

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JANUARY, 1936.



General, Physical, and Inorganic Chemistry.

Intensity of the hydrogen α - and β -lines as determined by the frequency of the electrical field in electrodeless discharge. O. STUHLMAN, jun., and M. S. McCAY (Physical Rev., 1934, [ii], 45, 750—751; cf. A., 1935, 799). L. S. T.

Striation of the positive column in the glow discharge of hydrogen. H. H. PAUL (Z. Physik, 1935, 97, 330—354).—Probe measurements in the positive column suggest that striations are due to an electric double layer formed by positive and negative ions; this explains the increasing difficulty of obtaining striations with increasing purity of H_2 . A. B. D. C.

Reproducibility of the relative energy distribution of the continuous H_2 spectrum emitted by a hydrogen discharge tube. V. E. GONSALVES (Physica, 1935, 2, 1003—1015).—The H discharge tube may be used as an ultra-violet standard. The intensity of the total emission between 1850 and 3200 Å. is const. between 3.0 and 3.4 mm. if the current is const. The relative energy distribution is independent of the current between 150 and 250 m. amp. if the pressure is const., and does not change in the region 1—3.5 mm. for currents between 150 and 250 m. amp. T. G. P.

Nuclear moments of lithium, potassium, and sodium. M. FOX and I. I. RABI (Physical Rev., 1935, [ii], 48, 746—751).—The at. beam method of "zero moments" gave, for the hyperfine structure separations of the normal 2S_1 state of Li, K, and Na, the vals. 0.0268 ± 0.0003 , 0.0154 ± 0.0002 , and 0.0596 ± 0.0006 cm.⁻¹, respectively. The calc. nuclear magnetic moments are $Li^{7} 3.20$, $K^{39} 0.397$, and $Na^{23} 2.08$ nuclear magnetons. The nuclear spin was $3/2$ for Li; a higher resolution arrangement gave an upper limit of $5/2$ for the spin of the K^{41} nucleus, and $2/2$, or greater, for Li^6 , the magnetic moment of the nucleus being of the order of that of the deuteron. N. M. B.

Vacuum arc spectra of rubidium and lithium. S. DATTA and P. C. BOSE (Z. Physik, 1935, 97, 321—329). A. B. D. C.

Rotation structure of the $b'x$ band system of the nitrogen molecule in the Schumann region. V. M. TSCHULANOVSKI (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 155—156; cf. A., 1934, 575, 935).—A preliminary report of new data. J. W. S.

Ultra-violet absorption spectrum of oxygen. L. HERMAN and (MME.) R. HERMAN (Compt. rend., 1935, 201, 714—716; cf. A., 1934, 828).—Data for

the low- and high-pressure absorption bands of O_2 at $\lambda\lambda$ 2400—2800 Å. are compared and discussed.

H. J. E.

Far ultra-violet absorption spectrum of oxygen. W. C. PRICE and G. COLLINS (Physical Rev., 1935, [ii], 48, 714—719).—The spectrum was photographed under high dispersion in the region 1300—650 Å., and frequencies of the vibrational progressions are tabulated. The bands are explained as going to the various excited states of O_2^+ as limits. Results support Mulliken's assignment of the visible O_2^+ bands to the transition $^4\Sigma_g^- \rightarrow ^4\Pi_u$. The distances of these states of O_2^+ from the ground state of O_2 are 18.2 and 16.1 volts. N. M. B.

Influence of an electric field on the absorption spectrum of sodium. N. T. ZIE and W. W. PO (Compt. rend., 1935, 201, 716—718).—The no. of members of the principal series observed decreases with increasing field strength. Certain of the forbidden $S-D$ and $S-S$ transitions were observed.

H. J. E.

Nuclear moment of aluminium. F. W. BROWN and R. K. COOK (Physical Rev., 1934, [ii], 45, 731).—A tentative val. of 4.8 for the $g(I)$ factor has been calc. L. S. T.

New absorption spectrum of diatomic sulphur vapour in the Schumann region. K. WIELAND, W. MEHLI, and E. MIESCHER (Helv. phys. Acta, 1934, 7, 843—849; Chem. Zentr., 1935, i, 1978).—Data are given for two band systems between 1600 and 1870 Å., both originating from the S_2 mol. The heat of dissociation of S_2 in the $^3\Sigma$ state is 1.68 volts. J. S. A.

Deep terms in the isoelectronic sequence VI to Cu VII. P. G. KRÜGER and (MISS) H. T. GILROY (Physical Rev., 1935, [ii], 48, 720—721; cf. A., 1932, 208).—The $3d^5 6S_{5/2}$ and $3d^4 4p^6 P^0$ terms of this sequence have been identified by the use of const. second differences in the radiated frequencies from terms involving an electron transition to the ground state. N. M. B.

New terms in the spectrum of Fe II. J. C. DOBBIE (Proc. Roy. Soc., 1935, A, 151, 703—726).—An analysis of the spectrum of Fe II between 2327 and 9000 Å. has resulted in the discovery of numerous new terms, many of which belong to the doublet system; >900 lines, not previously classified, have been accounted for by the new terms. A fairly close approximation to Russell-Saunders coupling is found in the spectrum. The separations between the terms of higher and lower multiplicity derived

from the same parent terms are nearly all large compared with the intervals between the levels of these terms. L. L. B.

Absolute intensity of the zinc resonance line 2139 Å. and life of 2^1P_1 state of zinc. W. BILLETER (Helv. phys. Acta, 1934, 7, 841—842; Chem. Zentr., 1935, i, 1979—1980).—The abs. intensity is calc. as $f(2139)=1.17$, and the life of the 2^1P_1 state as 1.78×10^{-9} sec. J. S. A.

Ionisation potentials of Ge V, As VI, Se VII, Sb VI, and Te VII. P. G. KRUGER and W. E. SHOUPP (Physical Rev., 1934, [ii], 45, 759).—Radiations represented by $d^{10}1S_0$, d^9p , $3P_1^0$, $1P_1^0$, $3D_1^0$ have been found in the above. Term vals. of the $d^{10}1S_0$ terms are given and ionisation potentials are 93, 127, 166, 107, and 137 volts, respectively. L. S. T.

Influence of pressure on the discharge radiation of cadmium vapour. V. A. FABRIKANT and A. S. KANEL (Compt. rend. Acad. Sci., U.R.S.S., 1935, 3, 257—258).—Preliminary notice. W. R. A.

Hyperfine structure and the gross structure analysis of the spectrum of doubly-ionised antimony. J. S. BADAMI (Nature, 1935, 136, 836). L. S. T.

Ultra-violet fluorescence spectra of iodine vapour. F. DUSCHINSKY and P. PRINGSHEIM (Physica, 1935, 2, 923—932).—The fluorescence bands at 3400 Å. (Oldenberg, A., 1924, ii, 579) occurring in I vapour in presence of N_2 have been studied. I in presence of He gives a different spectrum in the same region, which is also obtained with N_2 at higher temp. The bands may also be obtained as a sensitised fluorescence in presence of Hg, accompanied by HgI bands. Modification of the usual energy level system of I is necessary if the bands are to be explained by transference. The 4400 Å. band of HgI has been investigated. T. G. P.

Hyperfine structure and nuclear magnetic moment of Cs I. L. P. GRANATH and R. K. STRANATHAN (Physical Rev., 1935, [ii], 48, 725—731).—The hyperfine structure of the lines $\lambda\lambda$ 8761, 4593, 4555, 3889, and 3877 of the arc spectrum of Cs was observed. The interval factors for the $6^2S_{1/2}$, $6^2P_{1/2}$, $7^2P_{1/2}$, and $8^2P_{1/2}$ states were 0.0767, 0.00925, 0.00329, and 0.0017 cm^{-1} , respectively. Assuming a nuclear spin of 7/2, the calc. nuclear magnetic moments are 2.66, 2.38, 2.62, and 3.01 nuclear magnetons for the respective states. N. M. B.

Additional terms in the spectrum of La III. R. C. GIBBS and G. K. SCHOEPFLE (Physical Rev., 1934, [ii], 45, 747).—The ns^2S and nd^2D series have been extended, one more pair of $2P$ terms has been located, and certain of the $2F$ and $2G$ terms have been determined. L. S. T.

Temperature classification of samarium lines. A. S. KING (Astrophys. J., 1935, 82, 140—191).—A temp. classification for 4477 Sm lines between 2900 and 8700 Å. is given. L. S. T.

Luminosity in the mercury discharge. R. D. RUSK and A. L. PECKHAM (Physical Rev., 1934, [ii], 45, 751).—Recombination of slow electrons

and positive ions is a negligible factor in producing luminosity. L. S. T.

Intensification by drying of Hg lines in a mercury-hydrogen discharge. H. BECK (Z. Physik, 1935, 97, 382—389).—Protons are most likely the source of increased intensity of the Hg lines on drying of the Hg- H_2 mixture. A. B. D. C.

Determination of the absorption coefficient, $K(\lambda_0)$, of the mercury resonance line, 2536.5 Å., by the resonance scattering method. G. P. BALIN (Physikal. Z. Sovietunion, 1935, 8, 93—99).—The theory of the method of Goos and Meyer (A., 1926, 334) for determining absorption coeffs. by resonance scattering is discussed and extended. If the density of the saturated vapour used is not too great, the vals. of $K(\lambda_0)$ are in good agreement with those obtained by other methods. A. J. M.

Paschen-Back effect with Bellevue electro-magnet supplied with supplementary coils. P. JAQUINOT and T. BELLING (Compt. rend., 1935, 201, 778—779).—The effect has been studied with the Hg lines 5789—5790 and 5770 Å., and a field of 65,800 gauss. Displacements and doubling agree with theory. R. S. B.

Line absorption of thallium doublet = 3519.29 Å. during thermal excitation of the metastable $6^2P_{3/2}$ level. F. MÜLLER (Helv. phys. Acta, 1934, 7, 813—840; Chem. Zentr., 1935, i, 1979).—Determination of the line absorption as a function of the TI pressure confirms the application of the Maxwell-Boltzmann partition law to metastable states. J. S. A.

Term values in the spectrum of lead v. G. K. SCHOEPFLE (Physical Rev., 1934, [ii], 45, 747).—65 terms, involving approx. 200 lines, have now been established. L. S. T.

Absorption spectrum of lead vapour in the Schumann region. N. V. KREMENEVSKI (Compt. rend. Acad. Sci., U.R.S.S., 1935, 3, 251—252).—The absorption spectrum of Pb vapour was examined between 2200 and 1350 Å. and between 420° and 1070°; the results are discussed. W. R. A.

Determination of the temperatures of gases from the intensities of band spectra. O. OLDENBERG (Physical Rev., 1934, [ii], 45, 738; cf. A., 1934, 1153).—Processes leading to normal and to abnormal rotation, i.e., rotation > the thermal val., are discussed. L. S. T.

Intensity measurements in the ultra-violet with the aid of the photon counter. I. L. ROICH (Physikal. Z. Sovietunion, 1935, 8, 223—226).—The Planck-Wien formula for black-body radiation has been confirmed in the ultra-violet using Schein's photon counter. T. G. P.

Mechanism of high-frequency discharges. H. BECK (Z. Physik, 1935, 97, 355—375).—Electrical and optical observations on high-frequency discharges have shown that spectral intensity, no. of excited levels, and electron temp. are very similar to those in the positive column of d.-c. discharges. A. B. D. C.

Cathode head-like discharge. H. BECK (Z. Physik, 1935, 97, 376—381).—This discharge, in

appearance similar to the symmetrical striations of anode columns, has been observed in Hg, Zn, and Cd; current-voltage characteristics are given together with conditions of its formation.

A. B. D. C.

Nature of luminous streamers from the condensed spark in vacuo. C. F. BAREFORD (Phil. Mag., 1935, [vii], 20, 825—834).—In the condensed spark in high vac. sharply defined luminous streamers, occurring in both the positive and negative phases of the oscillating current of the spark, pass through a hole bored in one of the electrodes and extend into the exhausted space beyond it. The spectra of the streamers show lines due to neutral and ionised atoms of the metal of the electrode opposite the hole. There is some evidence that aggregates rather than single atoms are concerned in the formation of the streamers.

N. M. B.

Spectroscopic observation of recurrent phenomena in discharge tubes. R. H. SLOANE and C. M. MINNIS (Proc. Physical Soc., 1935, 47, 1019—1028).—Irregular moving striations are photographed synchronously by forming an image of the positive column of a discharge tube along a spectrograph slit which is covered and uncovered by a mechanical shutter synchronised with the striations by a photo-electric device. The photographs for pure A show no appreciable recombination in the dark phase, and those for A-Hg mixtures show excitation of only the Hg lines in the dark phase; an explanation is proposed.

N. M. B.

Pre-discharge currents and striking conditions in gas-filled hot-cathode tubes. I. RUNGE (Z. tech. Phys., 1935, 16, 38—42; Chem. Zentr., 1935, i, 2140).

J. S. A.

Air afterglow. F. H. NEWMAN (Phil. Mag., 1935, [vii], 20, 777—781).—A detailed study of the spectra of air and O₂ afterglows shows that poisoning of the discharge-tube walls is necessary for glow formation; the effect persists after the discharge has ceased, but is eliminated by heating the tube. The bands in air are superposed on a continuous spectrum; band positions are given. Traces of H₂O, COMe₃, and C₆H₆ vapour quenched the afterglows, but CS₂ gave the characteristic blue flame. The afterglows are attributed to the oxidation of NO by O₃, both these gases being formed in the discharge tube.

N. M. B.

Pressure effects of foreign gases on spectral lines. H. MARGENAU (Physical Rev., 1935, [ii], 48, 755—765; cf. A., 1933, 201).—Mathematical. The effect of pressure on the shape and position of a spectral line is examined.

N. M. B.

Spectro-photometric comparison of the zodiacal light and the light of the night sky. J. CABANNES and J. DUFAY (Compt. rend., 1935, 201, 696—699).—The spectrum of the zodiacal light does not contain the line λ 5577 or the bands $\lambda\lambda$ 4838, 4825 Å.

H. J. E.

Fine structure of the K edges of magnesium and aluminium. J. VELDKAMP (Physica, 1935, 2, 933—934).—Sandström's explanation (Diss., Upsala,

1935) of the fine structure of the K edges of Mg and Al is incorrect. Another interpretation is given.

T. G. P.

Atomic scattering factors of nickel, copper, and zinc. G. W. BRINDLEY and F. W. SPIERS (Phil. Mag., 1935, [vii], 20, 865—881; cf. A., 1935, 16).—At. scattering factors of Ni, Cu, and Zn for Cu K α radiation have been measured. Abs. vals. of the reflected intensities were obtained by comparison with reflexions from KCl. The results are compared with those of previous workers.

T. G. P.

Width of K α lines of gaseous krypton and of elements in chemical compounds. E. WILHELMI (Z. Physik, 1935, 97, 312—320).—Results are given for Kr, Rb in RbCl, Br in KBr, and Cu in CuO and CuF₂; that for Kr shows state of aggregation to have no effect, whilst the others show effects due to chemical combination.

A. B. D. C.

K-Series spectrum of thorium. J. C. HUDSON, H. G. VOGT, and A. H. ARMSTRONG (Physical Rev., 1934, [ii], 45, 755).

L. S. T.

L-Emission spectrum of argon. M. BAČKOVSKÝ and V. DOLEJŠEK (Nature, 1935, 136, 643).—Vals. for the L-series of A, measured directly by means of the ionic tube, agree with those calc. by interpolation of the data of Siegbahn and Magnusson (A., 1935, 909).

L. S. T.

Relative energy of the L α satellites excited by cathode rays in the atomic number range 47—52. F. R. HIRSH, jun. (Physical Rev., 1935, [ii], 48, 722—724; cf. A., 1934, 233).—Measurement of the integrated relative energy of the L α satellites with respect to their parent L α_1 line have been extended photographically from Ag (47) to Te (52). In this range the satellites decrease rapidly in relative energy with increasing at. no., in agreement with the Coster-Kronig theory.

N. M. B.

L α [X-ray] emission of mercury, platinum, and tungsten. (MLLE.) Y. CAUCHOIS (Compt. rend., 1935, 201, 721—722; cf. A., 1935, 800).—Data for the satellites to the L α radiation of Hg, Pt, and W are recorded.

H. J. E.

Occurrence of the reversed absorption edges of the long wave-lengths of X-rays. M. BAČKOVSKÝ and V. DOLEJŠEK (Nature, 1935, 136, 836—837).

L. S. T.

Enhancement of X-ray satellites by the Auger effect. F. R. HIRSH, jun. (Physical Rev., 1935, [ii], 48, 776—777).

N. M. B.

Soft X-ray spectra of aluminium and magnesium: wave-length measurements. T. H. OSGOOD (Physical Rev., 1934, [ii], 45, 753).—Vals. are given for the λ of the sharp edge of the wide line in the L spectrum of Mg and Al.

L. S. T.

Photo-electric emission and surface chemistry. C. OUELLET (Natural. Canad., 1935, 62, 271—281; cf. A., 1935, 697).—A general survey of the relation of photo-electric emission to surface phenomena, and the use of the photo-electric counter.

N. M. B.

Photo-electric properties of pure and gas-contaminated magnesium. R. J. CASHMAN and W. S. HUXFORD (Physical Rev., 1935, [ii], 48, 734—741;

cf. A., 1933, 662).—The threshold characteristic of all gas-free surfaces obtained by successive distillations is at 3430 ± 20 Å. The val. at 5100 Å., previously ascribed to pure Mg, is attributed to Mg contaminated with H_2 . A trace of O_2 causes a max. excursion of the long-wave limit to about 5700 Å. The formation of polar mols. on the Mg surface will account for the threshold shift observed when H_2 or O_2 is present. A method of purifying Mg by multiple distillations is described. N. M. B.

Positive and negative thermionic emission from molybdenum. H. B. WAHLIN and J. A. REYNOLDS (Physical Rev., 1935, [ii], 48, 751—754).—In view of discordant results reported, an investigation under rigorous outgassing gave the val. 4.17 volts for the electron work function and 8.35 volts for that of the positive ion. The positive ion emission agrees with the Saha theory of ion formation (cf. Moon, A., 1932, 1185). N. M. B.

Potential drop and ionisation at mercury arc cathode. E. S. LAMAR and K. T. COMPTON (Physical Rev., 1935, [ii], 48, 777; cf. A., 1931, 780).—A correction. N. M. B.

Electron temperatures in the positive column in mixtures of neon and argon or mercury. H. B. DORGELO, H. ALTING, and C. J. BOERS (Physica, 1935, 2, 959—967).—The electron temp. falls rapidly during the increase in partial pressure of A up to 15% in Ne-A mixtures at const. total pressure (5 mm.) and const. current (2 amp.). In Ne-Hg mixtures the electron temp. falls with increasing partial pressure of Hg. The results are explained on a development of Schottky's diffusion theory. T. G. P.

Ion optical images with electrical lenses. J. KOCH and W. WALCHER (Z. Physik, 1935, 97, 131—137).—Images have been obtained with K ion rays. A. B. D. C.

Sudden losses of energy undergone by high-energy electrons. L. LEFRINCE-RINGUET (Compt. rend., 1935, 201, 712—714; cf. A., 1935, 801).—Electrons of approx. 2×10^6 e.v. suffer large energy losses in traversing A or Pb, 5—10 times as frequently as would be expected from theory. H. J. E.

Quantum-like loss of velocity of slow electrons and effective cross-section in molecular gases. H. LÖHNER (Ann. Physik, 1935, [v], 24, 349—360).—Measurements of the loss of velocity of electrons by Lenard's counter-potential method indicate that inelastic collision begins at 4.25, 2.45, 2.45, 3.65, 7.2, and 7.1 volts for H_2 , N_2 , NO, CO, N_2O , and CO_2 , respectively. A relationship exists between the loss of velocity and the effective cross-section of the mol. J. W. S.

Total ionisation produced by electron collisions in nitrogen. G. A. ANSLOW (Physical Rev., 1934, [ii], 45, 750).—The total ionisation produced in N_2 by electrons with energies up to 1500 volts has been measured. L. S. T.

Double excitation of helium by electron impact. H. S. W. MASSEY (Proc. Camb. Phil. Soc., 1935, 31, 604—608).—The calc. probability of ex-

citation of helium by electron impact to doubly excited levels agrees qualitatively with experimental data. Reasons are given for the lack of quant. agreement. W. R. A.

Velocity distribution of electrons moving in an electric field. B. DAVIDOV (Physikal. Z. Sovietunion, 1935, 8, 59—70).—Theoretical. The velocity distribution of electrons moving in a gas under a const. electric field is calc. taking into account only elastic collisions between mols. and electrons. The distributions of velocities with regard to magnitude and direction, and formulæ for the mean energy and motion of the electrons are obtained. A. J. M.

Paths of electrons in magnetons when space-charge effects are considered. I. H. AVENDER, A. THOMA, and D. M. TOMBS (Z. Physik, 1935, 97, 202—210).—Theoretical. A. B. D. C.

The positive electron. A. T. WATERMAN (Amer. J. Sci., 1935, [v], 30, 541—548).—A review.

Excitation function of mercury for atomic collision. K. GAILER (Ann. Physik, 1935, [v], 24, 421—439).—The mutual excitation of H and Hg was investigated by the use of positive rays. In the case of H positive rays passed through Hg, only the Hg becomes excited. The excitation of the Hg at higher potentials is brought about almost entirely by neutral H atoms, excitation by H^+ being at least 20 times smaller. The excitation function of Hg for collision with H is determined and compared with that for electron collision. The results are discussed from the viewpoint of "transferable energy." A. J. M.

Electron collisions in mercury vapour: the 9.8 volt loss. C. L. CROSS and J. A. ELDRIDGE (Proc. Iowa Acad. Sci., 1934, 41, 257).—Data for the magnetic analysis of electrons which have passed through Hg vapour are given. CH. ABS. (e)

Homogeneous dissociation of hydrogen molecules by collision with positive ions. A. SCHECHTER (J. Chem. Physics, 1935, 3, 433—434).—Special experimental conditions are given of work previously described (cf. A., 1934, 977) in view of reported failure of later investigators to obtain similar results (cf. Kunsman, A., 1935, 4). N. M. B.

Disappearance of hydrogen in presence of positive ions. C. H. KUNSMAN and R. A. NELSON (J. Chem. Physics, 1935, 3, 754).—A reply to Schechter (preceding abstract). F. L. U.

Collisions of slow electrons with methane molecules. H. L. BROSE and J. E. KEYSTON (Phil. Mag., 1935, [vii], 20, 902—912).—The effective cross-sections of CH_4 mols. with respect to slow electrons of different velocities have been determined and are discussed. T. G. P.

Effective cross-section and charging cross-section of helium with respect to He^+ . A. ROSTAGNI (Ann. Physik, 1935, [v], 24, 543—544).—The results of Wolf (A., 1935, 1294) give the charging cross-section $>$ total effective cross-section. This may be due to inconstancy of field along the collector, and to the neglect of secondary electron emission. A. J. M.

At. wt. of germanium. I. Analysis of germanium tetrabromide. O. HÖNIGSCHMID, K. WINTERSBERGER, and F. WITNER (*Z. anorg. Chem.*, 1935, 225, 81—89; cf. A., 1934, 1053).—The mean of 10 analyses of GeBr_4 by nephelometric titration with AgNO_3 gives Ge 72.588 ± 0.008 , and the mean of 10 gravimetric analyses 72.586 ± 0.012 . The final val., 72.59, agrees with that of Baxter and Cooper (A., 1924, ii, 690; 1926, 5), but not with Aston's 72.65 ± 0.05 (A., 1931, 1208). F. L. U.

Rare earths. XLVI. At. wt. of gadolinium. C. R. NAESER [with B. S. HOPKINS] (*J. Amer. Chem. Soc.*, 1935, 57, 2183—2184).—From the ratio $\text{GdCl}_3 : \text{Ag}$ the at. wt. of Gd is 156.85 ± 0.011 . E. S. H.

At. wt. of tantalum. Analysis of tantalum pentachloride. O. HÖNIGSCHMID and R. SCHLEE (*Z. anorg. Chem.*, 1935, 225, 64—68).—The prep. of pure TaCl_5 from tantalite is described. The mean of 6 determinations of the Cl content of TaCl_5 by nephelometric titration with AgNO_3 gave Ta 180.88 ± 0.01 , agreeing with the val. previously obtained by analysis of TaBr_5 (A., 1935, 140). F. L. U.

Properties of the hydrogen isotopes as revealed by the mass-spectrograph. W. BLEAKNEY (*Physical Rev.*, 1934, [ii], 45, 762).—A mass-spectrograph dealing with gases at very low pressure shows that no exchange takes place nor is equilibrium established when a non-equilibrium mixture is in contact with H_2O , Hg, soft glass, Pyrex glass, or stopcock grease. Certain catalysts, however, e.g., Ni and Cr_2O_3 , established equilibrium at temp. as low as that of liquid air. L. S. T.

Relative abundance of the silicon isotopes. A. MCKELLAR (*Physical Rev.*, 1934, [ii], 45, 761).—Measurements of the violet bands of SiN indicate an approx. abundance ratio $\text{Si}^{28} : \text{Si}^{29} : \text{Si}^{30} = 89.6 : 6.2 : 4.2$. The abundance of Si^{29} and Si^{30} relative to Si^{28} is slightly > that estimated by Aston. An at. wt. > the accepted val. is obtained. L. S. T.

Isotopes of nickel. J. DE GIER and P. ZEEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1935, 38, 810—813).— Ni^{64} has been detected by the parabola method, but Ni^{61} (Aston, A., 1935, 802) was not found. The abundance figures are Ni^{58} 68.1%, Ni^{60} 27.2%, Ni^{62} 3.8%, and Ni^{64} 0.9%. R. S.

Interference-spectroscopic examination of the gold hydride band spectrum in search of the isotope effect due to the suspected gold isotopes. S. IMANISHI (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1935, 28, 129—134).—No evidence for the existence of Au^{199} could be obtained. This is in agreement with Dempster (A., 1935, 677). R. S.

Periodic classification of the rare earths. H. YAGODA (*J. Amer. Chem. Soc.*, 1935, 57, 2329—2330).—The tendency of the rare earths to form stable trivalent compounds is said to mask the fact that the properties of these elements in other valency states are a periodic function of at. no. Examples are given. E. S. H.

New periodic table. P. VAN RYSELBERGHE (*J. Chem. Educ.*, 1935, 12, 474—475).—The new table emphasises the importance of the azimuthal quantum

no. of the last electron added in the building up of the successive elements. L. S. T.

Radioactive fluctuations. A. E. RUARK and I. DEVOL (*Physical Rev.*, 1935, [ii], 48, 772).—Mathematical. Expressions are found for the fluctuations in the emission of sources which decay appreciably during the time of a single experiment, and for fluctuations in the counts recorded by a detector which receives only a fraction of the particles or rays emitted by a source. N. M. B.

Renewed activity of radium bromide after heating. C. T. KNIPP (*Trans. Illinois State Acad. Sci.*, 1934, 27, 128—129).—A minute amount of RaBr_2 was sealed on the end of a rod by means of very thin Pyrex glass. The no. and length of the tracks in a Wilson chamber due to the specimen increased to a max. in 6—10 days. CH. ABS. (e)

^{43}K and the radioactivity of potassium. H. J. WALKE (*Nature*, 1935, 136, 755).—Recent evidence supports the view (A., 1935, 275, 558) that ^{40}K and not ^{43}K (*ibid.*, 1185) is the source of the natural β -radioactivity of K. L. S. T.

Temporal sequence of α - and γ -radiation of radium. W. JOHNER and E. STAHEL (*Helv. phys. Acta*, 1934, 7, 638—639; *Chem. Zentr.*, 1935, i, 2132—2133).—It is proposed to determine the relative order of α - and γ -ray emission from Ra by examination of the absorption of the K lines, excited by inner absorption of the γ -radiation, in Tl, Au, and Hg filters. Absorption corresponding with the Rn spectrum would indicate emission of γ -radiation after loss of the α -particle. Preliminary results indicate emission of Ra K radiation. J. S. A.

Absorption of γ -rays by barium sulphate, gypsum, water, and flesh. J. S. ROGERS (*Brit. J. Radiol.*, 1934, [ii], 7, 176—186; *Chem. Zentr.*, 1935, i, 2133).—The absorption has been determined photographically, and conclusions have been reached as to gypsum thicknesses for protection from γ -rays, and radiation intensities for penetration of varying flesh thicknesses. J. S. A.

γ -Ray emission of various targets under bombardment by deuterium ions. L. R. HAFSTAD, M. A. TUVE, and C. F. BROWN (*Physical Rev.*, 1934, [ii], 45, 746—747).—Powerful γ -ray emission from Be, C, and CaF_2 bombarded by deuterons is described. There is faint or doubtful emission from SiO_2 and Al, but none from Ag. L. S. T.

Experiments with neutrons slowed down at different temperatures. C. H. WESTCOTT and H. NIEWODNICZANSKI (*Proc. Camb. Phil. Soc.*, 1935, 31, 617—624).—Neutrons were slowed down by paraffin wax at the temp. of liquid N_2 and liquid H_2 . The absorption produced by certain substances increased as the temp. was lowered. The no. of transformations also increased, the increase depending on the thickness of the paraffin layer. When liquid H_2 was substituted for paraffin similar effects were produced. W. R. A.

Disintegration by slow neutrons. J. CHADWICK and M. GOLDHABER (*Proc. Camb. Phil. Soc.*, 1935, 31, 612—616).—Details of work (A., 1935, 277) are

given and a different interpretation of the results observed with B. The reaction between B and slow neutrons is $B^{10} + n^1 \rightarrow Li^7 + He^4$. The disintegration process with nitrogen is $N^{14} + n^1 \rightarrow B^{11} + He^4$. No increase was found for H, D, He, Be, C, O, F, Ne, Na, Mg, Al, Cl, A, Ca, Ni, Cu, Zn, In, and U. W. R. A.

Excitation of secondary γ -rays by neutrons. I. General; phenomena in paraffin. II. Measurements with iron, copper, cadmium, and lead. R. FLEISCHMANN (Z. Physik, 1935, 97, 242—264, 265—267).—Nuclear γ -rays have been excited by slow neutrons in H, Fe, Cu, Cd, and Pb, and absorption of the γ -rays by paraffin, Al, and Pb has been determined. The mass of the neutron is 1.0083. A. B. D. C.

Absorption and detection of slow neutrons. D. P. MITCHELL, J. R. DUNNING, E. SEGRÈ, and G. B. PEGRAM (Physical Rev., 1935, [ii], 48, 774—775; cf. A., 1935, 1441).—The disintegrations of B and Li were examined in terms of the absorption observed in B, Li, and Cd. Absorption-transmission curves show slight departure from the exponential.

N. M. B.

Scattering of slow neutrons by iron and other substances. D. BUDNITZKI and I. KURTSCHATOV (Physikal. Z. Sovietunion, 1935, 8, 170—178).—The free paths of slow neutrons in C, Fe, Cu, and Pb have been found by using their reflexion, and are compared with vals. obtained by Dunning *et al.* (Physical Rev., 1935, [ii], 47, 416) for fast and slow neutrons. In calculating paths the selective sensitivity of the indicator and the absorption of neutrons by H_2O must be considered. T. G. P.

Absorption of slow neutrons by iron. I. KARA, L. ROSENKEVITSCH, C. SINELNIKOV, and A. WALTHER (Physikal. Z. Sovietunion, 1935, 8, 215—218).—Absorption in Fe and Cu is < recorded by Fermi (A., 1935, 910). T. G. P.

Selective absorption of neutrons. I. KARA, L. ROSENKEVITSCH, C. SINELNIKOV, and A. WALTHER (Physikal. Z. Sovietunion, 1935, 8, 219—222; cf. preceding abstract).—Absorption of neutrons by Cu is independent of the change in concn. of B_2O_3 in H_2O surrounding the indicator. This is explained by the selective absorption of B. The average vals. of sensitivity increase in the order B, Ag, Cu. The cross-section for absorption decreases rapidly with increased velocity of neutrons. T. G. P.

Evaluation of the accuracy of Bethe and Peierls' formula concerning the decomposition of the deuteron with γ -radiation. V. J. MAMASACHLISOV (Physikal. Z. Sovietunion, 1935, 8, 206—207; cf. A., 1935, 279). T. G. P.

Disintegration of lithium by deuterons. T. W. BONNER and W. M. BRUBAKER (Physical Rev., 1935, [ii], 48, 742—746; cf. A., 1935, 1049).—The energy distribution of the neutrons from the disintegration of Li by 0.85 m.e.v. deuterons was determined by the method of recoil protons in a high-pressure cloud chamber. Results indicate that the neutrons come from the reactions ${}^3Li^7 + {}^1H^2 \rightarrow {}^2He^4 + {}^0n^1$, the neutrons (95% of the disintegrations) having a continuous energy distribution; and ${}^3Li^7 + {}^1H^2 \rightarrow$

${}^4Be^8 + {}^0n^1$, the neutrons (5% of the disintegrations) being nearly homogeneous, with a max. energy of 13.3 ± 0.5 m.e.v. The calc. mass of ${}^4Be^8$ is 0.3 ± 0.75 m.e.v. > that of two α -particles. N. M. B.

Transmutation of deuterium by deuterons. K. D. ALEXOPOULOUS (Naturwiss., 1935, 23, 817).—Experiments are described which indicate that no γ -radiation is emitted in the nuclear reaction between deuterons. A. J. M.

Disintegration of lithium by lithium ions. V. PETUHOV, C. SINELNIKOV, and A. WALTHER (Physikal. Z. Sovietunion, 1935, 8, 212—214).—The excitation function and abs. yield of the transmutation ${}^3Li^6 + {}^3Li^6 \rightarrow {}^3He^4$ are \times vals. predicted by Gamow's formula. The contrary result of Whitmer and Pool (Physical Rev., 1935, [ii], 47, 795) is probably due to protons in the ionic beam. T. G. P.

Artificial radioactivity. II. D. VAN DER VEEN (Chem. Weekblad, 1935, 32, 667—671).—A further review (see A., 1934, 826).

Synthesis of radio-elements with deuterons accelerated by an impulse generator. F. JOLIOU, A. LAZARD, and P. SAVEL (Compt. rend., 1935, 201, 826—828).—Preliminary results for the conversion ${}^6C^{12} + {}^1D^2 = {}^7N^{13} + {}^0n^1$ are recorded. Production of ${}^7N^{13}$ becomes measurable with accelerating voltages $> 0.95 \times 10^6$ volts. H. J. E.

Induced radioactivity by bombarding magnesium with α -particles. C. D. ELLIS and W. J. HENDERSON (Nature, 1935, 136, 755).—In addition to Al^{28} (β -ray period 137 sec.) two other radioactive bodies, probably Al^{29} and Si^{27} , emitting β -rays with a period of approx. 11 min. and positrons with a period of 5—7 min., respectively, are produced. Relative yields indicate that Mg^{25} has a strong resonance level for α -particles of energy $< 5.4 \times 10^6$ volts, and that Mg^{24} and/or Mg^{26} have one for α -particles of energies between 5.4 and 6.1×10^6 volts. L. S. T.

Radio-elements produced by neutrons. P. PREISWERK and H. VON HALBAN (Compt. rend., 1935, 201, 722—724).—The induced activities of half-periods 97 and 4 min. observed on bombarding Tl with neutrons are attributed to ${}_{81}Tl^{204}$ and ${}_{81}Tl^{206}$, respectively. No activity was observed on irradiating Bi with neutrons. P gave a product of half-period 15 ± 1.5 days, attributed to ${}_{15}P^{32}$. H. J. E.

Radioactivity of some rare-earths induced by neutron bombardment. (SIR) J. C. McLENNAN and W. H. RANN (Nature, 1935, 136, 831—832; cf. A., 1935, 1049, 1050).—Bombardment of rare-earth oxides or oxalates by retarded neutrons from a Be+Ra source gave the following vals. for the half-periods: Nd 35 ± 5 min., Gd 6.4 ± 0.3 hr., Dy 2.5 ± 0.1 hr., Er 5.8 ± 0.2 min., 2.7 ± 0.2 hr., Ho 2.6 hr., and Lu 3.6 ± 0.4 hr. L. S. T.

Nature of the high-energy particles of penetrating radiation and the status of ionisation and radiation formulæ. E. J. WILLIAMS (Physical Rev., 1934, [ii], 45, 729—730).—A discussion. L. S. T.

Alterations of intensity of cosmic radiation on the Hafelekar (2300 metres). V. F. HESS, H. T. GRAZLADEI, and R. STEINMAURER (Sitzungsber. Akad. Wiss. Wien, 1934, IIa, 143, 313—338; Helv. phys. Acta, 1934, 7, 669—670; Chem. Zentr., 1935, i, 2134). J. S. A.

Frequency and intensity of cosmic-ray bursts from lead. H. GEIGER and O. ZEILLER (Z. Physik, 1935, 97, 300—311). A. B. D. C.

Shower production in small thicknesses of lead and other elements. J. E. MORGAN and W. M. NIELSEN (Physical Rev., 1935, [ii], 48, 773—774).—The increase in counting rate, for dual and triple coincident discharge of the counters, as a function of Pb thickness is examined. N. M. B.

System of masses of light atoms deduced from nuclear reactions alone. L. ISAKOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 301—304).—19 equations of nuclear reactions of light nuclei have been collected, together with their uncertainties. Solution of these equations by the method of least squares, the individual equations being weighted according to their uncertainties, gives a system of at. mass vals. for H^1 to Be^{11} . Vals. for H^1 , H^2 , He^4 , Li^6 , and Li^7 are in good agreement with mass-spectrograph vals. corr. for the error in the ratio He : O (1.8 parts in 10,000). It is shown that Be^8 should be radioactive, although direct observation of its activity is difficult. A. J. M.

Nuclear theory. K. NAKABAYASI (Z. Physik, 1935, 97, 211—220).—Mass defects and nuclear radii are calc. A. B. D. C.

Pair production by magnetic multipole radiation. J. C. JAEGER (Proc. Camb. Phil. Soc., 1935, 31, 609—611).—Pair production by magnetic multipole radiation has been calc. for dipoles, quadripoles, and octopoles. The probability of pair production decreases with the order of the multipole. W. R. A.

Neutrino theory of light. III. R. DE L. KRONIG (Physica, 1935, 2, 968—980; cf. A., 1935, 1187).—Characteristics of neutrino-fields in relation to radiation-fields are deduced. T. G. P.

Properties of ultimate particles. G. WATAGHIN (Ann. Acad. Brasil. Sci., 1935, 7, 273—276).—Modern views on the constitution of matter are discussed and the development of the conception of the electron, positron, photon, etc. is traced historically. D. R. D.

Evidence for a resonance level in the B^{10} nucleus. E. POLLARD (Physical Rev., 1934, [ii] 45, 555—556). L. S. T.

Atomic frequencies in alkali metals. B. N. SEN (Gazzetta, 1935, 65, 907—908; cf. A., 1934, 719).—The calc. at. frequencies (ν) of the alkali metals (except Li) are in good agreement with experimental and other calc. vals. Since these elements have marked photo-electric properties, it seems likely that the discrepancy in the calc. val. of ν for S and Se is due to the existence of allotropic forms and not to their photo-electric property, which in the case of S is very weak. O. J. W.

Permutation degeneration in vector models of atoms. M. MARKOV (Compt. rend. Acad. Sci., U.R.S.S., 1935, 3, 103—104).—From the general permutation theory identities of the kind derived by Van Vleck for two equiv. p electrons arise for other kinds of electrons. W. R. A.

Calculation of the self-consistent field with exchange for lithium. V. A. FOCK and M. I. PETRASHEN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 295—296).—The difference between the observed and calc. term vals. for Li largely disappears when the self-consistent field method is used with quantum exchange instead of without it. The use of wave functions of the generalised self-consistent field gives the intensity of the principal line of each series with great precision. A. J. M.

Electromagnetic field theory. T. LEWIS (Phil. Mag., 1935, [vii], 20, 1000—1025).—Theoretical. Pure field theory based on Maxwell's equations and the principle of least action leads to a satisfactory theory of the electron. T. G. P.

γ -Transformation of electromagnetic fields. W. H. WATSON (Physical Rev., 1935, [ii], 48, 776; cf. Schrödinger, A., 1935, 912).—Mathematical. N. M. B.

Elements of the quantum theory. V. B. The rigid rotator (concluded). S. DUSHMAN (J. Chem. Educ., 1935, 12, 485—491; cf. A., 1935, 1298). L. S. T.

Collision problems and the conservation laws. (A) J. L. SYNGE. (B) B. HOFFMANN (Physical Rev., 1934, [ii], 45, 500—501, 734—735).—Theoretical. L. S. T.

Ultra-violet radiation of chemical reactions. O. VIKTORIN (Chem. Listy, 1935, 29, 245—249).—Ultra-violet radiation is shown by means of an Al or CuI photocathode to accompany the reactions of oxidation of pyrogallol by atm. O_2 , of $K_2C_2O_4$ by Br, of EtOH by CrO_3 , of glucose by $KMnO_4$, of $Na_2S_2O_4$ in alkaline media, and of Al at the anode, and of neutralisation of HNO_3 by NaOH. R. T.

Variation of spectra of detonations with the nature of the surrounding gas. A. MICHEL-LÉVY and H. MURAOUR (Compt. rend., 1935, 201, 828—830).—With $C(NO_2)_4 + PhMe$ in A, Kr, O_2 , CO_2 , air, and Cl_2 continuous emission predominated. In N_2 , He, and H_2 bands were observed. The luminosity is attributed to excitation of the surrounding gas by the shock wave. H. J. E.

Colour of smoky quartz. N. M. MOHLER (Physical Rev., 1934, [ii], 45, 743).—Absorption spectra (200—700 $m\mu$) of smoky quartz before and after decoloration by heat and recoloration by exposure to Ra, and the spectra of irradiated clear crystal, and fused specimens, support the view that the colour of smoky quartz is due to radioactive action. L. S. T.

The 4502 Å. band of NH. R. W. LUNT, R. W. B. PEARSE, and E. C. W. SMITH (Proc. Roy. Soc., 1935, A, 151, 602—609; cf. A., 1935, 679, 912).—A new band at 4502 Å., degraded to the red, has been observed in the spectrum of a hollow-cathode discharge in streaming NH_3 . The band arises from a

${}^4\Pi \rightarrow {}^1\Sigma$ transition. The rotational consts. for the new ${}^1\Sigma^+$ level have been calc. L. L. B.

Beryllium deuteride spectra. P. G. KOONTZ (Physical Rev., 1935, [ii], 48, 707—713).—The spectra of the BeD green bands at 4990 Å. and the ultra-violet BeD⁺ bands at 2200—3100 Å. were photographed. Rotational analyses of the former and rotational and vibrational analyses of the latter are tabulated. The electronic isotope shift in the ultra-violet is 0.8 cm.⁻¹ Rotational consts. are evaluated, and the slight discrepancy between the ratio of the B_e consts. for the deuterides and hydrides and the ratio of the reduced masses is discussed. N. M. B.

Fine structure of the C bands of calcium deuteride. B. GRUNDSTRÖM (Z. Physik, 1935, 97, 171—176). A. B. D. C.

E Band system of calcium hydride. W. W. WATSON and R. L. WEBER (Physical Rev., 1935, [ii], 48, 732—734).—The E band system of CaH at 4900 Å. is the $\Delta v=0$ sequence of a ${}^2\Pi \rightarrow {}^2\Sigma$ transition, the lower state being the normal ${}^2\Sigma^+$ state. Frequency assignments and calc. mol. consts. are tabulated. There is evidence of strong interaction between the E state and other near CaH states. N. M. B.

Dissociation energy of carbon monoxide. F. BRONS (Nature, 1935, 136, 796, and Physica, 1935, 11, 1108—1113).—The structure of the fourth positive group in the spectrum of CO confirms the val. 8.41 volts for dissociation energy (cf. A., 1934, 828). L. S. T.

Vibrational analysis of the hafnium oxide band spectrum. R. W. SHAW and H. C. KETCHAM (Physical Rev., 1934, [ii], 45, 753).—Approx. 100 bands arising from the HfO mol. have been observed in the region λ 6350—3330 Å. in an arc flame. No rotational structure has been observed. L. S. T.

Ultra-violet band spectrum of N₂O₃. E. H. MELVIN and O. R. WULF (Physical Rev., 1934, [ii], 45, 751—752).—Mixtures of NO and small amounts of NO₂ give a group of bands in the near ultra-violet probably due to N₂O₃. A process of dissociation of the N₂O₃ mol. in the region 2400—2200 Å. is indicated. L. S. T.

Emission spectrum of the selenium oxide SeO. L. BLOCH, E. BLOCH, and C. S. PLAW (Compt. rend., 1935, 201, 824—825; cf. A., 1935, 1443).—The spectrum of a high-frequency discharge in SeO₂ vapour has a no. of bands at λ 3800—2880 Å., degraded to the red, attributed to SeO. The fundamental vibrational frequencies of SeO in the normal and excited state were 908.9 and 533.4 cm.⁻¹, respectively; energy of dissociation 5.31 e.v. H. J. E.

Spectra of SeO and SeO₂. R. K. ASUNDI, M. JAN-KHAN, and R. SAMUEL (Nature, 1935, 136, 642—643; cf. A., 1935, 1188).—The emission bands of SeO and the absorption bands of SeO₂ have been analysed. The energy of dissociation of unexcited SeO is 4.17 volts. L. S. T.

Vibrational analysis of BaCl and BeCl bands. A. E. PARKER (Physical Rev., 1934, [ii], 45, 752; cf. A., 1934, 1153).—A band system due to BeCl,

a ${}^2\Pi \rightarrow {}^2\Sigma$ transition degrading to the red, has been photographed. L. S. T.

Photo-dissociation of polyatomic molecules in the Schumann ultra-violet. A. TERENIN and H. NEUMANN (J. Chem. Physics, 1935, 3, 436—437).—Threshold energies of dissociation were obtained for the vapours of H₂O, MeOH, EtOH, HCO₂H, AcOH, MeCN, NH₃, and I. N. M. B.

Spectrum, fluorescence, and photochemical decomposition of acraldehyde. H. W. THOMPSON and J. W. LENNETT (J.C.S., 1935, 1452—1459).—Absorption by the vapour was observed at λ 3800—2900 and < 2320 Å. In the first region there were sharp bands, degraded to the red, and max. absorption was at approx. 3450 Å. The bands at < 2320 Å. were narrow and diffuse. No fluorescence was observed on irradiating with λ 3800—3000 Å. The photochemical decomp. (λ 3665, 3135 Å.) yielded polymerised C₂H₃·CHO, CO, and small amounts of C₂H₂. The quantum yield for the decomp. (λ 3665 Å.) was approx. 10⁻². That for the polymerisation was 2.3. Both vals. increased with decreasing λ . H. J. E.

Influence of temperature on methyl iodide absorption spectrum in [quartz] ultra-violet. A. HENRICI and H. GRIENEISEN (Z. physikal. Chem., 1935, B, 30, 1—39; cf. A., 1933, 445).—Numerous new bands have been observed, particularly at higher temp. The electron transition responsible for the B bands is either in the C-I linking or in a non-linking I electron shell (cf. A., 1935, 562). Most of these bands may be accounted for by assuming vibrational frequencies of 525, \perp 880, and 1237 cm.⁻¹ in the ground state and 508, \perp 780, 1090, and \perp 1250 cm.⁻¹ in the excited electronic state. A resolution of various bands, observed at higher temp., is interpreted as removal of a degeneracy. Several bands exhibit exceptional weakening with rise of temp. and apparently represent transitions to a new electron term, 49,220 cm.⁻¹, the probability of transition to which varies with temp. In this term the frequencies have become 495, \perp 805, and 985 cm.⁻¹ R. C.

Optical absorption of substituted benzenes. E. STEURER (Z. physikal. Chem., 1935, B, 30, 157—158).—The absorption curves of ψ -cumene, mesitylene, and *p*-xylene have been determined and the results compared with those of Conrad-Billroth (A., 1935, 913). R. C.

Optical absorption of porphyrins. III. A. STERN and H. WENDERLEIN (Z. physikal. Chem., 1935, 174, 321—334; cf. A., 1935, 1444).—The absorption curves of two chloroporphyrin-*e*₅ Me₂ esters accord with the structure previously suggested (A., 1933, 402). The curve of 4-de-ethoxyphyloerythrin Me₁ ester exhibits only a small shift towards the blue compared with that of the corresponding porphyrin with Et substituted in the β -position. Absorption curves of derivatives of the chlorophyll-*b* series reveal regularities similar to those observed in the *a* series. The effect on the light absorption of the hydrogenation of the vinyl group in methylphæophorbide-*a* and -*b* has been examined. R. C.

Determination of ionisation by ultra-violet spectrophotometry: its validity and application to the measurement of the strength of very weak bases. L. A. FLEXSER, L. P. HAMMETT, and A. DINGWALL (J. Amer. Chem. Soc., 1935, 57, 2103—2115).—Ultra-violet absorption spectra of BzOH, 2:4-C₆H₃(NO₂)₂·OH, NH₂Ph, COPh₂, anthraquinone, CH₂Ph·CO₂H, and *p*-NO₂·C₆H₄·CO₂H in different solvents have been determined. The technique of ionisation determination by this method is described and discussed. The strengths of the very weak bases COPh₂, BzOH, and CH₂Ph·CO₂H have been measured.

E. S. H.

Interpretation of vibration spectrum of organic molecules with the aid of the isotopy effect. E. BARTHOLOMÉ and H. SACHSSE (Z. physikal. Chem., 1935, B, 30, 40—52).—The magnitude of the change in a frequency when in a H compound D is substituted for H is a measure of the participation of the substituted atom in that particular mol. vibration. In numerous cases substitution reduces the symmetry of the original mol., resulting in a resolution of vibrations which are degenerate in the H compound; from the resolution the degree of degeneracy and hence the symmetry character of the original frequency may be deduced. Comparison of the infra-red absorption spectra of MeOH and MeOD has made it possible to identify the normal vibrations; in an appreciable proportion of the mols. there is no free rotation of the OH relative to the Me. The 827 cm.⁻¹ band of C₂H₆ is a degenerate σ -vibration, and 1465 and 1495 cm.⁻¹ are σ -bands. The identification of the normal vibrations of C₂H₆ is largely completed.

R. C.

Infra-red spectrum of heavy water. E. F. BARKER and W. W. SLEATOR (J. Chem. Physics, 1935, 3, 660—663).—The absorption bands ν_2 and ν_3 for D₂O and ν_2 and ν_1 for HDO have been located in water vapour containing 90 and 40% of D. ν_3 for HDO is masked by the corresponding band for H₂O. The fine structure of the ν_2 bands agrees approx. with that calc. from mol. dimensions.

F. L. U.

Infra-red absorption spectrum of methyl deuteride. N. GINSBURG and E. F. BARKER (J. Chem. Physics, 1935, 3, 668—674; cf. A., 1934, 716).—The six fundamental vibrational frequencies of MeD have been observed and the fine structure of the bands resolved. Moments of inertia and inter-nuclear distances are calc.

F. L. U.

Infra-red absorption of cyanides and thiocyanates. W. GORDY and D. WILLIAMS (J. Chem. Physics, 1935, 3, 664—667; cf. A., 1934, 1288).—The absorption of MeCN, CH₂Ph·CN, MeCNS, and aq. solutions of HCN and of some simple and complex metal cyanides shows in all cases a characteristic band in the region 4.38—4.90 μ . Slight variations in the position are attributed to changes in the vibrational energy of the bound CN groups. An additional band shown by highly ionised cyanide solutions is attributed to CN'.

F. L. U.

Infra-red absorption spectra of plant and animal tissue and of various other substances. R. STAIR and W. W. COBLENTZ (J. Res. Nat. Bur. Stand., 1935, 15, 295—316).—The infra-red absorption

spectra to 15 μ has been studied for pure rubber, gutta-percha hydrocarbon, balata hydrocarbon, polyindene, polystyrene, indene, styrene, Cellophane, pokeweed pith, onion skin, moonwort-seed septum, cotton-seed wing, chitin, pith of feathers, fish bladder, dragon-fly wing, bat-wing, ovalbumin, egg membrane, gelatin, polyvinyl acetate and chloroacetate, glyptal resin, shellac, paraffin oil, sperm oil, linseed oil, CCl₄, (CH₂Cl)₂, PhEt, PhCl, *o*-C₆H₄Cl₂, EtOAc, PrⁿBr, BuⁿBr, and C₂HCl₅.

J. W. S.

Origin of the wing accompanying the Rayleigh line in liquids. S. C. SIRKAR (Nature, 1935, 136, 759—760).—The changes in intensity of the wings which accompany the dissolution of C₆H₆, C₁₀H₈, or Ph₂O in cyclohexane do not support the hypothesis of Gross and Vuks (A., 1935, 914).

L. S. T.

Determination of degree of depolarisation of light scattered by molecules. H. VOLKMANN (Ann. Physik, 1935, [v], 24, 457—484).—An apparatus is described by which the degree of depolarisation (Δ) of light scattered in CH₄, H₂, CO₂, and N₂O has been determined. The accuracy of former determinations is discussed. Δ for CH₄ is 0, indicating tetrahedral symmetry. The influence of the Raman effect on Δ for CH₄ is <0.001. Δ for CO₂ is 0.0724 \pm 0.003; for H₂, 0.009 \pm 0.001; for N₂O, 0.102 \pm 0.004.

A. J. M.

Rotational Raman spectrum of nitrous oxide. D. BENDER (Physical Rev., 1934, [ii], 45, 732).—Comparison of the rotational Raman spectra of N₂O and CO₂ shows no resolution of N₂O, the mol. of which is asymmetric.

L. S. T.

Raman effect in fuming sulphuric acid. J. CHÉDIN (Compt. rend., 1935, 201, 724—726).—Vals. are recorded for oleum with 10—68% of SO₃, and for H₂SO₄. Oleums rich in SO₃ have no Raman lines in common with H₂SO₄. This is attributed to formation of H₂S₂O₇.

H. J. E.

Raman spectrum of sodium nitrate, sodium acetate, and acetic acid. E. R. LAIRD and D. A. FRANKLIN (Physical Rev., 1934, [ii], 45, 738).—The Raman one-line spectrum for NaNO₃ solutions has been re-examined. The slight change in λ between dil. and conc. solutions and the marked change in λ for the crystals and the appearance of other lines in the solid have been confirmed. With solutions of NaOAc, there is no difference in appearance or position of the five lines found. The solid gives a strong continuous background with faint lines in approx. the same positions as solutions. All lines, except one, are different from those found for AcOH, in which the no. and position of the lines change markedly from the glacial acid to a 28% solution.

L. S. T.

Raman spectrum of arsenic trichloride. D. M. YOST and T. F. ANDERSON (J. Chem. Physics, 1935, 3, 754).—It is pointed out, with reference to a paper by Brodski and Sack (A., 1935, 1189), that central forces alone do not suffice for the treatment of mols. of the AsCl₃ type.

F. L. U.

Raman spectra of oxalic acid. J. H. HIBBEN (J. Chem. Physics, 1935, 3, 675—679).—Raman spectra of H₂C₂O₄, H₂C₂O₄·2H₂O, and of aq. and

EtOH solutions have been determined. The results indicate that in the anhyd. acid and aq. solutions the two $\cdot\text{CO}_2\text{H}$ groups behave differently, whilst in EtOH they behave similarly. Shifts due to C:O oscillations are either absent or are far weaker in the dihydrate. Chemical interpretations are suggested.

F. L. U.

Raman spectrum of the isomeric chloronitrobenzenes. R. MANZONI-ANSIDEI (Gazzetta, 1935, 65, 871—877).—Raman lines are recorded for *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$. The vals. of the frequency characteristic of the NO_2 group are: *o*- 1528, *m*- 1535, *p*- 1548 cm^{-1} . Measurements of other workers are discussed.

O. J. W.

Raman effect. XLV. Raman spectrum of organic substances. Poly-substituted benzenes. VII. K. W. F. KOHLRAUSCH and G. P. YPSILANTI. XLVI. Poly-substituted benzenes. VIII. A. W. REITZ and G. P. YPSILANTI. XLVII. Aromatic polycarboxylic acids. A. PONGRATZ and R. SEKA. XLVIII. Nuclear-substituted ethyl benzoates. K. W. F. KOHLRAUSCH and W. STOCKMAYER (Monatsh., 1935, 66, 285—298, 299—306, 307—315, 316—326).—XLV. The Raman spectra of *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$, *o*- and *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{OH}$, *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CN}$, *o*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{F}$, *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{Br}_2$, *p*- $\text{C}_6\text{H}_4\text{BrI}$, *p*- $\text{C}_6\text{H}_4\text{F}\cdot\text{NH}_2$, *p*- $\text{C}_6\text{H}_4\text{FI}$, and *p*- $\text{C}_6\text{H}_4\text{F}\cdot\text{OH}$ have been determined. Three lines found in the Raman spectrum of these substances occur also in that of C_6H_6 , and the degrees of depolarisation of these lines are almost identical with the corresponding ones for C_6H_6 . Only the line 1156 cm^{-1} occurs in *o*-, *m*-, and *p*-di-derivatives, in mono-derivatives, and in C_6H_6 itself. The lines 615, 999, and 1020 cm^{-1} occur independently of the substituent in mono-substituted derivatives, but in the di-derivatives 634 (corresponding with 615) occurs only in the spectrum of *p*-compounds, 994 only in that of *m*-compounds, and 1037 only in that of *o*-compounds. The special characteristics of the spectra of *p*-compounds are discussed.

XLVI. The Raman spectra of compounds of the type $\text{C}_6\text{H}_4\text{X}\cdot\text{OMe}$ [$\text{X}=\text{NH}_2$ (*o*, *m*, and *p*), OH (*o*, *m*, and *p*), Me (*o*, *m*, and *p*), F (*p*), Cl (*o* and *p*), Br (*o* and *p*), I (*o*, *m*, and *p*), CN (*p*)] have been determined. All *p*-derivatives show lines at 634, 1169, and 1590 cm^{-1} .

XLVII. The Raman spectra of *m*- and *p*- $\text{C}_6\text{H}_4(\text{CO}_2\text{X})_2$ ($\text{X}=\text{Me}$, Et), 1:2:3- and 1:3:5- $\text{C}_6\text{H}_3(\text{CO}_2\text{Me})_3$ have been determined. The positions of the double linkings in the nucleus with respect to the substituent groups cannot be found by a study of the constitutive effects of substituents on the frequencies of the nucleus.

XLVIII. The Raman spectra of compounds of the type $\text{C}_6\text{H}_4\text{X}\cdot\text{CO}_2\text{Et}$ ($\text{X}=\text{NH}_2$, OH , Cl , Br , NO_2 , *o*-, *m*-, and *p* in each case) have been determined. The effect of X on the inner vibrations of the NO_2 and CO_2R groups is discussed. The effect is strongest in the *o*-position, and the characteristic frequencies of the NO_2 and CO groups are increased by the introduction of further substituents, the increase being the greater the higher is the substituent in the series OH , NH_2 , Me , Cl , Br , CO_2R , NO_2 , *i.e.*, in the order in which

substituents tend to increase the dissociation const. of BzOH .

A. J. M.

Raman effect and organic chemistry: isopropylacetylene, isopropylethylene, and some of their derivatives. B. GREDY (Bull. Soc. chim., 1935, [v], 2, 1951—1958).—Raman lines are recorded for $\text{CPr}^{\beta}:\text{CH}$, $\text{CHPr}^{\beta}:\text{CH}_2$, and some of their derivatives. Lines characteristic of the double and triple linkings are found in all the substances. The influence of substituted Cl or Br on the double linking frequency at about 1600 cm^{-1} is confirmed.

O. J. W.

Raman effect and organic chemistry. Raman spectra of the ethylenic compounds $\text{CH}_2:\text{CHR}$. M. BOURGUEL and L. PLAUX (Bull. Soc. chim., 1935, [v], 2, 1958—1969).—Measurements are recorded for > 20 substances of the type $\text{CH}_2:\text{CHR}$ ($\text{R}=\text{a}$ variety of atoms and radicals). These all have five characteristic frequencies, each of which may vary within narrow limits. For butene the vals. are: 1295, 1417, 1642, 3004, and 3083 cm^{-1} . The various radicals R are classified according to their influence on the 1600 frequency. In derivatives of the type $\text{CH}_2:\text{CH}\cdot\text{CH}_2\text{R}'$ this frequency is const. at 1642 cm^{-1} .

O. J. W.

Raman spectra of methyldiethylcarbinol, benzyldimethylcarbinol, and the corresponding olefines. J. SAVARD (Compt. rend., 1935, 201, 833—835; cf. A., 1935, 681).—Data are recorded and compared.

H. J. E.

Polarisation of Raman radiation. F. HEIDENREICH (Z. Physik, 1935, 97, 277—299).—The method of circular polarisation (cf. Hanle, A., 1933, 114) has been applied to Raman displacements of $\text{C}_2\text{H}_2\text{Cl}_2$ (*cis* and *trans*), C_2Cl_4 , C_2Cl_6 , cyclohexane (I), and Ac_2O . Pure rotation broadening should be shown by inverted circular polarisation, as do PhMe , C_6H_6 , AcOH , and Ac_2O ; EtOH , H_2O , and (I) do not give inverted polarisation, and indicate that all broadening due to liquids is not rotation broadening. Sirkar's polarisation dispersion (cf. A., 1934, 942) could not be observed.

A. B. D. C.

Depolarisation in the Raman spectra of halogenated derivatives of ethyl acetate. H. C. CHENG (J. Chim. phys., 1935, 32, 541—548; cf. A., 1934, 1056).—Raman spectra of AcOH , EtOAc , $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$, $\text{CHCl}_2\cdot\text{CO}_2\text{Et}$, and $\text{CCl}_3\cdot\text{CO}_2\text{Et}$ have been measured, and the fundamental frequencies of $\text{C}\cdot\text{CO}_2\text{Et}$, CH_2Cl , CHCl_2 , and CCl_3 ascertained. Various depolarised lines are fully discussed in relation to the groupings in the molecules.

T. G. P.

Intensity and polarisation of Raman radiation from liquids. A. V. RAO (Z. Physik, 1935, 97, 154—157).—The relative intensity and polarisation of Q branches of the different Raman lines of C_6H_6 , CCl_4 , CHCl_3 , and AsCl_3 have been determined; the total depolarisation obtained from the Raman lines is an appreciable fraction of the depolarisation of the total scattered radiation.

A. B. D. C.

Raman effect of organic molecules. Vibration spectra of acrylonitrile and ethylene oxide. B. TMM and R. MECKE (Z. Physik, 1935, 97, 221—224).—Frequencies are given for $\text{C}_2\text{H}_3\cdot\text{CN}$ and

(CH₂)₂O, and are classed as valency frequencies of the vinyl groups, ring frequencies, and CH frequencies.

A. B. D. C.

Relation between the ultra-violet absorption spectrum and the Raman spectrum of pyridine.

V. HENRI and P. ANGENOT (Compt. rend., 1935, 201, 895—896).—Fundamental frequencies of 600, 857, 993, 1031, and 1159 cm.⁻¹ have been observed in the ultra-violet absorption spectrum of the vapour of C₅H₅N (I) at various pressures. The frequencies correspond with those of the Raman spectrum of (I) and C₆H₆, since CH and N have nearly the same mass. For the higher electronic level the frequency 542 cm.⁻¹ has been observed. Ultra-violet light of $\lambda < 2750 \text{ \AA}$. falling on (I) is photochemically active and causes predissociation.

R. S. B.

Application of the Raman effect to the *cis-trans* isomerism of methylcyclohexanols.

J. TABUTEAU (Compt. rend., 1935, 201, 897—898).—The Raman spectra of *cis*- and *trans*-*o*-, *m*-, and *p*-methylcyclohexanol differ most for frequencies 300—900 cm.⁻¹ The spectra of the *cis*-alcohols and -acetates have many lines in common, but with the *trans*-compounds the no. of common lines is much less. The distinction between *cis*- and *trans*-isomerides decreases in the order *o*, *m*, *p*, and is $<$ with the borneols and myrtanols owing to the relatively small mass of the Me.

R. S. B.

Stability of the Lenard light centres in zinc sulphide. N. RIEHL (Ann. Physik, 1935, [v], 24, 536—542).—An investigation has been made to discover whether the Lenard light centres change spontaneously in the course of time, depending on the history of the phosphor. ZnS phosphors which have been kept in the dark for some years show a decreased sensitivity to α -ray phosphorescence and probably also to ordinary light phosphorescence, showing that spontaneous changes in the lattice or light centres have taken place. X-Ray analysis shows that the ageing is not due to a change of the wurtzite lattice into the Zn-blende lattice. The aged phosphor can be partly regenerated by prolonged heating at 500°. The thermodynamic instability of the light centres may be due to the rapid cooling of the phosphor when first prepared, the equilibrium being frozen, for minerals which have cooled comparatively slowly show but feeble phosphorescence. The existence of phosphorescent minerals indicates that the capacity to phosphoresce is not completely lost by ageing.

A. J. M.

Luminescent properties of zinc sulphide in relation to X-rays. L. LEVY and D. W. WEST (Brit. J. Radiol., 1935, 8, 184—185).—The afterglow and latent fluorescence of "Fluorazure" ZnS intensifying screens becomes very feeble if a trace of Ni is added before firing the powder. A screen made from ZnS and CdS is superior to one from CdWO₄.

CH. ABS. (e)

Polarised fluorescence of organic compounds. S. M. MITRA (Z. Physik, 1935, 97, 138—153).—Variation in polarisation of fluorescence radiation from succinylfluorescein and eosin with temp., viscosity, and concn. of solution, and λ of the exciting radiation is given for the solvents glycerol, castor oil, sugar solutions, collodion, and gelatin.

A. B. D. C.

Rôle of oxidation-reduction potential and acidity in quenching of fluorescence in solutions.

K. WEBER (Z. physikal. Chem., 1935, B, 30, 69—83).

—For quinine sulphate and aesculin the logarithm of the concn., k , of halogen ion which halves the fluorescence intensity increases linearly as the reduction-oxidation potential, E , of the halogen ion becomes increasingly negative, whilst for fluorescein and uranine the relation between k and E is more complex. k rises with [H⁺]. Following Schneider (A., 1935, 681) and assuming quenching by halogen ions to be a sensitised photo-oxidation, a reaction mechanism is postulated which leads to quenching formulae agreeing with experiment. These latter yield quantitatively the observed relation between k and E , so that from k the differences between the E vals. of the halogens may be derived. For the quenching of the fluorescence of the above substances by cations there is no connexion between k and E , suggesting that oxidation-reduction reactions play no part.

R. C.

Photochemical reactions connected with the quenching of fluorescence of dyes by ferrous ions in solution.

J. WEISS (Nature, 1935, 136, 794—795; cf. A., 1935, 1211).—Irradiation of different dyes, e.g., methylene-blue, thionine, brilliant-cresyl-blue, etc., in acid FeSO₄ with the visible radiation of a strong C arc produces bleaching or a change in colour, due to the formation of leuco-dyes, which is irreversible when the Fe⁺⁺⁺ is pptd. by hydrolysis. With the above dyes the process is completely reversible in the dark, the Fe⁺⁺⁺ being reduced by the leuco-dye. The direct, unsensitised photochemical process is obtained by irradiating 0.5M-FeSO₄ in H₂SO₄ with light from a strong Hg arc, H₂ being formed when O₂ is excluded. The bearing of these results on biological problems is discussed.

L. S. T.

Dependence of fluorescence spectra on the viscosity of the solvent.

A. JABLONSKI (Physikal. Z. Sovietunion, 1935, 8, 105—108).—The results of Tumermann (A., 1935, 807) are not inconsistent with those of Jablonski (A., 1932, 213).

A. J. M.

Photoluminescence.

F. OBERHAUSER and R. CABRERA (Anal. Fac. Filos. Univ. Chile, 1934, 1, 28—44; cf. A., 1929, 793).—Org. acids containing a trace of fluorescein exhibit fluorescence and phosphorescence when exposed to light sources.

F. R. G.

Diffusion in the bulb of a mercury rectifier.

D. R. KANASKOV (Physikal. Z. Sovietunion, 1935, 8, 119—135).—The dark space in a Hg rectifier has been examined with a Langmuir probe. Linear relations exist between (a) log random electron current or (b) log concn. of electrons, or (c) the potential, at a point along the axis of the tube and the distance of the point from the cathode.

T. G. P.

Bulk and superficial conductivities of cuprous oxide.

L. DUBAR (Compt. rend., 1935, 201, 883—885).—Using conductors of different surface the bulk and superficial conductivities (σ , ω) of Cu₂O have been determined in dry air at 15.8°; $\sigma = 1.61 \times 10^{-8}$ mho cm./cm.² and $\omega = 21.7 \times 10^{-8}$ mho cm./cm. σ is unaffected by H₂O vapour, but ω decreases owing to

adsorption. ω is greatly reduced by the action of dil. H_3PO_4 . R. S. B.

Investigations on electrets. A. GEMANT (Phil. Mag., 1935, [vii], 20, 929—952).—The main results of Eguchi (A., 1925, ii, 462) have been verified. Electrets prepared by allowing substances to solidify in a field of 5—10 kv. per cm. are the electrical analogues of permanent magnets. The field on their free surface may be utilised provided they are nearly short-circuited and kept dry. The charge is acquired either by ionic space charges (heterocharge) or by the orientation of dipole mols. (homocharge) which may be accompanied by a secondary piezoelectric effect. Acidic substances yield ions producing heterocharge, whilst non-dissociating dipoles, chiefly esters, yield homocharge. For mixtures an additive law is valid. T. G. P.

Elimination of peculiarities in the dielectric behaviour of water vapour. J. D. STRANATHAN (Physical Rev., 1934, [ii], 45, 741).—The breaks in the pressure-($K-1$) curves for H_2O vapour have been eliminated by using a brass condenser, and quartz or Pyrex insulators, and by exercising a strict control on the rate at which the vapour enters the condenser. The electric moment of the H_2O mol. is 1.83×10^{-18} . L. S. T.

Dipole moments and structure of quinoline derivatives.—See A., 1935, 1506.

Physical methods in chemistry. IV. Dipole measurement and its application to chemistry. P. C. HENRIQUEZ and L. J. N. VAN DER HULST (Chem. Weekblad, 1935, 32, 636—645).—The calculation of at., electronic, and orientation polarisation and the relationships between dipole moment and structure are discussed. D. R. D.

Configuration of the mercuric halides. W. J. CURRAN and H. H. WENZKE (J. Amer. Chem. Soc., 1935, 57, 2162—2163).—Electric moments of $HgPh_2$, $HgCl_2$, $HgBr_2$, and HgI_2 have been determined. The vals. are < those calc. from solubility data. The configuration of these compounds is not linear. E. S. H.

Dipole measurements with isomeric platocomplexes. K. A. JENSEN (Z. anorg. Chem., 1935, 225, 97—114).—Determinations of the dipole moments of compounds $[PtX_2(SR_2)_2]$ ($X=Cl, Br, I, NO_2, NO_3$, and $R=Et, Pr^a, Pr^b, Bu^a, Bu^b, CHMeEt, CH_2Ph$) give $2.2-2.5 \times 10^{-18}$ e.s. unit for the α -compounds and about 9×10^{-18} (Cl, Br) or 13×10^{-18} (NO_2, NO_3) for the β -compounds. The results indicate that the α -compounds are *trans*- and the β *cis*-isomerides. Cryoscopic measurements in C_6H_6 show both the α - and β -chlorides to have simple mols., the latter being associated in conc. solutions. No interconversion of the α - and β -forms occurs in C_6H_6 , but it does in the case of $[PtCl_2(Et_2Sc)_2]$. F. L. U.

Dipole moments of ethyl and isoamyl borates and triphenyl phosphate. E. G. COWLEY and J. R. PARTINGTON (Nature, 1935, 136, 643).—The vals. obtained in C_6H_6 at 20° are 0.75, 0.81, and 2.79 *D*, respectively. P_∞ and P_E are 50.5 and 38.63, 94.3 and 80.20, 252.5 and 87.41 c.c., respectively. L. S. T.

Dipole moments of certain organic compounds. J. N. PEARCE and L. F. BERHENKE (Proc. Iowa Acad. Sci., 1934, 41, 141—142).—The dielectric consts. of *p*- $C_6H_4Br \cdot CHO$, *p*- $C_6H_4Me \cdot CHO$, *p*- $OH \cdot C_6H_4 \cdot CHO$, and *p*-anisaldehyde in dioxan at 25° gave dipole moments 2.20, 3.27, 4.18, and 3.70×10^{-18} , respectively. The angle between the CHO moment and the line through the 1:4 C atoms of the C_6H_6 nucleus was 51° . Those between the directions of the OH and CHO group moments were $50^\circ, 49^\circ$, respectively. CH. ABS. (e)

Structure of antipyrine [and pyramidone] in aqueous solution. G. DEVOTO (Atti R. Accad. Lincei, 1935, 21, 819—820).—The dielectric consts. of aq. antipyrine (I) and pyramidone (II) of various concns. have been determined at 25° ($\lambda 90$ cm.). $d\epsilon/dc=1.5$ for (I) and -6.7 for (II), indicating that polar structures for these compounds are untenable. D. R. D.

Transitions in camphor and chemically related compounds. I. Dipole rotation in crystalline solids. W. A. YAGER and S. O. MORGAN. II. Vibration of atomic groups. A. H. WHITE and S. O. MORGAN (J. Amer. Chem. Soc., 1935, 57, 2071—2078, 2078—2086).—I. Determination of the dielectric properties of *d*- and *dl*-camphor, *d*-camphoric anhydride, borneol, *isoborneol*, and bornyl chloride shows that these compounds undergo transitions in the solid state. Above the transition temp. the dielectric const. of the solid is that normally expected of the polar substance in the liquid state; below the transition temp. the dielectric const. has a low val., approx. equal to n^2 . This behaviour is explained by the rotation of dipoles in the solid.

II. An increase of about 18 g.-cal./ $^\circ C$./mol. in the sp. heat of *d*-camphor at the transition at -30° has been observed; it is assumed that energetic intramol. vibration arises. The total polarisation behaviour of *d*-camphor in dil. solution is explained by assuming that at room temp. dipole moment is < and at. polarisation > was formerly supposed, and that at. polarisation begins to decline with falling temp. below -10° , when the transition to the more rigid mols. begins. Similar transitions, observed in crystals of *cyclohexane* derivatives, appear to be due to transformations from the rigid to the pliable forms of the mols. forming the crystals. E. S. H.

Calculation of dipole interaction. R. P. BELL (Trans. Faraday Soc., 1935, 31, 1557—1560).—The method proposed by Martin (A., 1934, 1063) for calculating dipole interaction is shown to be valid for sufficiently small vals. of the dipole moment. F. L. U.

Reactivity and dipole moment. E. HERTEL and E. DUMONT (Z. physikal. Chem., 1935, B, 30, 139—148; cf. A., 1935, 1232).—Measurement of the dipole moments of *p*-substituted derivatives of $NPhMe_2$ and the corresponding substitution products of C_6H_6 has shown that the effect of a substituent on the reactivity of a functional group (NMe_2) runs parallel with its contribution to the dipole moment of the compound. It is suggested in explanation that the group moment of a substituent is the result chiefly of a considerable dissymmetry in the distribution

of charge about the point of attachment to the ring, and that the reactivity of a functional group is determined by the state of the nuclear C to which it is attached, this in its turn being a function of the states of the other C atoms of the ring. R. C.

Index of refraction of HCl from 1 to 10 μ . R. ROLLEFSON and A. H. ROLLEFSON (J. Chem. Physics, 1935, 3, 434).—Dispersion measurements over 1—10 μ show that the dispersion curve is matched best by using the vals. 1.00×10^{-10} and 1.18×10^{-18} e.s.u. for the effective charge of the rotator-vibrator and the electric moment of the rotator, respectively. N. M. B.

Double refraction of chitin tendons. J. M. DIEHL and G. VAN ITTERSON, jun. (Kolloid-Z., 1935, 73, 142—146).—When chitin is immersed in glycerol-quinoline mixtures its double refraction changes from positive to negative as n of the liquid mixture increases. E. S. H.

Maximum rotations of carboxylic acids containing a phenylethyl group.—See this vol., 70.

Optical rotatory power of solutions in an electric field. J. KUNZ and A. McLEAN (Nature, 1935, 136, 795—796).—Changes in optical rotatory power are observed when solutions of 2-*l*-menthyl H 3-nitrophthalate in C_6H_6 or PhMe are placed in an electric field. This behaviour is distinct from the Kerr effect and is attributed to the electric moment induced in the solvent mols. by the electric field. Anomalous effects are obtained with the 2-Et ester. L. S. T.

Magnetic birefringence in solutions of paramagnetic salts of rare earths. S. W. CHINCHALKAR (Phil. Mag., 1935, [vii], 20, 856—858; cf. A., 1932, 677).—The results of Haenny (cf. *ibid.*, 909) are reduced to the same equiv. concn., and the connexion between the birefringence and the orbital moment of the ion is discussed. N. M. B.

Temperature variation of the electro-optical Kerr effect of nitrobenzene at its transition point. W. HERZOG (Z. Physik, 1935, 97, 233—241).—No discontinuity was observed at the Wolfke-Mazur transition point (cf. A., 1932, 329). A. B. D. C.

Magneto-optics. C. G. DARWIN (Proc. Roy. Soc., 1935, A, 151, 512—539).—Theoretical. A formal method suitable for the discussion of magneto-optics, irrespective of the underlying at. theory, is developed. The magneto-optic effects of material of any at. character are discussed. The formulæ are applied to test the experimental results of the Kerr effect. L. L. B.

Discussion of experiments on the time-lag in the magneto-optic effect. G. F. HULL (Physical Rev., 1934, [ii], 45, 738). L. S. T.

Affinity in Hume-Rothery phases. U. DEHLINGER (Metallwirts., 1935, 14, 145—149; Chem. Zentr., 1935, i, 2130).—Theoretical. The affinity in Hume-Rothery phases is explained by the attribution of a definite lattice linking to each valency electron. The energy levels are calc. from Bloch's wave theory of metallic electrons, where λ must be an integral sub-multiple of the lattice spacing. Highly

symmetrical lattices, for which there are insufficient electrons for twofold occupation of each linking, can be formed only at high temp., when free rotation within the lattice is possible. J. S. A.

Planar configuration of quadricovalent nickel, palladium, and platinum: dithio-oxalate derivatives. E. G. COX, W. WARDLAW, and K. C. WEBSTER (J.C.S., 1935, 1475—1480).—The three salts $K_2[M^{II}(COS)_4]$ ($M^{II} = Ni, Pt, \text{ and } Pd$) have been prepared, and are shown to be isomorphous. The four valencies to the metal atom are co-planar in each case. The crystals are monoclinic; 4 mols. in unit cell; space-group $A2/a (C_{2h}^6)$. The principal interat. distances were Ni-S 2.30, Pd-S 2.44, Pt-S 2.44, C-S 1.83, K-O 2.57—3.0, K-S 3.73 (min.) Å. Crystallographic and X-ray data are given. H. J. E.

Electronic structures of molecules. XIV. Linear triatomic molecules, especially carbon dioxide. R. S. MULLIKEN (J. Chem. Physics, 1935, 3, 720—739; cf. A., 1935, 1188).—Electron configurations of a no. of triat. linear mols. are given, and ionisation potentials of CO_2 , CS_2 , N_2O , and $HgCl_2$ are interpreted in relation to these. An explanation of the triangular form of NO_2 is given. F. L. U.

"Most probable" locations of the valency electrons in the carbon atom. W. P. DAVEY (Physical Rev., 1934, [ii], 45, 763).—Theoretical. L. S. T.

Deuterium. II. III. D. MACGILLAVRY (Chem. Weekblad, 1935, 32, 650—655, 679—684; cf. A., 1935, 1185).—A further review.

Deuterium and X-ray absorption. D. K. FROMAN (Physical Rev., 1934, [ii], 45, 731).—The presence of D_2 in ordinary H_2 does not account for the peculiarity in its absorption of X-rays in the range 0.5—0.6 Å. L. S. T.

Sputtering of metals by incidence of slow ions and measurement of sputtering swelling values. H. LÜDER (Z. Physik, 1935, 97, 158—170).—Degree of sputtering by positive ions of energies of 40 volts and upwards was determined from the resistance of the sputtered wire. Swelling val. or min. energy of sputtering was determined for A^+ ions incident on Ni, Cu, Fe, and W, for K^+ , Cs^+ , and Li^+ incident on W, and for Cs^+ on Cu. A. B. D. C.

Molecular ions from heated salts of some of the alkali metals. L. L. BARNES (Physical Rev., 1934, [ii], 45, 751).—At temp. just < m.p., KCl give an ion of mass K_2Cl^+ , and K_2SO_4 one of mass $K_3SO_4^+$. Salts of other alkali metals give similar ions. L. S. T.

Periodic system of energy coefficients. A. E. FERSMAN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 173—176; cf. A., 1935, 1305).—The *VEK* vals. (energy of unit valency of an ion) for a large no. of ions are tabulated according to the periodic classification, and correlated. J. W. S.

Solution of variation problems in quantum mechanics. A. SCHUCHOVICKI (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 161—164).—Mathematical. J. W. S.

Temperatures and heat effects of genotypic transformation of alkali salts of long-chain fatty acids. P. A. THIESSEN and J. VON KLENCK [with H. GOCKOWIACK and J. STAUFF] (*Z. physikal. Chem.*, 1935, **174**, 335—358; cf. *A.*, 1933, 1004, 1011).—The temp. at which the heat effect, Q , corresponding with genotypic transformation sets in has been determined. The dielectric const.-temp. curve is discontinuous at the transformation point. For a single crystal of Na stearate on heating up through 49° the double refraction undergoes an abrupt irreversible change in sign. Q increases with the chain length and also runs parallel with the radius of the cation. Above the transformation temp. the sp. heat rises discontinuously. R. C.

Kinetic interpretation of internal effects. V. NJEGOVAN (*Z. Physik*, 1935, **97**, 390—394).—Rotation and vibration of elastic mol. of an ideal gas effectively decrease the radius of the mol. and so liberate energy. This hypothesis is applied to thermal dissociation, ionisation, and gas degeneracy. A. B. D. C.

Movement of a heavy drop in the acoustic field. S. V. GORBATSHEV and A. B. SEVERNY (*Kolloid-Z.*, 1935, **73**, 146—154).—Theoretical. E. S. H.

Relation between internuclear distances and force constants of molecules and its application to polyatomic molecules. R. M. BADGER (*J. Chem. Physics*, 1935, **3**, 710—714; cf. *A.*, 1934, 477).—The relation between internuclear distances and force consts. found for diat. mols. persists in polyat. mols. This fact provides a method whereby internuclear distances in the latter can be calc. from vibrational data alone. F. L. U.

Mean free paths of molecules and wave mechanics. J. A. EEDRIDGE (*Proc. Iowa Acad. Sci.*, 1934, **41**, 257).—Direct determinations of the mean free path of H_2 , N_2 , and O_2 yield vals. for the effective cross-section of the mol. which are 4—5 times those based on viscosity data; theoretical factor should be > 2 . CH. ABS. (e)

Electrostatic interaction in atoms. R. F. BACHER and S. GOUDSMIT (*Physical Rev.*, 1934, [ii], **45**, 767). L. S. T.

Vibrations and internal rotation of a chain of four atoms. L. S. KASSEL and C. W. MONTGOMERY (*Physical Rev.*, 1934, [ii], **45**, 766).—The dynamical behaviour of a chain of four equal atoms with tetrahedral bond angles has been studied in an attempt to classify the infra-red and Raman spectra of the higher hydrocarbons. Extra Raman lines observed by Kohlrusch and the tendency of long-chain hydrocarbons to exist in a linear form are explained. L. S. T.

Hydrocarbon linking additivity. V. DEITZ (*J. Chem. Physics*, 1935, **3**, 436).—Corrections previously proposed for obtaining linking additivity (cf. *A.*, 1935, 284) are tested with the help of experimental data (cf. Kistiakowsky, *ibid.*, 825) on the heats of hydrogenation of some olefines. N. M. B.

Fundamental frequencies of the cyanogen molecule. S. C. WOO, T. K. LIU, and T. C. CHU

(*J. Chinese Chem. Soc.*, 1935, **3**, 301—307).—The fundamental frequencies assigned by Kistiakowski *et al.* (*A.*, 1934, 30, 145) are criticised. The restoring force consts. of linkings in the mols. HCN, ClCN, BrCN, $(CN)_2$, and C_2H_2 have been calc. from the fundamental frequencies of the valency vibrations. All the cyanides have the same type of CN linking. The frequencies have been re-assigned on the basis of the above calculations, the selection rule for infrared and Raman spectra, and heats of formation of linkings. A. J. M.

Quantum-mechanical discussion of orientation of substituents in aromatic molecules. G. W. WHELAND and L. PAULING (*J. Amer. Chem. Soc.*, 1935, **57**, 2086—2095).—Using the method of mol. orbitals, the charge distribution in aromatic mols. undergoing substitution is discussed quantitatively, taking into consideration the inductive effect, the resonance effect, and the polarising effect of the attacking group. With reasonable vals. for the parameters involved, the calc. charge distributions for several aromatic compounds are in qual. agreement with experimental results regarding position and rate of substitution. E. S. H.

Effect of surface tension on flow from Poncelet apertures. H. LAUFFER (*Forsch. Ing.*, 1934, **5**, A, 266—274; *Chem. Zentr.*, 1935, i, 1987).—Theoretical. Contrary to accepted views, the flow from small apertures at low pressure is augmented by the influence of surface tension. J. S. A.

Aluminium alkoxides and their parachors. R. A. ROBINSON and D. A. PEAK (*J. Physical Chem.*, 1935, **39**, 1125—1133).—Surface tension and density data and parachor vals. are given for *Al acetylacetonate* (I), m.p. 192°, *aluminioethyl acetoacetate* (II), m.p. 78—79°, *Al diethylmalonate* (III), m.p. 95—96°, *Cr acetylacetonate*, m.p. 212°, $[Al(OEt)_3]_4$, m.p. 146—151°, $[Al(OPr^a)_3]_4$, m.p. 106—108°, $[Al(OPr^b)_3]_4$, m.p. 118°, $[Al(OBu^a)_3]_4$, m.p. 102—106°, $[Al(OBu^b)_3]_4$, m.p. 208—210°, sec.- $[Al(OBu)_3]_4$, b.p. 174—176°/5 mm., *Sb(OEt)_3*, b.p. 99.5°/13 mm. Assuming singlet linkings in (I), (II), and (III), the mean parachor of Al is 39.5. The parachor deficiencies which occur in the alkoxides may be accounted for by an 8-membered ring in which the O are attached to Al by singlet linkings. R. S.

The parachor as a function of density and molecular volume of a substance in its different chemical states. I. R. MOROZOV (*J. Gen. Chem. Russ.*, 1935, **5**, 1020—1023).—The parachor is calc. from $P = (V + V_1)(2dV_1/V)^{\frac{1}{2}}$, where V is the sum of the vols. of the constituent atoms, V_1 is the mol. vol. of the substance, and d is the density. R. T.

Investigations on diffusion of cathode rays by means of the cloud chamber. I. GUNTHER (*Ann. Physik*, 1935, [v], **24**, 377—392).—The directional distribution of cathode rays after passing various thickness of matter was particularly studied. The results suggest that the passage of rays through matter is a combination of absorption and diffusion processes. J. W. S.

Absorption of short-wave-length X-rays. W. V. MAYNEORD and J. E. ROBERTS (*Nature*, 1935, **136**,

793).—For elements up to Ca the mean absorption per electron for X-rays of λ 59 X is in agreement with the Klein-Nishina formula. The photo-electric absorption coeff. per electron varies according to (at. no.)³.
L. S. T.

Widths of X-ray bands in solids. J. REHNER, jun. (Physical Rev., 1934, [ii], 45, 735).—Theoretical (cf. A., 1934, 576).
L. S. T.

X-Ray and magnetic measurements of KCl powders in relation to lattice distortion and photochemical coloration. G. W. BRINDLEY, F. W. SPIERS, and F. E. HOARE (Phil. Mag., 1935, [vii], 20, 1041—1054).—Comparisons of high-order spectra of finely-ground and pptd. KCl show that the greater photo-coloration of the former, which has been attributed to flaws and cracks (Smekal), is not due to lattice distortion. The question of extinction is considered in detail. Grinding reduces the diamagnetic susceptibility of KCl only from 39.3×10^{-6} to 38.8×10^{-6} , confirming the above conclusion.
T. G. P.

Examination of electro-deposited nickel coatings by X-ray diffraction. W. A. WOOD (Phil. Mag., 1935, [vii], 20, 964—971).—Specimens of electro-deposited Ni differing in hardness and initial brightness have been examined. Brightness is associated with the selective orientation of the metal grains, and hardness with the degree of diffusion of the X-ray diffraction spectra. The grain size has been estimated from the broadening of the spectral lines for a series of deposits of known hardness.
T. G. P.

X-Ray examination of lattice distortion in copper and nickel powders. G. W. BRINDLEY and F. W. SPIERS (Phil. Mag., 1935, [vii], 20, 882—893; cf. A., 1935, 150).—The scattering factors for Cu $K\alpha$ radiation of finely filed Cu and Ni are < those of chemically prepared powders. The diminution increases with the order of the spectrum. The average displacements due to lattice distortion caused by filing are 0.106 Å. for Cu and 0.083 Å. for Ni, and are explicable if distortion is a random displacement of atoms from the points of the undistorted lattice. Scattering factors for the (200) reflexions indicate, however, that distortion is not entirely random.
T. G. P.

Discontinuous variation in the diffusion of X-rays with the angle of diffusion. J. LAVAL (Compt. rend., 1935, 201, 889—891).—For a beam of X-rays of λ incident at an angle ϕ on Al, Cr, Ni, In, Mo, Ag, Sb, Pt, and Au the diffusion of the rays varies discontinuously with $\sin \phi/2$. For similarly placed discontinuities $\lambda \sin \phi/2$ is a linear function of at. no.
R. S. B.

Effect of additions of cadmium on growth of zinc crystals. E. P. T. TYNDALL (Proc. Iowa Acad. Sci., 1934, 41, 252).—In Zn containing several tenths of 1% of Cd, mosaic formation was largely prevented (cf. Hoyem and Tyndall, A., 1929, 246).
CH. ABS. (e)

Relation between the mechanical strain and the intensity of X-rays reflected by a quartz plate. I. E. FUKUSHIMA (Bull. Inst. Phys. Chem.

Res. Japan, 1935, 14, 1105—1112).—Intensities of X-rays reflected from a strained quartz plate have been measured. The distribution of intensity depends on the distribution of strain.
R. S.

Relation between amorphous and crystalline scattering and its application to crystal analysis. N. S. GINGRICH and B. E. WARREN (Physical Rev., 1934, [ii], 45, 762—763).—An expression for the average radial distribution of atoms about any one atom, expressed as a series over the no. of lines in the powder pattern, is given. Interat. distances can be obtained directly without determining a complete structure.
L. S. T.

Structure of layer lattices. W. LOTMAR (Z. Krist., 1935, 91, 187—191).—To explain the observed broadening of (*hkl*) reflexions in layer lattices as compared with the (*hko*) and (*00l*), a particular distortion is suggested which leaves the (*hko*) planes undisturbed.
B. W. R.

Alternating axes and symmetry symbols in crystallography. J. D. H. DONNAY (J. Washington Acad. Sci., 1935, 25, 476—488).—A discussion of the use and nomenclature of the alternating axis, regarded as a single symmetry operation, in point- and space-group theory. The international point-group symbols are tabulated with the other notations in use.
B. W. R.

Advantages of employing four-index notation for crystals of rhombohedral symmetry. H. UNGEMACH (Z. Krist., 1935, 91, 97—113).—The reasons for preferring the Bravais to the Miller system for crystallographic calculation and description are given.
B. W. R.

Growth of metal crystals in metal vapour. IV. M. STRAUMANIS (Z. physikal. Chem., 1935, B, 30, 132—138; cf. A., 1934, 946).—Experiments have been made on the sublimation of Te and Se in H₂ and the equilibrium crystal forms determined. The results do not wholly agree with Stranski's theory of homopolar crystal growth.
R. C.

X-Ray diffraction in solutions. J. A. PRINS and R. FONTEYNE (Physica, 1935, 2, 1016—1028; cf. A., 1935, 931).—“Superarrangement” of the cations is present with ThCl₄, UO₂Cl₂, La(NO₃)₃, Cd(NO₃)₂, Zn(NO₃)₂, Ni(NO₃)₂, ZnCl₂, ZnI₂, and NiCl₂; it is probable with the multivalent anions of Na₂WO₄, Na₂MoO₄, H₂PtCl₆, HIO₄, HClO₄, and H₂SO₄. No such arrangement is found in univalent cations. HIO₃; CdI₂ in H₂O or EtOH; CdCl₂, Hg(NO₃)₂, Na₃(PW₁₂O₄₀), Ce₂(SO₄)₃, and Zr(NO₃)₄ in H₂O exhibit only gaseous distribution. Superarrangement is related to solvation. d^{18} and n_D^{20} have been determined for *M*/15 to *M*/85 aq. Th(NO₃)₄.
T. G. P.

Cybotactic group structure of isopentane near the critical point. C. A. BENZ (Proc. Iowa Acad. Sci., 1934, 41, 249—250; cf. A., 1934, 1297).—X-Ray diffraction intensity curves were measured at various points on the isothermal diagram. There is no sharp transition as the gaseous state is approached. Cybotactic groups appear in regions commonly known as gas if the sp. vol. is kept near that of a liquid.
CH. ABS. (e)

Dimorphism of trinitroresorcinol, bromobenzhydrazine, and benzaldehyde-*p*-nitrophenylhydrazone. R. FISCHER and A. KOFLER (Mikrochem., 1935, 19, 38—46).—The following stable (*s*) and metastable (*ms*) forms are obtained on vac. sublimation. Trinitroresorcinol: (*s*), m.p. 177°, monoclinic prisms of high optic axial angle; (*ms*), m.p. 165.5°, trigonal prisms, uniaxial and optically negative. "Bromobenzhydrazine": (*s*), m.p. 165°, rectangular monoclinic prisms with high double refraction; (*ms*) monoclinic plates, m.p. 159°. Benzaldehyde-*p*-nitrophenylhydrazone: (*s*), stout monoclinic rods, m.p. 261°; (*ms*), thin ill-formed monoclinic crystals, m.p. 234—236°. J. S. A.

Silicon disulphide, a fibrous inorganic compound with chain molecules. E. ZINTL and K. LOOSEN (Z. physikal. Chem., 1935, 174, 301—311).—In respect of the character of the constituent units of its lattice SiS_2 is intermediate between the mols. of the mol. lattice of CO_2 and the three-dimensional macromols. of SiO_2 in quartz. It forms on sublimation flexible fibres, which consist of one-dimensional macromols. oriented parallel to each other. The crystals are rhombic and the probable space-group is V_2^6 . R. C.

Orthonitric acid, H_3NO_4 . E. ZINTL and W. HAUCKE (Z. physikal. Chem., 1935, 174, 312—316).—Comparison of the powder diagram of $\text{HNO}_3 \cdot \text{H}_2\text{O}$ with those of the five low-pressure modifications of NH_4NO_3 and that of H_3PO_4 makes it appear not improbable that $\text{HNO}_3 \cdot \text{H}_2\text{O}$ is orthonitric acid. R. C.

Crystal growth of the alkali halides. Z. GYUJAI (Z. Krist., 1935, 91, 142—153).—Crystallisation from conc. solution, vapour, and melt of NaCl and KCl is studied microscopically, and the chief directions of growth from the nucleus are described. B. W. R.

Crystal structure of $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$. C. D. WEST (Z. Krist., 1935, 91, 181—186).—This typical member of the isomorphous orthorhombic pentamines $[\text{R}(\text{NH}_3)_5\text{X}]\text{Y}_2$ has a_0 13.32, b_0 6.71, c_0 10.42 Å., space-group V_8^{16} . The 16 necessary parameters are determined, and the structure is compared with that of the hexamines $\text{R}(\text{NH}_3)_6\text{Y}_2$. B. W. R.

Structure of green basic cobalt bromide. W. FEITKNECHT and W. LOTMAR (Z. Krist., 1935, 91, 136—141).—The three isomorphous basic compounds, basic Zn bromide III, green Co bromide and iodide, are investigated by X-rays. The existence of regular layers of pure hydroxide groups at intervals of 8.2 Å. is established; the intervening material is randomly arranged, and its origin and relations are discussed. B. W. R.

Crystal structure of nickel sulphate heptahydrate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$. C. A. BEEVERS and C. M. SCHWARTZ (Z. Krist., 1935, 91, 157—169).—The at. parameters of the orthorhombic variety have been determined, using Patterson's method for the location of Ni and S and a double Fourier analysis for the remaining parameters. 6 H_2O surround Ni forming an almost octahedral group. The structure is compared with that of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. B. W. R.

Crystal structure of potassium persulphate, $\text{K}_2\text{S}_2\text{O}_8$. R. C. KEEN (Z. Krist., 1935, 91, 129—135).—The cell is triclinic, a_0 5.10, b_0 6.83, c_0 5.40 Å., α 106° 54', β 90° 10', γ 102° 35', space-group C_1^1 . At. parameters are found from intensity measurements. B. W. R.

Crystallography of the copper-pyridine-saccharin complex. J. BENTEMA, P. TERPSTRA, and J. J. DE VRIEZE (Pharm. Weekblad, 1935, 72, 1287—1294).— $\text{Cu}(\text{C}_5\text{H}_5\text{N}, \text{H}_2\text{O}, \text{C}_6\text{H}_5\text{O}_3\text{NS})_2$ (A., 1933, 732) forms rhombic bipyramidal crystals with 4 mols. in the unit cell of dimensions a 9.50, b 21.57, c 13.16 Å., space-group V_8^{20} . Full crystallographic data are given and the orientation of the constituent mols. is discussed. D. R. D.

Structure of natural wollastonite. M. BARNICK (Naturwiss., 1935, 23, 770—771).—X-Ray methods give monoclinic symmetry for wollastonite (a 15.33, b 7.28, c 7.07 Å.; $\alpha = \gamma = 90^\circ$, β 95° 24' 30"). The unit cell contains 12 $(\text{CaO}, \text{SiO}_2)$. It does not possess a chain structure, but has Si_3O_9 rings. A. J. M.

Crystal structure of hexagonal silver iodide. L. HELMHOLZ (J. Chem. Physics, 1935, 3, 740—747).—Hexagonal AgI has been examined by powder, Laue, and oscillation methods. At -180° the structure is essentially that of wurtzite with the ideal parameter val., whilst at room temp. the Ag atoms appear to be distributed at random among four positions tetrahedrally surrounding the ideal position. On the basis of these structures an explanation of some of the peculiarities of AgI is offered. F. L. U.

Crystal structure of silver azide. M. BASSIÈRE (Compt. rend., 1935, 201, 735—737).—The crystals are orthorhombic (a 5.58, b 5.93, c 6.04, all ± 0.03 Å.; 4 mols. in unit cell; space-group V_8^{20}). The crystal is built up from Ag and N_3 ions. The N_3 group is linear, the N-N distance being 1.18 ± 0.04 Å., as in other azides. H. J. E.

Molecular structure of di-iodoethane. Iodine bond resonance and molecular structure of di-iodoethylene. Molecular packing in their crystal lattices. H. P. KLUG (J. Chem. Physics, 1935, 3, 747—753).—Distances between the I atoms of $(\text{CH}_2\text{I})_2$ and of *s-trans*- $\text{C}_2\text{H}_2\text{I}_2$ in mol. models predicted theoretically agree well with these distances within the crystal cells as given by X-ray data (A., 1935, 1195). These models, in conjunction with Mack's concept of the at. domain radius in crystals, lead to a picture of mol. packing which agrees with observed physical properties of the crystals. F. L. U.

Molecular map of resorcinol. J. M. ROBERTSON (Nature, 1935, 136, 755—756).—The electron density map obtained by a quant. X-ray analysis of resorcinol (I) is reproduced. The complete structure is described. OH belonging to adjacent (I) mols. approach to within 2.66 Å., indicating the existence of a strong (OH) linking or secondary valency force between mols. L. S. T.

Crystal structure of pyrene. J. DIAR and A. C. GUHA (Z. Krist., 1935, 91, 123—128).—Pyrene is monoclinic prismatic, a_0 13.74, b_0 9.22, c_0 8.45 Å., β 102½°, 4 mols. in cell, space-group C_{2h}^2 . Tentative mol. orientations are suggested. B. W. R.

An orthorhombic crystalline modification of 1:2:5:6-dibenzanthracene. K. S. KRISHNAN and S. BANERJEE (Z. Krist., 1935, 91, 170—172).—This substance is normally monoclinic; an orthorhombic bipyramidal form occurs occasionally when cryst. from EtOAc. M.p. and *d* are nearly the same as for the normal form. B. W. R.

Magnetic anisotropy and crystal structure of 1:2:5:6-dibenzanthracene. K. S. KRISHNAN and S. BANERJEE (Z. Krist., 1935, 91, 173—180).—Measurement of the anisotropy and the absolute susceptibility for very small crystals (0.02 mg.) is described. Measurements on both monoclinic and orthorhombic dibenzanthracene enable the directions of the lengths of the mols. and the angles of tilt of the mol. planes to be determined. B. W. R.

Thread diagram for polyvinyl alcohol. F. HALLE and W. HOFMANN (Naturwiss., 1935, 23, 770).—Polyvinyl alcohol gives a typical thread diagram similar to that of a natural fibre; identity period in the direction of the thread axis is 2.57 ± 0.02 Å. It is composed of crystallites which readily arrange themselves parallel on stretching, especially when warmed. A. J. M.

X-Ray structure investigations on elastic tissue with special reference to extension and shrinkage. H. KOLPAK (Kolloid-Z., 1935, 73, 129—142).—The results previously reported (A., 1934, 244) are confirmed and extended, and discussed in relation to current theories of valency chain structures. E. S. H.

Electron diffraction by gases. L. R. MAXWELL, S. B. HENDRICKS, and V. M. MOSLEY (J. Chem. Physics, 1935, 3, 699—709; cf. A., 1934, 17, 835).—The C-O-C valency angle in 4:4'-di-iododiphenyl ether has been found to be $118 \pm 3^\circ$ by the electron diffraction method. This is $>$ the O valency angle for simpler mols. such as F_2O , Cl_2O , and Me_2O . By the same method P and As mols. have been shown to have regular tetrahedral structure, the at. separations being respectively 2.21 and 2.44 Å. F. L. U.

Electron diffraction pattern from the natural (111) face of diamond. R. BEECHING (Phil. Mag., 1935, [vii], 20, 841—855).—Intensity measurements on the pattern were made, relative intensities of the main spots were determined, and tolerances in the Bragg angles were compared with the widths of the corresponding Kikuchi lines (cf. A., 1935, 570). The inner potential was measured, and various qual. observations were made. A case where a spot has been partly suppressed by Kikuchi lines is recorded. N. M. B.

"Extra" electron diffraction rings. (A) L. H. GERMER. (B) G. I. FINCH (Nature, 1935, 136, 832).—(A) Calculations show that the exit face theory (A., 1935, 287) of the origin of these rings is untenable.

(B) Germer's calculations agree with the view that the "extra" rings are due to surface contamination (*ibid.*, 1452). L. S. T.

Electron diffraction in rubber films. K. I. KRILOV (Physikal. Z. Sovietunion, 1935, 8, 136—152).—The diffraction patterns from crêpe rubber

films are rings. Stretched films gave points generally explicable on Susich's X-ray structure (A., 1928, 1186), but certain modifications are necessary. Unstretched chloroprene gave spots of an orthorhombic unit: *a*, 10.93, *b* 8.23 Å. (for crêpe a 12.23, *b* 8.3 Å.). No spots were obtained with Na-butadiene rubber. T. G. P.

Permanent polarisation of Rochelle salt. H. MÜLLER (Physical Rev., 1934, [ii], 45, 736; cf. A., 1935, 288). L. S. T.

Dielectric properties of Rochelle salt. J. E. FORBES and H. MÜLLER (Physical Rev., 1934, [ii], 45, 736—737; cf. A., 1935, 228). L. S. T.

Magnetisation of imperfect crystals. F. BRITTER (Physical Rev., 1934, [ii], 45, 742; cf. A., 1934, 945). L. S. T.

Dependence of internal friction on magnetisation in iron. W. T. COOKE (Physical Rev., 1934, [ii], 45, 742). L. S. T.

Approach to the theoretical magnetisation curve. T. D. YENSEN (Physical Rev., 1934, [ii], 45, 743).—The curves reproduced for Fe, Fe-Si and Fe-Ni alloys show that the approach to the theoretical curves, based on the Langevin-Weiss theory, depends not only on lattice orientation, but also on purity of material. L. S. T.

Separation of magnetic viscosity and eddy-current lag. A. V. MITKEVITSCH (Compt. rend. Acad. Sci. U.S.S.R., 1935, 3, 209—211).—Eddy-current lags can be detected through the sp. influence of previous changes in magnetic induction. C. W. G.

Rotatory power of quartz for rays perpendicular to the optic axis and its dispersion between 2537 and 5780 Å. G. BRUHAT and L. WEIL (Compt. rend., 1935, 201, 887—889).—The ratio of the rotatory powers of quartz for rays perpendicular and parallel to the optic axis is (mean) 0.54 ± 0.01 . The dispersion is the same for both rays. R. S. B.

Quantum mechanical investigation of the cohesive forces of metallic copper. K. FUCHS (Proc. Roy. Soc., 1935, A, 151, 585—602).—The wave functions and energies of the 4s electrons of Cu have been calc. by a method analogous to that used by Wigner and Seitz for Na (A., 1933, 660). The right order of magnitude is obtained for the lattice const. and for the heat of vaporisation, but to obtain the correct compressibility, the interaction between the ions in the lattice due to the overlapping of the closed shells must be considered. For Cu, the face-centred structure will have lower energy than the body-centred, but for Na the two structures have almost equal energies. Thus the calculations show why Cu has a close-packed structure, but fail to show why Na should have one cubic structure rather than the other. L. L. B.

Effect of photochemical colouring on the extension and strength limits of single crystals of rock-salt. M. N. PODASCHEVSKI (Physikal. Z. Sovietunion, 1935, 8, 81—92).—The extension and strength limits of single NaCl crystals are increased by photochemical coloration, the result being the

same whether the coloration is produced by X-rays or ultra-violet light. A. J. M.

Plastic properties of silver chloride and sodium chloride single crystals. A. V. STEPANOV (Physikal. Z. Sovietunion, 1935, 8, 25—40).—The plastic properties of single crystals of AgCl and NaCl are compared to show that they are connected with the polarisation effect of the lattice. Single crystals of AgCl show a high degree of plasticity and metallic properties in general. AgCl which has been exposed to light is not so plastic. The elastic limit along the cubic axis of a crystal tempered at 350° was 70 g. per sq. mm. Deformation on extension is similar to that of a metal belonging to the cubic system. The elastic limits for crystals of AgCl and NaCl are similar. The deformation work for NaCl is > for AgCl. At room temp. AgCl is more plastic than NaCl. A. J. M.

Tension coefficient of [electrical] resistance of the single hexagonal crystals, zinc and cadmium. M. ALLEN (Physical Rev., 1934, [ii], 45, 757). L. S. T.

Allotropy of calcium. M. C. NEUBERGER (Z. Elektrochem., 1935, 41, 790).—Published work is considered. E. S. H.

Thermodynamics of stationary systems. I. The thermo-element. II. The diffusion element. B. BRUŽS (Proc. Roy. Soc., 1935, A, 151, 640—651, 651—665).—I. A quant. application of the first and second laws of thermodynamics to stationary systems is connected with an introduction of certain arbitrary assumptions, of which two are distinguished. The first is the "non-interaction" assumption of Kelvin, leading to the well-known relations connecting the Seebeck, Peltier, and Thomson coeffs. The second postulates the existence of a const. ratio between the Joule and the polarisation effects, and leads to a new relationship between the Seebeck coeff. and the thermal and electrical conductivities of the material.

II. The above treatment of the thermo-element is extended to the problem of the diffusion element, and it is shown that a close correspondence exists between thermo- and diffusion element. The problem of the diffusion element reduces to a knowledge of the diffusion and electrical conductivities. L. L. B.

Influence of a magnetic field on the high-frequency conductivity of an ionised medium. E. V. APPLETON and D. B. BOOHARIWALLA (Proc. Physical Soc., 1935, 47, 1074—1084; cf. *ibid.*, 1932, 44, 246).—The relation between the transverse high-frequency conductivity and the pressure of ionised air under the influence of an imposed magnetic field was investigated. The pressure for max. conductivity varies with field intensity. The relation of results to ionospheric conductivity is discussed. N. M. B.

Change in resistance of bismuth single crystals at the m.p. J. H. SCHROEDER (Proc. Iowa Acad. Sci., 1934, 41, 254).—Measurements of resistance for various crystal orientations are recorded up to temp. > the m.p. The change from solid to liquid did not occur suddenly at the m.p., but began 1.5° < and continued 1.5° > m.p. CH. ABS. (e)

Change in resistance of single crystals of bismuth in a magnetic field at low temperatures. W. J. DE HAAS, J. W. BLOM, and L. SCHUBNIKOV (Physica, 1935, 2, 907—914; cf. A., 1930, 1102, 1353).—The influence of magnetic fields (4000—22,000 gauss) on the resistance of Bi single crystals is greater at 1.35° and 4.22° abs. than at 14.15° abs.

T. G. P.

Magneto-resistance of bismuth films at low temperature. C. T. LANE (Physical Rev., 1934, [ii], 45, 733—744).—The magneto-resistance of films 0.1—4 μ thick has been measured at -180° and 20°. There is a change in direction of the $[\Delta R_{-180^\circ}/\Delta R_{20^\circ}]$ -thickness curve at a thickness < 1 μ , and the magneto-resistance approaches temp. independence as the film thickness approaches zero. L. S. T.

Resistance of single crystals of gallium in a magnetic field. III. W. J. DE HAAS and J. W. BLOM (Physica, 1935, 2, 952—958; cf. A., 1934, 588).—Change of resistance of single crystals of Ga with the pseudo-tetragonal axis parallel to the length of the wire in a magnetic field perpendicular to the wire has been measured at liquid He temp. At 1.35° and 4.22° abs. the influence of the magnetic field is independent of temp., but > at liquid H₂ temp. T. G. P.

Electrical resistance of tantalum wires charged with hydrogen. A. SIEVERTS and H. BRÜNING (Z. physikal. Chem., 1935, 174, 365—369).—For H₂ pressures, p , up to ~1 atm., the amount sorbed by Ta at 500° and 600° is $\propto \sqrt{p}$; at 400° there are deviations from this relation. The resulting increase in resistance is at 500° and 600° $\propto \sqrt{p}$, whilst at 400° this is approx. Comparison of these results with similar data for the system Pd-H₂ indicates that the sorption has not involved the formation of a new phase. R. C.

Electrical conductance of colloidal solutions at high frequencies. H. J. CURTIS and H. FRICKE (Physical Rev., 1935, [ii], 48, 775; cf. *ibid.*, 47, 974).—Suspensions of powdered glass and kaolin, and colloidal Al₂O₃, V₂O₅, starch, and gelatin showed a marked increase in conductance at frequencies \succ 16,000 kc. per sec. The phenomenon is attributed to a form of Debye-Falkenhagen effect. N. M. B.

Diamagnetism of the tervalent bismuth ion. S. S. BHATNAGAR and B. S. BAHL (Current Sci., 1935, 4, 234).—The val. calc. for Bi⁺⁺⁺ is in agreement with the experimental val. (A., 1935, 1453). From Kido's work the predicted difference between the diamagnetism of Bi⁺⁺⁺⁺ and Bi⁺⁺⁺ should be of the order of 12.87, as is obtained. W. R. A.

Theory of dispersion of magnetic permeability in ferro-magnetic bodies. L. LANDAU and E. LIFSCHITZ (Physikal. L. Sovietunion, 1935, 8, 153—169).—The distribution of magnetic moments in a ferromagnetic crystal is investigated. The crystal consists of elementary layers magnetised to saturation. T. G. P.

Ionic diamagnetism in the solid state and in solution. H. FAHLENBRACH (Ann. Physik, 1935, [v], 24, 485—488).—The results of Frivold *et al.* (A., 1935, 1197) on the susceptibility of solutions may

be explained by the work of Cabrera *et al.* (A., 1933, 766, 1002, 1233). The results of Flordahl *et al.* (A., 1935, 1197) are also discussed. A. J. M.

Magnetic moment of the manganic ion. L. C. JACKSON (Proc. Physical Soc., 1935, 47, 1029—1031).—The magnetic susceptibility of Mn^{III} acetylacetonate was measured for a powdered specimen in the range $292-16.9^\circ$ abs. The law $\chi(T+5.5)=\text{const.}$ is obeyed down to about 75° abs., below which the susceptibility increases more rapidly. The calc. magneton no. of the Mn^{+++} ion is 4.98, in agreement with the Bose-Stoner theory. N. M. B.

Diamagnetic study of structure. F. W. GRAY and J. H. CRUICKSHANK (Trans. Faraday Soc., 1935, 31, 1491—1510).—A new method of treating at. and mol. diamagnetic data is described, whereby deviations of the observed diamagnetism of mols. from that calc. from the diamagnetism of free atoms may be used to establish the modes of linking of atoms in mols. Details are worked out for C_6H_6 , $C_{10}H_8$, $\cdot CO_2H$, H_2O , and H_2O_2 . F. L. U.

Effect of crystalline fields on the magnetic susceptibilities of Sm^{+++} and Eu^{+++} , and the heat capacity of Sm^{+++} . (MISS) A. FRANK (Physical Rev., 1935, [ii], 48, 765—771; cf. A., 1932, 217).—Mathematical. The temp. variation of the paramagnetic susceptibility of Sm^{+++} is calc. on the assumption that the ion is subject to a cryst. field which can be represented by a potential expression. Eu behaves, in contrast, like the free ion even in presence of a cryst. field. The contribution to the heat capacity of Sm^{+++} at various temp. due to the excited levels is calc. Results are compared with available experimental data. N. M. B.

Magnetic susceptibility of mixtures of oxides of the rare earths: mixtures of neodymium with praseodymium and of neodymium with samarium [oxides]. I. L. MAZZA (Atti R. Accad. Lincei, 1935, [vi], 21, 813—818).—The mixtures of the oxides were obtained by calcining the co-pptd. oxalates. In the system $Sm_2O_3-Nd_2O_3$, the magnetic susceptibility follows the simple additive law. In the system $Pr_2O_{11}-Nd_2O_3$, this could not be established, but the deviations are attributed to mutual reduction and oxidation of these oxides during the calcining. For Nd_2O_3 $\kappa=3.10 \times 10^{-7}$; for Sm_2O_3 , 6.1×10^{-6} ; and for Pr_6O_{11} , 1.56×10^{-7} . D. R. D.

Propagation of elastic waves in ice. I. M. EWING, A. P. CRARY, and A. M. THORNE, jun. II. A. P. CRARY and M. EWING (Physical Rev., 1934, [ii], 45, 749). L. S. T.

Propagation of sound and supersonic waves in gases. H. L. SAXTON (Physical Rev., 1934, [ii], 45, 749).—The derivation of equations for velocity and the absorption const. is outlined. L. S. T.

Vibrations of air and carbon dioxide in closed bulb resonators. K. VOECKLER (Ann. Physik, 1935, [v], 24, 361—376).—The frequency of vibration is in accord with the theory of Rayleigh and Thiesen, and the damping is of the order of magnitude predicted by the theory. The damping is less in CO_2

than in air and is diminished by addition of H_2O vapour. J. W. S.

Collision excitation of intramolecular vibrations in gases and gas mixtures studied by sound dispersion measurements. III. Measurements with nitrous oxide. A. EUCKEN and H. JAACKS (Z. physikal. Chem., 1935, B, 30, 85—112; cf. A., 1935, 155).—From determinations of the λ of ultrasonic waves in pure N_2O and mixtures of N_2O with foreign gases the variation of collision efficiency with temp. and pressure at -60° to 200° and 0.3—1 atm. has been measured. The deactivation of N_2O mols. by either N_2O or NH_3 mols. occurs by binary collisions. The difference between physical and chemical collision excitation of mol. vibration is discussed in relation to the collision efficiency in presence of H_2 , D_2 , and He. Measurements have been made with CO_2 mixed with a little H_2O to determine the effect of H_2O on the vibrational excitation of CO_2 . The reported dispersion of the rotational heat of H_2 in the ultrasonic region (A., 1934, 588) could not be confirmed (cf. *ibid.*, 950). R. C.

Experiments at very low temperatures obtained by the magnetic method. II. New superconductors. N. KURTI and F. SIMON (Proc. Roy. Soc., 1935, A, 151, 610—623; cf. A., 1935, 290).—The experimental technique of cooling down additional substances with the paramagnetic salts by applying the magnetic method (*loc. cit.*) is discussed. The measurement of the magnetic behaviour of a metal can be used to detect superconductivity, and to find the transition point and the threshold vals. Cd, Zr, and Hf become superconducting in the new temp. region, the normal transition points being 0.54° , 0.70° , and 0.35° abs. Au, Cu, Bi, Mg, and Ge did not become superconducting down to 0.05° abs. L. L. B.

Theory of anomalies in specific heats. L. LANDAU (Physikal. Z. Sovietunion, 1935, 8, 113—118). T. G. P.

Characteristic point of pure substances. F. MICHAUD (J. Chim. phys., 1935, 32, 527—540).—The characteristic point of a solid body is defined as the point of contact of the tangent passing through the origin to the curve giving at. or mol. heat capacity as a function of abs. temp. The co-ordinates of this point define the characteristic temp. and characteristic heat capacity. The point with the same abscissa on the curve at. or mol. entropy/abs. temp. is the characteristic entropy. The characteristic point plays a part in comparisons of heat properties of solids analogous to that of the crit. point in comparisons of thermo-elastic properties of fluids. The curves $S/\text{temp.}$ for certain substances are approx. superposable by a simple translation of the co-ordinates. The characteristic entropies of pure substances of the same atomicity are approx. equal amongst themselves, diat. and triat. mols. having twice and three times the characteristic entropy of a normal metal. A more rigorous comparison is effected by plotting log heat capacity/entropy. Such curves are a criterion of the existence of allotropic changes. Anomalies are discussed. T. G. P.

Specific heats of solid substances at higher temperatures. XX. Molecular heats of the alloys of palladium and antimony in comparison with the sum of the atomic heats of the free elements. XXI. Molecular heats of the compound PtSb_2 in comparison with the sum of the atomic heats of the free composing elements. XXII. Molecular heats of the supposed binary compounds of copper and palladium. T. J. POPPEMA and F. M. JAEGER (Proc. K. Akad. Wetensch. Amsterdam., 1935, 38, 822—833, 833—836, 836—841; cf. A., 1935, 924).—XX. The sp. heats of Sb measured under different conditions are not quite const., but no transformation point could be observed at 414° . At. heat data between 100° and 600° are tabulated and sp. heats of PdSb , PdSb_2 , and Pd_3Sb over a range of temp. are given. The difference between the mol. heats C'_p , and the sum of the at. heats Σ is small, but increases with rise of temp. and % of Pd. The change $\beta\text{-Pd}_3\text{Sb} \rightarrow \alpha\text{-Pd}_3\text{Sb} - 4800 \text{ g.-cal. per g. occurs at } 950^\circ$.

XXI. Sp. heat data are given for PtSb_2 up to 600° . $C'_p - \Sigma$ increases from -8% of C'_p at 200° to -19% at 600° .

XXII. Alloys of the composition CuPd and Cu_3Pd have been prepared and the sp. heats determined up to 900° . $C'_p - \Sigma$ is small, and it is concluded, in conjunction with X-ray measurements, that the alloys are chiefly composed of solid solutions.

R. S.

Specific heat of Ag_2HgI_4 in relation to the crystal structure. J. A. A. KETELAAR (Z. physikal. Chem., 1935, B, 30, 53—60; cf. A., 1934, 1056).—The sp. heat has been measured at $20\text{--}100^\circ$. From 37° it rises anomalously, and immediately below the transition point at 50° reaches three times the normal val., to which it falls discontinuously at transition. The heat of transition is 0.32 for the homogeneous, and $1.13 \text{ g.-cal. per g.}$ for the heterogeneous, part. The explanation of the sp. heat anomaly is that with rise in temp. even below the transition point there is increasing misplacing of the metal atoms (cf. *ibid.*, 947). An "averaged structure" may be interpreted either as a statistical distribution of the atoms over the available lattice points or as the result of repeated twinning (cf. *ibid.*, 16); X-ray examination affords no means of decision. With $\alpha\text{-Ag}_2\text{HgI}_4$, however, the high electrical conductivity and considerable heat of transition $\beta \rightarrow \alpha$ decide for the former alternative.

R. C.

Specific heat of iron nitrides. S. SATOH (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 28, 135—139; cf. A., 1933, 27).—The sp. heat of a series of Fe-N alloys is a max. at 9.7% N. This is discussed in relation to the Fe-N equilibrium diagram. R. S.

Evaporation as mechanical subdivision to molecules. P. V. ZOLOTAREV (Trans. Inst. Chem. Tech. Ivanovo, 1935, 50—53).—Mathematical. The heat of evaporation of a given substance is shown to be \propto the work expended in breaking it down to its constituent mols. Formulae are derived for calculating Avogadro's const. for different types of mols., and for solids and liquids.

R. T.

Determination of fixed points at low temperatures with a hydrogen thermometer. S.

AOYAMA and E. KANDA (Bull. Chem. Soc. Japan, 1935, 10, 472—481).—Existing vals. for the b.p. of O_2 and N_2 and the sublimation point of CO_2 are confirmed by means of the H thermometer described. Temp. are determined to within $\pm 0.036^\circ$ at 0° and $\pm 0.025^\circ$ at -200° .

J. G. A. G.

Melting curve of oxygen to 170 kg. per sq. cm. J. H. C. LISMAN and W. H. KEESOM (Physica, 1935, 2, 901—906; cf. A., 1935, 1197).—Points on the melting curve of O_2 have been determined up to $167.7 \text{ kg. per sq. cm.}$ and 56.25° abs. Extrapolation gives the triple point $54.32(5)^\circ \text{ abs.}$ The density of solid $\gamma\text{-O}_2$ at the triple point calc. from Clapeyron's equation is $1.37(2)$.

T. G. P.

Polarisation effects in thallos fluoride. E. HAYEK (Z. anorg. Chem., 1935, 225, 47—48).— TlF has b.p. $655^\circ \pm 10^\circ$, d_4^{20} 8.36. Attempts to prepare a subfluoride analogous to Ag_2F were unsuccessful.

F. L. U.

Transition points of hexachloroethane. E. H. WIEBENGA (Z. anorg. Chem., 1935, 225, 38—42).—Transition temp. of C_2Cl_6 , determined both thermally and dilatometrically, are: rhombic = triclinic 43.6° , triclinic = cubic 71.1° . The transition reported at 125° does not occur. The rates of transformation, although slow, are finite except at the actual transition temp.

F. L. U.

New form of thermodynamic diagrams. K. PAVLOV and A. PRIVVAROVA (Chimstr., 1935, 7, 33—37).—A graphical method is described.

CH. ABS. (e)

Influence of the degree of dispersion on physico-chemical constants. IV. E. COHEN and J. J. A. BLEKKINGH (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 842—849).—Crystals of KCl of 0.1, 0.5, and 5 mm. mean cross-section have been prepared. $d = 1.9891 \pm 0.0004$ in each case. R. S.

International Bureau of Physico-Chemical Standards. VII. Physical constants of twenty organic compounds. J. TIMMERMANS and (MME.) HENNAUT-ROLAND (J. Chim. phys., 1935, 32, 501—526; cf. A., 1934, 480).—The following data for b.p./760 mm., f.p., and d_4^{15} have been determined: $n\text{-C}_5\text{H}_{12}$ 36.10° , -129.1° , 0.63114; $n\text{-C}_7\text{H}_{16}$ 98.35° , -90° , 0.68785; $(\text{CH}_2\text{OH})_2$ 197.85° , -12.6° , 1.11710, glycerol —, —, 1.26443; Et_2S 92.10° , -103.3° , 0.84102; $\text{HCO}\cdot\text{NH}_2$ —, 2.55° , 1.13756; PhF 84.85° , -41.9° , 1.03091, CH_2PhCl 179.35° , -39.2° , 1.10426; $\text{CH}_2\text{Ph}\cdot\text{OH}$ 205.45° , -15.3° , 1.04927; anisole 153.80° , -37.5° , 0.99858; COPhMe 202.00° , 19.6° , 1.03236. The data include the relations between b.p. and pressure, coeffs. of dilatation, refractive indices, viscosity coeffs., and surface tensions. The crit. solution temp. of $n\text{-C}_5\text{H}_{10}$ in PhNO_2 is 24.5° . Earlier data are tabulated.

T. G. P.

Isotherms of methane between 0° and 150° and densities 19 and 53 Amagat (pressures between 20 and 80 atm.). A. MICHELS and G. W. NEDERBRAGT (Physica, 1935, 2, 1000—1002; cf. A., 1934, 837).—Isotherms of pure methane (b.p. const. to 0.03°) have been determined at 25° intervals between 0° and 150° .

T. G. P.

Acetylmethylcarbinol. J. R. POUND and A. M. WILSON (J. Physical Chem., 1935, 39, 1135—1138).—The v.p. of acetoin between 0° and the b.p. (144°) has been determined and the polymerisation has been studied by measurement of *n* and *d*. Crystallographic and thermal data relating to the polymeride are given. R. S.

Difference in vapour pressures of ortho- and para-deuterium. F. G. BRICKWEDDE, R. B. SCOTT, and H. S. TAYLOR (J. Chem. Physics, 1935, 3, 653—660; cf. A., 1934, 1164).—The differences in v.p. of the mixture of ortho- and para-D₂ in equilibrium at 20.4° abs. and of the normal mixture have been determined between 15° and 20.4 abs. The speed of the uncatalysed change for normal liquid D₂ is about 0.001 of that for H₂. F. L. U.

Vapour pressures of neon of different isotopic compositions. W. H. KEESOM and J. HAANTJES (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 810).—The differences in v.p. of Ne of five different isotopic compositions (at. wt. 20.043—21.157) have been determined. At const. temp., v.p. is a linear function of at. wt. The divergence between the theoretical and observed dependence on temp. of $\log p_{20}/\log p_{22}$ for the solid state is attributed to a difference between the potential energy of Ne²⁰ and Ne²² and to variation in the zero-point energy. It is concluded, from data for the liquid state, that the sp. heat of Ne²⁰ is > that of Ne²². The triple point of Ne²² is 0.134° > that of Ne²⁰ and the melting heat of Ne²² is the greater by 1.18 g.-cal. per mol. R. S.

Measurement of v.p. of mercury from absorption of resonance radiation. H. VON HALBAN, jun. (Helv. Phys. Acta, 1934, 7, 856—875; Chem. Zentr., 1935, i, 1980).—The v.p. of Hg at -18° and -53.4° is calc. from abs. measurements of the absorption of the 2537 Å. resonance line by saturated Hg vapour at those temp. The accuracy is independent of the v.p. and unaffected by other gases at pressures below those causing broadening of the absorption line. J. S. A.

Vapour pressure of metals and their velocity of vaporisation in a vacuum. J. A. M. VAN LIEMPT (Rec. trav. chim., 1935, 54, 847—852).—Formulae are derived relating the velocity of sublimation in a vac., v.p., and heat of sublimation with the at. wt., m.p., and at. vol. of the metal and the temp. The equations agree with experiment. J. W. S.

Vapour pressure of zinc, lead, cadmium, cuprous, and silver chlorides. D. N. TARASENKOV and P. A. KOSHMAKOV (J. Gen. Chem. Russ., 1935, 5, 830—835).—The v.p. have been determined at 516—728°/7.4—723 mm. for ZnCl₂, at 650—942°/4.5—692 mm. for PbCl₂, at 618—952°/3—722 mm. for CdCl₂, at 632—1070°/3—216 mm. for Cu₂Cl₂, and at 882—1120°/3.7—59 mm. for AgCl. R. T.

Variation of the volume of elements in the act of fusion. I. L. LOSANA (Gazzetta, 1935, 65, 851—864).—The change in vol. in passing from the solid to the liquid state of the alkali metals is found to be (m.p. given in parentheses): Li (180.2°) 0.184, Na (97.7°) 0.512, K (62.1°) 1.072, Rb (38.8°) 1.472,

Cs (28.8°) 1.900 c.c. per g.-atom. These vals. were obtained by measuring the increased upthrust of a given wt. of metal at the m.p. in petroleum or vaseline oil by means of a hydrostatic balance. The vals. for Rb and Cs were confirmed by measurements of the m.p. at pressures from 1 to 135 atm. The change in vol. on fusion of elements in relation to their position in the periodic classification is discussed. O. J. W.

Aggregative states. An empirical law. E. I. ACHUMOV (J. Gen. Chem. Russ., 1935, 5, 843—847).—The empirical expression $\beta(T_b - T_c) = C$, where β is the coeff. of expansion of a liquid between the m.p. T_c and the b.p. T_b , and C is a const., is shown to hold for a no. of org. liquids. R. T.

Thermal expansion of cast and rolled zinc. H. G. JONES (Proc. Physical Soc., 1935, 47, 1117—1128).—Data tabulated and plotted for steady and continuously rising temp. show marked differences in the coeffs. for cast and rolled Zn. On rolling, the random orientation of crystals in the cast Zn is broken up, and most of the long axes are set perpendicular to the plane of rolling, but no change is produced in the vol. coeff. For small crystals the continuous expansion is small, but increases with the size of the crystals. Discontinuities in the continuous expansion are traced to the long axis. N. M. B.

Linear thermal expansion of sodium tungstate between 20° and 600°. J. B. AUSTIN and R. H. H. PIERCE, jun. (J. Chem. Physics, 1935, 3, 683—686; cf. A., 1933, 342).—The results, obtained by an interferometric method, show that at atm. pressure Na₂WO₄ is trimorphous. The transition III—II occurs at 585°, and II—I at a slightly lower temp., II being stable over a very short range. F. L. U.

Thermal stability of the lower atmosphere. A. L. HALES (Proc. Roy. Soc., 1935, A, 151, 624—640).—Mathematical. Equations for the conduction of heat by turbulence, and for the stability of a compressible fluid when the hotter fluid is below, are deduced. Super-adiabatic lapse rates are possible in limited regions of the atm. L. L. B.

Thermal conductivity law in moving media. Derivation of a molecular kinetic theory of thermal conductivity with an investigation of the limits of the Fourier method. M. LANG (Ann. Physik, 1935, [v], 24, 393—408).—Theoretical. A. J. M.

Viscosity of liquid phosphorus. A. N. CAMPBELL and S. KATZ (J. Amer. Chem. Soc., 1935, 57, 2051—2055).—Viscosity has been determined between 20° and 140°. There is evidence of association in liquid P below 45°, but no evidence of a change of viscosity when heated P is suddenly chilled. E. S. H.

Viscosity of liquid methane and ethylene in relation to temperature. N. S. RUDENKO and L. V. SCHUBNIKOV (Physikal. Z. Sovietunion, 1935, 8, 179—184).—Measurements have been made between 90° and 111° abs. for CH₄ and between 110° and 169° abs. for C₂H₄. T. G. P.

Complex viscosity. A. GEMANT (Trans. Faraday Soc., 1935, 31, 1582—1590; cf. A., 1935, 1065).—

Maxwell's theory of the behaviour of materials exhibiting both viscosity and plasticity is generalised and developed so as to take account of mol. vibrations. The theory is applied to dielectric losses due to dipole rotation.
F. L. U.

Definition and correction of diffusion constants of gases. J. KUUSINEN (Ann. Physik, 1935, [v], 24, 445—446).—The work of Trautz and Müller (A., 1935, 575) is criticised on the ground that a false interpretation of Fick's law was used. The Maxwell-Chapman method leads to results identical with those obtained by the correct use of Fick's law.
A. J. M.

Definitions of diffusion constants. J. KUUSINEN (Ann. Physik, 1935, [v], 24, 447—456).—A general definition of the diffusion const. of a binary mixture is derived.
A. J. M.

Criticism of certain researches on the physico-chemical analysis of binary systems. V. F. UST-KATSHKINTZEV (J. Gen. Chem. Russ., 1935, 5, 892—898).—The experimental data given by Terpugov (A., 1933, 354; 1934, 1167) for the systems $\text{Et}_2\text{O}-\text{AsCl}_3$ and $-\text{H}_2\text{SO}_4$, by Usanovitsch *et al.* (A., 1934, 1167) for $\text{Et}_2\text{O}-\text{SbBr}_3$, and by Pushin *et al.* (A., 1932, 1197) for $\text{C}_5\text{H}_5\text{N}-\text{AcOH}$ do not confirm the conclusions reached by the authors relative to the existence of compounds. In general, systems which exhibit deviations from the additive rule for certain properties may follow it for others, and, in particular, max. and min. on curves which represent temp coeffs. of various properties cannot be accepted as evidence of compound formation.
R. T.

Association and molecular polarisation. V. Simultaneous formation of double and triple complexes in dipole association. I. SAKURADA (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 1120—1126; cf. A., 1935, 927).—The equilibrium consts. for double and triple dipole association can be calc. from dielectric data, and it is concluded that such complexes exist simultaneously in the mixtures CCl_4-PhCl , CCl_4-PhBr , $\text{C}_6\text{H}_{14}-\text{PhNO}_2$, and C_6H_6 -quinoline. The heats of association have been calc. from the variation of the equilibrium consts. with temp.
R. S.

Simultaneous formation of double and triple complexes in dipole association. E. HERTEL and E. DUMONT (Z. physikal. Chem., 1935, B, 30, 149—151).—Polemical against Sakurada (A., 1935, 927).
R. C.

Viscosity of sulphuric acid [solutions]. S. D. BESKOV and O. A. SLIZKOVSKAJA (Chimstr., 1935, 7, 32—33).—Vals. for H_2SO_4 (d 1.33—1.84) between 5° and 90° are recorded. The η of $\text{H}_2\text{SO}_4-\text{H}_2\text{O}$ mixtures does not follow the additive law.
CH. ABS. (e)

Viscosity of solutions of salts in methyl alcohol. G. JONES and H. J. FURNWALT (J. Amer. Chem. Soc., 1935, 57, 2041—2045).—Determinations of d and η at 25° have been carried out for solutions of KCl, KBr, KI, and NH_4Cl over a wide concn. range in MeOH. The results for d can be expressed by an equation of the form suggested by Root (A., 1933,

347). The data for η are used to test the validity of several equations connecting η with concn.

E. S. H.

Viscosity of sugar and dextrin solutions containing salts. J. H. C. MERCKEL (Kolloid-Z., 1935, 73, 171—174).—The influence of NaI, NaBr, NaCNS, NaCl, NaBrO_3 , NaIO_3 , and NaF on the viscosity of sucrose or dextrin solutions is in the order of their lyotropic nos.
E. S. H.

S-Shaped viscosity curves. M. USANOVITSCH (J. Gen. Chem. Russ., 1935, 5, 996—1001).—S-Shaped viscosity-composition curves are obtained in binary systems of which one component is associated when this forms an unassociated compound with the other component. The rule is exemplified by the systems $\text{PhNO}_2-\text{H}_2\text{SO}_4$ and $\text{AsCl}_3-\text{Et}_2\text{O}$.
R. T.

Concentrated solutions. I. Conductivity, viscosity, and density of fused $\text{NH}_4\text{Ag}(\text{NO}_3)_2$ and of its concentrated solutions. M. S. SKANAVI-GRIGORIEVA and E. B. SCHTERNIN (J. Gen. Chem. Russ., 1935, 5, 799—806).—The conductivity κ of the fused salt rises abruptly at 113° , and then continues to increase at a slower rate with rising temp.; η falls linearly over the same range. Up to 10% H_2O has little effect on κ at 100° , but further addition of H_2O leads to a rapid rise in κ to a max. in 75% solutions. At 25° a well-defined max. val. of κ is found for 60% solutions. Composition- d and $-\eta$ curves are given for numerous aq. systems at 25° .
R. T.

Conductivity and viscosity in the systems (A) sulphuric acid-nitrobenzene, (B) nitrobenzene-acetic acid, (C) sulphuric acid-acetic acid. M. USANOVITSCH (J. Gen. Chem. Russ., 1935, 5, 701—708, 709—711, 712—718).—(A) [with G. KOZMINA and V. TARTAKOVSKAJA]. The conductivity curves ($0-30^\circ$) have a well-defined min., suggestive of the compound $2\text{PhNO}_2, \text{H}_2\text{SO}_4$. The temp. coeff. of conductivity curves have 2 max. and a min., corresponding with 2:1, 1:1, and 1:2 compounds of PhNO_2 and H_2SO_4 . The η -composition curves do not possess max. or min.

(B) [with A. TENENBAUM]. The system ($20-80^\circ$) is non-conducting, and the composition curves do not suggest compound formation. The formation of electrolytic solutions when two non-electrolytes are mixed is ascribed exclusively to compound formation.

(C) [with A. NAUMOVA]. The temp. coeff. of conductivity-composition curves ($0-30^\circ$) suggest 1:1 and 1:2 compounds.
R. T.

Viscosity coefficients in the system fused $\text{KCl}-\text{MgCl}_2$. S. KARPATSCHEV and A. STROMBERG (J. Gen. Chem. Russ., 1935, 5, 625—630).—The viscosity isotherms ($550-650^\circ$) suggest the compound $\text{MgCl}_2, 2\text{KCl}$.
R. T.

Chemical composition and optical properties of solutions. I. Quaternary system $\text{KCl}-\text{NaCl}-\text{MgCl}_2-\text{H}_2\text{O}$ at 15° . E. I. ACHUMOV and M. P. GOLOVKOV (J. Gen. Chem. Russ., 1935, 5, 500—509).—Composition- n curves for the above system are of the same general shape as are those connecting composition with other physical properties.
R. T.

Equilibria in liquid mixtures and solutions.
IV. B. p. and composition of vapour of solutions of carbonyl chloride in dichloroethane and xylene. V. A. KIREEV, S. I. KAPLAN, and V. N. ZLOBIN (J. Appl. Chem. Russ., 1935, 8, 949—951).—B.p. and composition of the vapour phase at the b.p. have been determined for 0—35% COCl_2 in xylene and in $\text{C}_2\text{H}_4\text{Cl}_2$. R. T.

Fugacity of salts present in boiling solutions. P. ZOLOTAREV and J. OBUDOVSKAJA (Trans. Inst. Chem. Tech. Ivanovo, 1935, 54—55).—The salt content of river- H_2O falls from 134.6 to 3.4 mg. per litre after one distillation; the same salts are present in the distillate as were originally present. The phenomenon is ascribed to sputtering at the heated walls of the vessel above the surface of the liquid, leading to the formation of an aerosol of the salts. R. T.

Röntgen analysis of β -phases of Cu-Be and Al-Zn alloys at high temperatures. G. F. KOSOLAPOV and A. K. TRAPESNIKOV (Metallwirt., 1935, 14, 45—46; Chem. Zentr., 1935, i, 2243).—The β -phase of a Cu-Be alloy (7.2% Be) exists above 620°, with a random-distributed body-centred lattice, a 2.79 Å. The α -phase has the Cu lattice, and the γ -phase at room temp. a CsCl structure, a (570°) 2.72 Å. Al-Zn alloy with 40% of Al exhibits the Zn and Al lattices at room temp., and a single face-centred γ -phase at 410°. J. S. A.

X-Ray studies on the systems tin-antimony and tin-arsenic. G. HÄGG and A. G. HYBINETTE (Phil. Mag., 1935, [vii], 20, 913—929).—The homogeneous phase extending from 45 to 55 at.-% Sb has a deformed NaCl structure. The unit cell at the Sn limit is a rhombohedron with r 6.117 Å., α 89.70°, and vol. 228.9 Å.³ With increasing Sb content the vol. and deformation increase until r is 6.138 Å., α 89.18°, and vol. 231.2 Å.³ As is insol. in the Sn phase. Two intermediate phases of narrow range exist at Sn_3As_2 and SnS . The Laue symmetry of the former is D_{3d} . The unit cell is a rhombohedron with r 12.23 Å. and α 19.22°. The structure probably corresponds with the ideal formula Sn_4As_3 , where some As is replaced by Sn. The probable space-group is D_{3d}^2 . The phase at SnAs has the NaCl structure with lattice const. 5.716 Å. As dissolves 21 at.-% Sn, which increases the rhombohedral edge and diminishes the angle of the As phase. T. G. P.

Alloys of rhodium with copper. O. E. ZVJAGINTZEV and B. K. BRUNOVSKI (Ann. Inst. Platine, 1935, No. 12, 37—66).—Cu-Rh alloys are easily oxidised in air. With 0—20 at.-% Rh they are homogeneous and have the structure of Cu. From 90—100 at.-% Rh they have the Rh structure. Between these limits there are two phases, except where the compounds Cu_2Rh_3 and CuRh_3 (both with a face-centred cubic structure) exist. There is also a partial change of structure at Cu_3Rh . CH. ABS. (e)

Modulus of elasticity of copper-beryllium alloys. L. GUILLET (Compt. rend., 1935, 201, 960—962).—The modulus of elasticity and Rockwell hardness increase linearly with [Be] up to approx. 18 and 12% Be, respectively. For [Be] > 12% the

hardness increase is less. The elasticity of the alloy with 15% of Be equals that of steel. H. J. E.

Structure of zinc-cadmium eutectic. M. STRAUMANIS and N. BRAKŠS (Z. physikal. Chem., 1935, B, 30, 117—131; cf. A., 1912, ii, 744).—The eutectic consists of comparatively coarse fibres which grow into the melt perpendicularly to the surface of cooling and are built up of alternating parallel crystal leaflets of Zn and Cd, running lengthwise. These leaflets, which are somewhat crumpled, are so arranged in the fibres that their wide basal faces are in contact and the diagonal axes of the first position make an angle of 0—5° with the fibre axis. The leaflets are thinner the more rapid is the cooling. It is inferred that the structure of eutectics is determined primarily by the crystallophysical properties of the components, surface tension playing a part only in exceptional circumstances. R. C.

Binary systems of alkali metals. I. C. GORIA (Gazzetta, 1935, 65, 865—870).—The system Rb-K shows limited solubility in the solid state and a eutectic at 34° with 15 at.-% K. In the Rb-Na system there is a eutectic at -5.2° with 92 at.-% Rb, but no solid solutions or compounds are formed. O. J. W.

Electrical resistance of wires of palladium-silver and palladium-gold alloys charged with hydrogen. A. SIEVERTS and H. HAGEN (Z. physikal. Chem., 1935, 174, 247—261).—The pressure-concn. (p - c) isotherms for alloys with 5 and 10% Ag are similar to those for pure Pd; at 155° there is a hysteresis loop and at 200° an approx. flat portion on the isotherm, but no hysteresis. The isotherms for alloys with 20—50% Ag are all parabolic. Up to 30 at.-% Ag the pressure-resistance (p - R) isotherms are similar to those of Pd, but for a given c and p the increase in R caused by the H is the smaller the larger is the proportion of Ag. For alloys with 30 and 40% Ag ΔR is negative over a certain range of temp. and p , whilst for 50% ΔR rises again. Pd-Au alloys behave similarly to Pd-Ag alloys of the same at. composition, but both the H absorption and ΔR for the Ag alloys are $>$ for the Au alloys at the same temp. and p . R. C.

Resistance thermometry below 10° abs. J. D. BABBITT and K. MENDELSSOHN (Phil. Mag., 1935, [vii], 20, 1025—1041).—The resistances of phosphor-bronze wires have been measured at low temp. The superconductive component responsible for the temp. dependency below 7° abs. is Sn-P, transition point 8.9° abs. A binary alloy of definite composition properly treated is suitable for low-temp. thermometry, e.g., 5% Pb-Ag. T. G. P.

Experiments on a superconductive alloy in a magnetic field. J. M. C. JONKER and W. J. DE HAAS (Physica, 1935, 2, 935—942).—Resistance may be detected by studying the dying-out of the persisting current in a ring composed in part of Pb wire and in part of the alloy, when the latter is placed in a longitudinal magnetic field. The magnetic transition curve of a 64.8% Tl-Pb alloy has been studied. In a magnetic field slightly $>$ the penetration val. there is no resistance $> 5 \times 10^{-11}$ ohm. The magnetic threshold depends on the measuring current. T. G. P.

Intermetallic compounds. W. KLEMM (Angew. Chem., 1935, 48, 713).—A review in which the general differences between intermetallic and salt-like compounds are discussed. R. S. B.

New methods and results for the detection of intermetallic compounds. G. GRUBE (Angew. Chem., 1935, 48, 714—719).—A review of experimental methods, including the study of magnetic susceptibility (χ). For Pd-Mn below 500° χ rises rapidly with increasing % of Mn. The classification of compounds is discussed. R. S. B.

Structure of intermetallic phases. G. HÄGG (Angew. Chem., 1935, 48, 720—723).—A review of structural relations from the viewpoint of the position of the constituents in the periodic table. R. S. B.

Energy and space problems in the formation of intermetallic compounds. W. BILTZ (Angew. Chem., 1935, 48, 729—734).—A lecture. E. S. H.

Magnetism and chemical linking in intermetallic phases. E. VOOR (Angew. Chem., 1935, 48, 734—740).—A crit. discussion of published work. E. S. H.

Theory of transition of metallic mixed phases. III. Diagrams of state for partly ordered mixed phases. G. BORELIUS (Ann. Physik, 1935, [v], 24, 489—506).—Theoretical. The theory previously put forward (A., 1934, 724, 1166) is applied to alloys in which the constituents are not in stoichiometrical proportions. The general thermodynamic theory underlying the equilibria in binary alloys is considered. The zero-point entropy and zero-point energy are discussed as measures of the at. ordering. A. J. M.

Effect of thermal agitation on atomic arrangement in alloys. II. W. L. BRAGG and E. J. WILLIAMS (Proc. Roy. Soc., 1935, A, 151, 540—566).—Theoretical. The treatment given previously (A., 1934, 954) for the order-disorder transformation in alloys, and a recent extension of it by Bethe (A., 1935, 1193), are compared with the formal methods of Borelius, Gorsky, and Dehlinger (A., 1928, 822, 1078; 1933, 896). The energy contents of the alloys CuZn and Cu₃Au as deduced theoretically are compared with those found experimentally by Sykes (A., 1935, 576). Expressions are given for the dependence of temp. on composition. L. L. B.

Solid solutions with a varying number of atoms in the unit cell. G. HÄGG (Z. Krist., 1935, 91, 114—122).—"Interstitial solution" is suggested to describe those solid solutions formed by adding or subtracting one kind of atom *A* in a given lattice *B*. For stability, a rigid skeleton lattice *B* and small substituent atoms *A* are desirable. The interstitial solutions can be classified according to the means whereby electrical neutrality is maintained. Valency change in one kind of atom may make an interstitial solution possible. The electrical conductivity of such lattices is discussed. B. W. R.

Separation of binary liquid mixtures into two layers. R. V. MERZLIN and V. F. UST-KATSCHKINTZEV (J. Gen. Chem. Russ., 1935, 5, 771—778).—Phase diagrams for KCl-H₂O-NEt₃, -C₅H₅N, and

-piperidine have been constructed at 0—80°. The systems H₂O-C₅H₅N and -piperidine appear to have a high lower crit. miscibility temp. R. T.

Physico-chemical properties of certain aqueous systems containing amines, and capable of stratification. R. V. MERZLIN (J. Gen. Chem. Russ., 1935, 5, 886—891).—The composition- d and -surface tension (σ) and σ -temp. curves have been determined for the systems H₂O- β -collidine and -NEt₃; the composition- η curve for the latter suggests a 1:1 compound. The data suggest formation of thermolabile compounds in both systems. R. T.

Viscosity of binary systems at critical zones. R. V. MERZLIN (J. Gen. Chem. Russ., 1935, 5, 899—903).—Binary liquid systems exhibit irrational max. in the η -composition curves at the lower crit. temp. zone; at the upper crit. temp. two types of curve are possible, (a) in which the curves exhibit a negative deviation from additivity, due to dissociation of associated complexes, and (b) in which electrolytic dissociation of the complexes is superimposed on this effect. R. T.

Mutual solubility and surface tension. II. Surface tension and dipole moment. V. K. SEMENTSCHENKO and T. N. IVANOVA (J. Gen. Chem. Russ., 1935, 5, 807—813).—The surface tension, σ , of H₂O, nicotine (I), and PhNO₂ (II) at 25° is depressed by PrCO-NH₂ (III), PrCl, PrCHO (IV), PrCN, PrOH, and PrCO₂H (V), to an extent which increases with the concn. In the case of H₂O no obvious connexion exists between surface activity and dipole moment, μ ; in (I) and (II) it rises with increasing μ for substances not containing N, and falls for those containing N. The crit. temp. of miscibility of (I) with H₂O is raised by (III) and (V), is unaffected by PrOH, and lowered by the remaining substances, to an extent which increases linearly with the concn. The val. of σ at 70° at a H₂O-(I) interface rises with increasing concn. of PrCl, (IV), and PrCN, but is practically unaffected by PrOH, and is lowered by (III) and (V). R. T.

Homogenisation by means of amines of certain aqueous amine systems with an upper critical temperature of stratification. R. V. MERZLIN and V. F. UST-KATSCHKINTZEV (J. Gen. Chem. Russ., 1935, 5, 904—919).—Phase diagrams have been constructed for the systems H₂O-NHPh-NH₂ (I)-piperidine (II), -C₅H₅N, -NH₂-CH₂Ph (III), and -NH₂Ph, and for H₂O-NH₂Ph-(II), -C₅H₅N, and -(III), at 0—50°. No connexion is apparent between the dipole moment, dissociation coeff., or dielectric const. of the amines and their homogenising action at any arbitrarily fixed temp. Within the temp. range studied the homogenising action rises in the series (I) < (III) < C₅H₅N < (II), but falls with rise of temp. for C₅H₅N and (III), and rises for (II); the principle of corresponding temp. should be taken into account in comparing the activity of a series of homogenisers. R. T.

Solubility of ammonium oxalate in water. A. E. HILL and E. F. DISTLER (J. Amer. Chem. Soc., 1935, 57, 2203—2204).—Data are recorded for the

range 0—100°. The solid phase throughout is the monohydrate. E. S. H.

Solubility of sodium cyanide in water and in aqueous sodium hydroxide. V. A. KIREEV and L. I. VAGRANSKAJA (J. Gen. Chem. Russ., 1935, 5, 963—966).—The solubility of NaCN at 0°, 25°, and 40° falls linearly with increasing [NaOH]. R. T.

Solubility of cobaltous nitrate in aqueous nitric acid, and the transition point of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to $\text{Co}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. A. VALDMAN and L. L. KLATSCHKO-GURVITSCH (J. Gen. Chem. Russ., 1935, 5, 791—794).—Aq. $\text{Co}(\text{NO}_3)_2$ saturated at 80° solidifies on cooling to 25°, to yield 39.5% of trihydrate (I) and 60.5% of hexahydrate (II). (I) alone can be prepared by cooling to 56°, and (II) alone by saturating at 56° and cooling. The transition point of (II) to (I) falls from 54° in absence of HNO_3 to 42° in presence of 30% of HNO_3 . R. T.

Determination of solubility of the complex K_2SiF_6 under various conditions. A. A. VASSILIEV and N. N. MARTIANOV (Z. anal. Chem., 1935, 103, 103—106).—The solubility of K_2SiF_6 in H_2O at 17° has been determined titrimetrically. The solubility is lower in 50% aq. EtOH, and is further decreased in presence of 2% of KCl. J. S. A.

Solubility of phosphoric acid. A. E. MAKOVETZKI and M. A. OSTROUMOV (Trans. Kirov Inst. Chem. Tech. Kazan, 1935, No. 3, 103—106).—The best solvents for separating H_3PO_4 from its aq. solutions are isoamyl alcohol and fusel oil. H_3PO_4 is almost insol. in CHCl_3 , CCl_4 , liquid SO_2 , PhMe, xylene, benzene, kerosene, and turpentine.

CH. ABS. (e)

Solubility of 6-nitro-3-methylbenzoic acid in benzene, toluene, and water. A. GIACALONE (Gazzetta, 1935, 65, 844—850).—The solubility of 6:3- $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CO}_2\text{H}$ (I) has been measured in C_6H_6 and in PhMe between 10° and 80° and in H_2O between 10° and 100°. In the first two solvents the influence of temp. is given by $S = K \times 2^{t/10}$, where K is a const. (I) crystallises from C_6H_6 in two forms, of which only one is stable at higher temp. The solubility in H_2O is very small up to 50°, but increases rapidly above 60° due to formation of hydrates.

O. J. W.

Solubility of several compounds of the mannose series in alcohols. F. W. UPSON, E. A. FLUEVOG, and W. D. ALBERT (J. Physical Chem., 1935, 39, 1079—1094).—The solubilities of *l*-rhamnose (I), α -*d*-mannose (II), β -*d*-mannose (III), *d*-mannono- γ -lactone (IV), *d*-mannono- δ -lactone (V), α -methyl-*d*-mannoside, and *d*-mannitol (VI) in MeOH, EtOH, $\text{CH}_2\text{:CH} \cdot \text{CH}_2 \cdot \text{OH}$, $\text{Pr}^{\alpha}\text{OH}$, $\text{Pr}^{\beta}\text{OH}$, $\text{Bu}^{\alpha}\text{OH}$, $\text{Bu}^{\beta}\text{OH}$, and *sec.*-BuOH have been determined at different temp. (I) is the most sol. and (VI) the least sol. in all cases. (II) is more sol. than (III), whilst (IV) is almost twice as sol. as (V). R. S.

Solute as liquid. W. D. BANCROFT (Science, 1935, 82, 388—389).—A discussion. L. S. T.

Equilibrium distribution of acetic acid between isopropyl ether and water. A. A. SMITH and J. C. ELGIN (J. Physical Chem., 1935, 39, 1149—1153).—Distribution data are given for 20°. The

results, considered in relation to Almquist's equation (A., 1934, 22), suggest that AcOH forms double mols. in $\text{Pr}^{\beta}\text{O}$. R. S.

Equilibria and surface phenomena in the system water-formic acid-phenol. V. I. NESTEROVA, N. N. PETIN, and K. V. TOPTSCHIEVA (J. Gen. Chem. Russ., 1935, 5, 848—861).—The partition coeff. of HCO_2H (I) between H_2O and PhOH at 20° rises with increasing concn. to 1.075*M*, and then falls to 1.507*M*-(I), at which concn. the system becomes homogeneous. The conductivity of the PhOH layer rises uninterruptedly to the crit. point, whilst that of the aq. layer rises to a max., and then falls with increasing $[\text{HCO}_2\text{H}]$. The dissociation coeff. of (I) rises with increasing $[\text{HCO}_2\text{H}]$ in the PhOH, but remains const. in the aq. layer. The surface tension at the air- H_2O interface remains const., but that at the H_2O -PhOH interface rises linearly with increasing $[\text{HCO}_2\text{H}]$ to the crit. point. R. T.

Solubility of deuterium and hydrogen in solid palladium. A. SIEVERTS and G. ZAPF (Z. physikal. Chem., 1935, 174, 359—364).—The solubilities have been determined at 300—1100°. The ratio of the solubility of D to that of H is 0.67 at 300° and 0.91 at 1000° and approaches 1 at higher temp. The solubility of either at a given temp. is $\propto \sqrt{\text{gas pressure}}$. R. C.

Colloid-chemical phenomena in metals. I. Gases in aluminium. J. A. KLJATSCHKO (Kolloid-Z., 1935, 73, 226—236).—Mainly a discussion of published work. The vol. of gas liberated from Al and duralumin when heated at different temp. and the proportion of H_2 contained therein have been measured. E. S. H.

Accommodation coefficient of hydrogen on iron. H. H. ROWLEY and W. V. EVANS (J. Amer. Chem. Soc., 1935, 57, 2059—2064).—The accommodation coeff. is 0.31 at 450—350° abs. and increases steadily with falling temp. to 0.55 at 120° abs. Comparison with other work suggests that the exchange of energy between H_2 gas mols. and an adsorbed layer of H_2 is measured in each case. An attempt to remove this adsorbed layer reduces the accommodation coeff. to 0.18 at 350° abs. E. S. H.

Sorption of gases by minerals. V. [Extra-Japanese zeolites.] VI. J. SAMESHIMA and N. MORITA (Bull. Chem. Soc. Japan, 1935, 10, 485—490, 490—494).—V. The rate of absorption of NH_3 and CO_2 at 1 atm. by the dehydrated minerals has been determined at 25°. Thomsonite, scolecite, epistilbite, and phillipsite absorb large vols. of NH_3 , probably forming compounds, but only very small quantities of CO_2 are absorbed; the absorption depends on the temp. of dehydration.

VI. Sepiolite absorbs large vols. of NH_3 and CO_2 , and belongs to the SiO_2 gel class. Asbestos, acid clay, and bentonite absorb large vols. of NH_3 , but only very small quantities of CO_2 . Talc, serpentine, and vivianite absorb only very small quantities of NH_3 and CO_2 . J. G. A. G.

Adsorption of alkali metals on metal surfaces. VI. Selective photo-electric effect. J. H. DE BOER and C. F. VEENEMANS (Physica, 1935, 2, 915—

922; cf. A., 1935, 929).—The photo-electric emission of a cathode has been measured at increasing vals. of the covering fraction for $\lambda\lambda > 3600 \text{ \AA.}$ and 2537 \AA. With the longer $\lambda\lambda$ emission is due solely to the normal photo-electric effect, but at 2537 \AA. the selective effect contributes.

T. G. P.

Mechanism of displacement adsorption of gases and vapours. P. K. MIGAL (J. Gen. Chem. Russ., 1935, 5, 614—621).—The molar heat effect observed when an adsorbed gas is replaced by a vapour (CHCl_3 , CCl_4 , MeOH , CS_2 , EtI , EtOH , Et_2O) may be expressed by $q = \lambda + [(C_2/\alpha_2) - (C_1/\alpha_1)]\beta P$, where λ is the heat of condensation of 1 g.-mol. of vapour, C_1 and C_2 are the sp. heats of the gas and vapour, respectively, α_1 and α_2 are the coeffs. of thermal compression, β is the compression coeff., and P is the deformative force due to the adsorbent. When the capillary activity of the second adsorbate is $>$ that of the first, adsorption on the first adsorbate, but not displacement, occurs, but under converse conditions, adsorption takes place with replacement of the first adsorbate.

R. T.

Velocity of adsorption of gases on porous adsorbents. G. DAMKÖHLER (Z. physikal. Chem., 1935, 174, 222—238).—Langmuir's theory of adsorption velocity is applicable only to pore-free adsorbents and leads to a val. of 10^{-5} — 10^{-10} sec. for the time, τ , required for the establishment of adsorption equilibrium. A theory of velocity of adsorption on porous adsorbents is developed, making various simplifying assumptions and taking the rate-determining process to be diffusion in the pores. This diffusion can be regarded as consisting of a Knudsen mol. streaming in a capillary and a surface diffusion in Volmer's sense on the pore walls. The two diffusion consts. and the pore size are estimated, and the theory indicates that if τ is several min. the mean pore length is of the order of several mm. Langmuir's theory is not applicable to Berl and Weingaertner's experiments (A., 1935, 696), but these are reconcilable with the new theory.

R. C.

Heats of adsorption of gases and vapours on crystallogenic adsorbents. A. B. LAMB and E. N. OHL (J. Amer. Chem. Soc., 1935, 57, 2154—2161).—Heats of adsorption of several gases and vapours on dehydrated chabasite, thomsonite, and brucite have been determined at 0° . In cases where adsorption is considerable, the mol. heats are $>$ those previously observed with C or SiO_2 , but can be represented by the same empirical equation.

E. S. H.

Liquid-side resistance against gas absorption by a liquid drop. (A) Theoretical. (B) Experimental. S. HATTA and A. BABA (J. Soc. Chem. Ind. Japan, 1935, 38, 544—546B, 546—550B).—(A) The resistance to gas absorption due to turbulence on the liquid side of the interface has been calc. for falling drops with (i) no damping of the initial turbulence due to drop formation, (ii) gradual damping during fall, and (iii) immediate disappearance of turbulence, in which case absorption follows a diffusion law. The frictional resistance offered to a falling drop is discussed.

(B) The absorption of CO_2 by falling drops of H_2O

has been studied at 20° . Absorption during drop formation is negligible compared with that during time of fall. $C/C_\infty = 6q^2/\pi^2 - 3q$ (C = mean concn. at time t , C_∞ = saturated concn., $q = Dt/a^2$, where D = diffusion coeff. of dissolved gas, a = radius of drop), in agreement with (iii). $D = 1.08 \times 10^{-3}$ sq. cm. per sec., which is 60—70 times the published val.

R. S. B.

Surface tension of the system sulphuric acid-water. L. E. SABININA and L. I. TERPUGOV (J. Gen. Chem. Russ., 1935, 5, 783—787).—The temp. coeff. of surface tension-composition curves (10 — 50°) exhibits a min. corresponding with $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$. The max. deviation from the additive rule for σ is found for the same concn.

R. T.

Measurements of surface tension of solutions of potassium and lithium salts of higher fatty acids by the ring method with exclusion of atmospheric carbon dioxide and with special regard to other disturbing influences. I. A. LOTTERMOSER and E. GIESE (Kolloid-Z., 1935, 73, 155—170).—The lack of reproducibility of surface tension measurements of soap solutions cannot be overcome entirely by exclusion of CO_2 . Other sources of error are the enrichment of the solute by adsorption at the Pt ring and at other surfaces in the apparatus. Whilst these effects cannot be eliminated, means are considered whereby they may be reduced to a min. and kept const.

E. S. H.

Cation exchange in permutites, especially hydrogen and heavy-metal permutites. A. RENOLD (Kolloid-Beih., 1935, 43, 1—142).—A comprehensive investigation and discussion of the prep. and exchange reactions of permutites of H, alkali and alkaline-earth metals, Cd, Ni, Cu, Hg, and Ag.

E. S. H.

Transmission of surface perturbations to within real crystals. V. D. BALAREV [with V. CHRISTOFOROVA] (Z. physikal. Chem., 1935, B, 30, 152—156; cf. A., 1935, 1069).—Admixture with NaCl, KCl, or PbCl_2 causes the dehydration and rehydration curves for $\text{BaCl}_2 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{BaCl}_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{O}$ to approach; this can be due only to the transmission of surface energy from the points of contact of the two salts (cf. *ibid.*, 447).

R. C.

Sorption phenomena and chemical processes. VII. Permutoid reactions. I. PUTILOVA (J. Gen. Chem. Russ., 1935, 5, 934—937).—Experimental data for the heat effect of the reaction between nitroalizarin and aq. $\text{Cu}(\text{OAc})_2$ agree with those calc. from the Le Chatelier theorem.

R. T.

Surface potentials and force-area relations of unimolecular films. II. *d*-Pimaric acid and tetrahydro-*d*-pimaric acid. W. D. HARKINS, H. E. RIES, jun., and E. F. CARMAN (J. Amer. Chem. Soc., 1935, 57, 2224—2227; cf. A., 1934, 141).—The max. thickness of the mono-layer is about 12 \AA. for both compounds. The coeffs. of compressibility have been calc. The structures of the pimaric acids are compared with that of cholesterol, and their orientations in surface films are related to the different positions of the polar groups. The surface potential of tetrahydro-*d*-pimaric acid is about 200 mv., whilst that of

d-pimic acid is about 100 mv. In the latter case an unprecedented decrease in surface potential on compression is observed. These facts may be related to an increasing intramol. dipole compensation on compression.

E. S. H.

Unimolecular films of molecules which lie flat on the surface of water. I. Surface pressures and potentials of films of long molecules: polymerides of γ -hydroxydecoic acid. W. D. HARKINS, E. F. CARMAN, and H. E. RIES, jun. (J. Chem. Physics, 1935, 3, 692—698).—Improvements in the apparatus of Harkins and Fischer (A., 1934, 141) are described. The relation between surface pressure and area per mol. (*A*) has been determined for a series of linear polymerides of γ -hydroxydecoic acid with mol. wts. from 780 to 25,200. The films have high compressibilities and *A* is approx. \propto mol. wt. The mols. are oriented parallel to the surface. Their dimensions are calc. Differences between films with perpendicular and with parallel orientation are tabulated. Measurements of the surface potentials show that the contribution of each polar group is $>$ that of the dipole of vertically oriented stearic acid. The films are not very sensitive to changes in [H⁺].

F. L. U.

Theory of physico-chemical periodic processes. I. A. A. VITT and F. M. SCHEMJAKIN (J. Gen. Chem. Russ., 1935, 5, 814—817).—Mathematical.

R. T.

Emission wave theory of periodic reactions. VIII. F. M. SCHEMJAKIN (J. Gen. Chem. Russ., 1935, 5, 943—949; cf. A., 1935, 453).—In general, the periodicity const. is given by $K = \lambda V$, where λ is the distance between two Liesegang rings, and *V* is the velocity of propagation, at limiting conens. of the substrates, whilst at optimal conens. $K = V/4$; the latter relation also applies to micro-periodic phenomena. These findings are in accord with the theoretical considerations of Christiansen *et al.* (A., 1934, 955).

R. T.

Relation between volumes of substances in the free state and in solution. I. I. ZASLAVSKI, A. A. ASTASCHEVA, and I. A. SAKOV (Trans Inst. Chem. Tech. Ivanovo, 1935, 47—49).—The mol. wt.-equiv. vol. curves of chlorides of metals in the solid state and in solution exhibit parallel variations.

R. T.

Viscosity of aqueous solutions of electrolytes. II. Comparison of specific ionic viscosities with other ionic properties of homologous elements. H. TOLLERT (Z. physikal. Chem., 1935, 174, 239—246; cf. A., 1935, 443).—The lattice energies of the alkali chlorides and Na halides, the ionic radii in the lattice, the ionic hydration vals. and heats of hydration, and the mol. ionisation energies of the alkali chlorides all run parallel with the sp. ionic viscosities in 0.1*N* solution. It is inferred that the hydrated ions up to 0.1*N* are in a state of equilibrium with free H₂O which is a function of the at. no. in the same kind of way as are the above ionic properties.

R. C.

Refractometric investigations of aqueous solutions of salt mixtures. System barium chloride-potassium chloride. G. SPACU and E. POPPER

(Z. physikal. Chem., 1935, B, 30, 113—116; cf. A., 1934, 723).—The existence in solution of complex anions corresponding with the compounds [BaCl₄]K₂ and [BaCl₅(H₂O)]BaK is said to have been established.

R. C.

Structure of solutions of strong electrolytes in alcohols and water. G. W. STEWART (Proc. Iowa Acad. Sci., 1934, 41, 250—251; cf. A., 1934, 591).—Aq. LiCl behaves as a submicroscopic emulsion, consisting of a LiCl-H₂O structure in H₂O as a solvent. Aq. MgCl₂, (NH₄)₂SO₄, NH₄Cl, and NaCl are similar. A solution of LiCl in EtOH shows a composite liquid structure, which behaves as if liquid alcoholate were thoroughly mixed with the EtOH, the two forming a single cybotactic structure.

CH. ABS. (e)

Measurement of the size of colloidal particles from the intensity of light transmitted through the solutions. N. N. ANDREEV (J. Gen. Chem. Russ., 1935, 5, 529—534).—The radius of suspended colourless particles (colophony) can be derived from the absorption of transmitted light by a modified Mie formula (Ann. Physik, 1908, [iv], 25, 377).

R. T.

Donnan effect in ultrafiltration of colloidal solutions. A. RABINOVITSCH, P. VASILEV, and T. GATOVSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 109—112).—In ultrafiltration the vol. of the initial sol is diminished by the same amount as the vol. of the ultrafiltrate is increased. By assuming complete dissociation of sols and ultrafiltrates new equations, based on those of Donnan, are derived; they yield theoretical vals. for Fe₂O₃, WO₃, TiO₂, and V₂O₅ sols in good agreement with experimental data.

W. R. A.

Uranium colloids. II. S. I. DIJATSCHKOVSKI and M. F. IVANOVA (J. Gen. Chem. Russ., 1935, 5, 638—642; cf. A., 1927, 1137).—Highly disperse, photosensitive sols of uranyl tartrate are described.

R. T.

Formation of zirconate hydrosols and their disintegration by certain neutral salts. A. W. THOMAS and H. S. OWENS (J. Amer. Chem. Soc., 1935, 57, 2131—2135).—The anions citrate, glycollate, lactate, malate, mucate, pyruvate, tartrate, H₂PO₄['], P₂O₇^{''''} reverse cationic basic Zr chloride micelles to anionic zirconate micelles. The conditions are: (1) ability of the salt anion to displace aquo-groups from the cationic micelle, (2) the formation of a sol. anionic complex, (3) the equilibrium const. of the anionic complex must be $>$ the solubility product of ZrO(OH)₂. The basic Zr sols can be brought into crystalloidal solution by addition of K acetate, tartrate, or glycollate.

E. S. H.

Distance between colloidal particles in the iridescent films of certain iron oxide sols. W. HELLER (Compt. rend., 1935, 201, 831—833; cf. A., 1930, 439).—Vals. are recorded for the distances between layers at various conens. and for varying periods of ageing.

H. J. E.

Magnetic study of sols of hydrated ferric oxide. A. BOUTARIC and R. BONNEVIALE (Bull. Soc. chim., 1935, [v], 2, 1998—2008).—The measured sp. susceptibilities, χ , of Fe₂O₃ sols, containing up to

75 g. of Fe_2O_3 per litre, obey the mixture law. The val. of χ for Fe_2O_3 does not vary appreciably with the length of dialysis, but decreases with increasing age of the sol, the decrease being faster at higher temp.

O. J. W.

Osmotic pressure and mol. wt. of cellulose acetate. A. DOBRY (Bull. Soc. chim., 1935, [v], 2, 1882—1884).—From the limiting val. of the osmotic pressure at zero concn. in various solvents the mol. wt. of cellulose acetate is found to be 66,500.

O. J. W.

Viscosity of solutions of cellulose in cuprammonium. O. KRATKY and G. SAITO (Cellulosechem., 1935, 16, 85—90).—Data are recorded for η of 0.1, 0.25, and 0.5% solutions of modified celluloses regenerated from alkali-cellulose aged in air, and these are approx. expressed by the equation $\eta_{sp}/c = A + Bc$, in which A and B are consts. The term Bc is regarded as due to mechanical interaction of the long chain mols. or micelles with each other. The ratio length/width of the particles calc. on this hypothesis agrees approx. with that calc. from Staudinger's equation.

A. G.

Dissolution of cellulose nitrate. I—III. T. TOMONARI (J. Soc. Chem. Ind. Japan, 1935, 38, 517—528B; cf. A., 1934, 637).—The solubility of various types of cellulose nitrate in org. solvents and in aq. $\text{HNO}_3 + \text{H}_2\text{SO}_4$, and the relative η for solutions, have been determined at 0—25°. Dissolution of di- and tri-nitrates in aq. $\text{HNO}_3 + \text{H}_2\text{SO}_4$ is hindered by the presence of an unknown constituent.

R. S. B.

Action of alcohols on organosols (especially polystyrene, caoutchouc, and cellulose acetate). H. ERBRING and K. SAKURADA (Kolloid-Z., 1935, 73, 191—201).—The pptg. effects of a homologous series of alcohols increases with increasing mol. polarisation, except for organosols of paraffin and caoutchouc, where the reverse effect is observed, and polystyrene in COMeEt , in which the pptg. val. is independent of mol. polarisation. In general the concn. of alcohol required for pptn. increases with increasing viscosity of the system. By addition of alcohols to polystyrene in C_6H_6 a liquid-liquid system is formed at first.

E. S. H.

Coagulation of organosols of cellulose nitrate by electrolytes. II. S. PAPKOV and M. TSCHVEL-EVA (Kolloid-Z., 1935, 73, 202—203; cf. A., 1935, 1319).—The coagulation of sols of cellulose nitrate in COMe_2 by H_2O in presence and in absence of electrolytes has been studied. The stability of the sols cannot be traced to the charge on the particles; the existence of such a charge is doubtful.

E. S. H.

Variation of flocculation threshold in starch sols. H. KOBER and F. DITTMAR (Kolloid-Z., 1935, 73, 219—226).—Capillary-active substances, such as sulphonated fatty acids, have very little influence on the coagulation of starch sols except in presence of salts, when small concns. cause turbidity or flocculation according to the concns. of electrolyte and sol. The effect also varies with the degree of hydrolysis of the starch which occurs during prep. of the sol.

E. S. H.

Imbibition of organic solvents by Yamagata imbibing clay. M. UTIDA (J. Soc. Chem. Ind. Japan, 1935, 38, 513—514B).—The quantity of org. solvent imbibed is $<$ for H_2O , but no systematic relation applies. The relative η of the system clay sol- H_2O - EtOH is infinite near the max. point of the system H_2O - EtOH .

R. S. B.

Imbibition of electrolyte solution by Yamagata imbibing clay. M. UTIDA (J. Soc. Chem. Ind. Japan, 1935, 38, 514B).—The swelling of clay in aq. HCl , NaOH , and NaCl is compared with η for the systems clay sol-electrolyte. A base exchange occurs, as with zeolites, the reaction velocity increasing rapidly with concn. of electrolyte.

R. S. B.

Structure viscosity of lyophilic sols. I. Gelatin sol. N. PESKOV and S. AVERBUCH (Kolloid-Z., 1935, 73, 182—191).—A viscosimeter for use with lyophilic sols is described. The deviations from the Hagen-Poiseuille law shown by gelatin sols are traced to the inner structure and orientation of the particles. The influence of acids and alkalis on η is ascribed to the electro-viscous effect, the increase in dispersity, the possible increase in swelling power, and the change in the form of the micelles. Deviations from the law disappear at 34° in 2% electrolysed gelatin, and at 30° when acids or bases are added to give $p_H < 3.5$ or > 5.5 .

E. S. H.

Silicic acid gels. V. Determination of the hydrogen-ion concentration of gel mixtures. C. B. HURD and R. L. GRIFFETH (J. Physical Chem., 1935, 39, 1155—1159; cf. A., 1934, 730).—The quinhydrone (I) method can be used for the determination of the p_H of SiO_2 gels. The vals. obtained are < 7 and const. during setting, whilst the time of setting is unaffected by the presence of (I).

R. S.

Cryolysis, diffusion, and particle size. II. Investigations with myosin. F. E. M. LANGE and F. F. NORD (Biochem. Z., 1935, 281, 444—446).—A table shows the diffusion coeffs. for myosin (unfrozen) at temp. down to -79° . The decrease of these coeffs. with chilling points to an irreversible aggregating action.

P. W. C.

Ideal and real protein solutions. G. ETTISCH and R. HAVEMANN (Z. physikal. Chem., 1935, 174, 199—221).—If a homodisperse quartz suspension is allowed to sediment in presence of a protein the increase in the sedimented vol. compared with the val. in absence of the protein is a max. at the isoelectric p_H (I). This is a more precise method for the location of I than mere observation of the sedimented vol. alone. For ovalbumin and serum-albumin the val. of I so obtained falls with increasing protein concn., c , when the latter is $>$ a certain val. It follows therefore that at the higher c the mean valency of the protein mol. (cf. A., 1934, 36) is a function of c . Cataphoresis measurements show that at concns. $> 0.5\%$ I of ovalbumin is not const. at $p_H 4.93$, but moves to lower p_H with rising c . These observations are attributed to electrical interaction between the isoelectric protein mols. in the more conc. (non-ideal) solutions. In such solutions the mols. behave as poly poles, and at I the NH_3^+ and CO_2^- groups of

different mols. approach as close as possible. This theory accounts for the above phenomena and also for the effect of neutral salts on I . R. C.

Diffusion of colouring matters in gelatin and morphology of their reactions with electrolytes. S. VEIL (Bull. Soc. chim., 1935, [v], 2, 1830—1832).—The use of characteristic diffusion figures in gelatin (cf. A., 1934, 1172) for the purpose of qual. analysis is extended to the case of colouring matters.

O. J. W.

Diffusion in gelatin and rhythmic precipitation of magnesium hydroxide. G. AMMON and R. AMMON (Kolloid-Z., 1935, 73, 204—219).—The formation of periodic structures of $Mg(OH)_2$ in gelatin by interaction of aq. NH_3 and $MgCl_2$ has been studied in relation to the diffusion coeffs. of the two reagents, the ratio of the distances between successive rings, and the viscosity of the gelatin. The results of other investigators are discussed in the light of these results.

E. S. H.

Quinone-gelatin gels. J. BUCHHOLZ (Kolloid-Z., 1935, 73, 237).—The phenomenon previously reported has been observed with tolu-, naphtha-, and anthra-quinone.

E. S. H.

Lyophilic colloids. XXV. Coacervation. II. Complex coacervation of the system gum arabic-gelatin. H. G. B. DE JONG and W. A. L. DEKKER (Kolloid-Beih., 1935, 43, 143—212; cf. A., 1935, 821).—Determinations of η , turbidity, and electrophoretic velocity have been carried out. Neutral salts inhibit coacervation; a valency influence, but not a lyotropic influence, is noted. Coacervation is still observed in very dil. solutions. The composition relations for optimum coacervation vary with p_H . The behaviour of the coacervate droplets in the electric field is described.

E. S. H.

Phenomena of electrofiltration in the electrolysis of gels. J. SWYNGEDAuw (Compt. rend., 1935, 201, 821—823; cf. A., 1934, 961).—A discussion.

H. J. E.

Generalised thermodynamic notation. H. A. C. MCKAY (J. Chem. Physics, 1935, 3, 715—719)

F. L. U.

Quantity parameter, intensity parameter, and stable equilibrium. M. PLANCK (Physica, 1935, 2, 1029—1032).—Polemical. (cf. A., 1935, 1076).

T. G. P.

Displacement of equilibrium and the laws of moderation [i.e., of Le Chatelier and van 't Hoff]. D. MATURO (Rev. Fac. Quím. Ind. Agric., 1934, 3, 109—118).—Mathematical.

D. R. D.

Reversible thermo-elastic systems. Generalised coefficients. D. MATURO (Rev. Fac. Quím. Ind. Agric., 1934, 3, 119—130).—Mathematical.

D. R. D.

Osmotic equilibrium and real solutions. D. MATURO (Rev. Fac. Quím. Ind. Agric., 1934, 3, 131—146).—Theoretical. A rigid thermodynamic treatment of equilibria across a semi-permeable membrane.

D. R. D.

Partial molal quantities in an infinitely dilute solution. I. R. KRITSCHESKI and J. S. KASARNOVSKI (J. Amer. Chem. Soc., 1935, 57, 2171—2172).—Theoretical.

E. S. H.

Equilibrium studies on the exchange reaction between acetylene and heavy water. L. H. REYERSON and B. GILLESPIE (J. Amer. Chem. Soc., 1935, 57, 2250—2251).—Average vals. of K_x for the reaction $C_2H_2 + HDO = C_2HD + H_2O$ are 0.365, 0.45, and 0.51 at 0° , 25° , and 100° , respectively. E. S. H.

Second dissociation constant of carbonic acid. Y. KAUKO and V. MANTERE (Suomen Kem., 1935, 8, B, 34; cf. A., 1935, 823).—Extrapolation of measurements in dil. solution gives $K_2 = 5.0 \times 10^{-11}$ at 18° .

R. S.

Peculiar behaviour of aqueous carbonic acid. Y. KAUKO (Suomen Kem., 1935, 8, B, 39—41).—Recorded vals. for the dissociation consts. of H_2CO_3 are discussed. The author's val. for the second const. is $5.3 \pm 0.3 \times 10^{-11}$ at 25° . A slow change occurs in the solution.

R. S. B.

Relative strengths of acids in *n*-butyl alcohol. L. A. WOOTEN and L. P. HAMMETT (J. Amer. Chem. Soc., 1935, 57, 2289—2296).—The relative strengths of 33 carboxylic and phenolic acids have been determined by the potentiometric method. The effect of a substituent on variation in relative strength with changing medium is that to be expected from the electric moment of the substituent and the dielectric const. of the medium, when the substituent is introduced into the mol. at some distance from CO_2H . Some other influence is preponderant when substitution is adjacent to CO_2H .

E. S. H.

Existence of boric acid complexes with one and with two molecules of a diol in aqueous solutions. J. BÖESEKEN and N. VERMAAS, and (in part) W. H. ZAAYER, and J. L. LEEFERS (Rec. trav. chim., 1935, 54, 853—860).—From the equations representing the equilibria involved in the titration of diols with KBO_2 (cf. A., 1932, 1204), and the evaluation of K_1 (2.5×10^{-6} at 18° for mannitol; 3.7×10^{-6} at 18.5° for sorbitol) and K_2 (1.10 and 2.11×10^{-4} , respectively), it is possible to calculate the concn. of all the components present in solution. Rotatory dispersions, in close agreement with the experimental vals., are calc. The rotatory dispersion curve for a solution containing an excess of borate is different from that containing an excess of mannitol. A preliminary analysis of the system $NaBO_2$ -sorbitol indicates that the system is less simple.

J. W. B.

Activity of chloride ions in some solutions of complex chlorides of cobalt and chromium (III). M. CHATELET and F. KERTÉSZ (Compt. rend., 1935, 201, 817—819).—Electrode potential measurements with $AgCl$ electrodes are recorded for aq. KCl , $BaCl_2$, $[CoCl(NH_3)_5]Cl_2$, $[CoH_2O(NH_3)_5]Cl_2$, and $[CrCl(NH_3)_5]Cl_2$ (0.0002—1 molar). For the two Co salts there is only one ionised Cl. For the Cr salt the ionisation of the second Cl increases with dilution.

H. J. E.

Amphoteric hydrated oxides, solutions of their hydrolysing salts, and their compounds of high mol. wt. XXX. Iso- and hetero-polytungstic acids, especially the mechanism of formation of arseno- and phospho-tungstic acids. G. JANDER and H. BANTHIE (Z. anorg. Chem., 1935, 225, 162—172; cf. A., 1934, 1319).—In aq. solutions containing

$\text{WO}_4^{''}$ and $\text{PO}_4^{'''}$ (or $\text{AsO}_4^{'''}$) increasing $[\text{H}^+]$ leads to the successive formation of hexatungstic acids, and hetero-acids in which $\text{P}(\text{As}) : \text{W} = 1 : 6, 1 : 12,$ or $2 : 18$. The systems have been studied by the diffusion method. F. L. U.

Test of mass law on concentrated molten solutions by potential measurements. L. HOLUB, F. NEUBERT, and F. SAUERWALD (Z. physikal. Chem., 1935, 174, 161—198).—Equilibrium consts. and activities have been determined by potentiometric measurements for the systems Pb-Sn-Cl_2 , Pb-Cl_2 , Cd-Pb-Cl_2 , Cd-Cl_2 , Pb-Ag-Cl_2 , Pb-Ag-Br_2 , Pb-Ag-I_2 , Tl-Cd-Cl_2 , Tl-Pb-Cl_2 , and Cd-Sn-Cl_2 . The equilibrium consts. determined directly with cells of the Daniell type differ from the vals. calc. from activities, indicating that activities cannot generally be determined electrochemically owing to irreversibility of the necessary electrodes. The Lorenz-van Laar mass law (A., 1926, 355) fails completely in almost every case. There are large deviations from the ideal mass law, and in some cases where the const. has approx. the correct val. this is due to the accidental compensation of opposed deviations from ideality on the part of the substances involved. It has not been possible to determine at what concns. there is ideality of behaviour of the mols. and ions. In attempting to determine the mol. state of reactants from the constancy of the appropriate mass law quotients it is found that quotients which are most nearly const. do not always correspond with the most probable reaction; both simple and associated mols. or ions may be present simultaneously. R. C.

Physical chemistry of lipins. III.—See A., 1935, 1523.

Thermodynamical calculations of solubilities of nitrogen and hydrogen in water at high pressures. I. R. KRITSCHEVSKI and J. S. KASARNOVSKI (J. Amer. Chem. Soc., 1935, 57, 2168—2171).—A thermodynamic equation, which allows the calculation of the solubility of slightly sol. gases in solvents with small v.p., is given. The equation is verified for N_2 and H_2 in H_2O at $0-100^\circ$ and pressures up to 1000 atm. Partial mol. vols. of N_2 and H_2 in aq. solution are calc. E. S. H.

Deliquescence and efflorescence. A. DAMIENS (Bull. Soc. chim., 1935, [v], 2, 1893—1901; cf. A., 1934, 490).—It is suggested that the terms "deliquescent" and "efflorescent" should be replaced by "critical hygrometric state" defined by $100p/P$, where p and P are the v.p. of the system and the v.p. of H_2O , respectively. Hygrometric data recorded in various parts of France during several years are discussed. O. J. W.

Determination of critical hygrometric states. M. DIENIS (Bull. Soc. chim., 1935, [v], 2, 1901—1907; cf. preceding abstract).—The aq. v.p. of various saturated salt solutions and solid salt hydrates has been measured at 20° and 25° . The "crit. hygrometric states" are recorded. O. J. W.

Fusion curves of mixtures of water and deuterium oxide. Solution equilibrium in the system water-deuterium oxide. M. DEŽELIĆ (Z. anorg. Chem., 1935, 225, 173—174).— H_2O and D_2O

form an unbroken series of solid solutions, the f.p. of which is a linear function of the composition. Separation by means of fractional crystallisation is therefore impossible. F. L. U.

Thermal analysis of the system $\text{POCl}_3-\text{SO}_2\text{Cl}_2$. G. P. LUTSCHINSKI and A. I. LICHATSHEVA (Z. anorg. Chem., 1935, 225, 175—176).—The m.p.—composition diagram of $\text{POCl}_3+\text{SO}_2\text{Cl}_2$ is of the simple eutectic type. The eutectic point is at -73.8° and 25.1 mol.-% of POCl_3 . F. L. U.

Thermal analysis of the system argon-boron trifluoride. Compounds with the inert gases of the atmosphere. H. S. BOOTH and K. S. WILLSON (J. Amer. Chem. Soc., 1935, 57, 2273—2280).—F.p.—composition curves show maxima at ratios of 1 atom of A to 1, 2, 3, 6, 8, and 16 mols. of BF_3 , indicating that compounds are formed. The compounds are unstable and decompose above their m.p.; A_2BF_3 appears to be the most stable. The influence of pressure on f.p. suggests the equilibrium $\text{A} + x\text{BF}_3 \rightleftharpoons \text{A}_x\text{BF}_3$ or $\text{A}_x\text{BF}_3 + y\text{BF}_3 \rightleftharpoons \text{A}_{x+y}\text{BF}_3$. E. S. H.

Critical phenomena of the system argon-boron trifluoride. H. S. BOOTH and K. S. WILLSON (J. Amer. Chem. Soc., 1935, 57, 2280—2284).—Retrograde condensation and immiscibility are observed. The compounds formed in this system (cf. preceding abstract) are completely dissociated in the crit. temp. region and scarcely affect the results. E. S. H.

Dissociation of ferrous carbonate. J. KRUSTINSONS (Z. anorg. Chem., 1935, 225, 93—96).—Dissociation pressures of FeCO_3 have been determined over the range $250-290^\circ$. The calc. heat of dissociation is 20.9 kg.-cal. F. L. U.

Dissociation of NiS. D. N. TARASENKOV and A. V. BOGOSLOVSKAJA (J. Gen. Chem. Russ., 1935, 5, 836—838).—NiS gradually loses S when heated in N_2 at 700° , and the v.p. gradually diminishes as the composition of the product approaches that of Ni_3S_2 . This suggests that the NiS ordinarily prepared from Ni and S is a solid solution of S in some other sulphide. R. T.

Direct determination of zinc vapour concentration in the thermal reduction of zinc oxide. O. DONY-HÉNAULT and C. DECROLY (Compt. rend., 1935, 201, 726—728).—The $[\text{Zn}]$ in the vapour phase has been determined by allowing the gas in the reduction vessel (at $920-1075^\circ$) to expand into a second evacuated vessel, cooling the latter, and determining its Zn content. H. J. E.

Solubility product constant of calcium carbonate in sea-water. R. REVELLE and R. H. FLEMING (Proc. 5th Pacific Sci. Cong., 1933, 3, 2089—2092).—The solubility product of CaCO_3 in sea- H_2O is 2.37×10^{-6} . The activity coeff. of Ca^{++} for normal salinity is 0.225. Sea- H_2O is approx. saturated with CaCO_3 . CH. ABS. (e)

Equilibrium in the system $\text{H}_2\text{O-MgBr}_2$. F. H. GETMAN (Rec. trav. chim., 1935, 54, 866—872).—Solubility data are recorded for -42.7° to 100° and extrapolated to 172.4° , the m.p. of $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$. F.p. data for MgBr_2 solutions are also given. The only hydrates formed are $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$ and

MgBr₂·10H₂O, the transition temp. being 0.83°. The eutectic temp. for MgBr₂·10H₂O, ice, and solution is -42.7°. Attempts to obtain MgBr₂·4H₂O by heating MgCl₂·6H₂O were unsuccessful. J. W. S.

System alkali oxide-CaO-Al₂O₃-SiO₂-CO₂. V. Stable equilibria in the system Na₂O-SiO₂-CO₂ and pressures of CO₂ in the reaction between K₂CO₃ and K₂SiO₃. C. KRÖGER and E. FINGAS (Z. anorg. Chem., 1935, 225, 1-23; cf. A., 1935, 935).—The reaction of Na₂CO₃ with Na₂Si₂O₅, Na₂Si₃O₇, and Na₆Si₂O₇ and mixtures of these has been studied by measuring the pressure (*p*) of CO₂ over the systems at various temp. (*t*). CO₂ is absorbed only when the ratio Na₂O/SiO₂ > 0.5. *p-t* diagrams are given for this system and for the system K₂O-SiO₂-CO₂. Thermal data relating to the formation of several Na silicates are calc. Dissociation pressures of cryst. and fused Na₂CO₃ and K₂CO₃ have been determined. F. L. Ü.

Double decomposition in absence of a solvent. XXVIII. V. P. RADISCHTSHEV (J. Gen. Chem. Russ., 1935, 5, 455-490).—Equilibrium data are recorded for the system NaCl-NaBr-NaI-KCl-KBr-KI, which is treated as a combination of 9 binary, 2 ternary, and 4 quaternary systems. The solid phases are binary, ternary, and quaternary solid solutions. R. T.

Heat capacity and free energy of formation of naphthalene. J. N. PEARCE and W. B. TANNER (Proc. Iowa Acad. Sci., 1934, 41, 123-126).—The heat capacity of C₁₀H₈ has been measured from liquid air temp. to 298.1° abs.; vals. for changes in heat content, entropy, and free energy accompanying its formation from its elements are calc. CH. ABS. (e)

Difference in the heats of formation of the two isomerides of butane. Estimate of the heat of formation of tetramethylmethane. F. D. ROSSINI (J. Chem. Physics, 1935, 3, 438; cf. A., 1934, 966, 1071).—Computed vals. (kg.-cal. per mol.) are: *n*-C₄H₁₀ (gas) → *iso*-C₄H₁₀ (gas), -1.63 ± 0.15; *n*-C₅H₁₂ (gas) → CMe₄ (gas), -4.9 ± 1.0; 5C (graphite) + 6H₂ → CMe₄, -40.7 ± 1.2; 5C (diamond) + 6H₂ → CMe₄, -41.8 ± 1.2. N. M. B.

Ionic migration as a molecular-kinetic problem. A. MAGNUS (Z. physikal. Chem., 1935, 174, 262-268).—Regarding the solvent, not as a continuous medium, but as a system the mol. motions of which are controlled by the laws of the kinetic theory of gases, the steady mobility of ions is accounted for by supposing that between two collisions with solvent mols. the ion is accelerated in the direction of the electric field, then slowed down again by the next collision. From known ionic mobilities the mean free paths can be calc., and prove, especially for small and doubly-charged ions, to be ≪ the calc. mol.-kinetic vals. and independent of temp., a discrepancy which is attributed to attraction between the ions and the H₂O dipoles. R. C.

Mobility of the hydrogen and hydroxyl ions in aqueous solution. I. G. WANNIER (Ann. Physik, 1935, [v], 24, 543-544).—The explanation of the high mobilities of H' and OH' on the basis of a proton transfer from one H₂O mol. to the next is discussed.

H' and OH' should approximate to Na' in mobility, and an interpretation of the proton transference is offered on the basis of the tetrahedral structure of H₂O, H₃O', and OH'. H₃O has one potential "hole" and 3 protons, H₂O 2 holes and 2 protons, OH' 3 holes and one proton, so that in a sense OH' is the mirror image of H₃O'. The effect of a field on the ions does not require further assumptions.

A. J. M.

Electrolysis of copper in rock-salt. S. A. ARZIBISCHEV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 157-160; cf. A., 1935, 39).—Data recorded previously are corr. and discussed. Cu diffuses readily in either NaCl or KCl, although the ionic radii of K' and Cu'' are very different. Au also diffuses readily in KCl or NaCl. J. W. S.

Thermodynamics of the electric cell in heterogeneous systems. D. MATURO (Rev. Fac. Quim. Ind. Agric., 1934, 3, 159-167).—Mathematical.

D. R. D.

The concentration cell and Nernst's formula. D. MATURO (Rev. Fac. Quim. Ind. Agric., 1934, 3, 168-176).—The equations already deduced (cf. preceding abstract) are applied to the study of the contact potential between a metal and a solution of one of its salts. D. R. D.

Potentials of cells in liquid ammonia solutions. Thermodynamic constants of the amminocadmium chlorides and of cadmium chloride. C. S. GARNER, E. W. GREEN, and D. M. YOST (J. Amer. Chem. Soc., 1935, 57, 2055-2058).—E.m.f. of the cells Zn(amalgam, N₂)[ZnCl₂·6NH₃(s)], NH₄Cl in NH₃(l), CdCl₂·6NH₃(s)[Cd(amalgam, N₂)] have been determined at 25°. When Zn and Cd are present as pure metals $E_{298.2}^{\circ} = 0.3605$ volt. The standard free energies, heat contents, and virtual entropies of CdCl₂ and CdCl₂·*x*NH₃ (where *x* = 1, 2, 4, 6, 10) have been calc. E. S. H.

Becquerel cells. G. ATHANASIU (Ann. Physique, 1935, [xi], 4, 377-449; cf. A., 1925, ii, 1067).—For cells with Ag-AgI and Hg-Hg₂I₂ electrodes the positive photo-voltaic effect is increased by the H ions of the electrolyte, and may be destroyed or reversed by the OH ions. This is explained by assuming that the electrolyte is a "receiver" of products liberated in the photo-chemical reaction. Lowering of temp. increases the photo-voltaic effect; this is explained by regarding the electrode as the seat of two opposing reactions, a photo-chemical, on which temp. has little effect, and a purely thermal inverse reaction. Ag-AgI electrodes show sensitivity max. at 0.4225 and 0.30 μ, coinciding with the absorption max. of AgI; 0.4225 μ coincides with the photo-conductivity max. of AgI. For Hg-Hg₂I₂ electrodes the max. is at 0.400 μ, and the sensitivity threshold at 0.530-0.540 μ. The Cu-CuO electrode sensitivity ranges from 1 μ, in the infra-red, to a max. at 0.400 μ. Ag electrodes covered with a thick cryst. layer of Ag₂S show a sensitivity max. at 1.35-1.4 μ, coinciding with the photo-conductivity max.; this is also the case for Cu electrodes covered with Cu₂O by thermal and by electrical deposition. The sensitivity max. is at 0.480 μ, and the photo-voltaic and photo-cryst. effects are compared. Results, in general,

support the theoretical explanations previously reported. N. M. B.

Polarographic studies with the dropping mercury cathode. LV. Influence of air on solutions of salvarsan derivatives. R. BRDIČKA (Coll. Czech. Chem. Comm., 1935, 7, 457—466; cf. A., 1934, 1241).—Traces of toxic oxidation products (I) present in neosalvarsan (II), syntharsan (III), and myosalvarsan (IV) may be determined electro-polarimetrically. (II) is most sensitive to oxidation and has been studied most fully. Using an atm. of H_2 and a dropping Hg cathode it is shown that (II), (III), and (IV) are not electro-reduced in presence of NaCl, LiCl, and $LiNO_3$, but waves appear in the polarograms, due to electro-reducible (IV) (present even in the purest specimens). Solutions which have been oxidised by O_2 , and from which dissolved O_2 has been expelled by H_2 , give more pronounced waves owing to increased concn. of (I); the latter may be determined from the height of the waves. (III) gives smaller waves than corresponding solutions of (II) owing to its greater purity, but is otherwise similar; (IV) is more slowly oxidised than (II). In presence of LiCl, Na^+ gives a wave of the polarograms at -2.0 volt, owing to the diffusion current associated with the deposition of Na, and the % of Na can be determined from the height of this wave.

R. S. B.

Electrode polarisation in separation of metal from solutions of complex cyanides. O. ESSIN and A. MATANZEV (Z. physikal. Chem., 1935, 174, 384—394).—Analysis of Glasstone's experimental data (A., 1929, 654; 1930, 864) has shown that the existence of concn. polarisation caused by accumulation of CN^- at the cathode leads in several cases to relations between polarisation and c.d. which are analogous to the equation for H overvoltage. For the discharge of Hg from cyanide solutions, this demonstrates the existence of chemical polarisation, supposedly due to delayed discharge in the sense of Volmer's theory of overvoltage. In the separation of Cu there is no chemical polarisation, but rather a depolarising action. For the separation of Ag and Cd the experimental data are indecisive. R. C.

Organic depolarisers. W. F. HUNTER and L. F. STONE (J. Physical Chem., 1935, 39, 1139—1147).—The single potentials of a no. of depolarisers have been measured against Pt, Au, Ag, Sn, and Ni cathodes. A general interpretation in terms of the electron affinity of depolarisers and the work function of electrodes is advanced. R. S.

Acid-base titration in alcohol-water mixtures. III. Titration of alkaloids and alkaloid salts.—See this vol., 91.

Electrometric control of displacement reactions. (MLLE.) S. VEIL (Compt. rend., 1935, 201, 885—887).—The e.m.f. produced by Pt and Zn when in contact and immersed in $0.2N$ - $CuSO_4$ decreases rapidly from the Volta p.d. to a min., then rises to a max., and oscillates. R. S. B.

Determination of activity of unsaturated organic compounds from the e.m.f. of their reaction with sodium. B. V. TRONOV and L. P.

KULEV (J. Gen. Chem. Russ., 1935, 5, 1007—1015).—The e.m.f. between Na and Pt electrodes in C_6H_6 solutions of ketones, keto-acids, aldehydes (except MeCHO), nitriles (except MeCN), amines, C_5H_5N , cyclohexanone, and mesitylene oxide is greatly increased in presence of NaI, whilst that of carboxylic acids, esters (including nitrates), alcohols, unsaturated hydrocarbons, pyrrole, and nitromethane is unaffected; $PhNO_2$ and isoamyl nitrite occupy an intermediate position. R. T.

Explosion regions. XXVI. Shape of explosion regions and their diameters. W. P. JORISEN (Rec. trav. chim., 1935, 54, 888—892; cf. A., 1933, 469, 573, 790).—Theoretical. J. W. S.

Heavy hydrogen. V. Elementary reactions of light and heavy hydrogen. Thermal conversion of ortho-deuterium and the interaction of hydrogen and deuterium. VI. Ratio of the magnetic moment of the proton to the magnetic moment of the deuteron. A. FARKAS and L. FARKAS (Proc. Roy. Soc., 1935, A, 152, 124—151, 152—157).—V. In the temp. range 850 — 1000° abs. and at pressures 3—74 mm. the reconversion of ortho- D_2 (i) and the interaction of H_2 and D_2 (ii) proceed in the homogeneous gas phase according to the mechanisms: (i) $D+o-D_2 \rightleftharpoons p-D_2+D$ and (ii) $D+H_2 \rightleftharpoons HD+H$, $H+D_2 \rightleftharpoons HD+D$. Reaction (i) proceeds 2.4 times, and reaction (ii) 1.5 times, more slowly than the reconversion of para- H_2 at the same temp. and pressure. In (i) this is mainly due to the different collision frequency and concn. of D atoms. The difference in the energies of activation involved in the reactions $D+D_2 \rightleftharpoons D_2+D$ and $H+H_2 \rightleftharpoons H_2+H$ is only 510 g.-cal., but in (ii), the different reaction rate is due to the fact that the energy of activation for the partial reaction $H+D_2 \rightleftharpoons HD+D$ is about 1.7 kg.-cal. > that for $D+H_2 \rightleftharpoons HD+H$. This behaviour is explained by assuming that the activated complexes HHH, DHH, HDD, and DDD possess zero-point energies similar to the mols. H_2 , HD, and D_2 . A scheme for the energy levels involved in these interchanges is worked out.

VI. From a comparison of the velocity coeffs. of the ortho-para H_2 and D_2 conversions, in the presence of O_2 , using the theory of Kalckar and Teller (A., 1934, 940), the ratio of the magnetic moment of the proton to that of the deuteron is found to be 3.96 ± 0.11 . J. L. B.

Mechanism of the chain reaction in oxygen-hydrogen mixtures. M. PRETTRE (Compt. rend., 1935, 201, 728—730; cf. A., 1935, 827).—The activation energy of the H_2-O_2 reaction in reaction vessels coated with KCl is $95,000 \pm 6000$ g.-cal. The reaction kinetics under these conditions are consistent with the Haber chain mechanism. H. J. E.

Explosion of mixtures of combustible gases with air by nuclear drops of water and other nuclei and by X-rays. V. Experimental conditions required for ignition of hydrogen-air mixtures and nuclei. VI. Nuclear drop-ignition temperatures of ethylene-air mixtures passing through a silica combustion tube; relation between wall and gas temperature and effect on

ignition temperatures of the central thermocouple sheath. VII. Effect of a variety of nuclei, mainly mineral dusts, to ignite and explode a mixture of hydrogen and air; exceptional efficacy of Ni_2O_3 dust to ignite mixtures of air with hydrogen, ethylene, or methane. R. O. KING and G. MOLE (J. Inst. Petroleum Tech., 1935, 21, 838—845, 845—853, 853—859; cf. A., 1934, 1074).—V. An apparatus for direct measurement of the steam-forming activities (from dry H_2 and air) of various combustion-tube surfaces, e.g., Cr-Ni steel, Ni steel, and SiO_2 , is described. The over-all steam-forming effect varies in a particular tube with the variety, temp., and distribution of surface oxide, and steam is not formed at a const. rate until the oxide attains equilibrium with the H_2 in the existing conditions. Self- (T_s) and nuclear-ignition temp. (T_n) were determined in the same apparatus. T_s varies with surface activity, and it is concluded that self-ignition occurs in the boundary layer adjacent to the hot surface.

VI. The wall temp. in the Ni-steel tube was $16-30^\circ >$ the temp. indicated by a central thermocouple, and the differences were always $2-5^\circ$ greater when the tube was coated with oxide. Experiments showed that the surface of the thermocouple sheath was without effect on T_s of C_2H_4 -air mixtures. Ignition in this mixture may begin in the gaseous mixture apart from a free surface. T_s diminishes on changing from the active steel surface to the relatively inactive SiO_2 surface and the range of inflammability increases to a remarkable extent. Nuclear ignition is obtainable when ignition from the surface is prevented by steam dilution of the adjacent layer of gaseous mixture, the effect then being obtained on the surface of the nuclei in the gaseous stream. The effect is obtained when oxidation nuclei reach a suitable concn., or it may be induced by providing nuclear centres, e.g., H_2O or dust.

VII. Added nuclei such as compounds of Fe, Pb, Zn, Ni, and Cr all proved effective to explode a mixture of H_2 and air, Ni_2O_3 having an exceptional igniting effect; T_n was as low as 430° for Ni_2O_3 , compared with $640-690^\circ$ for other nuclei, for a 40% H_2 mixture supplied to a Cr-Ni steel tube at 300 c.c. per min. In a SiO_2 tube for H_2 -air, the min. T_s under given conditions was 566° compared with T_n 395° . Ni_2O_3 has a smaller igniting effect on C_2H_4 -air mixtures than on H_2 -air, the max. igniting effect occurring when the $[\text{C}_2\text{H}_4]$ is about 50% $>$ is required for combining proportions. For CH_4 -air, using Ni_2O_3 , T_n is about $75^\circ < T_n$ and the min. T_n is obtained when the $[\text{CH}_4]$ is 50% $<$ is required for combining proportions. C. C.

Ignition of firedamp by compression.—See B., 1935, 1124.

Homogeneous unimolecular decomposition of gaseous alkyl nitrites. IV. Decomposition of isopropyl nitrite. E. W. R. STEACIE and G. T. SHAW (Proc. Roy. Soc., 1935, A, 151, 685—693).—The thermal decomp. of Pr^iNO_2 between 170° and 210° is homogeneous and of the first order. The main reaction is $\text{Pr}^i\text{NO}_2 = \text{NO} + 0.5\text{COMe}_2 + 0.5\text{Pr}^i\text{OH}$, analogous to those of the other alkyl nitrites investigated (cf. A., 1934, 847, 1312). The reaction rate is

given by $k = 1.26 \times 10^{14} e^{-37,000/RT}$ sec.⁻¹ Comparison of the rates and activation energies of Pr^oNO_2 and Pr^iNO_2 shows that there is no appreciable variation due to chemical configuration. L. L. B.

Thermal decomposition of triethylamine. H. A. TAYLOR and E. E. JUTERBOCK (J. Physical Chem., 1935, 39, 1103—1110; cf. A., 1932, 1002).—The decomp. is unimol. at high pressures between 450° and 500° and tends to become bimol. at lower pressures. In the initial stages, the energy of activation is approx. 50,000 g.-cal. A sevenfold increase of surface and additions of N_2 and NH_3 are without effect, but marked differences occur when H_2 is added. It is suggested that the intermediate products are Et_3N_2 and C_4H_{10} , which ultimately yield CH_4 and N_2 . R. S.

Mechanism of slow oxidation of propane. R. N. PEASE (J. Amer. Chem. Soc., 1935, 57, 2296—2299).—At 300° , with mixtures containing 10—30% of O_2 , the primary products are MeOH , MeCHO , CO , and H_2O . The results are interpreted in terms of Rice's radical-chain theory, on the assumption that OMe and Pr are the chain carriers. Similar mechanisms may apply to the oxidation of CH_4 and C_3H_8 . E. S. H.

Thermal decomposition of nitromethane. H. A. TAYLOR and V. V. VESSELOVSKY (J. Physical Chem., 1935, 39, 1095—1101; cf. A., 1931, 175).—The reaction is unimol. in its early stages and has an energy of activation of 61,000 g.-cal. The gaseous and solid products have been analysed and the intermediate formation of MeNO is postulated. Increase of surface affects the later stages of the reaction, additions of He , N_2 , NO , and CO_2 are without effect, whilst O_2 reacts. R. S.

Induction period in gaseous thermal explosions. O. K. RICE, A. O. ALLEN, and H. C. CAMPBELL (J. Amer. Chem. Soc., 1935, 57, 2212—2222).—When the differential equation connecting temp. with time in an exothermic gas reaction is integrated, a sudden rise of temp., corresponding with an explosion, is indicated above a definite pressure. An approx. method for calculating the induction period in thermal explosions has been obtained from such curves, and applied to explosions of Me_2N_2 and EtN_3 . Approx. heats of decomp. of these compounds have been obtained. E. S. H.

Temperature coefficients in the acid hydration of sodium pyrophosphate. S. J. KIEHL and E. CLAUSSEN, jun. (J. Amer. Chem. Soc., 1935, 57, 2284—2289).—The rate of conversion of $\text{Na}_4\text{P}_2\text{O}_7$ into Na_3PO_4 in HCl solution has been determined at $30-90^\circ$ and an empirical equation developed. Temp. coeffs. for 15° intervals have been calc. E. S. H.

Kinetics of the permanganate-oxalate reaction. I. Effect of various salts on the rate of reaction. R. W. FESSENDEN and B. C. REDMON (J. Amer. Chem. Soc., 1935, 57, 2246—2249).—A negative salt effect has been found in this reaction. Zn^{++} , Cd^{++} , and Al^{+++} , which show apparent positive effects, form complex oxalates and thus decrease $[\text{C}_2\text{O}_4^{--}]$. E. S. H.

Oxidation under pressure of ferrous sulphate in neutral and acid solution. G. AGDE and F. SCHIMMEL (Z. anorg. Chem., 1935, 225, 29—32).—The influence of temp., $[\text{FeSO}_4]$, and pressure of O_2 on the oxidation of aq. FeSO_4 has been determined. Under suitable conditions the oxidation is nearly complete. A part of the product is in the form of insol. basic salt, unless the required amount of free H_2SO_4 is added. The presence of the latter does not affect the extent or the rate of oxidation. F. L. U.

Kinetics of the reaction between permanganate and manganous ions. M. J. POLISSAR (J. Physical Chem., 1935, 39, 1057—1066).—The reaction between Mn^{++} and MnO_4^- has been studied visually and by a semi-quant. $\text{H}_2\text{C}_2\text{O}_4$ -I method. It is autocatalytic, catalysis being due to the MnO_2 formed. The rate increases with the concn. of reactants, but diminishes with increasing acidity. MnO_2 prepared in neutral solution is more effective than that prepared in acid solution, probably owing to its greater dispersion. Determinations of MnO_2 by the $\text{H}_2\text{C}_2\text{O}_4$ method may be carried out only at low $[\text{Mn}^{++}]$. The course of the reaction is altered by addition of SO_4^{--} or F^- , which form complex manganic ions, whilst sunlight has no appreciable effect. R. S.

Hydrolysis velocity of ketimines: steric hindrance effect. J. B. CULBERTSON, W. REYNOLDS, and C. MAIN (Proc. Iowa Acad. Sci., 1934, 41, 170—171).—Data are recorded for the rates of hydrolysis of 2:6-, 2:5-, 2:4-, and 3:5-dimethyldiphenyl ketimine hydrochlorides. CH. ABS. (e)

Hydrolysis of phenyl furyl ketimine: relative negativity effect. J. B. CULBERTSON and L. HINES (Proc. Iowa Acad. Sci., 1934, 41, 172).—Data for the rate of hydrolysis at 0° and 25° are recorded. The rule that the ketimine salts are more resistant to hydrolysis the more negative are the radicals attached to the C:NH is supported. CH. ABS. (e)

Velocity of decomposition of diazo-compounds in water. XVIII. E. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1935, 38, 528—532B; cf. A., 1935, 1082).—The velocity coeffs. for the decomp. of 4:4'-tetrazo-, 2:2'-dimethyl-, 2:2'-dimethoxy-, and 2:2'-disulpho-4:4'-tetrazo-diphenyl chloride at 30° are respectively 1.31, 10.3, 0.0483 (extrapolated) and 2.42×10^{-4} . The temp. coeffs. have been determined. R. S. B.

Reaction rate of acetic anhydride and water. E. K. PLYLER and E. S. BARR (J. Chem. Physics, 1935, 3, 679—682; cf. A., 1934, 829).—By measuring the intensity of infra-red absorption bands characteristic of AcOH and Ac_2O , reaction velocities of $\text{Ac}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{AcOH}$ have been determined. The reaction is approx. unimol. at all concns. studied, and the velocity coeff. decreases with time. An extended application of the method is suggested. F. L. U.

Kinetics of addition of hypochlorous acid to double linkings. I. Crotonic acid. E. A. SCHILOV and N. P. KANJAEV (Trans. Inst. Chem. Tech. Ivanovo, 1935, 19—46).—The reaction of addition of HOCl (I) to crotonic acid (II), or its anion, is one of the first order with respect to (II), and of the second

with respect to (I); the reaction is retarded by H^+ , and unaffected by neutral salts, whilst Cl^- acts catalytically in acid solutions only, so that in presence of HCl the velocity of reaction $-d[\text{HOCl}]/dt = (k'[\text{H}^+] + k''n)[\text{HOCl}][\text{crotonic acid}][\text{Cl}^-]$, where n is the dissociation const. of (II). The temp. coeff. of the reaction in presence of HCl is 1.62 per 10° . The order of the reaction varies greatly with changes in the concn. of the substrates and in the p_{H} of the medium. The reaction in acid media is supposed to consist of addition of the complex $\text{HOCl} \cdot \text{HCl}$ to the $\text{C}=\text{C}$, followed by regrouping and elimination of HCl , whilst in alkaline media, in which OCl^- is the catalyst, the complex ion $\text{HOCl} \cdot \text{OCl}^-$ is assumed to react directly with (II). R. T.

Time course of the heat effects in rapid chemical changes.—See this vol., 91.

Oxidation of hæmoglobin to methæmoglobin by oxygen. II.—See this vol., 92.

Kinetics of displacement of silver from silver nitrate solutions by metallic lead. S. KRZYŻAŃSKI (Z. anorg. Chem., 1935, 225, 151—161).—The reaction is of zero order for initial concns. within the limits 0.125—1N- AgNO_3 . The temp. coeff. of the velocity is of the same order as that of the diffusion coeff. F. L. U.

Dust explosions. A. A. VAN DER DUSSEN (Rec. trav. chim., 1935, 54, 873—884).—The quantities of Al-S mixture, coal, or anthracene dust required to be suspended in unit vol. of air to cause explosion on ignition have been measured. The effects of non-combustible powders in suppressing such explosions follow the order $\text{K}_2\text{SO}_4 > (\text{NH}_4)_2\text{SO}_4 > \text{stone dust} > \text{fuller's earth}$. J. W. S.

Corrosion of iron.—See B., 1935, 1145.

Sensitised explosions. I. Hydrogen-oxygen reaction catalysed by nitrogen peroxide. S. G. FOORD and R. G. W. NORRISH (Proc. Roy. Soc., 1935, A, 152, 196—220; cf. A., 1933, 236).—The region of ignition, which occurs between narrow limits of concn. of catalyst, is bounded by regions of slow reaction, the velocity of which is increased by light which generates O atoms from the NO_2 . There is no distinction in the mode of generation of the slow and explosive reactions; both intervene sharply at the end of an induction period, during which the no. of chains grows at first slowly and then rapidly to a crit. val. The induction periods are reduced by irradiation to < 1 sec. over nearly the whole range of catalytic effect of NO_2 . The data support the view that the branching initially exceeds the extinction of chains over the whole region of catalysis, and that an equilibrium concn. of chains is ultimately imposed on the slow reaction by the self-neutralisation of chains, and by an increase in their extinction due to products of reaction. The process becomes adiabatic when the no. of chains exceeds a crit. val. NO_2 exercises a triple rôle in affecting the origin, branching, and extinction of chains. L. L. B.

Oxidation of carbon monoxide catalysed by nitrogen dioxide. R. H. CRIST and O. C. ROEHLING (J. Amer. Chem. Soc., 1935, 57, 2196—2203; cf. A.,

1934, 1314).—The rate is first order with respect to O_2 at high concns. of NO_2 , and at low concns. it is $\propto [O_2]$ and $[CO]^2$.
E. S. H.

Aqueous solutions of stannic chloride. III. Autocatalytic character of the flocculation. J. GUÉRON (Bull. Soc. chim., 1935, [v], 2, 1993—1998; cf. A., 1934, 960).—The curves previously given for the rate of hydrolysis of aq. $SnCl_4$ solutions can be represented satisfactorily by an equation of the autocatalytic type. The bearing of this on the structure of the colloidal particles formed during the flocculation is discussed.
O. J. W.

Thermal decomposition of sugars and its catalytic acceleration.—See this vol., 56.

Influence of pectin on inversion of sucrose. S. BERLINGOZZI and M. TESTONI (Annali Chim. Appl., 1935, 25, 489—496).—The presence of pectin lowers the velocity of inversion of sucrose (I) in aq. citric acid, the effect being max. at 35° and tending to decrease with rise in temp. For the same temp., inhibition with high concns. of (I) is $>$ that with low concns.
F. O. H.

Effect of salts on the velocity of inversion of sucrose at 25° . J. N. PEARCE and M. THOMAS (Proc. Iowa Acad. Sci., 1934, 41, 139).—For equal molal concns. of different salts the velocity coeff. increased in the order $KCl < NaCl < LiCl < BaCl_2 < Al(NO_3)_3$. The salt effect is best explained on the basis of ionic hydration.
CH. ABS. (c)

Polar and non-polar effects in esterification. C. N. HINSHELWOOD and A. R. LEGARD (J.C.S., 1935, 1588—1591; cf. A., 1935, 828).—The H^+ -catalysed rates of esterification by $EtOH$ of Bu^vCO_2H and CCl_3CO_2H are $<$ of $AcOH$, and the energies of activation are raised. The influence of Cl is probably polar, but that of Me is of another kind.
J. G. A. G.

Titanium. Chlorination of titanium dioxide. A. V. PAMFILOV, A. S. CHUDAKOV, and E. G. SCHANTDEL (J. Gen. Chem. Russ., 1935, 5, 605—608).—Max. utilisation of Cl_2 is found at 400° in presence of birch C and MnO_2 ; in absence of catalysts, velocity of reaction rises continuously with temp. Considerable quantities of $COCl_2$ are produced during the reaction.
R. T.

Displacement of noble metals from solutions of their salts by hydrogen at atmospheric or increased pressure. Displacement of (I) Pd from solutions of $PdCl_2$, (II) Pt from solutions of H_2PtCl_6 . V. V. IPATIEV and V. G. TRONEV (J. Gen. Chem. Russ., 1935, 5, 643—652, 661—666).—I. The reaction $PdCl_2 + H_2 \rightarrow Pd + 2HCl$ is of an autocatalytic nature, and proceeds at considerable velocity at room temp. and atm. pressure; its velocity is determined by the rate of diffusion of H_2 into the solution. The reaction is retarded by increasing the $[HCl]$ or by adding oxidising agents, but is unaffected by ions of less noble metals, which are displaced only after complete displacement of Pd .

II. The reaction consists of the steps $H_2PtCl_6 \rightarrow H_2PtCl_4 \rightarrow Pt$; the above considerations are also applicable to it.
R. T.

Active nitrogen of long duration, law of decay and of increased brightness on compression. (LORD) RAYLEIGH (Proc. Roy. Soc., 1935, A, 151, 567—584).—The catalytic destruction of active N_2 caused by the walls of the vessel is reduced to a min. by coating the walls with H_2SO_4 or HPO_3 . Using HPO_3 and a large bulb, the glow remains visible for > 6 hr. A photometric examination over a wide intensity range of the decay of the glow at const. vol., using (a) a bulb coated with Apiezon oil (considerable wall activity), and (b) a bulb coated with HPO_3 , shows that for (a) the decay proceeds according to an exponential law, being apparently a first order reaction, whilst for (b) the data indicate a reaction of the second, or possibly the third, order. The increase of luminosity under compression has been studied photometrically; the intrinsic brightness \propto (concn.)². This indicates a bimol. reaction in which the excess of neutral N_2 mols. have no part.
L. L. B.

Chlorination of propane. II. The heterogeneous reaction. L. H. REYERSON and S. YUSTER (J. Physical Chem., 1935, 39, 1111—1123; cf. A., 1935, 1082).—The reaction in presence of Al_2O_3 , Cu , and $CuCl_2$ catalysts deposited on SiO_2 gel has been investigated and the energies of activation have been determined. Al_2O_3 gave some H_2O , but good results were obtained with $CuCl_2$. The amount of Cl_2 reacting increased with rise of temp., but when 100% conversion was attained, the temp. could be considerably reduced without diminishing the % of reaction. This hysteresis effect is interpreted on the basis of the relation between the heat of reaction and the energy of activation. Production of the higher chlorinated products is favoured by high $[Cl_2]$, high temp., and greater rates of flow, whilst secondary chlorination of $CH_3CMe_2CH_2$ arising from the pyrolysis of $PrCl$ has been shown to occur.
R. S.

Hydrogenation catalysis. II. Technique of hydrogenation. A. S. GINSBERG (J. Gen. Chem. Russ., 1935, 5, 795—798).—A simple method of hydrogenation consists in shaking a given wt. of unsaturated substance in $EtOH$ with 1 g. of powdered Fe or Ni , and 0.1 g. of Pd (as $PdCl_2 \cdot 2NaCl$) in an atm. of H_2 . The decrease, V , in vol. of the gas is measured after 15 min., and the H no. (vol. of H_2 at n.t.p. absorbed by 1 g. of substance) is given by $V(B-d)/760(1+\alpha t)p - K$, where B is the barometric pressure, d the v.p. of H_2O at temp. t , $\alpha = 1/273$, p the wt. of substance taken, and K the vol. of H_2 absorbed by the catalyst alone. Instructions for recovering Pd from the used catalyst are given.
R. T.

Conversion of fatty acids and their esters into higher alcohols by catalytic reduction under pressure.—See B., 1935, 1149.

Reduction of a catalyst for ammonia synthesis.—See B., 1935, 1141.

Catalytic oxidation of sulphur dioxide.—See B., 1935, 1141.

Methane formation in gas mixtures containing carbon monoxide and dioxide in contact with various nickel catalysts.—See B., 1935, 1124.

Electrolytic separation factor of hydrogen isotopes under various experimental conditions. A. EUCKEN and K. BRATZLER (*Z. physikal. Chem.*, 1935, 174, 273—290).—Separation factors, S , varying from 2.7 to 17 have been observed. Using cathodes of Pt, Au, Ag, Cu, Pb, graphite, and Hg no relation between the material or overvoltage of the cathode and S could be detected. After anodic polarisation of the cathode, unless this is Hg, S is for some time abnormally high, which suggests that the max. separation will be obtained by electrolysis with a.c., or better, commutated d.c. This effect appears to be due not only to electrolytic liberation of O, but to sorption of O by the cathode from the solution or air, forming a surface oxide; probably the catalytic power of the surface for the union of H atoms to H₂ mols. is in this way increased, so that very rapid removal of the H atoms liberated is achieved. Small amounts of α -naphthoquinoline depress S considerably (cf. A., 1935, 309), possibly owing to the formation of intermediate reduction products the H and D atoms of which are able to equilibrate themselves with the solvent. For a given electrode metal S , if it is already large, rises with the c.d. There is no direct connexion between S and the slope of the logarithmic c.d.—potential curve. R. C.

Efficiency of separation of hydrogen and deuterium by electrolysis. T. H. ODDIE (*Proc. Physical Soc.*, 1935, 47, 1060—1067).—A method is described, taking account of evaporation and spraying losses, for determining the efficiency α of concn. of D₂O by electrolysis of H₂O—D₂O mixtures. α is independent of the [H⁺] of the electrolyte and the nature of the electrodes, but increases with rising c.d. $\alpha = 4.0 \pm 0.2$ for c.d. 0.6, and 4.6 ± 0.1 for c.d. 2 amp. per sq. cm., in agreement with theory. N. M. B.

Electrolytic separation of lithium isotopes. A. EUCKEN and K. BRATZLER (*Z. physikal. Chem.*, 1935, 174, 269—272).—Experiments in which aq. Li₂SO₄ was electrolysed with a flowing Hg cathode, and the Li set free reconverted into Li₂SO₄, and again electrolysed and so on five times gave finally a specimen of Li the at. wt. of which differed from that of ordinary Li by an amount within the limit of experimental error. The separation factor, S , was at most 1.070. Bell's calculation of S (A., 1934, 738) is criticised. R. C.

Kinetics of formation of anode films on metals. II. **Films of lead chloride on lead.** L. J. KURTZ (*Compt. rend. Acad. Sci. U.R.S.S.*, 1935, 3, 305—308; cf. A., 1935, 1083).—When 0.5*N*-HCl saturated with PbCl₂ is electrolysed with a Pb anode, the latter is first covered with "islands" of cryst. PbCl₂, which later spread over the whole surface and increase in thickness. The electrical conductivity of the PbCl₂ film increases with increase of c.d., as for AgCl and AgBr films. PbCl₂ films have very small porosity. The kinetics of the growth of PbCl₂ films are studied in the same way as for AgCl films, but the polarisation curves show some differences owing to the greater porosity of the AgCl films. A. J. M.

Reaction mechanism at a graphite anode. V. SIHVONEN (*Suomen Kem.*, 1935, 8, B, 35; cf. A.,

1934, 1186).—The electrode processes occurring in presence of fused alkali and carbonate electrolytes are discussed. R. S.

Electro-deposition of nickel from nickel chloride solutions.—See B., 1935, 1147.

Nickel-plating of aluminium.—See B., 1935, 1147.

Electric currents flowing over rusting iron. U. R. EVANS (*Nature*, 1935, 136, 792—793).—An arrangement for investigating currents flowing over an Fe surface in contact with 0.01*N*-NaHCO₃ during rusting is described. Intense anodic action occurs immediately around a scratched line where rusting is rapid, while cathodic areas are free from attack. L. S. T.

Electrodeposition of tin alloys from alkaline stannate baths.—See B., 1935, 1098.

Chemical reactions in rarified gases under the influence of electric discharges. P. JOLIBOIS (*Bull. Soc. chim.*, 1935, [v], 2, 2035—2052).—A lecture.

Chemical reaction in the electric discharge. I. **Chemical effects of impulse discharges.** E. J. B. WILLEY (*Proc. Roy. Soc.*, 1935, A, 152, 158—171).—Wrede's results for N₂ (A., 1930, 394) may be confirmed by chemical means and by simpler apparatus. The controlled impulse discharge is far superior, as regards both abs. and power yields, to a.c. and d.c. discharges. Some probable consequences of the action of an impulse discharge on a gas are discussed. It is considered that, if the breakdown period is not too short compared with the total duration of the discharge, and if the development of the positive column does not lead to a destruction of products first formed in this induction period, the total effects may approximate to those found in cathodic reactions. L. L. B.

Effect of light on periodic reactions. V. K. NIKIFOROV (*J. Chim. phys.*, 1935, 32, 585—587).—Wave equations yield the correct order for the ratio between the distances apart of Liesegang rings in the presence and absence of light in the reaction $2\text{AgNO}_3 + \text{K}_2\text{Cr}_2\text{O}_7 = \text{Ag}_2\text{Cr}_2\text{O}_7 + 2\text{KNO}_3$ (Kofman, A., 1934, 346). T. G. P.

Separation of the mercury isotopes by a photochemical method. K. ZUBER (*Nature*, 1935, 136, 796).—A partial separation of Hg²⁰⁰ and Hg²⁰² from ordinary Hg has been effected by irradiation of Hg vapour in a magnetic field with the Hg resonance line 2537 Å. L. S. T.

Question of further maxima of the density curves of photographic emulsions after the appearance of solarisation. H. BORST (*Phot. Ind.*, 1935, 33, 1056, 1058).—With some plates (*e.g.*, Agfa Normal), but not with others (*e.g.*, Perutz Orthochromatic), second and third max. can be shown to occur in the density curve, after the first solarisation, on prolonged exposure (to Uviol or Nitrax lamp). Measurement of the densities of the direct blackening produced (not developed), by red light, shows similar variations, but these densities are always much <

those obtained by development, and cannot therefore be concerned with the causes of the recurring max.

J. L.

Mechanism of the desensitisation of photographic plates. II. M. BLAU and H. WAMBACHER (*Z. wiss. Phot.*, 1935, **34**, 253—266; cf. *A.*, 1935, 177, 1331).—About 300 experiments were made to examine the relation of the density curves obtained from desensitised emulsions (Agfa Contrast) to the O_2 content of the surrounding atm., and also to the concn. of the desensitiser. Graphs are given showing the relation between various factors, e.g., intensity of light against concn. of desensitiser, for const. density production. Previous results are substantiated, that desensitisation is dependent on the presence of O_2 , without which there is no residual effect; the dye acts as O_2 carrier for reoxidation of nascent Ag. Other theories are discussed in detail. Solarisation, unobtainable in desensitised plates at atm. pressure, appears on exposure in vac. Similarly, increased densities were obtainable in emulsions bathed in KBr or KI solutions, when exposed in vac.; bathing in $NaNO_2$ or Na salicylate was, however, not affected by the presence or absence of O_2 .

J. L.

Law of blackening of the photographic plate. H. KIENLE (*Naturwiss.*, 1935, **23**, 762—767).—The failure of the photographic reciprocity law is examined particularly in connexion with intermittent illumination. For each emulsion there is a lower-frequency limit of illumination, independent of intensity, above which the Talbot law holds. The curves expressing deviations from the reciprocity law are parallel for all λ at all temp. investigated.

A. J. M.

Photographic photometry. H. KIENLE (*Naturwiss.*, 1935, **23**, 759—762).—Theoretical discussion. The assignation of a scale to intensities of blackening produced on a photographic plate can be of val. only when the method of determining the intensities is stated. The different effect on the plate of intermittent and continuous illumination when the same total quantity of light falls on the plate is discussed.

A. J. M.

Heterogeneous reaction kinetics. Effect of light exposure on the kinetics of thermal decomposition of silver oxalate. A. F. BENTON and G. L. CUNNINGHAM (*J. Amer. Chem. Soc.*, 1935, **57**, 2227—2234).—Exposure to light, especially $\lambda < 520$ $m\mu$, accelerates the subsequent thermal reaction; the effect is relatively less at higher decomp. temp. Contact with O_2 during exposure results in initial poisoning. In the earlier stages of thermal decomp., the extent of reaction at any time, t , approx. $\propto t^m$, where m is 3.5 for unexposed samples, but is progressively less with increasing exposure.

E. S. H.

Change of sodium nitroprusside into Prussian-blue. E. JUSTIN-MUELLER (*Bull. Soc. chim.*, 1935, [v], **2**, 1932—1936).—When exposed to sunlight in an open vessel an aq. solution of Na nitroprusside (I) is decomposed giving $NaNO_2$, HCN, and $Na_2Fe_2(CN)_6$. The last named, in presence of NaOH, is converted into Prussian-blue. When (I) is exposed to sunlight in a closed vessel NO is evolved. The structure of (I) is discussed.

O. J. W.

Reaction between ethylene and chlorine in presence of chlorine acceptors. Photochlorination of ethylene. T. D. STEWART and B. WEIDENBAUM (*J. Amer. Chem. Soc.*, 1935, **57**, 2036—2040).—The rate of photochlorination of $C_2H_4 \propto [Cl_2]$ at const. light intensity and is independent of $[C_2H_4]$. In $H_2-Cl_2-C_2H_4$ mixtures, illuminated or in the dark, practically no H_2 reacts, although the $C_2H_4-Cl_2$ reaction goes to completion. The reaction of C_2H_4 with Cl_2 in $C_2H_4Cl_2$ solution is very rapid and involves $< 10\%$ of the Cl_2 in substitution; in pentane solution 37—73% of Cl_2 is used for substitution, the amount increasing as the $C_2H_4 : Cl_2$ ratio increases.

E. S. H.

Photobromination of tetrachloroethylene and of chloroform with special reference to the effects of oxygen. J. WILLARD and F. DANIELS (*J. Amer. Chem. Soc.*, 1935, **57**, 2240—2245).—Photobromination of C_2Cl_4 is inhibited by the reaction product, and depends little on $[C_2Cl_4]$; the temp. effect is small. Small amounts of O_2 accelerate the reaction, but large amounts almost completely inhibit it, probably because of a competing Br-sensitised photo-oxidation. $CHCl_3$ and Br react at 25° when illuminated with λ 2650 Å. in presence, but not in absence, of O_2 . The mechanism is discussed.

E. S. H.

Catalysis of acetylene polymerisation in ultra-violet light by mercury vapour. (A) F. TOUL. (B) W. KEMULA (*Coll. Czech. Chem. Comm.*, 1935, **7**, 491—492, 493—494).—(A) Polemical against Kemula (cf. *A.*, 1935, 1208).

(B) A reply.

R. S. B.

Primary process in the photochemical and thermal decomposition of azomethane. F. PATAT (*Naturwiss.*, 1935, **23**, 801).—The photochemical decomp. of Me_2N_2 under various pressures at temp. from 20° to 266° by light of λ 366 $m\mu$ has a zero temp. coeff. in respect of the quantum yield. The primary process is $Me_2N_2 \rightarrow 2Me + N_2$ and the existence of a chain reaction involving the interaction of Me with Me_2N_2 is excluded.

W. O. K.

Photochemical decomposition of methylamine and ethylamine. H. J. ÉMELÉUS and L. J. JOLLEY (*J.C.S.*, 1935, 1612—1617; cf. *A.*, 1931, 1251).—The absorption spectra of NH_2Me and NH_2Et are on the short- λ side of approx. 244 and 237 $m\mu$, respectively, and the frequency differences between the bands lead to the frequencies 670 and 726 cm^{-1} , respectively, which are probably characteristic of the excited $\cdot NH_2$. The bands of long λ have fine structure. In the light of the Hg lamp and the Al spark, the chief products from NH_2Me are H_2 , NH_3 , and a liquid, with small quantities of CH_4 and N_2 . Similarly, NH_2Et gives the same gaseous products and small quantities of C_2H_6 and C_2H_4 . Photo-oxidation of NH_2Me affords chiefly NH_3 and a liquid, and smaller quantities of CO, N_2 , H_2 , and CH_4 . In each case, < 0.7 mol. is decomposed per quantum absorbed.

J. G. A. G.

Photochemical decomposition of nitrosoisopropylacetone and β -nitroso- β - ϵ -dimethylhexane. K. D. ANDERSON, C. J. CRUMPLER, and D. L. HAMMICK (*J.C.S.*, 1935, 1679—1684; cf. *A.*, 1903, i, 322; 1935,

307).—The quantum efficiency of the decomp. of the monomeric forms of nitrosoisopropylacetone (I) and β -nitroso- β -dimethylhexane (II) in C_6H_6 solution is approx. unity in light of λ 6400—7100 Å. (I) and (II) give $H_2N_2O_2$ and its decomp. products; (I) also yields mesityl oxide and (II) affords, probably, β -dimethyl- Δ^{β} -hexene. The reaction probably proceeds by the primary elimination of HON.

J. G. A. G.

Primary photochemical reactions. VIII. Quantum yield of the photolysis of methyl *n*-butyl ketone. B. M. BLOCH and R. G. W. NORRISH (J.C.S., 1935, 1638—1642; cf. A., 1934, 852).—In light of λ 2480—2770 Å., the quantum efficiency, γ , of the decomp. of COMeBu (I) at 760 mm. and 127° by the primary processes (I) \rightarrow CO + CH₃ + C₄H₉ and (I) \rightarrow C₃H₆ + COMe, is approx. 0.03 and 0.27, respectively. γ for condensation or polymerisation is approx. 0.04. The absorption spectrum is diffuse and fluorescence was not observed. It is probable that the energy of a considerable proportion of the excited mols. which do not decompose is degraded by an internal redistribution process. J. G. A. G.

Products and processes of ionisation in methyl chloride as determined by a mass spectrometer. S. H. BAUER and T. R. HOGNESS (J. Chem. Physics, 1935, 3, 687—692).—The following ions, in order of decreasing intensity, are generated as primary products in the decomp. of MeCl by electrons: MeCl⁺, Me⁺, CCl⁺, CH₂⁺, Cl⁺, HCl⁺, CH⁺, C⁺, H⁺. Appearance potentials for MeCl⁺, Me⁺, and Cl⁺ are respectively 11.0, 14.7, and 26 volts. Experimental details are given. F. L. U.

Inversion of sucrose solutions in tropical sunlight. N. A. YAJNIK, D. N. GOYLE, and M. L. WADHERA (Z. anorg. Chem., 1935, 225, 24—28).—Aq. sucrose solutions contained in Jena glass vessels undergo inversion when exposed to tropical sunlight in the absence of acid. When acid (0.25*N*) is present the rate of inversion is increased by sunlight. These experiments confirm Dhar's observations (A., 1922, ii, 39). F. L. U.

Photochemical oxidation of hæmoglobin.—See this vol., 92.

Action of radon on polymethylenes: cyclopentane and cyclopentene. G. B. HEISIG (J. Physical Chem., 1935, 39, 1067—1073; cf. A., 1932, 918).—V.-p. data are given for cyclopentane and -pentene and the $-M/N$ vals. for the Rn polymerisation are 1.7 and 4.5, respectively. $-M/N$ is inversely $\propto \Delta(H_2 + CH_4)100 / -\Delta HC$ and increases above 2 with a negative heat of formation. R. S.

Decomposition of ozone by the action of α -particles. P. C. CAPRON and R. CLOETENS (Bull. Soc. chim. Belg., 1935, 44, 441—466).— M/I data for C₂H₂ have been used to calculate M/I vals. in the decomp. of O₃ (3—20 mm. in about 700 mm. O₂). It is shown graphically that the velocity of decomp. $\propto [O_3]$ and increases with the radiation intensity. Considering O₃ ions alone, the ionic yield is approx. const. for a given intensity. R. S.

Separation by rectification of neon into its isotopic components. W. H. KÆESOM and J.

HAANTJES (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 809).—Ne of at. wt. 21.157 has been prepared after 14 rectifications. R. S.

Influence of hydrogen-ion concentration on oxidation and reduction reactions. A. K. BABKO (Z. anal. Chem., 1935, 103, 98—103).—In oxidation-reduction reactions not directly involving H⁺, but involving compounds of multivalent ions with O, H⁺ lowers the stability of the compounds, and raises the oxidation-reduction potential ϵ . Expressions for the influence of [H⁺] on ϵ are derived. J. S. A.

Change of isotopic composition of water by distillation. J. HORIUTI and G. OKAMOTO (Bull. Chem. Soc. Japan, 1935, 10, 503—505).—The % of D in the distillate is < that in the original liquid when H₂O containing 2.6% of D is distilled between -7° and 22°. J. G. A. G.

Purification of water and its p_H value. S. B. ELLIS and S. J. KIEHL (J. Amer. Chem. Soc., 1935, 57, 2145—2149).—Technique for purifying H₂O is critically discussed. The purest H₂O, collected in Ag vessels, had p_H 7.01 at 27.5°, as determined by the glass electrode. E. S. H.

Action of alkali hydroxide solutions on ultramarine-blue. K. LESCHEWSKI and E. PODSCHUS (Z. anorg. Chem., 1935, 225, 43—46; cf. A., 1934, 1318).—Aq. LiOH (1—2.5*N*) when boiled with ultramarine-blue (I) decolorises it and yields a cryst. product (II) containing no S. KOH is relatively inactive, but at a concn. of 7.5*N* removes all S on prolonged boiling, giving a cryst. product having a lattice different from that of (I) or (II). In both cases the Na of (I) is almost completely exchanged for Li or K. F. L. U.

Hydrolysis of solutions of cupric sulphate. O. BINDER (Compt. rend., 1935, 201, 893—894).—The slow hydrolysis of CuSO₄ has been studied by boiling solutions for 0.25—12 hr., and determining the change in acidity by the glass electrode and the composition of the ppt. by X-rays and analysis. Hydrolysis increases with the time of boiling and the change in acidity increases with concn. (c). Insol. solid phases are 4CuO,SO₃,4H₂O (c < 0.06 mol. per litre) and 3CuO,SO₃,2H₂O (c > 0.06). R. S. B.

Substitution of copper and silver by silver. A. P. SERGEEV and A. A. KOSHUCHOVSKI (J. Appl. Chem. Russ., 1935, 8, 1073—1075).—A ppt. of Cu is obtained on the surface of Ag foil (I) when the latter is immersed in aq. CuSO₄ containing excess of KCl or NaCl. When (I) is wrapped up in filter-paper moistened in H₂O, and the packet is placed on conc. aq. AgNO₃, crystals of Ag deposit on the filter-paper; the system acts as a concn. cell, in which Ag is dissolved from the foil, and pptd. at the boundary between conc. and dil. AgNO₃. R. T.

Electrometric and analytical evidence for the composition of precipitated basic copper perchlorate. R. A. BEEBE and S. GOLDWASSER (J. Physical Chem., 1935, 39, 1075—1078; cf. A., 1932, 243).—The composition of Cu(ClO₄)₂.6CuO.xH₂O has been determined electrometrically and by direct analysis. R. S.

Preparation of sulphur and magnesium sulphate from sulphur dioxide and magnesia. II. H. HAGISAWA (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 1161—1176).—The velocity of absorption of dil. SO_2 by aq. $\text{Mg}(\text{OH})_2$ has been studied. When conc. aq. $\text{Mg}(\text{HSO}_3)_2$ is heated with MgO (+S) in a sealed tube at 130—140°, the reaction $3\text{Mg}(\text{HSO}_3)_2 + \text{MgO} = 4\text{MgSO}_4 + 3\text{H}_2\text{O} + 2\text{S}$ is complete. R. S.

Preparation and properties of mono-, di-, and tri-calcium phosphates. H. W. E. LARSON (Ind. Eng. Chem. [Anal.], 1935, 7, 401—406).— $\text{CaH}_4(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, $\text{Ca}_2\text{H}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, and $\text{Ca}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ have been prepared. Their solubilities, p_{H} of the solutions, n , and behaviour on heating have been determined. E. S. H.

Reactions of phosphates with soils. II. **Action of lime on monocalcium phosphate in presence of anhydrous calcium sulphate.** J. CLARENS and H. MARGULIS (Bull. Soc. chim., 1935, [v], 2, 1980—1985; cf. B., 1934, 642).—When solutions of H_3PO_4 and $\text{Ca}(\text{OH})_2$ are mixed in presence of anhyd. CaSO_4 pptn. of CaHPO_4 first takes place. With further addition of $\text{Ca}(\text{OH})_2$ the CaHPO_4 is converted into $\text{Ca}_3(\text{PO}_4)_2$. O. J. W.

Decomposition of barium sulphate by chlorine.—See B., 1935, 1141.

Cadminitrites of univalent metals. A. FERRARI, A. BARONI, and C. COLLA (Gazzetta, 1935, 65, 797—809; cf. following abstract).—The prep. of $\text{KCd}(\text{NO}_2)_3$ and of the compounds $\text{MCd}(\text{NO}_2)_3$ ($\text{M}=\text{Rb}, \text{Cs}, \text{Tl}, \text{NH}_4$) is described. They crystallise in the monometric system, 1 mol. per unit cell, and have, in the order given, a 5.325, 5.375, 5.390, 5.340, 5.355 Å., and $d_{\text{calc.}}$ 3.183, 3.509, 4.063, 4.958, 2.902, respectively. Arguments in favour of the structure $\text{M}_2\text{Cd}[\text{Cd}(\text{NO}_2)_6]$ are given, but, as with the Hg compounds, the cationic Cd cannot be replaced by other metals. O. J. W.

Mercurinitrites of univalent metals. A. FERRARI and C. COLLA (Gazzetta, 1935, 65, 789—797).—The prep. of the compounds $\text{MHg}(\text{NO}_2)_3$ ($\text{M}=\text{Rb}, \text{Cs}, \text{Tl}$) is described. The corresponding K and NH_4 compounds could not be obtained. These double nitrites crystallise in the monometric system with 1 mol. per unit cell. For the Rb, Cs, and Tl compounds $a=5.540, 5.475, 5.385$ Å., and $d_{\text{calc.}}=4.35, 4.77, 5.77$, respectively. The Hg and M are at the corners and centre of the cube, but the position of the NO_2 is uncertain. It seems probable that the formulæ of these substances should be doubled, viz., $\text{M}_2\text{Hg}[\text{Hg}(\text{NO}_2)_6]$. The Hg outside the complex cannot, however, be replaced by any other metal. O. J. W.

Mercury powder. A. GALATZKY (Bull. Soc. chim., 1935, [v], 2, 1801—1807).—Very finely-divided Hg powder is prepared by reducing HgO suspended in H_2O with N_2H_4 and other reducing agents. The grey powder has an appreciable v.p., forms an amalgam by simple contact with Au or Sn, and is readily dissolved by 25% HNO_3 . It is probably a mixture of Hg with small amounts of HgO . O. J. W.

Rare earths. XLV. **Preparation of rare-earth amalgams by displacement.** D. H. WEST

[with B. S. HOPKINS] (J. Amer. Chem. Soc., 1935, 57, 2185—2186).—Amalgams of Ce, Nd, "didymium," and Yt have been prepared by the action of Na amalgam on conc. alcoholic solutions of their chlorides. The metals (except Yt) can be obtained free from Hg by heating the amalgams in vac. E. S. H.

Production of rare-earth metals by thermal decomposition of their amalgams. L. F. AUDRIETH (Metallwirts., 1935, 14, 3—5; Chem. Zentr., 1935, i, 2145—2146).—Amalgams of Ce, La, Nd, Sm, and Y are made by electrolysis of EtOH solutions of the anhyd. chlorides with an Hg cathode. The amalgam is conc. in vac. at 250°, and Hg is removed completely by heating the residue at >1000°. Crucibles lined with pure rare-earth oxides, grading outwards into Al_2O_3 , must be used. Ce is cubic face-centred, a 5.14 Å.; La and Nd are hexagonal with a 3.75, 3.65, c 6.06, 5.88 Å., respectively. J. S. A.

Action of Clerici's solution on gypsum. G. PEHRMANN (Zentr. Min., 1935, A, 54—55; Chem. Zentr., 1935, i, 2146—2147).—Clerici's solution attacks gypsum (I) and deposits Ti_2SO_4 , thereby making the apparent d of (I) too high. J. S. A.

Preparation of carbon suboxide. A. KLEMENC, R. WECHSBERG, and G. WAGNER (Monatsh., 1935, 66, 337—344).—Pure C_3O_2 may be obtained by the dehydration of $\text{CH}_2(\text{CO}_2\text{H})_2$, and from diacetyltartaric anhydride, and subsequent fractionation of the products. A. J. M.

Preparation of pure carbon monoxide. G. MEYER, R. A. HENKES, and A. SLOOFF (Rec. trav. chim., 1935, 54, 797—799).—CO cannot be freed completely from H_2 by fractional distillation. Pure CO is obtained by decomp. of $\text{Ni}(\text{CO})_4$ at 200°, and a laboratory apparatus for this purpose is described. J. W. S.

Silicates. III. **Behaviour of talc on heating with MgO and Mg, Co, and Mn chlorides.** E. THILO (Z. anorg. Chem., 1935, 225, 49—63; cf. A., 1933, 794).—Experiments are described showing that, although the chemical composition and cryst. structure of pyrophyllite and talc are closely analogous, the latter behaves quite differently towards MgO and anhyd. MgCl_2 , CoCl_2 , and MnCl_2 when heated with them. An explanation based on the respective lattice structures is offered. F. L. U.

Formation of "persilicate." H. DITZ (Z. anorg. Chem., 1935, 225, 90—92).—Comments on a paper by Krauss and Oettner (A., 1935, 833). F. L. U.

Carbides of lead and silver. E. MONTIGNIE (Bull. Soc. chim., 1935, [v], 2, 1807—1809).— PbC_2 is obtained by adding CaC_2 to a solution of $\text{Pb}(\text{OAc})_2$ in MeOH. It is stable at room temp., but is easily hydrolysed, and in acid solution evolves C_2H_2 . Pb cyanide could not be prepared. Org. Ag salts do not give Ag_2C_2 when strongly heated. O. J. W.

Attempted concentration of the heavy nitrogen isotope. M. H. WAHL, J. F. HUFFMAN, and J. A. HIPPLE, jun. (J. Chem. Physics, 1935, 3, 434—435).—A study of the isotopic reaction $\text{N}^{15}\text{H}_3 + \text{N}^{14}\text{H}_4\text{OH} = \text{N}^{14}\text{H}_3 + \text{N}^{15}\text{H}_4\text{OH}$ showed that the distribution of N^{15} was slightly favoured in the NH_4OH mol. The

ratio of the v.p. of $N^{14}H_3$ and $N^{15}H_3$, determined by fractional distillation of anhyd. NH_3 , was 1.0052 ± 0.0013 .
N. M. B.

Corrosive action of solutions of ammonium nitrate in liquid ammonia on metals.—See B., 1935, 1091.

Action of hydrogen sulphide on hydrogen sulphite solutions. J. JANICKIS (Z. anorg. Chem., 1935, 225, 177—203; cf. A., 1931, 1255).—The products of the action of H_2S on aq. $KHSO_3$ at p_H 5.1—2.3 are S_2O_3'' , S_nO_6'' ($n=2-5$), S, and H'. At first S_2O_3'' and S_3O_6'' are chiefly formed. The production of higher polythionates is favoured by increase of $[H^-]$ or of $[S_2O_3'']$, but there is no evidence that S_3O_6'' takes part in it. The occurrence of the reaction $H_2SO_2 + 2HS_2O_3' \rightarrow S_5O_6'' + 2H_2O$ is supported by the above observations and by the qual. detection of H_2SO_2 in the reaction mixture. S_4O_6'' and S_3O_6'' are successive degradation products of S_5O_6'' according to:
 $S_5O_6'' + HSO_3' \rightarrow S_4O_6'' + S_2O_3'' + H'$;
 $S_4O_6'' + HSO_3' \rightarrow S_3O_6'' + S_2O_3'' + H'$.
F. L. U.

Reaction of sulphur dioxide with water under pressure.—See B., 1935, 1091.

Hydrogen sulphites. III. Reduction of sodium hydrogen sulphite by zinc amalgam. II. T. MUROOKA (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 1154—1160).—Reduction of HSO_3' by the amalgam method can be carried out in the presence of H_2SO_3 or H_2SO_4 . The yield decreases as the temp. rises, and the best result is obtained when the quantity of amalgam is 1.2 times the theoretical. The solid remaining after reduction has the approx. composition $3ZnSO_3 \cdot Na_2SO_3 + Zn(OH)_2$.
R. S.

Thermal decomposition of $CrO_4 \cdot 3NH_3$. W. F. EHRET and A. GREENSTONE (J. Amer. Chem. Soc., 1935, 57, 2330—2331).— $CrO_4 \cdot 3NH_3$ does not lose NH_3 in vac. at room temp., but at $120 \pm 10^\circ$ a vigorous reaction occurs and a solid residue, $CrO_3 \cdot NH_3$, is formed. The presence of small amounts of impurities has a marked influence on the rate of decomp.; the reaction does not occur in the dark. $CrO_3 \cdot NH_3$ has d 2.073; it is stable in air, but hydrolysed by H_2O .
E. S. H.

Formation of masked complexes in normal and basic solutions of chromium and aluminium salts. A. KÜNTZEL, C. RIESS, and G. KÖNIGFELD (Collegium, 1935, 484—502; cf. B., 1935, 818).—Cr acido-complexes are formed with both sulphates and chlorides, but analogous Al complexes are not formed. Conductivity measurements show that Al sulphato-complexes are not present in aq. $Al_2(SO_4)_3$ which has been boiled and cooled again, but are formed in aq. $Cr_2(SO_4)_3$. The hydrolysis of Cr salts occurs in three successive stages, but that of Al salts is in one stage. Masking occurs on adding a neutral salt containing an anion common to both aq. Cr and Al salts; the rate of masking is greater in Al salts, but the masked Cr salts are more stable. Both basic Al and Cr salts form complexes; the change is complete in Al salts, but in Cr salts the degree of formation diminishes as the Cr salt is more aged.
D. W.

Isotopic exchange reactions with iodine. F. JULIUSBURGER, B. TOPLEY, and J. WEISS (J. Chem. Physics, 1935, 3, 437—438; cf. A., 1935, 1328).—The reaction $RX + I^- = RI + X^-$ (R =alkyl, $X=I$) was examined for two series of aliphatic I compounds by dissolving activated Na^+I^- in alcohol- H_2O , thereby obtaining radio-I ions in solution, adding the alkyl iodide, removing the partly activated org. iodide by pptn. with H_2O , and, after conversion into AgI, making Geiger-Müller counter measurements. Exchanges $>50\%$ were found. The upper limit of the activation energy for the interchange reaction $MeI + I^-$ in EtOH is 16.5 kg.-cal.
N. M. B.

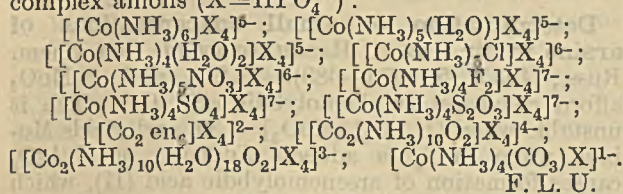
X-Ray investigation of method of preparing spongy iron by reducing hæmatite with gases. V. P. KASANZEV (Z. physikal. Chem., 1935, 174, 370—383).—X-Ray examination of the products of reduction with H_2 shows them to consist of a mechanical mixture of α -Fe, FeO, Fe_3O_4 , and Fe_2O_3 ; no solid solutions are present. The length of edge of the primary fine crystals of α -Fe has been measured. At 700° the reduction of Fe_2O_3 to Fe_3O_4 is more rapid than the subsequent stages of reduction. After reduction is 82.5% complete the product is mainly α -Fe with a small residue of Fe_3O_4 .
R. C.

Ageing and stability towards light of ferrous oxide hydrates in presence and absence of alkali nitrates. O. BAUDISCH (Ber., 1935, 68, [B], 2046—2049).—Colourless FeO hydrate is obtained by gradual addition of alkali to $FeCl_2$ and allowing to age under H_2O during $\frac{1}{2}$ —several hr. The suspension when agitated with O_2 gives α - Fe_2O_3 which probably contains γ - Fe_2O_3 on account of the magnetic properties. Ageing occurs very rapidly. Pptn. of $Fe(OH)_2$ in presence of air and nitrates causes almost immediate reduction of the latter to nitrites. It is probable that H_2O eliminated from the primary $Fe(OH)_2$ yields active H under the experimental conditions, $H_2O \rightarrow H + OH(H_2O_2)$ and corresponding with production of the latter compounds the oxidation of suitable org. compounds (lactic acid, uracil, thymine) occurs concurrently in the system. Neither reduction nor oxidation is observed with aged Fe^{II} hydrates. Even after very long periods in the dark nitrates are not reduced by Fe^{II} salts in the complete absence of O_2 . At. O, liberated from nitrates by light energy, has a powerful oxidising action and the nitrite thus produced reacts momentarily with excess of Fe^{II} ; according to the p_H of the medium, further and complete reduction of the O-N compounds ensues.
H. W.

Action of alkali sulphides on sodium nitroprusside. E. JUSTIN-MUELLER (J. Pharm. Chim., 1935, [viii], 22, 496—503).—The violet colour is due to the formation of an intermediate compound, $Na_3(CN)_5Fe(SNO)_2$, which rapidly decomposes into $Na(NO)S$ groups and $Na_2Fe_2(CN)_6$; these partly recombine to give $Fe_2S_4(NO)_2Na_2$ and the residual $Na_2Fe_2(CN)_6$ is transformed into $Fe[Fe_2(CN)_6]$ and finally into Prussian-blue.
E. H. S.

New group of complex compounds. Compounds with a complex anion, the central ion of which is a complex cation. III. Complex phos-

phato-anions with complex cobalt cations as central ions. H. BRINTZINGER and H. OSSWALD (Z. anorg. Chem., 1935, 225, 33—37; cf. A., 1935, 1091).—Determination of the ionic wt. by measuring the rate of diffusion of complex Co cations in $3N\text{-K}_2\text{HPO}_4$ indicates the existence of the following complex anions ($X=\text{HPO}_4''$):



F. L. U.

Mixed nickelnitrites of uni- and bi-valent metals. II. A. FERRARI and C. COLLA (Gazzetta, 1935, 65, 809—818; cf. A., 1935, 717).—The prep. of the triple nitrites $\text{M}^I\text{Cd}[\text{Ni}(\text{NO}_2)_6]$ ($\text{M}^I=\text{Ti, K}$) is described. These are isomorphous with $\text{K}_2\text{Pb}[\text{Ni}(\text{NO}_2)_6]$ and have a 10.37 and 10.28 Å., respectively. When M^I is Rb, Cs, or NH_4 , the triple nitrites with the general formula given above could not be obtained, as there is a great tendency to form solid solutions between nickelnitrites and cadmiumnitrites, with a 10.58, 10.81, and 10.41 Å., respectively.

O. J. W.

Red and green forms of Magnus' salt. H. D. K. DREW and H. J. TRESS (J.C.S., 1935, 1586—1588).—When the red form of Magnus' salt, $[\text{Pt}(\text{NH}_3)_4]\text{PtCl}_4$ (I), is treated with AgNO_3 followed by K_2PdCl_4 , $[\text{Pt}(\text{NH}_3)_4]\text{PdCl}_4$ is pptd., whereas the red triammine plato salt, $[\text{Pt}(\text{NH}_3)_3]_2\text{PtCl}_4$ (II), of Peyrone and Cleve gives the quite different chlorotriamminoplatinous palladochloride, $[\text{Pt}(\text{NH}_3)_3\text{Cl}]_2\text{PdCl}_4$. Contrary to Cox *et al.* (A., 1933, 41), (II) could not be converted into a green form, and (I) and (II) are not identical. Earlier work (A., 1906, ii, 289) was confirmed, but some H_2PtCl_4 solutions gave the red form of (I) even in the presence of much HCl, which usually favours the green isomeride. The red and green forms of (I) may be electro-isomerides. J. G. A. G.

Asymmetric platinum atom. VII.—See this vol., 84.

Microchemical spectral analysis in high-frequency spark. A. SCHLEICHER and N. BRECHTBERGEN (Z. anal. Chem., 1935, 103, 198; cf. A., 1935, 947).—Supplemental details are recorded. J. S. A.

Quantitative analysis of solutions by spectrographic means. O. S. DUFFENDACK, F. H. WILEY, and J. S. OWENS (Ind. Eng. Chem. [Anal.], 1935, 7, 410—413).—An uncondensed spark in air between a suitable solid electrode and the solution is photographed and, from measurements of the relative intensities of chosen spectral lines, the analysis for metals is made by comparison with previously constructed reference curves. The method has been applied to the determination of Na, K, Mg, and Ca in dil., mixed solutions of their salts. The error is about 2%. E. S. H.

Solubility of precipitates in acids. A. K. BABKO (Z. anal. Chem., 1935, 103, 190—196).—A general expression is given for the solubility of ppts. with varying acid conen., with or without the presence of excess of precipitant. J. S. A.

Electro-capillary method of qualitative analysis. S. I. DIJATSCHKOVSKI (J. Gen. Chem. Russ., 1935, 5, 728—730).—Theoretical aspects of electrolysis of solutions on filter-paper are discussed. R. T.

Analysis of anions. S. M. PUZEVSKAJA (J. Gen. Chem. Russ., 1935, 5, 498—499).—The procedure proposed by Birulia (A., 1933, 1260) is not feasible. R. T.

Application of the glass electrode to unbuffered systems. S. B. ELLIS and S. J. KIEHL (J. Amer. Chem. Soc., 1935, 57, 2139—2144).—General technique for p_{H} determination in unbuffered solutions is described. The method has been applied to very pure H_2O and to some very dil. salt solutions. E. S. H.

Application of bimetallic electrodes to titration of acids or alkalis. J. A. BOLTUNOV and M. A. VORSINA (J. Gen. Chem. Russ., 1935, 5, 519—528).—The bimetallic electrodes Pt-Ni, -Sb, -Co, -Pd, Pd-Ni, and Ni- Hg_2Cl_2 may be used repeatedly without inactivation for the titration of weak or strong acids ($\leq 0.001N$), and of alkalis, Pt-W, -Mo, -Ta, W-Ni, and C-Sb are less suitable, as they have to be reactivated after each determination, whilst Pt-Fe, -Cu, -C, -Al, -Pb, and -Sn electrodes do not give trustworthy results under any conditions. R. T.

Determination of small quantities of water by Crismer's method. L. DE BROUCKERE and A. GILLET (Bull. Soc. chim. Belg., 1935, 44, 473—503).—Crit. solution temp. (c.s.t.) have been determined for the mixtures MeOH- CS_2 , MeOH-EtOH- CS_2 , MeOH- $n\text{-C}_6\text{H}_{14}$, and MeOH-cyclohexane. Interaction occurs between MeOH and CS_2 at high temp., resulting in a progressive shift of the c.s.t., but this may be avoided by addition of EtOH, which lowers the c.s.t. Δ c.s.t. \propto the conen. of H_2O added, and small quantities can be determined by this means. The combustion analysis of an org. compound is given as an example. R. S.

Titrimetric determination of water and alcohols by their acid-catalysed reactions with acetic anhydride in organic media. G. TOENNIES and M. ELLIOTT (J. Amer. Chem. Soc., 1935, 57, 2136—2139).—General technique and scope of the method are described. The error in conen. of about 1% is $< \pm 1\%$; the lower limit of response is $< 0.001\%$. E. S. H.

Chromyl chloride test for chloride. L. MARTINI (Annali Chim. Appl., 1935, 25, 528—530).—A positive reaction with $\text{H}_2\text{SO}_4\text{-K}_2\text{Cr}_2\text{O}_7$ may be due to either Cl' or F'. The vapour is absorbed in dil. alkali, CrO_4'' confirmed as Pb salt, and Cl' or F' identified by the usual tests (CaCl_2 , AgNO_3 , etc.) with due consideration to the presence of I or Br. F. O. H.

Determination of fluorine in soluble and insoluble fluorides by its separation as K_2SiF_6 and subsequent titration of the complex. A. A. VASSILIEV [with N. N. MARTIANOV] (Z. anal. Chem., 1935, 103, 107—113).—Sol. fluorides are dissolved in H_2O and an equal vol. of aq. Na_2SiO_3 (0.01 g. of SiO_2 per c.c.) + KCl is added, and then acidified with 50% HCl (Me-orange). The solution is made 50%

with respect to EtOH. Pptd. K_2SiF_6 is collected, dissolved in CO_2 -free H_2O , and titrated with 0.1N-NaOH (phenolphthalein). The loss due to solubility of K_2SiF_6 is calc. from the vol. of solution and wash liquid. Insol. fluorides are fused with $SiO_2 + NaKCO_3$, and extracted with about 10% aq. $(NH_4)CO_3$. F' in an aliquot part of the solution is determined as above.

J. S. A.

Examination of therapeutic oxygen.—See B., 1935, 1117.

Determination of sulphur in soluble sulphides by photometric titration. S. HIRANO (J. Soc. Chem. Ind. Japan, 1935, 38, 598—601B).—The sol. sulphide is neutralised with HCl and titrated in presence of gum arabic with 0.01 and 0.001N-Pb $(NO_3)_2$ and $HgCl_2$, the end-point being determined photometrically. $BiCl_3$ may be similarly used in slightly acid solution. The method is trustworthy in presence of reducing agents (sulphite, thiosulphate) which preclude the use of the I method.

R. S. B.

Determination of sulphuric acid in presence of ferric salts. M. I. GARBER and I. V. SURIKOV (Trans. Butlerov Inst. Chem. Tech. Kazan, 1934, No. 2, 35—40).—Lunge's method (A., 1905, ii, 350) was superior to those of Allen and Bishop (A., 1913, ii, 722) and of Küster and Thiel (A., 1900, ii, 242).

CH. ABS. (e)

Determination of carbon disulphide and hydrogen sulphide in air.—See B., 1935, 1087.

Potassium thiocyanate as a primary standard substance. I. M. KOLTHOFF and J. J. LINGANE (J. Amer. Chem. Soc., 1935, 57, 2126—2131).—The side reactions occurring in the pptn. of Ag^+ solutions with KCNS have been investigated. KCNS is a suitable standard for work of ordinary accuracy ($\pm 0.1\%$). The solubility product of $AgCNS$ at 24° in 0.05N- KNO_3 is 3.2×10^{-12} .

E. S. H.

Stability of standard potassium thiocyanate solutions. E. N. TARAN (J. Gen. Chem. Russ., 1935, 5, 602—604).—The titre of 0.1N-KCNS rises, during 8 months of storage, to a greater extent (+1.5%) in presence of air and diffused light than in their absence (+0.63%). The variations are ascribed to development of micro-organisms.

R. T.

Kjeldahl method. IV. Metallic catalysts and metallic interferences. R. A. OSBORNE and J. B. WILKIE (J. Assoc. Off. Agric. Chem., 1935, 18, 604—609; cf. A., 1934, 857).—Hg is the most satisfactory catalyst, but it must be pptd. as HgS before distillation of NH_3 . Te, Ti, Fe, and Cu are also satisfactory. Se, Mo, V, W, and Ag are satisfactory in ordinary amounts (< 0.003 g.-mol. per g. of material) or under less violent conditions of digestion. Pt and larger amounts of Se, V, and MnO_4' interfere. Mixed catalysts are not recommended for the digestion of samples of flour.

E. C. S.

Micro-determination of phosphorus. A. D. BRAUN (Trud. Vseso. Inst. Exp. Med., 1934, 1, No. 3, 171—174).—The Fiske-Subbarow method was modified by replacing the mixture of sulphite and H sulphite by 30% CH_2O .

CH. ABS. (e)

Oxidative determination of hypophosphite. L. MARTINI (Annali Chim. Appl., 1935, 25, 525—

528).—The sample (0.1 g. in 50 c.c. H_2O) is boiled for 10 min. with 16% H_2SO_4 (10 c.c.) and 0.1N- $KMnO_4$ (50 c.c.). The ppt. of Mn oxides is dissolved by addition of excess (25 c.c.) of 0.1N- $H_2C_2O_4$ and the solution is re-titrated with 0.1N- $KMnO_4$. The difficulty of dehydrating $NaH_2PO_2 \cdot H_2O$ is demonstrated.

F. O. H.

Determination of small concentrations of arsine in air. B. A. RASCHKOVAN (J. Gen. Chem. Russ., 1935, 5, 675—689).— H_2SO_4 and H_2MoO_4 afford colourless sulphomolybdic acid (I), which is unstable when $[H_2SO_4]/[MoO_3] < 30$, and yields Mo-blue when $SnCl_2$ is added. Addition of H_3AsO_3 causes formation of arsenomolybdic acid (II), which is in equilibrium with (I) and H_2SO_4 ; when $[H_2SO_4]/[MoO_3] > 75$, (II) is not formed, and no coloration results with $SnCl_2$. The following procedure, based on the above considerations, is proposed for determination of AsH_3 ($< 2 \times 10^{-8}$ g.) in air: the sample of air is shaken with 10—20 c.c. of 65% HNO_3 , and a known vol. of the acid is evaporated to dryness after 24 hr. The residue is dissolved in a known vol. of H_2O , and 1 c.c. of the solution is shaken with 1 c.c. of a solution containing 3.4 g. of $(NH_4)_2MoO_4$ and 3 c.c. of conc. H_2SO_4 per 100 c.c. 15 min. later, the mixture is shaken with 0.05 c.c. of aq. $SnCl_2$ (prepared by dissolving 25 g. of Sn in 30 c.c. of conc. HCl, adding a further 20 c.c. of HCl, and diluting to 1 litre), and the coloration is compared with that of a standard solution.

R. T.

Determination of small amounts of boron by means of quinalizarin. G. S. SMITH (Analyst, 1935, 60, 735—739).—A difference in colour produced by equal amounts of quinalizarin with 1 c.c. of test solution + 9 c.c. of H_2SO_4 ; and 10 c.c. of solution of 9 : 1 H_2SO_4 , indicates the presence of H_3BO_3 , and may be matched against a standard solution of H_3BO_3 . The method is suitable for determining $1—40 \times 10^{-6}$ g. of B. Al-Si alloys may be dissolved in 10% NaOH, the solution after acidification being examined for B as above.

J. S. A.

Determination of carbon monoxide in admixture with hydrogen and methane. G. MEYER and A. SLOOFF (Rec. trav. chim., 1935, 54, 800—803).—CO in a mixture of CO, H_2 , and CH_4 may be oxidised to CO_2 by passage over I_2O_5 at $120—130^\circ$, the CO_2 being retained by a liquid-air trap during measurement of the decrease of vol. Combustion of a second sample with CuO completes the analysis.

J. W. S.

Dependence of the detection of carbon monoxide with palladium salt solutions on various additions. W. DALLER (Z. anal. Chem., 1935, 103, 83—88).—The presence of excess of acid or of chlorides hinders the deposition of Pd; salts of weak acids, e.g., NaOAc, favour the action. Solutions of Na_2PdCl_4 containing excess of Na_2SO_3 are somewhat slowly reduced by CO but not by H_2 , and may be used for the analysis of CO- H_2 mixtures. CH_4 reduces Pd solutions at 100° , or at 50° in presence of NaOAc.

J. S. A.

Determination of the CO_2 pressure of natural waters. A. PEKKARINEN (Suomen Kem., 1935, 8, B, 34—35).—If a stream of air containing a known % of CO_2 is passed through dil. $NaHCO_3$ and the solu-

tion is then shaken with a known vol. of air, the % of CO_2 taken up is equal to that of the first air. This principle has been applied to the determination of free CO_2 in natural H_2O . R. S.

Electro-analytical determination of alkalis. K. ABRESCH (*Angew. Chem.*, 1935, 48, 683—685; cf. B., 1935, 1059).—K and Na are separated by the perchlorate or platinichloride method, and are then each determined by the polarographic method (cf. B., 1933, 944; A., 1933, 1024). K and Na can be determined in this manner conveniently and rapidly in solutions containing also Fe, Al, Ca, Mg, etc.

A. B. M.

Application of spectrum analysis to determination of alkalis and alkaline earths. V. Direct photometric determination of alkali metals. W. H. JANSEN, J. HEYES, and C. RICHTER (*Z. physikal. Chem.*, 1935, 174, 291—300; cf. A., 1935, 185).—The liquid under examination is fed into a compressed air- C_2H_2 flame and the principal strong line of the element to be determined, picked out by a monochromator, falls on a photo-electric cell. The magnitude of the photo-electric current, which is measured by allowing it to charge a Lindemann electrometer, is within certain limits of concn. of the element in the flame a linear function of the concn., which is therefore determined by interpolation of data obtained with solutions of known concn. The experimental error is $\pm 5\%$. R. C.

J. Lawrence Smith fusion [method]. M. O. LAMAR, W. M. HAZEL, and W. J. O'LEARY (*Ind. Eng. Chem. [Anal.]*, 1935, 7, 429—431).—Modified procedure is recommended. E. S. H.

Determination of calcium phosphates. H. TRAPP (*J. pr. Chem.*, 1935, [ii], 144, 93—105).—Ca in $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ can be determined (max. error, $+0.17\%$ to -0.18%) by dissolving the sample (0.7—0.1 g.) in 30 c.c. of 30% AcOH +1 c.c. of HCl (d 1.19) at 100° , diluting to 400 c.c., and adding 4 g. of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ to the boiling solution. The ppt. is ignited, treated with $(\text{NH}_4)_2\text{CO}_3$, and weighed as CaCO_3 . Similar results are obtained by dissolving $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in HCl , diluting with H_2O to 250 c.c., adding NH_3 until the solution is red to phenolphthalein, and then 25 c.c. of 10% NH_3 . The mixture is heated for several hr. on the water-bath, kept overnight, and the pptd. $\text{Ca}_3(\text{PO}_4)_2$ is washed with H_2O and weighed. Difficulties in the alkalimetric determination, $3\text{CaHPO}_4 \cdot 2\text{H}_2\text{O} + 2\text{NaOH} = \text{Ca}_3(\text{PO}_4)_2 + \text{Na}_2\text{HPO}_4$, by use of excess of 0.1N-NaOH and back-titration with acid are due to the tenacious occlusion of alkali by the ppt.; the optimum conditions are defined. Under suitable conditions, pptn. of P_2O_5 by MoO_4^{2-} is quant. and the ratio $\text{MoO}_3 : \text{P}_2\text{O}_5$ is const. Variations are due to the ignition, whereby reduction to ill-defined lower oxides readily occurs. Repeated alternate treatment with NH_3 and ignition of the blue residues leads to its complete dissolution with the exception of a residue containing Fe_2O_3 , Al_2O_3 , CaO , and P_2O_5 . The proportion of the blue matter in the residue varies with the conditions of ignition; it is richer in P_2O_5 than the portion sol. in NH_3 .

H. W.

Spectrographic micro-determination of zinc [in plant material]. L. H. ROGERS (*Ind. Eng. Chem. [Anal.]*, 1935, 7, 421—422).—The method is applicable when the concn. of Zn is 0.1—0.005%. Fe interferes in concns. of about 1%, but a procedure for making allowance is suggested. E. S. H.

Quantitative separation of lead from other cations by the chromate method. Z. KARAOGLANOV and M. MICHOV (*Z. anal. Chem.*, 1935, 103, 113—119).—Pb is quantitatively pptd. as PbCrO_4 by $(\text{NH}_4)_2\text{CrO}_4$ in HNO_3 solution, and may be so separated from Cu, Ni, Ag, Ca, Ba, Mn, Zn, Cd, Sr, Fe^{+++} , or Al. J. S. A.

Separation of lead from copper, cobalt, nickel, and cadmium by carbon dioxide in pyridine solution. A. JÍLEK, J. KOT'Á, and J. VŘEŠT'AL (*Chem. Listy*, 1935, 29, 299—304).—The solution of nitrates, containing alkali metals and > 0.2 g. of Cu, is made alkaline with 10% aq. $\text{C}_5\text{H}_5\text{N}$, the vol. is made up to 100 c.c., CO_2 is passed for 5 min., 2 c.c. of aq. NH_3 are added, and CO_2 is passed for a further 40 min. The ppt. of PbCO_3 is collected, washed with aq.-alcoholic $\text{C}_5\text{H}_5\text{N}-\text{NH}_3$ mixture saturated with CO_2 , ignited, and weighed as PbO ; Cu is determined electrolytically in the filtrate. Pb is separated from Ni and Co similarly, except that NH_3 is omitted from the solutions. A similar method cannot be applied to separation of Pb from Cd. R. T.

Use of ceric sulphate in determining cuprous oxide obtained by reducing sugars on Fehling's solution. R. A. STEGEMAN and D. T. ENGLIS (*Trans. Illinois State Acad. Sci.*, 1934, 27, 75—76).— Cu_2O is treated with excess of $\text{Ce}(\text{SO}_4)_2$ and the latter titrated back with standard FeSO_4 (o-phenanthroline as internal indicator). The results are better than those by the KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ methods.

CH. ABS. (e)

Determination of mercury in mercuric cyanide. E. CATELAIN (*J. Pharm. Chim.*, 1935, [viii], 22, 454—456).— $\text{Hg}(\text{CN})_2$ acidified with HCl affords HgS quantitatively when boiled with $\text{Na}_2\text{S}_2\text{O}_3$. Traces of S are removed with Na_2SO_3 and the residue is weighed. J. L. D.

Volumetric determination of mercuric chloride by means of lead sulphide. N. A. TANANAEV and V. D. PONOMAREV (*J. Appl. Chem. Russ.*, 1935, 8, 1076—1078).—25 ml. of approx. 0.1N- HgCl_2 are boiled during 15 min. with 25 ml. of an aq. suspension of freshly pptd. PbS , the solution is filtered, the filtrate+washings are boiled, and titrated with 0.1N- Na_2CO_3 (phenolphthalein); the HgCl_2 content is calc. according to the reaction $\text{HgCl}_2 + \text{PbS} \rightarrow \text{HgS} + \text{PbCl}_2$. The mean error is -0.4% . R. T.

Analytical reactions for detecting salts of cerium and other elements with methylene-blue. L. PASSERINI and L. MICHELOTTI (*Gazzetta*, 1935, 65, 824—832).—Complex compounds with characteristic colours are formed when an aq. solution of methylene-blue is added to solutions containing the following ions: Ce^{+++} , Hg^{++} , PtCl_6^{--} , Au^{+++} , Ir^{+++} , Pd^{++} , MoO_4^{--} , $\text{Fe}(\text{CN})_6^{--}$, $\text{Fe}(\text{CN})_6^{--}$, CNS^+ , $\text{Cr}_2\text{O}_7^{--}$. With many other ions no characteristic colours are formed. The intense scarlet coloration formed with

Ce⁺⁺⁺ salts can be used for detecting this element in presence of all other elements of the third analytical group, including Fe and Cr. The composition of many of the coloured ppt. is given. O. J. W.

Colour reactions of rare-earth metals with pyrogallol and gallic acid. II. F. M. SCHEMJAKIN and T. V. VASCHEDTSCHENKO (J. Gen. Chem. Russ., 1935, 5, 667—674; cf. A., 1934, 621).—The phenomena observed when solutions of Ce(NO₃)₃, NH₃, and pyrogallol or gallic acid (I) are mixed are represented on triaxial diagrams. A colorimetric method for Ce^{III} determination, based on the diagrams, consists in placing 4 c.c. of 0.001*M*-(I) in a Nessler cylinder, adding 4 c.c. of 0.0001—0.0002*M*-Ce^{III}, and 2 c.c. of 0.1*M*-NH₃ containing 1% of Na₂SO₃, filling the remaining space with Et₂O, and comparing the intensity of coloration with that of a standard solution after < 2 min. R. T.

Oxidation mechanisms in aqueous solution. [Manganic sulphate as a reagent.] A. R. J. P. UBBELOHDE (J.C.S., 1935, 1605—1607).—A solution of Mn₂(SO₄)₃, stable when kept in the dark, is prepared by adding 3 c.c. of conc. H₂SO₄ followed by six 2-c.c. portions of 0.5*N*-KMnO₄ at 3-min. intervals to 50 c.c. of MnSO₄ solution (15.1 g. of MnSO₄ in 1000 c.c. of 6*N*-H₂SO₄) with continuous cooling. 2 c.c. of conc. H₂SO₄ are added after 8 c.c. and 12 c.c. of KMnO₄ have been added. The reagent rapidly oxidises nitrites, oxalates, VII to VV, H₂O₂, and Fe^{II} in the presence of Cl⁻. The reactions are stoichiometric and the end-points are well defined, thus affording superior results to titrations with KMnO₄. J. G. A. G.

Bismuthate method for [determination of] manganese. II. B. PARK (Ind. Eng. Chem. [Anal.], 1935, 7, 427; cf. A., 1926, 704).—Modified procedure is recommended. E. S. H.

Absolute colorimetry. XII. **Absolute colorimetric determination of iron.** A. THIEL and O. PETER (Z. anal. Chem., 1935, 103, 161—166; cf. A., 1934, 1324).—For the determination of Fe⁺⁺⁺, the sample is acidified with HCl (against Congo-red), and sulphosalicylic acid is added. The extinction of the red colour produced towards filtered blue or blue-green light is determined by comparison with the standard grey solution, Fe⁺⁺⁺ being calc. from the extinction coeff. For the determination of total Fe, the above solution is made alkaline with aq. NH₃. Rapid atm. oxidation of Fe⁺⁺ occurs, and the yellow colour due to total Fe is colorimetric as before, using light of 462 mμ. Citrates and tartrates interfere. J. S. A.

Simple reaction for cobalt ion. A. V. VOLOKITIN (J. Appl. Chem. Russ., 1935, 8, 1095).—Crystals of MgCl₂·6H₂O acquire a bluish-green coloration when immersed in solutions containing Co. R. T.

Thiocyanate-acetone reaction for detecting minimal quantities of cobalt in presence of iron. H. DITZ and R. HELLEBRAND (Z. anorg. Chem., 1935, 225, 73—80; cf. A., 1934, 1085).—The sensitivity of the NH₄CNS-COEt₂ test for Co is greatly reduced if accompanying Fe is removed

either by Na₂CO₃ or by conversion into a complex fluoride. Removal of Fe by means of pptd. CaCO₃ leaves the sensitivity of the Co test unimpaired, so that 1.5 mg. of Co per litre can be detected in presence of 15 g. of Fe. F. L. U.

Analysis of iron and nickel present together. J. HANUŠ and J. VOŘÍŠEK (Chem. Listy, 1935, 29, 288—295).—When Ni : Fe < 1 : 40, a single pptn. of Fe suffices [acetate, succinate, and (CH₂)₆N₄ procedures], whilst when Ni : Fe > 1 : 40 a double pptn. is necessary for the first two methods, but does not give complete separation in the third method. The amount of Ni carried down with the Fe ppt. may be reduced by adding AcOH to 0.01*N* and NH₄Cl to 1%. The fraction of the Ni pptg. together with Fe is const. for a given Ni : Fe, irrespective of the vols. of solutions taken. R. T.

Determination of cobalt and nickel in zinc ores and electrolytic zinc.—See B., 1935, 1146.

Use of hydrogen peroxide and amyl acetate for micro-determination of chromium. W. B. S. BISHOP and F. P. DWYER (J. Proc. Austral. Chem. Inst., 1935, 2, 278—280).—Amyl acetate is the best solvent for extraction of the blue colour given by CrO₄²⁻+H₂O₂ in acid solution. 2×10⁻⁶ g. of Cr may be so detected. J. S. A.

Colorimetry of chromates at p_H greater than 7. V. N. SKVORTZOV (Trans. Butlerov Inst. Chem. Tech. Kazan, 1934, No. 2, 63—66).—A discussion. CH. ABS. (e)

Determination of chromium in titanium oxide. R. FLATT and X. VOGT (Bull. Soc. chim., 1935, [v], 2, 1985—1993).—The Cr is oxidised to chromate by fusing with a mixture of K₂CO₃ and KClO₃. After removal of most of the TiO₂ with HF the Cr is determined colorimetrically by means of the violet-red colour formed with diphenylcarbazide in acid solution. Using 10 g. of a commercial TiO₂ sample, 0.1—1.0 part of Cr in 10⁶ can be determined with an accuracy of 15%. O. J. W.

Colorimetric determination of molybdenum. Variables involved. L. C. HURD and H. O. ALLEN (Ind. Eng. Chem. [Anal.], 1935, 7, 396—398).—Modified procedure in the KCNS-SnCl₂ method is recommended. E. S. H.

Volumetric determination of tin with ceric sulphate. N. A. RUDNEV (Trans. Butlerov Inst. Chem. Tech. Kazan, 1934, No. 2, 51—62).—The titration of Sn⁺⁺ with Ce(SO₄)₂, with NHPh₂ as indicator, is described. CH. ABS. (e)

Colorimetric determination of titanium by means of gallic acid, as compared with the hydrogen peroxide method. F. M. SCHEMJAKIN and A. NEUMOLOTOVA (J. Gen. Chem. Russ., 1935, 5, 491—497).—4 c.c. of 5% NaOAc, 8 c.c. of 1% gallic acid, and a vol. of solution containing 3—800×10⁻⁷ g. of Ti are placed in a 50-c.c. cylinder in the order given, H₂O is added to the mark, and the coloration is compared with that given by a standard solution. Al does not interfere, but Fe, Mo, U, W, Th, Be, Mn, Zn, Ni, Co, and Ca should be removed. The order of accuracy is the same as for the H₂O₂ method, which,

however, is applicable to the determination of $\leq 6 \times 10^{-6}$ g. of Ti. R. T.

Colorimetric determination of titanium in presence of bromine compounds. G. P. LUTSCHINSKI and A. I. LICHATSHEVA (*Z. anal. Chem.*, 1935, 103, 196—198).—A high [H_2SO_4] and a large excess of H_2O_2 are added to the Ti solution, liberating Br quantitatively. Br is extracted with CHCl_3 , and Ti in the aq. layer determined from the yellow coloration remaining. J. S. A.

Detection of vanadium. E. I. KRETSCH (*J. Appl. Chem. Russ.*, 1935, 8, 1092—1094).—5—100 mg. of powdered salt or alloy are mixed with 0.05—0.1 g. of wood C and 0.2—0.5 g. of anhyd. AlCl_3 , and the mixture is gently heated for 1—2 sec. in a test-tube having a plug of glass-wool moistened with 75% H_2SO_4 inserted at about 7 cm. from the bottom, when an orange coloration indicates V (≤ 0.01 mg. as V_2O_5). Other elements not giving coloured chlorides volatile at $< 150^\circ$ do not interfere. R. T.

Persulphate method of determining vanadium. L. N. MONJAKOVA (*Rept. Cent. Inst. Met.*, 1934, No. 16, 197—199).—Factors affecting the method [e.g., the rate of reduction of V with Mohr's salt, and the time for oxidation of excess of Mohr's salt with $(\text{NH}_4)_2\text{S}_2\text{O}_8$], and its application for determining V in high-V steel were studied. CH. ABS. (e)

Possibility of determining bismuth as basic carbonate. F. HECHT and R. REISSNER (*Z. anal. Chem.*, 1935, 103, 186—189).—Bi, in solution as nitrate only, is treated at room temp. with the min. excess of aq. $(\text{NH}_4)_2\text{CO}_3$. The liquid is heated to boiling, and the ppt. of $(\text{BiO})_2\text{CO}_3$ is washed and dried at 100° . The method may be applied to micro-analytical determinations. J. S. A.

Micro-electrolytic determination of bismuth and lead, and their separation by graded potential. A. J. LINDSEY (*Analyst*, 1935, 60, 744—746).—Bi is deposited at 60 — 70° from dil. HNO_3 solution at a potential of 0.8 volt, in presence of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ as depolariser. Pb is deposited anodically as PbO_2 from dil. HNO_3 at 90 — 100° , at a potential of ≤ 1 volt. For the separation of Bi and Pb, Bi is first deposited as above. The solution and washings are treated with an excess of $\text{NaOH} + \text{Na}_2\text{O}_2$, and are finally acidified with HNO_3 . PbO_2 is deposited at a potential of 1.2 volts, and is preferably redissolved and re-deposited from 20% HNO_3 . J. S. A.

Determination of bismuth with [α]-naphthoquinoline. F. HECHT and R. REISSNER (*Z. anal. Chem.*, 1935, 103, 88—98).—To a solution containing Bi as $\text{Bi}_2(\text{SO}_4)_3 + 3\%$ free H_2SO_4 , 2.5% aq. α -naphthoquinoline sulphate (I) and some H_2SO_3 are added and then an excess of KI. $\text{C}_{13}\text{H}_9\text{N} \cdot \text{HBiI}_4 \cdot \text{H}_2\text{O}$ is pptd., and is collected on a glass filter. The ppt. is washed twice with a solution of (I) + KI (3 c.c. for 10 mg. Bi), followed by ≥ 6 c.c. of H_2O . The ppt. is dried at room temp., and the Bi calc. as if from $\text{C}_{13}\text{H}_9\text{N} \cdot \text{HBiI}_4$. Vols. of solution and wash liquid must be rigidly adhered to, to ensure compensation between H_2O in the ppt. and loss of $\text{C}_{13}\text{H}_9\text{N} \cdot \text{HI}$ during washing. J. S. A.

Use of a [heated] bar in determining m.p. R. DOLIQUE (*J. Pharm. Chim.*, 1935, [viii], 22, 441—451).—The temp. gradients along bars of different metals heated at one end and with different cross-sectional areas are studied and the method is applied to the determination of m.p. J. L. D.

Colour temperatures of the Hefner and acetylene flames. A. R. PEARSON and B. PLEASANCE (*Proc. Physical Soc.*, 1935, 47, 1032—1041).—The colour of the "cylindrical" C_2H_2 flame depends on gas pressure, rate of consumption, and height of flame. In view of discordant data for photometric purposes, results for various burners and conditions are given. The colour temp. for C_2H_2 flames is approx. 2380 — 2520° , and for the Hefner flame 1910° abs. N. M. B.

Simple thermo-regulator. H. P. BLOXAM (*J. Sci. Instr.*, 1935, 12, 361—363).—A bimetallic instrument with a general accuracy of ± 2 — 3° is described. It is suitable for temp. up to 300° . C. W. G.

Semi-automatic potentiometer for thermal analysis. R. J. M. PAYNE (*J. Sci. Instr.*, 1935, 12, 348—355).—A mechanically-driven potentiometer is combined with an inverse-rate recorder. C. W. G.

Determination of the b.p. of small quantities of substances. R. DOLIQUE (*Bull. Soc. chim.*, 1935, [v], 2, 1832—1847).—A differential Hg manometer is described, which can be used for measuring v.p. and b.p. with only a few drops of liquid. The apparatus can be made suitable for the fractional distillation of small amounts of liquid, and can be used for distinguishing a pure liquid from an azeotropic mixture. O. J. W.

Precision determination of lattice constants. E. R. JETTE and F. FOOTE (*J. Chem. Physics*, 1935, 3, 605—616).—Theoretical and experimental conditions necessary for the precise determination of lattice consts. are discussed with reference to symmetrical focussing cameras. Methods for the evaluation of standard errors and fiduciary limits of results from one film and from a set of films are developed. X-Ray targets of alloys have been used to obtain a larger no. and better distribution of lines. The influence of the no. of Miller indices of diffraction lines on the vals. of lattice consts. in non-cubic systems is shown. The importance of the method of prep. of the samples is emphasised. Lattice consts. of pure Al, Ni, Ag, Au, Si, Fe, Mo, W, Mg, Zn, Cd, Sb, Bi, and Sn have been measured. T. G. P.

New technique for obtaining X-ray powder patterns. R. A. STEPHEN and R. J. BARNES (*Nature*, 1935, 136, 793—794).—In the method described a flat specimen such as is met with in metallurgical practice is used, the intensity of each line can be easily calc., and the sharpness controlled, and the time of exposure is lessened in certain cases. L. S. T.

Variable-temperature X-ray powder camera. W. H. BARNES and W. F. HAMPTON (*Rev. Sci. Instr.*, 1935, [ii], 6, 342—344).—Temp. between -60° and 0° are obtained in the camera by circulating through it a suitable liquid precooled in a separate bath. C. W. G.

Two-crystal spectrometer for X-rays of wavelength $0.030 < \lambda < 0.215 \text{ \AA}$. T. R. KUYKENDALL and M. T. JONES (Rev. Sci. Instr., 1935, [ii], 6, 356—361).—Transmission and reflexion through the body of the crystals are employed instead of reflexion from the surface. Specially designed induction coils and a cascade Coolidge tube for a source of short- λ X-rays are described. C. W. G.

Trichromatic colorimeter. R. DONALDSON (Proc. Physical Soc., 1935, 47, 1068—1073).—A simplified instrument for use with a.c. or d.c. is described. The integrating properties of a diffusing sphere are employed to effect the mixture of the three instrumental stimuli; means are described for obtaining linearity of the scales. N. M. B.

Universal colorimeter-nephelometer. A. A. MALIGIN (J. Appl. Chem. Russ., 1935, 8, 1110—1115).—A double-wedge colorimeter, also adapted to nephelometry, is described. R. T.

Optical system of the disappearing-filament pyrometer. F. A. CUNNOLD (Proc. Roy. Soc., 1935, A, 152, 64—80).—Reflexion at the round filament is negligible in the usual type of disappearing-filament pyrometer. Perfect disappearance of the filament is not essential for the attainment of max. accuracy. The aperture limits suggested by previous workers may be considerably widened, enabling pyrometers transmitting much more light to be constructed. L. L. B.

Construction and use of a quartz quarter wave. G. BRUHAT and L. WEIL (Compt. rend., 1935, 201, 719—721). H. J. E.

Bismuth electrode. D. N. MEHTA and S. K. K. JATKAR (J. Indian Inst. Sci., 1935, 18A, 109—113).—The Bi electrode can be used for p_{H} 5.0—7.4. C. W. G.

Glass electrodes. P. L. VARNEY (Science, 1935, 82, 396—397).—A double-shank electrode is described. L. S. T.

Micro-hydrogen electrode. J. LÖBERING (Z. anal. Chem., 1935, 103, 180—183).—An electrode for use with < 0.1 c.c. of liquid is described. J. S. A.

Unpolarisable electrodes to carry action currents.—See A., 1935, 1552.

Application of controlled potential to micro-chemical electrolytic analysis. A. J. LINDSEY and H. J. S. SAND (Analyst, 1935, 60, 739—743).—Apparatus and procedure are described. J. S. A.

Sound-proof box for electrically driven laboratory centrifuges. N. POLLARD (Analyst, 1935, 60, 752—753). J. S. A.

Image errors of the electron microscope. W. GLASER (Z. Physik, 1935, 97, 177—201).—Comma and spherical aberration errors are discussed theoretically. A. B. D. C.

[Mechanical] relay for spark counters of the Greinacher type. H. TEICHMANN (Nature, 1935, 136, 871—872). L. S. T.

Magnetic properties of natural and artificial iron-oxygen compounds. I. Magnetic measurements on powder samples. W. LUYKEN and L. KRAEBER (Mitt. Kaiser-Wilh. Inst. Eisenforsch.,

1934, 16, 169—178; Chem. Zentr., 1935, i, 2141).—A magnetic balance, especially suited for measurement on paramagnetic substances, is described. Conditions necessary for abs. measurements on ferromagnetic material have been investigated. J. S. A.

Accurate measurement of volumes, and accurate titration. R. GOLTZ (J. Gen. Chem. Russ., 1935, 5, 779—782).—A burette adapted for the accurate delivery of liquids is described, and conditions for prep., standardisation, and storage of standard solutions are specified. R. T.

Absorber for titrimetric determination of traces of admixtures to gases. V. G. GUREVITSCH (J. Appl. Chem. Russ., 1935, 8, 1107—1109).—A wash-bottle for the absorption of traces of admixtures to gases is described. R. T.

Kjeldahl flasks and other apparatus of arsenic-free glass. G. LOCKEMANN (Z. anal. Chem., 1935, 103, 81—82).—The use of apparatus of special Jena As-free glass (cf. A., 1935, 948) is discussed. J. S. A.

Pyknometer. G. A. FESTER (Rev. Fac. Quím. Ind. Agric., 1934, 3, 177).—The apparatus consists of a tap-funnel attached to a narrow U-tube with a bulb on the other limb and a graduation mark above the bulb. The liquid is run in through the tap until the meniscus reaches the mark, and the excess in the funnel is washed out before weighing. D. R. D.

Absorption and titration flask for carbon dioxide determination. R. GARDNER (Ind. Eng. Chem. [Anal.], 1935, 7, 437—438).—A modification of Thomas' absorption unit (B., 1933, 574) is proposed. E. S. H.

Continuous distilling apparatus. F. M. SCHERTZ (Ind. Eng. Chem. [Anal.], 1935, 7, 441).—The apparatus is suitable for liquids with b.p. 20—100°, and minimises risk of fire. E. S. H.

Glass water-stills. B. SIEDE (Chem.-Ztg., 1935, 59, 925).—Modern resistance glasses enable satisfactory stills to be constructed. The simple all-glass apparatus without rubber or ground joints illustrated compares favourably with metal stills for efficiency. G. H. C.

Molecular still. W. H. STRAIN and W. M. ALLEN (Ind. Eng. Chem. [Anal.], 1935, 7, 443).—Apparatus, accommodating 1—2 g. of substance, suitable for the purification of biological products is described. E. S. H.

Automatic cut-off for electric stills. M. R. A. RAO and B. S. RAO (Ind. Eng. Chem. [Anal.], 1935, 7, 377). E. S. H.

Automatic still cut-off. A. H. HALE and F. D. TUENMLER (Ind. Eng. Chem. [Anal.], 1935, 7, 441). E. S. H.

All-glass valve. J. WILLARD (J. Amer. Chem. Soc., 1935, 57, 2328—2329). E. S. H.

Superiority of a Knudsen type vacuum gauge for large metal systems with organic vapour pumps, its design and operation. J. W. M. DUMOND and W. M. PICKELS, jun. (Rev. Sci. Instr., 1935, [ii], 6, 362—370).—A discussion of the advantages and disadvantages of different types of gauge. C. W. G.

Use of the Pirani gauge in finding vacuum leaks. T. R. CUYKENDALL (Rev. Sci. Instr., 1935, [ii], 6, 371—372).—Gauges may be made from C-filament lamps. Leaks are shown by the gauge if a stream of illuminating gas is played over the surface of the apparatus. C. W. G.

Precision oil gauge. S. PALKIN (Ind. Eng. Chem. [Anal.], 1935, 7, 434—435).—The gauge is suitable for measuring pressures < 40 mm. with a precision of about 0.033 mm. Hg. E. S. H.

Design of pressure control assembly. S. PALKIN (Ind. Eng. Chem. [Anal.], 1935, 7, 436).—The apparatus previously described (A., 1934, 1195) is modified. E. S. H.

Sampling apparatus for chemical-climatological and technical investigations. H. CAUER (Z. anal. Chem., 1935, 103, 166—180).—Portable and permanent installations of pump, flow meter, air filter, and absorption tubes for air sampling are described, and their uses indicated. J. S. A.

Cataphoresis chamber for measurement of the cataphoretic migration velocity of microscopic particles. R. HAVEMANN (Biochem. Z., 1935, 281, 402—407).—The usual methods for determination of ζ -potential and the theoretical requirements for microscopic measurement of cataphoresis in suspensions with the help of a closed chamber are discussed. The setting up of a suitable chamber is described. P. W. C.

Laboratory apparatus for ammonia synthesis. V. F. POSTNIKOV (Trans. Inst. Chem. Tech. Ivanovo, 1935, 66—67).—Apparatus for the study of catalytic NH_3 synthesis at 500°/100 atm. is described. R. T.

Precise method of measuring viscosity of solutions of organic substances. A. VAN DER WYK and K. H. MEYER (J. Chim. phys., 1935, 32, 549—563).—With the object of determining viscosities of dil. solutions of org. substances the errors in Ubbelohde's method have been examined in detail, and necessary precautions and corrections ascertained so that η may be found in the range 0.015—0.050 with an accuracy of 4×10^{-4} g./cm. sec. T. G. P.

Structure-capillary viscosimeter. V. Z. DANES (Kolloid-Z., 1935, 73, 174—181).—An overflow capillary viscosimeter with a very wide range of working pressures is described. Results are given for H_2O and some aq. solutions. E. S. H.

Durability of quartz glass ignition vessels. M. A. BESBOBODOV and T. A. LADE (J. Soc. Glass Tech., 1935, 19, 217—220T).—Measurements of the loss in wt. of transparent fused SiO_2 vessels when used for the ignition of various ppts. encountered in quant. analysis showed that, after three successive heatings, the corrosion was greatest with PbSO_4 (especially marked), ZnNH_4PO_4 , ZnCO_3 , and SnO_2 . Little or no loss in wt. was caused by the following, for the ignition of which fused SiO_2 vessels are recommended: KNO_3 , K_2PtCl_6 , MgSO_4 , HCl (conc.), Ni dimethyl-

glyoxime, mixtures of Al and Fe (or of Al, Fe, and Ti) hydroxides, NaCl and KCl (1:1), MgNH_4PO_4 , graphite ash, $\text{MgNH}_4\text{AsO}_4$, Na_2SO_4 , MnNH_4PO_4 , CaCO_3 , a mixture of $\text{K}_2\text{S}_2\text{O}_7$, Al_2O_3 , and Fe_2O_3 (the loss in wt. was = that of a Pt vessel used under similar conditions), CaC_2O_4 , and BaSO_4 . A. L. R.

Diacolation and filtration under pressure. C. ROHMANN and J. H. EHLERS (Pharm. Ztg., 1935, 80, 1196—1197).—A laboratory apparatus for maintaining const. pressures ± 1 atm. for a const. delivery of 1 c.c. per min. from the diaculator or filter over a period of 80 hr. is described. E. H. S.

Determination of the v.p. of compounds of metals. D. N. TARASENKOV, A. N. GRIGOROVITSCH, and A. V. BOGOSLOVSKAJA (J. Gen. Chem. Russ., 1935, 5, 924—933).—Jelinek's method (A., 1929, 1262) is preferred to that of Volmer (*ibid.*, 1226). The b.p. method gives trustworthy results for salts of high v.p., on condition that no decomp. occurs. Johnston's static method (A., 1908, ii, 358) is in particular convenient for determination of dissociation pressure when one of the products is a gas. R. T.

Stirring air within desiccators. F. J. ZINK (Ind. Eng. Chem. [Anal.], 1935, 7, 442—443).—Small fans mounted on pivots inside the desiccator are caused to rotate by a series of mechanically moved permanent magnets passing near the outside. E. S. H.

Reflux condenser for use with Erlenmeyer flasks. J. W. OLSON and C. E. PLASS (Ind. Eng. Chem. [Anal.], 1935, 7, 444). E. S. H.

Liquid absorption tube. W. D. TURNER (Ind. Eng. Chem. [Anal.], 1935, 7, 444). E. S. H.

Carbon dioxide from "dry ice." W. S. IDE (Ind. Eng. Chem. [Anal.], 1935, 7, 442).—Solid CO_2 is a convenient source of gaseous CO_2 for use in the determination of N by the micro-Dumas method. A suitable apparatus is described. E. S. H.

Continuous production of distilled water free from carbon dioxide and ammonia. F. G. STRAUB (Ind. Eng. Chem. [Anal.], 1935, 7, 433—434).—The apparatus described gives a distillate having a conductivity of 0.5—0.3 $\times 10^{-6}$ mho and p_{H} 6.8. E. S. H.

Calculation of ΔD in a crystal growth process. M. GORDON (Ind. Eng. Chem. [Anal.], 1935, 7, 386—387).—Mathematical. E. S. H.

Decantation of crystalline suspensions. I. General theory. II. Characteristic functions. G. BOZZA (Atti R. Accad. Lincei, 1935, [vi], 21, 697—700, 752—755).—Mathematical. O. J. W.

Decantation of suspensions of crystals. III. Continuous cylindrical decanting apparatus. G. BOZZA (Atti R. Accad. Lincei, 1935, 21, 809—813).—Theoretical. Formule correlating rate of flow, efficiency, the dimensions of the apparatus, concn. of suspended matter, etc. are evolved. D. R. D.

Geochemistry.

Reduced thickness of the atmospheric ozone [layer] during Polar winter. D. BARBIER, D. CHALONGE, and E. VASSY (Compt. rend., 1935, 201, 787—789).—The quantity of O_3 in the atm. has been studied spectroscopically at Abisko (Swedish Lapland) and compared with charts of air movements. Increased reduced thickness of O_3 coincided with an invasion of Arctic air, which is richer in O_3 than that of lower latitudes. The method permits the study of displacements of large masses of stratospheric air. Since air coming from regions to the north of the aurora zone is rich in O_3 the origin of the latter is problematical. R. S. B.

Visual spectroscopic study of atmospheric ozone. J. GAUZIT (Ann. Physique, 1935, [xi], 4, 450—532).—A simple spectrophotometer is described for the estimation of the abundance of atm. O_3 by observation of the Chappuis bands when the sun is a few degrees below the horizon, by the study of the O_3 absorption bands in the ultra-violet from observations of the blue sky, and by lunar spectrophotometry. Results of 156 measurements over 15 months show a max of O_3 in March–April, and a min. in August–September. The distribution of O_3 in a horizontal stratum was examined. Assuming the "thin layer" hypotheses, the estimated height of this layer is 20—50 km., with an average val. of 33 km. N. M. B.

Emanation content of air from the soil and underground tectonics. (Foundation of geophysical investigations on the basis of emanation measurements in air from soil.) H. ISRAËL-KÖHLER and F. BECKER (Naturwiss., 1935, 23, 818).—It is assumed that Fick's law of diffusion governs the distribution of Rn in the air derived from the upper layers of soil. Three cases are possible: (a) the emanation originates completely in the surrounding earth, (b) an active layer at a certain depth is covered by weaker and inactive layers, (c) the sources of Rn are tectonic clefts covered with weakly active sedimentary layers. In the normal case the Rn content of the air increases rapidly with depth and reaches a const. concn. at a depth of about 5 m. In other cases the concn. varies exponentially with the depth. A. J. M.

Daruvar thermal spring. S. MIHOLIĆ (Bull. Soc. Chim. Yougoslav., 1935, 6, 121—129).—The analytical data do not differ from those obtained in 1839. R. T.

Ansh-Bulat sulphate lake, and the possibilities of its exploitation. A. B. ZDANOVSKI and D. I. RJABTSCHIKOV (J. Appl. Chem. Russ., 1935, 8, 981—993).—The H_2O contains 17.4% of solutes, chiefly Na_2SO_4 6.9, $MgSO_4$ 2.5, and $NaCl$ 7.6%. $Na_2SO_4 \cdot 10H_2O$ crystallises out over the range 16° to -5° , and the mother-liquors yield 80 kg. of $NaCl$ per ton when conc. at 25° and then cooled to -10° . The final filtrates can be further conc. for the prep. of $MgCl_2$ and Br. R. T.

Distribution of nitrogen compounds in the sea near Southern California. E. G. MÖBERG and

R. H. FLEMING (Proc. 5th Pacific Sci. Cong., 1933, 3, 2085—2088).—The surface layer had 150 mg. of org. N and 30 mg. of NH_3 -N per cu.m., NO_2 ' and NO_3 ' being absent. The $[NH_3]$ was const. to a depth of 70 m. NO_3 ' was found at 40 m. and below.

CH. ABS. (e)

Abnormal density of water from the deep portions of Lake Baikal. J. MENDELEEV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 105—108).—The d of samples of H_2O from different depths of the lake increase with increasing depth of the sample. Comparative vals. for the sample before and after distillation show an almost const. diminution of d on distillation. W. R. A.

Sulphur bacteria in the "pink" waters of the Surakhani oilfields and their significance in the geochemistry of water. V. T. MALISCHEK and A. A. MALIANG (Compt. rend. Acad. Sci. U.S.S.R., 1935, 3, 221—224).—Bacterial oxidation and reduction are discussed. C. W. G.

Occurrence of selenium in the Colorado River and some of its tributaries. K. T. WILLIAMS and H. G. BYERS (Ind. Eng. Chem. [Anal.], 1935, 7, 431—432).—The Se content has been determined and its origins are traced. E. S. H.

Boron content of sea-water of the North Atlantic Coast. N. W. RAKESTRAW and H. E. MAHNCKE (Ind. Eng. Chem. [Anal.], 1935, 7, 425).—The variation with locality and depth has been investigated. E. S. H.

Coastal ground water at Yumigahama, Tottori. Y. TOYOHARA (Mem. Coll. Sci. Kyoto, 1935, A, 18, 295—309).—A theory based on hydrodynamical considerations holds good for the actual sea-shore as well as for models. C. W. G.

Geochemical characteristics of protocrystallisation. A. E. FERSMAN (Compt. rend. Acad. Sci. U.S.S.R., 1935, 3, 216—220).—Theoretical. C. W. G.

Granite of Schärding [Upper Austria]. G. HORNINGER (Tsch. Min. Petr. Mitt., 1935, 47, 26—79).—A description is given of the rock, with chemical analyses. L. J. S.

Baryte from Kitzbühel, Tyrol. H. LEITMEIER (Tsch. Min. Petr. Mitt., 1935, 47, 1—25).—White sparry baryte occurring as veins in dolomite has long been mined at this locality. The dolomite-rock contains BaO 0.15% (sol. in HCl and presumably as carbonate) near the veins and 0.08% at some distance from them, but there is no evidence that the baryte was accumulated by lateral secretion from the rock. At one place the mineral is violet-coloured, but this quickly fades on exposure to light, and is restored by exposure to Ra. L. J. S.

Wollastonite and parawollastonite. M. A. PEACOCK (Amer. J. Sci., 1935, [v], 30, 495—529).—Measurements of wollastonite crystals from Crestmore, California, show them to be triclinic, whilst crystals from the limestone blocks of Monte Somma, Vesuvius, are mostly monoclinic, but some are triclinic and others

consist of an intergrowth of the two kinds. In both kinds the angles and cleavages in the prism-zone parallel to the *b*-axis are identical, and the optical characters are the same, except that in the triclinic crystals the extinction is $2\frac{1}{2}^\circ$ to the *b*-axis. The name wollastonite is reserved for the more common triclinic form, and the monoclinic form is called parawollastonite. A third modification of CaSiO_3 is pseudo-wollastonite. L. J. S.

"Ferrosilite" as a natural mineral. N. L. BOWEN (Amer. J. Sci., 1935, [v], 30, 481—494).—"Ferrosilite," FeSiO_3 (A., 1932, 926), has been asserted to have no real existence (A., 1932, 997; 1933, 1120; 1935, 447). Minute acicular crystals found in the lithophysæ of an obsidian from Lake Naivasha are monoclinic with a prism angle of $90^\circ 50'$, α 1.763, β only slightly greater, γ 1.794, $c : \gamma = 34\frac{1}{2}^\circ$, $2V$ very small, suggesting a monoclinic pyroxene. From these data it is further concluded (by extrapolation in the systems $\text{CaSiO}_3\text{--FeSiO}_3$ and $\text{MgSiO}_3\text{--FeSiO}_3$) that the crystals have the composition FeSiO_3 , and the mineral is named clinoferrosilite. The systems $\text{CaSiO}_3\text{--FeSiO}_3$ and $\text{MgSiO}_3\text{--FeSiO}_3$ are now discussed afresh. Similar crystals were also found in lithophysal obsidians from Iceland, Wyoming, and California; analyses of the obsidians are given. L. J. S.

Composition of tectites. F. LOEWINSON-LESSING (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 181—185; cf. A., 1931, 60, 1028, 1146).—There are no eruptive rocks analogous to tectites, although many of the latter have acidity coeffs. and monobasic : dibasic oxide ratios similar to rocks of terrestrial origin. J. W. S.

Synthesis of pyrophyllite. R. SCHWARZ and G. TRAGESER (Z. anorg. Chem., 1935, 225, 142—150).—In the synthesis of pyrophyllite (I) from orthoclase or anorthite (A., 1935, 1101) montmorillonite is not formed. The natural occurrence of kaolin or (I) arising from feldspars may serve as a geological thermometer, since (I) is not formed below 400° . F. L. U.

Structural relationship of glauconite and mica. J. W. GRUNER (Amer. Min., 1935, 20, 699—713).—X-Ray investigation (data given) of 8 glauconites subjected to various treatments shows that glauconite (I) is a mica in structure. The average vals. from 6 specimens for the consts. are a_0 5.24, b_0 9.07, c_0 20.03 Å., β $95^\circ 00'$. (I) is as stable as biotite at temp. as high as 750° . It can absorb Tl ions, which probably replace K⁺ to $\approx 25\%$. The high SiO_2 and H_2O content of (I) is apparently due to the environment in which it is formed. Excess of sol. SiO_2 over sol. Al_2O_3 gives rise to a Si : Al ratio in the $(\text{Si}, \text{Al})_4\text{O}_{10}$ tetrahedral layer $>$ in mica, and may even cause substitution of a few Si for Fe⁺⁺⁺ or Al in approx. the positions having a covalency of 6. In comparison with a muscovite (I) may occasionally have vacant positions in its structure, and a suitable formula is $(\text{OH})_{6-10}\text{K}_{2-3}(\text{Mg}, \text{Fe}^{\text{II}}, \text{Ca})_{1-3}(\text{Fe}^{\text{III}}, \text{Al}, \text{Si})_{3-5}(\text{Si}_{13-14}\text{Al}_{2-3})\text{O}_{38-40}$. Probably one half of the H_2O given in analyses is adsorbed. L. S. T.

Primary native silver ores at Batopilas, Mexico, and Bullard's Peak, New Mexico. P. KRIEGER (Amer. Min., 1935, 20, 715—723).—At

Batopilas, native Ag is associated with safflorite, rammelsbergite, arsenopyrite (I), galena (II), and sphalerite (III). All the evidence indicates a primary origin for the Ag. The probable order of deposition is (i) sulphides, including pyrite, (II), and (III), (ii) Ni and Co arsenides and (I), and (iii) Ag minerals and Ag. At Bullard's Peak, native Ag is associated with a Ni-skutterudite in a manner similar to that of Ag and arsenides in the Cobalt district of Ontario. Primary origin of the Ag, and centrifugal replacement of the arsenide by Ag, are indicated. L. S. T.

Monazite from West Portland Township, Quebec. I. H. S. SPENCE. II. O. B. MUENCH (Amer. Min., 1935, 20, 724—732).—I. The waste dump of a felspar quarry at $45^\circ 45' 30''$ N, $75^\circ 36' 30''$ W contained tourmaline, cuxenite, monazite, allanite (?), titanite+ilmenite, fergusonite (?), cyrtolite, muscovite, tenerite, and specularite.

II. Analysis of the monazite by Fenner's method gave Th 3.44, and Pb 0.068%; U, by emanation method, 0.054%. The Pb-U ratio is 0.053, giving a val. of $388\text{--}391 \times 10^6$ years for the age of the mineral. The % of Pb obtained by a micro-analysis (A., 1935, 1216) is less (0.032—0.05%) than that obtained above by macro-methods. L. S. T.

Piedmontite from Los Angeles County, California. R. R. SIMONSON (Amer. Min., 1935, 20, 737—738).—Piedmontite occurs as small euhedral crystals in quartz-sericite-biotite schist and in quartzite from this locality. L. S. T.

Radioactivity of ferro-manganese formations in seas and lakes of the U.S.S.R. L. M. KURBATOV (Nature, 1935, 136, 871).—The Ra content of Fe-Mn bottom deposits of these lakes or seas varies from $1.2 \times 10^{-10}\%$ (Caspian Sea) to $31.8 \times 10^{-10}\%$ (Black Sea); it is much $<$ in deep-water concretions of the Pacific Ocean ($47.6\text{--}146.6 \times 10^{-10}\%$). Small concretions are more radioactive than large ones, and the surface layer is more active than the centre. The Th-X content is small. L. S. T.

Crystallised melanterite from Pfaffenreuth, Bavaria. F. MACHATSCHKI (Zentr. Min., 1935, A, 53—54; Chem. Zentr., 1935, i, 2148).—Native melanterite crystals, of octahedral habit, have been found; $a : b : c = 1.180 : 1 : 1.534$, $\beta = 104^\circ 23'$. J. S. A.

Maxixe beryl. K. SCHLOSSMACHER and H. KLANG (Zentr. Min., 1935, A, 37—44; Chem. Zentr., 1935, i, 2147).—Structure and characteristics of the stone are discussed. The blue pleochroic colour is rapidly lost on exposure to light. J. S. A.

Osmiridium. III. X-Ray analysis. O. E. ZVJAGINTZEV and B. K. BRUNOVSKI (Ann. Inst. Platine, 1935, No. 12, 5—15; cf. A., 1932, 1107).—Natural osmiridium has a fibrous structure, probably due to partial recrystallisation. CH. ABS. (e)

Gypsum crystals from Alfalfa County, Oklahoma. C. A. MERRITT (Amer. Min., 1935, 20, 674). L. S. T.

Method for removing iron oxide coatings from minerals. M. DROSDOFF and E. TRUOG (Amer. Min., 1935, 20, 669—673).—The mineral is suspended in H_2O , treated with H_2S , and then with 0.05N-HCl.

Silicates and apatite are practically unaffected. The action of H_2S on hematite, limonite, goethite, biotite, basalt, granite, and certain Fe-coated minerals is also described. L. S. T.

Angelite from Mono County, California. D. M. LEMMON (Amer. Min., 1935, 20, 664—668).—Angelite, basic Al phosphate, d 2.67, hardness 5, occurs as a hydrothermal mineral deposited from solutions which acted on the andalusite (I) deposit subsequent to the formation of (I), corundum, diaspore, topaz, etc. It is directly associated with lazulite, rutile, barite, pyrophyllite, muscovite, alunite, and quartz. Other occurrences are briefly described. L. S. T.

Pseudo-brookite. C. PALACHE (Amer. Min., 1935, 20, 660—663; cf. *ibid.*, 1934, 19, 16).—Pseudo-brookite from Thomas Mts., Utah, has [F. A. GONYER] Fe_2O_3 60.57, TiO_2 38.12, and MgO 1.26, total 99.95%, indicating an excess of approx. 4% of TiO_2 over that required by Fe_2TiO_5 . L. S. T.

Mineralogical classification of igneous rocks: comparison of recent proposals. S. J. SHAND (J. Geol., 1935, 43, 609—617).—Various classifications based on texture, colour, degree of saturation with SiO_2 , composition of the feldspar developed in a rock, and the ratio of Al_2O_3 to bases are compared and discussed. L. S. T.

Mixing and unmixing of silicate rock magmas. G. LINCK (Chem. Erde, 1935, 10, 126—128).—A criticism (cf. Grigoriov, Zentr. Min., 1935, 242). L. J. S.

Lias clay from Dobbertin [Mecklenburg]. F. K. SCHLÜNZ (Chem. Erde, 1935, 10, 116—125).—Chemical analyses and microscopical examination were made of the fractions of the clay $>1\mu$ and $<1\mu$. X-Ray patterns show the latter to be mainly halloysite. L. J. S.

Minerals of lead slags. W. FABER (Chem. Erde, 1935, 10, 67—115).—Chemical analyses and optical determinations are given of several fractions separated by heavy liquids from a Pb slag from the Harz. The minerals identified include α -celsian, willemite, fayalite, magnetite, Zn-blende, and wurtzite. The diagrams of the systems $CaO-FeO-SiO_2$ and $\gamma-Ca_2SiO_4-Mg_2SiO_4-Zn_2SiO_4-Fe_3SiO_4$ are discussed. L. J. S.

Recent and fossil red earth (terra rossa) formation. E. BLANCK and E. VON OLDERSHAUSEN (Chem. Erde, 1935, 10, 1—66).—Analyses are given of soils and of the underlying limestone from which they are derived in the district of the southern Frankenalb in the Altmühl valley in Bavaria. L. J. S.

Structure of dickite and other clay minerals. C. J. KSANDA and T. F. W. BARTH (Amer. Min., 1935, 20, 631—637).—X-Ray measurements of dickite from Schuylkill Co., Pa., give a_0 5.145, b_0 8.882, c_0 14.337, β 96° 45', d_{calc} 2.618, with four mols. of $Al_2Si_2O_5(OH)_4$ per unit cell; space-group C_{2h}^2 or C_4^1 . A test for piezo-electricity gave a negative result, making the latter improbable. Gruner's structure is, in the main, confirmed, but a certain difference renders proposed structures of kaolinite, nacrite, halloysite, and vermiculite uncertain. L. S. T.

Combined water in clay substance. O. KOERNER, K. PUKALL, and H. SALMANG (Z. anorg. Chem., 1935, 225, 69—72; cf. A., 1930, 720).—Isothermal dehydration of a very pure Zettlitz kaolin, extending over periods up to 1.5 years, shows that, contrary to the usual belief, the composition of the clay mol. is $Al_2O_3 \cdot 2SiO_2 \cdot 1.5H_2O$, the remaining H_2O being adsorbed. Dehydration proceeds by way of the mono- and hemi-hydrates. F. L. U.

Minerals of Franklin and Sterling Hill, New Jersey. C. PALACHE (U.S. Geol. Surv., 1935, Prof. Paper 180, 1—135).—Detailed descriptions are given of 148 minerals from this unique mineral locality; 30 of these minerals have not been found elsewhere. In addition to details from the lit., many new crystallographic and optical data and some new chemical analyses are given. Two new species are established: hydrohetaerolite, $2ZnO \cdot 2Mn_2O_3 \cdot H_2O$, tetragonal (?), as distinct from hetaerolite ($ZnO \cdot Mn_2O_3$); and magnesium chlorophoenicite, $(MgMn)_3As_2O_8 \cdot 7(Mg, Mn)(OH)_2$, monoclinic, differing from chlorophoenicite in containing Mg in place of Zn. The primary ore is a granular mixture of franklinite (43%), willemite (26%), calcite (25%), zincite (1%), with tephroite and other silicates (5%). It is suggested that hydroxides of Mn and Fe and hemimorphite were first formed by the metasomatic replacement of limestone, and that this deposit was altered by regional metamorphism in pre-Cambrian times, and further alterations by later intrusions of pegmatites giving the complex variety of minerals. L. J. S.

Heavy minerals of the "Erinpura" granite and microgranite of Danta state (N. Gujrat). N. L. SHARMA and S. PURKAYASTHA (Proc. Indian Acad. Sci., 1935, 11, B, 369—376).—Comparative mineralogical data are recorded and discussed. A. G. P.

Pre-Cambrian rocks of the Lake Superior Region. C. K. LEITH, R. J. LUND, and A. LEITH (U.S. Geol. Surv., 1935, Prof. Paper 184, 1—34).—The correlation of the rocks in relation to their geological age is discussed. The extensive deposits of banded jaspery Fe ores were probably derived from the weathering of volcanic rocks with chemical (or organic-algal) pptn. from solution and subsequent concn. by oxidation and leaching of SiO_2 by percolating surface waters. L. J. S.

Dark inclusions in a tonalite of Southern California. C. S. HURLBUT, jun. (Amer. Min., 1935, 20, 609—630).—Dark inclusions in a quartz diorite, known as the Bonsall tonalite (analysis given), are described. Plagioclase, hornblende, and biotite make up the bulk of the inclusions and are always present, whilst quartz, orthoclase, and pyroxene are sometimes found in small amounts. The inclusions and the tonalite are mineralogically similar, but the former are xenoliths of older rock (gabbro) and owe their present condition to reaction with the tonalite magma. L. S. T.

Paragenesis of the mineral assemblage at Crestmore, Riverside County, California. J. W. DALY (Amer. Min., 1935, 20, 638—659).—The geology of the district, the rocks, and the minerals are

described. The mode of formation of the latter is discussed, and the contact metamorphic minerals are grouped under the rocks to which they owe their origin.

L. S. T.

Radiometric prospecting of a [volcanic] flow of rhyolite. E. ROUË and (MME.) A. HÉE (Compt. rend., 1935, 201, 892—893).—The deposit at Welschbruch has been delimited radiometrically.

R. S. B.

Occurrence of vanadium in fossil coals. V. SILBERMINTZ (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 117—120).—800 samples of coal of different types and origins were considered. Analyses for V were made on 500 samples. Most samples show very slight content of V_2O_5 in the ash, but certain specimens contained up to 8.79% V_2O_5 . Most coals high in V_2O_5 are of the clarain-vitrain type and often have a lignite structure. The origin of V in coal appears to depend principally on local conditions. W. R. A.

Conversion of plant substances into fossil coals.—See B., 1935, 1122.

Origin of petroleum. G. A. FESTER and J. CRUELLAS (Rev. Fac. Quím. Ind. Agric., 1934, 3, 76—108).—The following theory is put forward, based on numerous analyses of relevant materials. Marine flora and fauna suffer decomp. in tropical climates, evolving gases (including H_2S) and leaving mainly fatty material, which by further decomp. is converted into petroleum. In colder climates, the cellulose and lignin do not decompose completely and coal etc. are produced. This theory is supported by the geographical distribution of petroleum and coal. The presence of colloidal V sulphides in South American petroleum is explained by the presence of vanadates (derived from the local igneous rocks) in the H_2O , the H_2S causing pptn. of the V. Analyses and other data concerning South American raphaellites and petroleum are given. D. R. D.

Organic Chemistry.

Free radicals. E. DARMOIS (Bull. Soc. chim., 1935, [v], 2, 2053—2067).—A lecture.

Thermal decomposition of nitromethane.—See this vol., 33.

Thermal decomposition of hexane at high pressures. J. N. PEARCE and J. W. NEWSOME (Proc. Iowa Acad. Sci., 1934, 41, 139—140).—Between 460° and 490°/14,000—15,000 lb. the gaseous product consists of 25% CH_4 , 47% C_2H_6 , 15% C_3H_8 , and 7% C_4H_{10} ; at 460° it contains 2.1% H_2 , 1.4% C_2H_4 , 1.5% C_3H_6 , and 2.1% C_4H_8 . At 497° both H_2 and C_2H_2 have disappeared and the C_3H_8 , C_4H_{10} , C_3H_6 , and C_4H_8 have fallen to 5.5%, 4.0%, 0.04%, and 0.16%, respectively. At this temp. abundant formation of C begins and the proportion of CH_4 increases. The liquid product contained cycloparaffins, C_6H_6 , substituted benzenes, and higher unsaturated compounds. CH. ABS. (r)

Polymerisation of ethylene under high pressures and in presence of phosphoric acid. V. N. IPATIEV and H. PINES (Ind. Eng. Chem., 1935, 27, 1364—1369).—The gaseous products of polymerisation of C_2H_4 under pressure in presence of H_3PO_4 at 250°, 280°, 300°, and 330° contain chiefly C_2H_4 and iso- C_4H_{10} (2.5% of the total product at 250° and 18.8% at 330°), produced by hydrogenation of Δ^{α} - and Δ^{β} - C_4H_8 . The liquid products b.p. < 60° are paraffins; olefines are present in all fractions, naphthenes occur in fractions b.p. > 110°, and fractions b.p. > 250° are mainly aromatic, the proportions of the lower paraffinoid and higher aromatic fractions increasing with rise of temp. of polymerisation. The thermal polymerisation of C_2H_4 in absence of H_3PO_4 gives rise almost exclusively to olefines and naphthenes and aromatic compounds are absent. At 180° C_2H_4 and H_3PO_4 give $(OH)_2PO \cdot OEt$, which decomposes at higher temp. with the formation of olefines and naphthenes. The latter are subsequently hydrogenated to paraffins and dehydrogenated to aromatics, respectively. There is no evidence of cracking. S. C.

Hydrogenation catalysis. II. Technique.—See this vol., 35.

Oxidation of γ - and β -methyl- Δ^{β} -pentene by selenium dioxide. A. GUILLEMONAT (Compt. rend., 1935, 201, 904—906; cf. A., 1935, 852).— γ -Methyl- Δ^{β} -pentene with SeO_2 in AcOH gives γ -methyl- Δ^{β} -penten- δ -ol (cf. A., 1910, i, 454) and β -methyl- Δ^{β} -pentene gives β -methyl- Δ^{β} -penten- α -ol, b.p. 61—63°/14 mm. (Ac derivative, b.p. 61—63°/12 mm.).

J. L. D.

Kinetics and mechanism of thermal transformations of unsaturated hydrocarbons. Polymerisation of $\Delta^{\alpha\gamma}$ -butadiene at atmospheric pressure. V. G. MOOR, N. V. STRIGALEVA, and L. V. SCHILAEVA (J. Gen. Chem. Russ., 1935, 5, 818—829).— C_4H_6 yields chiefly C_8H_{12} , b.p. 130°, when heated at 400°, whilst at higher temp. (450—700°) fractions of higher and of lower b.p. are obtained. The velocity of the reaction $2C_4H_6 \rightarrow C_8H_{12}$ varies with temp. according to $\log K = -6400/T + 7.32 \pm 0.04$; the energy of activation is 28 kg.-cal. per mol. R. T.

Oxidation with selenium dioxide. Y. R. NAVES and (MME.) M. G. IGOLEN (Bull. Inst. Pin, 1935, 234—238).—A review of its various applications.

J. L. D.

Acetylene series. VI. Oxidation of acetylenic hydrocarbons with permanganate. V. N. KRESTINSKI and M. K. KELBOVSKAJA (J. Gen. Chem. Russ., 1935, 5, 871—876).— C_2H_2 and dil. aq. $KMnO_4$ at 0° afford HCO_2H (I) and traces of $H_2C_2O_4$, $CPh:CH$ gives $BzOH$, CO_2 , and traces of (I), $CMe:CEt$ gives CO_2 , $AcOH$, and $EtCO_2H$, and $CBu^t:CH$ gives Bu^tCO_2H , CO_2 , and (I). Neutral intermediate oxidation products were not found in any case. R. T.

Atomic equilibria in hydrocarbon molecules of the $CH:C-CH_2R$ series. E. F. ZEBERG (J. Gen. Chem. Russ., 1935, 5, 1016—1019).— $\alpha\beta$ -Dibromo- γ -phenylpropane and KOH at 100—120°, with or without $EtOH$, afford $CPh:CH_2$ and traces of $CH_2Ph-CH:CH_2$. R. T.

Action of acetylene on acetyl chloride. A. CORNILLOT and R. ALQUIER (Compt. rend., 1935, 201, 857—838).—Condensation of AcCl with C_2H_2 in presence of AlCl_3 at 15° affords *Me* β -chlorovinyl ketone (I), b.p. $40^\circ/20$ mm. [semicarbazone, m.p. 180° (decomp.)], which probably has a *cis*-configuration and rapidly decomposes, even in the dark, with evolution of HCl to an amorphous mass. With boiling NaOH-EtOH (I) gives a 20—25% yield of $\text{C}_6\text{H}_3\text{Ac}_3$. J. W. B.

Use of copper to increase the yield of ethyl bromide. P. HENDRIXSON (Proc. Iowa Acad. Sci., 1934, 41, 165).—Addition of Cu to the reaction mixture of EtOH , H_2SO_4 , H_2O , and NaBr increases the yield of EtBr from 57% to 80%. The effect is due to the liberation of SO_2 , which reduces any free Br to HBr . CH. ABS. (r)

Photochlorination of ethylene.—See this vol., 37.

Chlorination of propane.—See this vol., 35.

Mechanism of slow oxidation of propane.—See this vol., 33.

Photobromination of tetrachloroethylene and of chloroform.—See this vol., 37.

Isotopic exchange reactions with iodine.—See this vol., 40.

Aluminium alkoxides and their parachors.—See this vol., 14.

Synthesis of octadecyl alcohols with branched chain. O. BRUNNER and G. WIEDEMANN (Monatsh., 1935, 66, 438—442).— $\text{CHEt}(\text{CO}_2\text{Et})_2$ is converted by myristyl iodide in presence of Na and PhMe into *Et*, ethyltetradecylmalonate, b.p. $132\text{—}136^\circ/14$ mm., hydrolysed and decarboxylated to α -ethylpalmitic acid, b.p. $215\text{—}220^\circ/10$ mm. (amide, m.p. $111\text{—}112^\circ$), the *Et* ester, b.p. $198\text{—}203^\circ/12$ mm., of which is reduced by Na and Bu°OH in light petroleum to β -ethylhexadecyl alcohol, m.p. 15° (non-cryst. phenylurethane; 4'-chlorodiphenylcarbamate, m.p. $105\text{—}106^\circ$). Analogously, *Et*, *n*-butyldodecylmalonate, b.p. $224\text{—}226^\circ/1$ mm., affords successively α -butylmyristic acid, b.p. $214\text{—}219^\circ/10$ mm. (*Et* ester, b.p. $189\text{—}192^\circ/10$ mm.; amide, m.p. $109\text{—}110^\circ$), and β -*n*-butyltetradecyl alcohol, b.p. $125\text{—}130^\circ/\text{high vac.}$, m.p. 1° (non-cryst. phenylurethane; 4'-chlorodiphenylcarbamate, m.p. $102\text{—}103^\circ$). *Et*, hexyldodecylmalonate, b.p. $222\text{—}225^\circ/12$ mm., yields successively α -hexyl-lauric acid, b.p. $218\text{—}222^\circ/12$ mm. (*Et* ester, b.p. $195\text{—}198^\circ/12$ mm.; amide, m.p. $110\text{—}111^\circ$), and β -hexyldodecyl alcohol, b.p. $120^\circ/\text{high vac.}$, f.p. -7.5° (non-cryst. phenylurethane; 4'-chlorodiphenylcarbamate, m.p. $77\text{—}78^\circ$). *Et*, dioctylmalonate, b.p. $220\text{—}225^\circ/15$ mm., affords α -octyldecoic acid, b.p. $212\text{—}218^\circ/13$ mm. (*Et* ester, b.p. $195\text{—}197^\circ/12$ mm.; amide, m.p. $122.5\text{—}123.5^\circ$), and β -octyldecoyl alcohol, b.p. $110\text{—}120^\circ/\text{high vac.}$, f.p. -8° (non-cryst. phenylurethane; 4'-chlorodiphenylcarbamate, m.p. 96°).

H. W.

Existence of boric acid complexes with one and two molecules of a diol in aqueous solution.—See this vol., 29.

Preparation of pure sorbitol and sorbose and the influence of this ketose on the conductivity of boric acid. J. BÖESEKEN and J. L. LEEFERS (Rec. trav. chim., 1935, 54, 861—865).—Details are given for the prep. of an efficient Ni-Co-Cr catalyst and its use in the reduction of glucose in 96% EtOH with H_2 at $150^\circ/150$ atm., to give cryst. sorbitol. An improved oxidation of sorbitol to sorbose using *Acetobacter suboxydans* is described, oxidation being complete in 3.5 days instead of 4—6 weeks, necessary with *B. xylinum*. Addition of $0.1M\text{-H}_3\text{BO}_3$ to $0.1M\text{-sorbose}$ causes a much greater increase in conductivity than does similar addition to fructose. J. W. B.

Fluorination of halogenomethyl ethers. I. Fluorination of trichlorodimethyl ether. H. S. BOOTH and P. E. BURCHFIELD (J. Amer. Chem. Soc., 1935, 57, 2069).—Treatment of $\text{CCl}_3\text{-Ome}$ with SbF_3 without a catalyst yields *Me chlorodifluoromethyl ether*, b.p. 55.3° , m.p. -105.1° , and *Me trifluoromethyl ether*, b.p. 30.1° , m.p. -96.2° . These compounds are only slowly hydrolysed by H_2O . E. S. H.

$\alpha\delta$ - and $\alpha\epsilon$ -Oxido-compounds. **Synthesis of $\alpha\epsilon$ -oxidodecane.** A. FRANKE, A. KROUPA, and O. SCHMID (Monatsh., 1935, 66, 406—432).—*Et* hexoylacetate (improved prep. from technical *Me* heptinene-carboxylate) is converted by the successive action of Na+EtOH and $\text{CH}_2(\text{CH}_2\text{Br})_2$ followed by heating of the product under diminished pressure into *anhydrodecan- α -ol- ϵ -one* (I), which readily adds H_2O giving *decan- α -ol- ϵ -one* (II), m.p. $24.5\text{—}25.3^\circ$, b.p. $144\text{—}148^\circ/11$ mm. (distillable only in complete absence of acidic or halogenic impurities), which does not reduce Fehling's solution or $\text{NH}_3\text{-Ag}_2\text{O}$, is little changed when heated at 100° , and according to optical evidence has the open structure $\text{C}_5\text{H}_{12}\text{-CO-}[\text{CH}_2]_3\text{-CH}_2\text{-OH}$. Oxidation of (II) with CrO_3 in AcOH affords δ -ketodecoic acid, m.p. 56.3° , and ϵ -keto-*n*-decyl δ -ketodecoate, m.p. 52° , probably formed through the semiacetal, since the direct esterification of acid by alcohol is somewhat difficult. (II) is unchanged by Al-Hg or Na-Hg in $\text{EtOH-H}_2\text{O}$, but is reduced by Na in 96% EtOH to *decane- $\alpha\epsilon$ -diol* (III), m.p. $23\text{—}24^\circ$, b.p. $155.5\text{—}157^\circ/11$ mm. Hydrogenation (Pt sponge in Et_2O) of (I) leads to $\alpha\epsilon$ -oxidodecane (IV), b.p. $198.5\text{—}200.5^\circ/747$ mm., which is transformed successively into $\alpha\epsilon$ -dibromo-*n*-decane, b.p. $150\text{—}151.5^\circ/10$ mm., $\alpha\epsilon$ -dicyano-*n*-decane, b.p. $187\text{—}193^\circ/9$ mm., and non-cryst. α -*n*-amylpimelic acid (diamide, m.p. 161.5° after softening at 160°); indications of the presence of isomeric diamides, and hence of $\alpha\delta$ -oxide in the initial material, are not observed. Elimination of H_2O from (III) by H_2SO_4 occurs at a noticeable rate with boiling 30% acid, and then leads mainly to an unsaturated alcohol, $\text{C}_{10}\text{H}_{20}\text{O}$, b.p. $228\text{—}231^\circ/1$ atm., with smaller amounts of an oxide essentially (IV). Interaction of $\text{Br}[\text{CH}_2]_6\text{-Br}$ with $\text{CH}_2\text{Ac-CO}_2\text{Et}$ appears to lead mainly to the cryst. diketone $\text{Ac}[\text{CH}_2]_3\text{-Ac}$. Treatment of dry NaOBz with $\text{Br}[\text{CH}_2]_6\text{-Br}$ at 200° affords ζ -bromohexyl benzoate (V), b.p. $187\text{—}190^\circ/9$ mm., and $\alpha\zeta$ -dibenzoyloxy-*n*-hexane, m.p. $55.5\text{—}56^\circ$ after softening at 55° . (V) and $\text{CH}_2\text{Ac-CO}_2\text{Et}$ in boiling EtOH containing NaOEt afford a product which

after successive acid and alkaline hydrolysis gives *nonan- α -ol- θ -one*, m.p. 23—23.5°. When heated with H_3PO_4 the ketol gives only complex substances of uncertain constitution, whereas (II) readily yields (VI).

H. W.

Constitution of adenylypyrophosphoric and adenosinediphosphoric acid. K. LOHMANN (Biochem. Z., 1935, 282, 120—123).—Examination of the electro-titration curve of adenosinediphosphoric acid (I) before and after hydrolysis indicates that it is adenylic acid (II) esterified with 1 H_3PO_4 and that adenylypyrophosphoric acid (III) is (II) esterified with 2 H_3PO_4 . Constitutional formulæ, based on these and other deductions, are given for (I) and (III). The NH_2 of the adenine residue is free in (I) and (III).

W. McC.

Introduction of chlorine into nitromethane-disulphonic acid. H. J. BACKER (Rec. trav. chim., 1935, 54, 899—904).—The following salts of nitromethanedisulphonic acid (A., 1931, 64) are described, crystallographic data (by TERPSTRA) being given for some of these: *dibrucine*+10 H_2O , Ba_2 +2 H_2O , K_3 , Tl_3 , and Ba_3 . All salts of type $MO_2N:C(SO_3M)_2$ are explosive. The action of Cl_2 on $KO_2N:C(SO_3K)_2$ in H_2O gives *K chloronitromethanedisulphonate* (I), whence the *strychnine*+2 H_2O , *brucine*+4 H_2O , Ba +3 H_2O , decomp. 150°, *Tl*, Ag +2 H_2O , and Ca +3 H_2O , salts of *chloronitromethanedisulphonic acid*+4 H_2O and +2 H_2O , m.p. 95.5° (explosive decomp.) (prep. from Ba salt), are obtained. (I) and aq. K_2SO_3 affords *K nitromethanedisulphonate* thus: (I)+ K_2SO_3 + H_2O \rightarrow $(SO_3K)_2CH\cdot NO_2$ + KCl + $KHSO_4$. J. W. B.

Influence of an element or of a negative group on the relative mobilities of alkyl radicals in their chloroformates. P. CARRÉ and H. PASSEDOUET (Compt. rend., 1935, 201, 898—900).—The effect of introducing Cl or Ph into the alkyl of alkyl chloroformates is to diminish the temp. of thermal decomp. (cf. A., 1935, 1105), *i.e.*, to increase the mobility of alkyl (cf. A., 1933, 806; 1934, 509). The Pr^a ester has a lower mobility than the allyl ester, but the β -phenylpropyl ester has a higher mobility than the cinnamyl ester. The suggestion that the tendency to migration is the greater the more electropositive is the migrating group is abandoned. J. L. D.

Condensation of carboxylic compounds with substances capable of forming organo-metallic compounds or tautomerides thereof under the influence of alkali metals and of their water-decomposable derivatives. G. V. TSHELINCEV (J. Gen. Chem. Russ., 1935, 5, 562—569).—Theoretical. Ester condensation reactions consist of the steps: $EtOAc + CH_2Na\cdot CO_2Et \rightleftharpoons ONa\cdot CMe(OEt)\cdot CO_2Et \rightleftharpoons CH_2Ac\cdot CO_2Et + NaOEt \rightleftharpoons ONa\cdot CMe\cdot CH\cdot CO_2Et + EtOH$. R. T.

Addition of hydrogen bromide to allylacetic acid. M. S. KHARASCH and M. C. McNAB (Chem. and Ind., 1935, 989—990; cf. A., 1933, 805).—A criticism of the views of Linstead *et al.* (A., 1935, 195). J. W. B.

Addition of hydrogen bromide to olefinic acids. R. P. LINSTAD and H. N. RYDON (Chem. and Ind., 1935, 1009).—A reply to the above. J. W. B.

Addition of hydrogen bromide to triple and double linkings. Undecynoic, undecenoic, and κ -epoxyundecenoic acids. P. L. HARRIS and J. C. SMITH (J.C.S., 1935, 1572—1576).—The reaction between Δ^1 -undecenoic acid and HBr is sensitive to "oxidants." In the presence of BzO_2H (I) (modified prep.) at 0° during 3 hr. κ -bromoundecenoic acid (II) is formed, whilst in the presence of $NHPh_2$ the reaction is slower and the ι -Br-acid (III) results. Undecenoic acid (IV) and (I) (in ligroin at 30° during 24 hr.) yield κ -epoxyundecenoic acid (V), m.p. 45.5° (after 10 days m.p. 50°), which reacts with HBr in air, forming mixed bromohydrins, m.p. 49—53°. In ligroin solution (IV) and HBr in air yield (III); in presence of (I) (0° during 15 min.) or (V) the product is (II). None of the catalysts is effective in absence of mol. O_2 . F. N. W.

p -Xenylamine as new reagent for the identification of fatty acids and fatty acid derivatives. Synthesis of the p -xenylamides [p -phenylanilides] of oleic and elaidic acid and their bromo-derivatives. W. KIMURA and M. NIHAYASHI (Ber., 1935, 68, [B], 2028—2034).—The p -phenylanilides are obtained by heating the requisite acid with p - $C_6H_4Ph\cdot NH_2$ (prep. from Ph_2 described) in a vac. or through the acid chlorides and their derivatives by bromination of the anilides or through the chlorides of the Br-acids. Their m.p. are 34—61° > those of the corresponding p -phenylphenacyl esters. The following are described: *ole*-, m.p. 120°, *elaid*-, m.p. 134—135°, *oleodibromostear*-, m.p. 87.5°, and *elaidodibromostear-p-phenylanilide*, m.p. 133.5°.

H. W.

Preparation in a high state of purity of long-chain compounds. I. Oleic acid. L. KEFFLER and J. H. McLEAN (J.S.C.I., 1935, 54, 362—367T).—The Pb salt method fails to remove the final 3—4% of saturated impurities in oleic acid, even when prepared from high-grade olive oil and a large excess of $Pb(OAc)_2$ is used. The higher unsaturated impurities can be completely removed by 10—12 recrystallisations of the Li salts from 5 vols. of 80% EtOH; the final 3—4% of saturated impurities can then be removed, within 0.2 or 0.3%, by repeated fractional distillation under much reduced pressure. Oleic esters which had "aged" by keeping for long periods have also been purified by repeated fractional distillation, but the pure products were highly susceptible to rancidity changes, as were also the samples known to contain highly saturated impurities. Improvements in fractional distillation of fatty esters are described.

Oleic acid. T. P. HILDITCH (Chem. and Ind., 1935, 1009).—A reply to Keffler *et al.* (see above).

J. W. B.

Unsaturated acids of natural oils. IV. The highly unsaturated acid of *Telfairia occidentalis*. E. H. FARMER and E. S. PAICE. V. α - and β -Licanic acids. W. B. BROWN and E. H. FARMER (J.C.S., 1935, 1630—1632, 1632—1633).—IV. *T. occidentalis* oil (7 months old) on saponification gives a mixture of fatty acids from which β -elæostearic acid (10% yield) is obtained. Freshly extracted (light petroleum) kernels give an oil containing

α - but no β -elaeostearic acid, although after irradiation (12 hr. in presence of S) the β -acid only is found.

V. Technical oiticica fat (I) or the kernel fat of *Licana rigida* normally yields α -licanic acid (*semicarbazone*, m.p. 110—111°; *Me ester*) on saponification, but after irradiation (8 hr. in presence of I or S) *isolicanic acid*, m.p. 99.5° (*semicarbazone*, m.p. 138°), is formed. The fatty acids from (I) contain stearic (1.4%) and palmitic acids (about 1%).

F. N. W.

Polymerisation of methyl esters of higher unsaturated fatty acids. XVI. Polymerisation of methyl stearolate. K. KINO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 28, 140—145).—Me stearolate heated in H_2 at 280—290° slowly polymerises to a bimol. product, which is not depolymerised when catalytically hydrogenated.

E. W. W.

Oxidation products of the unsaturated acids of linseed oil. L. C. A. NUNN and I. S. MACLEAN (Biochem. J., 1935, 29, 2742—2745; cf. A., 1935, 998).—The unsaturated acids of saponified linseed oil are oxidised by alkaline $KMnO_4$, the OH-acids are separated, and the remainder is steam-distilled. From the OH-acid fraction *isolinusic*, *linusic*, di-, tetra-, and hexa-hydroxystearic acids are separated, and from the steam distillate *Zn $\alpha\beta$ -dihydroxy-decane- $\alpha\kappa$ -dicarboxylate* is identified. The Δ^0 and Δ^u positions of the ethylenic linkings in linoleic acid are confirmed.

H. D.

Preparation of brassidic acid from colza oil. L. KEFFLER and A. M. MAIDEN (Bull. Soc. chim. Belg., 1935, 44, 467—472).—Brassidic acid obtained from colza oil by a variation of the method of Reimer *et al.* (A., 1887, 233) and purified by repeated crystallisation from EtOH solidifies at 59.9° and is 99% pure.

H. G. M.

Acid fraction of mean mol. wt. 354 from the seeds of *Butea frondosa*, Roxb.—See A., 1935, 1550.

Odour and constitution: γ -substituted γ -butyrolactones. B. ROTHSTEIN (Bull. Soc. chim., 1935, [v], 2, 1936—1944).— $\alpha\beta$ -Epoxy-saturated hydrocarbons condense with $CHNa(CO_2Et)_2$, the malonyl residue becoming attached to the α -C (the less substituted). The products on hydrolysis and loss of CO_2 yield γ -substituted γ -butyrolactones. The b.p., *n*, and *d* of the following are given: $CH_2 \left\langle \begin{array}{c} CH_2 \\ CO_2 \end{array} \right\rangle CHR$, R=Bu^a; amyl; Me·[CH₂]₆; Me·[CH₂]₇; Me·[CH₂]₈; Me·[CH₂]₉; b.p. 140°/0.30 mm.; Me·[CH₂]₁₀; m.p. 32°, b.p. 159°/0.43 mm.; Pr ^{β} ·[CH₂]₂; b.p. 135°/16 mm.; and Pr ^{β} ·[CH₂]₃; b.p. 145°/14 mm., the last four compounds being new. The odour of these compounds is described. The following epoxy-hydrocarbons (prepared from the appropriate chlorohydrin or by BzO₂H-oxidation of the corresponding ethylene) appear new: $CHR \left\langle \begin{array}{c} O \\ CH_2 \end{array} \right\rangle$

R=Bu^a, b.p. 123—124°/763 mm.; Me·[CH₂]₆; b.p. 75°/13 mm.; Me·[CH₂]₇; b.p. 94°/15 mm.; Me·[CH₂]₈; b.p. 124—125°/15 mm.; Me·[CH₂]₁₀; b.p. 138—139°/15 mm. α -Chloro- ζ -methylheptan- β -ol has b.p. 99—100°/12 mm.

H. G. M.

Oxidation of *dl*- α -hydroxystearic acid and its significance as regards the structure of cerebronic acid. (A) E. KLENK and F. DITT. (B) P. A. LEVENE and P. S. YANG (J. Biol. Chem., 1935, 749—750, 751).—(A) *dl*- α -Hydroxystearic acid and $KMnO_4$ in $COMe_2$ give other acids as well as margaric. The conclusions of Levene *et al.* (A., 1933, 1276) concerning cerebronic acid are thus invalidated.

(B) The above result is admitted, but the conclusions are upheld.

R. S. C.

Condensation of α -aldehydo- $\alpha\beta$ -dicarboxylic esters with esters of α -halogeno-substituted acids. M. N. SHTSCHUKINA and N. A. PREBRASHENSKI (Ber., 1935, 68, [B], 1991—1998).—The condensation is considered to consist of an *O*-alkylation of the $\cdot CH \cdot OH$ form of the aldehydosuccinic ester. Condensation of $CH_2Cl \cdot CO_2Et$ with $NaOEt$ and $Et_2 \alpha$ -aldehydo- β -ethylsuccinate (I) or directly with the Na derivative of (I) obtained from $CO_2Et \cdot CHEt \cdot CH_2 \cdot CO_2Et$ and HCO_2Et gives $Et_2 \alpha$ -carbethoxymethoxymethylene- β -ethylsuccinate (II), $CO_2Et \cdot CHEt \cdot C(CO_2Et) \cdot CH \cdot O \cdot CH_2 \cdot CO_2Et$, b.p. 207°/15 mm., 195°/4 mm., which does not colour fuchsin- H_2SO_3 or yield a semicarbazone, immediately adds Br, and reduces boiling $Ag_2O \cdot NH_3$. Hydrolysis of (II) with boiling 10% $H_2C_2O_4$ affords an acid, $C_8H_{12}O_5$, m.p. 102.5—103° (also obtained amongst other products by use of boiling 10% HCl), slowly hydrolysed by boiling HCl to ethylsuccinaldehydic acid [*semicarbazone*, m.p. 161—162° (decomp.)] and $OH \cdot CH_2 \cdot CO_2H$. Et aldehydosuccinate (III) and $CH_2Br \cdot CO_2Et$ analogously yield $Et_2 \alpha'$ -carbethoxy-*n*-propoxymethylenesuccinate, $CO_2Et \cdot CH_2 \cdot C(CO_2Et) \cdot CH \cdot O \cdot CHEt \cdot CO_2Et$, b.p. 187°/7 mm., 211.5°/22.5 mm., which gives the same reactions as (II). It is very slowly hydrolysed by boiling dil. $H_2C_2O_4$ to an acid, $C_8H_{12}O_5$, b.p. 182—184°/8 mm., and by boiling 10% HCl to $OH \cdot CHEt \cdot CO_2H$ and succinaldehydic acid (IV). The Na derivative of (III) and $CH_2Cl \cdot CO_2Et$ in boiling EtOH give $Et_2 \alpha'$ -carbethoxymethoxymethylenesuccinate, $CO_2Et \cdot CH_2 \cdot C(CO_2Et) \cdot CH \cdot O \cdot CH_2 \cdot CO_2Et$, b.p. 211—212°/20 mm., hydrolysed by 10% HCl to a non-aldehydic acid, m.p. 126—129°, and (IV). H. W.

Nature of oxidising graphite anode and comparative electrolysis of *d*- and *meso*-tartaric acid in sodium hydroxide. V. SIHVONEN and M. PYLKKANEN (Suomen Kem., 1935, 2, B, 37—39).—0.5*M*-Na tartrate has been anodically oxidised at 25° with Pt, Ni, Fe, and C anodes, using 3*N*-NaOH in the cathodic compartment. Quant. analysis has been made on the product for O_2 , $CHO \cdot CO_2H$ (I), HCO_2H , and H_2CO_3 , and qual. analysis for dihydroxymaleic (II) and tartaric (III) acid. The % of HCO_2H is approx. the same as that of the CO_2 , and hence there can be no decomp. at the anode of (I) into 2 mols. of HCO_2H . $H_2C_2O_4$ is present only as a trace. The formation of (III) is greatest with Fe. There is no formation of $OH \cdot CH(CO_2H)_2$ or $CO(CO_2H)_2$. The primary product is (II), and in agreement the oxidation yield of *d*- is slightly < that of *meso*-tartaric acid, since the formation of (II) is slightly easier with the latter. Occlusion of O_2 by C in presence of NaOH is slow, and the anodic p.d. remains positive a longer

time than with the other electrodes. Otherwise oxidation with C resembles that with Ni. There is no marked difference between the isomerides.

R. S. B.

Decomposition of citric acid by yeast.—See A., 1935, 1538.

Preparation of crystalline aldono-lactones. R. WEIDENHAGEN (Z. Wirts. Zuckerind., 1935, 85, 689—691).—*d*-Gluconic (I) and *d*-arabonic (II) acids are converted into mixtures of the lactone and Et ester when heated with HCl-EtOH for 8—10 hr. at 150°. Dissolution of the mixture from (I) in COMe₂ and addition of light petroleum affords cryst. *d*-gluconolactone in 40% yield. Similarly, an 84% yield of *d*-arabonolactone is obtained from the Ca salt of (II).

P. G. C.

alloMucic acid and a new tetrahydroxyadipic acid. T. POSTERNAK (Helv. Chim. Acta, 1935, 18, 1283—1287; see A., 1935, 846, 1483).—The Ca salt (+6H₂O) and *di*(phenylhydrazide), m.p. 227—230° (decomp.), of $\alpha\beta\gamma\delta$ -tetrahydroxyadipic acid are also described. The m.p. of the lactone is now given as 200—201° (decomp.).

J. W. B.

Combination of thiol acids with methyl- [and phenyl-]glyoxal. M. P. SCHUBERT (J. Biol. Chem., 1935, 111, 671—678).—Aq. AcCHO gives additive compounds (1:1) with SH·CH₂·CO₂H (*Hg* salt, decomp. about 220°), and its anilide (II), m.p. 70°, and with glutathione, amorphous. BzCHO gives similar compounds with (I), m.p. 159°, thiosinamine, m.p. 108°, (II), m.p. 149°, *o*-SH·C₆H₄·CO₂H, m.p. 142°, and cysteine betaine (III), amorphous. Cysteine and CS(NH₂)₂, probably by virtue of the free NH₂ of the ψ -form, react with loss of H₂O to give with AcCHO products, amorphous and m.p. 159°, and with BzCHO products, m.p. 141° and 222°, respectively. Cystine betaine, +H₂O, cryst. (*Ag* and *Co* salts; flavianate, m.p. 230°), is prepared; it is readily reduced by Sn-HCl. The flavianate of (II) has m.p. 210°.

R. S. C.

Optical rotation of configuratively related aldehydes. P. A. LEVENE and A. ROTHEN (J. Biol. Chem., 1935, 111, 739—747).—*l*-C₂H₁₁·OH leads to α -methylbutaldehyde, b.p. 90—92°, $[M]_D^{25} +20.3^\circ$ (homogeneous), and β -methyl-*n*-valeraldehyde, b.p. 122°, $[M]_D -8.7^\circ$ in heptane, CHMeEt·CH₂·CH₂Br, and thence δ -methylhexan- α -al, b.p. 144°, $[M]_D +12.0^\circ$ in heptane, and ϵ -methylheptan- α -al, b.p. 72°/25 mm., $[M]_D +12.9^\circ$ in heptane. $[M]$ are max. vals. This series resembles the corresponding acids, azides, and iodides in changes of $[M]$.

R. S. C.

Action of alkyl halides on thio-aldehydes and -esters. M. S. PLATONOV and S. B. ANISIMOV (J. Gen. Chem. Russ., 1935, 5, 622—624).—MeI or EtI and mono- or di-thioparaldehyde or Et thioacetate (110°; 20 hr.) yield SMe₃I or SEt₃I.

R. T.

Mechanism and application of the Fries isomerisation. V. C. SEKERA (Trans. Illinois State Acad. Sci., 1935, 27, 81—82; cf. A., 1928, 1010).—Anhyd. FeCl₃ and ZnCl₂ can replace AlCl₃ in this reaction, although they are not so effective.

CH. ABS. (r)

Determination of diacetyl. H. SCHMALFUSS and H. RETHORN (Z. Unters. Lebensm., 1935, 70, 233—240).—Ac₂ is heated at 100° with aq. NH₂OH, HCl, NiCl₂, and NH₃. The Ni dioximine so formed is collected, washed at 0°, and weighed. The mean error of the determination of 0.05 g. of Ac₂ is -0.2%.

E. C. S.

Properties and reactions of carbohydrates in liquid ammonia. C. O. MILLER and A. E. SIEHRS (Proc. Soc. Exp. Biol. Med., 1931—1932, 29, 535—538; cf. A., 1934, 638).—Arabinose, glucose, fructose, galactose, sucrose, maltose, and α -methylglucoside (I) are sol. in dry liquid NH₃ (II) at -33.5° and 25°. Glycogen (III) is dispersed in an opalescent solution. The presence of moisture causes caramel formation. Disaccharides and (I), but not monosaccharides, will crystallise from (II). Addition of a solution of KNH₂ causes pptn. of the K₁ salts of monosaccharides, the K₂ salts of disaccharides, and either, according to the proportions used, of (I); the salts are stable when dry. The K salt of (II) chars in air. Reducing sugars, but not sucrose, caramelize when sealed with KNH₂ at 20° for 24 hr.

CH. ABS. (r)

Sugar determination by the ferricyanide electrode.—See this vol., 126.

Use of ceric sulphate in determining cuprous oxide obtained by reducing sugars on Fehling's solution.—See this vol., 43.

Action of phosphate on hexoses. II. R. NODZU and K. MATSUI (Bull. Chem. Soc. Japan, 1935, 10, 467—471).—At p_H 6.2—7 under the conditions previously defined (A., 1935, 734) Na₂HPO₄, K₂HAsO₄, and Na₂SO₃ yield acetol (I) from glucose (II), but in smaller amounts than does K₂HPO₄. Alkali chlorides and sulphates are ineffective. Traces of Fe slightly increase, and of Zn or Cu decrease, the production of (I) by K₂HPO₄. Traces of Ca or Mg are without effect. (I) is obtained from pure (II) and K₂HPO₄.

R. S. C.

[2:3:6-Trimethylglucose anhydride.] K. HESS and F. NEUMANN (Ber., 1935, 68, [B], 2167; cf. A., 1933, 596, 1278).—A reply to Freudenberg et al. (A., 1935, 1484).

H. W.

Colorimetric determination of glucose and fructose by their osazones. V. S. BUTKEVITSCH and M. S. GAJEVSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 313—316).—A modification of Herzfeld's method (A., 1932, 416; 1933, 175) for the colorimetric determination of glucose and fructose is described. The accuracy is $\pm 2.5\%$.

P. G. C.

Reduction products of aromatic amines and sugars [condensation products]. P. KARRER, H. SALOMON, R. KUNZ, and A. SEEBACH (Helv. Chim. Acta, 1935, 18, 1338—1342).—The following compounds, all of type NHR·CH₂·[CH·OH]₄·CH₂·OH, are obtained by heating together *d*-glucose and the appropriate amine in MeOH or EtOH, and catalytic reduction of the product with H₂ (20—25 atm.) at 100° (Ni catalyst) or 30° (Pd-C): *N*-phenyl-, m.p. 134° (*benzylidene* derivative, m.p. 118—119°), *N*-*p*-tolyl-, m.p. 122°, *N*-*p*-ethoxyphenyl-, m.p. 123°, *N*-*p*-hydroxyphenyl-, m.p. 163°, *N*- β -(*p*-hydroxyphenyl)ethyl- (only

as its *hydrochloride*, m.p. 208°, and *N*-ethyl- (as its *hydrochloride*, m.p. 134°)-*D*-glucosamine. These compounds are not febrifuges.
J. W. B.

ψ-Galactal. H. LOHAUS and O. WIDMAIER (Annalen, 1935, 520, 301—304).—Hydrolysis of galactal triacetate (Levene *et al.*, A., 1931, 1400) with boiling H₂O affords *ψ*-galactal diacetate (I),

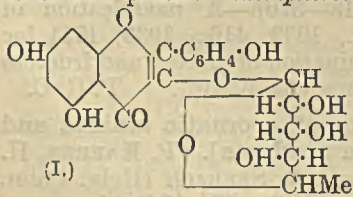
$$\text{OAc}\cdot\text{CH}_2\left\langle\begin{array}{l} \text{CH}\cdot\text{CH}(\text{OAc})\cdot\text{CH} \\ \text{O}\text{---}\text{CH}(\text{OH})\text{---}\text{CH} \end{array}\right.$$
 b.p. 163—165°/0.04 mm., $[\alpha]_D^{20}$ -26.9° [*p*-nitrophenylhydrazone, m.p. 176°; *acetal* (II), b.p. 136—138°/0.05 mm., $[\alpha]_D^{20}$ -39.70°], converted by Ba(OH)₂ into *isogalactal* (isolated as its *p*-nitrophenylhydrazone, m.p. 187°), which, when distilled, affords protoglucal (Bergmann *et al.*, A., 1934, 173). Reduction of (I) with Pd-H₂ gives its H₂-derivative, b.p. 148—153°/0.04 mm., $[\alpha]_D^{20}$ +44.2° [*p*-nitrophenylhydrazone, m.p. 148°; *acetal*, b.p. 107—108°/0.04 mm., $[\alpha]_D^{20}$ +23.78°, by similar reduction of (II)]. Galactal is reduced to its H₂-derivative, m.p. 128°, $[\alpha]_D$ +48.1°.
J. W. B.

Interaction of fructose and dinitrobenzene. L. VON SZÉCSÉNYI-NAGY (Biochem. Z., 1935, 281, 175—177).—*o*- but not *m*-C₆H₄(NO₂)₂ yields a deep violet colour with fructose.
W. McC.

Inversion of sucrose solutions in tropical sunlight.—See this vol., 38.

Thermal decomposition of sugars and its catalytic acceleration. E. H. RIESENFELD and F. MÜLLER (Ber., 1935, 68, [B], 2052—2054).—Technical sugar and sucrose are heated at 150° alone and with NaCl containing varied proportions of FeCl₃. Incipient caramelisation is observed in absence of catalyst, whereas addition of NaCl causes marked caramelisation and some carbonisation. The influence of > 0.005% of Fe (calc. on total mass) is inappreciable, but greater concns. cause more profound caramelisation and much greater separation of C. FeCl₃ alone induces carbonisation, but no caramelisation. K₂CO₃ and other salts behave similarly to NaCl.
H. W.

Robinobiose and kaempferolrhamnoside. G. ZEMPLÉN and A. GERECs (Ber., 1935, 68, [B], 2054—2059).—Contrary to Charaux (A., 1926, 1183), enzymic fission of robinine (*acetate*, m.p. 175° after softening at 135°, $[\alpha]_D^{20}$ -95.83° in CHCl₃) gives as least sol. product *kaempferol-1-rhamnoside* (I), m.p. 230° (decomp.) (*acetate*, m.p. 159° after softening at 116°, $[\alpha]_D^{20}$ -76.88° in CHCl₃), hydrolysed by boiling 1% HCl to kaempferol and *l*-rhamnose. The



mother-liquors from (I) yield *robinobiose*, $[\alpha]_D^{25}$ +2.72° to ±0° in H₂O [*acetate*, m.p. 113° after softening at 70°, $[\alpha]_D^{20}$ -19.23° in CHCl₃; *α-chloroacetate* (II), decomp. 180°, $[\alpha]_D^{20}$ -5.05° in CHCl₃], very similar to Charaux' robinose (III) and shown by oxidation with OI' to be *l-rhamnosido-D-galactose*. (II), Ag₂CO₃, and MeOH give *β-methylrobinoside acetate*, m.p. 153.5—154.5°, $[\alpha]_D^{24}$ -25.24° in CHCl₃. The sequence of

monoses in the non-isolated (III) is therefore *l-rhamnose-D-galactose-l-rhamnose*.
H. W.

Cellotriose. L. ZECHMEISTER and G. TÓTH (Ber., 1935, 68, [B], 2134—2136).—In reply to Hess *et al.*, (A., 1935, 1226, 1308) the homogeneity of the author's cellotriose is maintained.
H. W.

Influence of substitution in the benzene nucleus on enzymic fission of phenol-β-D-glucosides.—See A., 1935, 1536.

Emulsin. XXIV. Glucoside syntheses with emulsin. B. HELFERICH and U. LAMPERT (Ber., 1935, 68, [B], 2050—2051).—The dependence of the synthesis on the temp., nature of aglucone, β-glucosidase val. of the emulsin, and solvent is fully discussed. The prep. of *n*-butyl-β-D-glucoside in good yield is described.
H. W.

Determination of cardio-active glucosides by the step-photometer.—See A., 1935, 1531.

Arabogalactan of Siberian larch.—See this vol., 123.

Starch nitrates. E. BERL and W. C. KUNZE (Annalen, 1935, 520, 279—289).—When potato-starch (I) is nitrated with 1:1 H₃PO₄-HNO₃ the P₂O₅ content (approx. 0.3%) of the starch nitrate (II) is of the same order as the SO₃ content of (II) when H₂SO₄-HNO₃ is used, but the N content (13.1%) never reaches the theoretical val. (14.14%) for the trinitrate. With H₃PO₄-HNO₃ the η of (II), which rises to a max. at 12 hr. nitration and then slowly falls, is 10 times > when H₂SO₄-HNO₃ is used, and the stability of the product is higher (max. decomp. point 170°). X-Ray diagrams of (II) (3 interference rings) differ from those (9 rings) of (I), but hydrolysis of (II) gives a product different from (I). Microscopical examination of the grains of (II) shows a yellow outer section [amylopectin nitrate (III)] with a dark inner kernel [amylose nitrate (IV)], and by freezing moist in liquid air and subsequent flotation, separation into a lighter portion (smaller N content) and a heavier portion (higher N content) is effected. Addition of COMe₂ causes swelling, and the inner kernels split up into small granules, which, unlike (III), go into solution as the [COMe₂] is increased. The η of (II) is dependent on the composition of the nitrating mixture, duration and temp. of nitration, and the nature of (I). The η of (II) from sol. starch is only 0.1 that of ordinary (I), but is not related to the mol. (micelle) wt. of (I) as determined by osmotic pressure measurements. Samples of high mol. wt. give a product of lower η. In agreement with the above, separate nitration of amylopectin gives (III) of lower N content (11.82—12.05%) and very high η, whereas amylose gives (IV) with higher N content (13.45%) and low η. Previous heating of (I) with H₂O at 90—130°/0.715—2.7 atm. causes a 10³ increase in η of (II), but at 150—180°/4.7—10 atm., a sudden and rapid fall in η of (II) occurs.
J. W. B.

Phosphorus of starches. T. POSTERNAK (Helv. Chim. Acta, 1935, 18, 1351—1369).—A more detailed account of work previously summarised (A., 1934, 59, 390; 1935, 1549).
J. W. B.

"Bukuryo," sclerotia of *Pachyma Hoelen*, Rumph. I. Chemical structure of β -pachyman, the polysaccharide obtained from "Bukuryo," and its determination. K. TAKEDA (Mem. Tottori Agric. Coll., 1935, 3, 1—123).—Extraction of "Bukuryo" with EtOH-NaOH yielded β -pachyman (I), $(C_6H_{10}O_5)_n$, no m.p., but darkening at 230—235°, $[\alpha]_D^{20} +24.78^\circ$ in 5% NaOH, mol. wt. probably < that of starch [*trinitrate*, m.p. 195—199°, $[\alpha]_D^{20} -63.63^\circ$ in C_5H_5N -EtOAc (3:2); *triacetate* (II), decomp. 255—258°, $[\alpha]_D^{20} -68.75^\circ$ in $CHCl_3$; Me_2 ether (III), m.p. 265—268°, $[\alpha]_D^{20} -11.25^\circ$ in C_5H_5N - C_6H_6]. Hydrolysis of (I) with dil. or conc. H_2SO_4 or dil. HCl yielded glucose (IV), whilst takadiastase gave (IV) and a disaccharide (*osazone*, m.p. 177°) similar to, but not identical with, gentiobiose. Hydrolysis with $H_2C_2O_4$ or conc. HCl produced (IV) and an unstable *disaccharide*, $C_{12}H_{22}O_{11}$, m.p. 110° $[\alpha]_D^{20} +76.7^\circ$ in H_2O (*osazone*, m.p. 167°), insol. in 95% EtOH, which on keeping decomposes to (IV). Neither fructose nor mannose was found in the hydrolytic products. Acetolysis of (I) using $ZnCl_2$ yielded (II) and *biose octa-acetate*, m.p. 80—82°, $[\alpha]_D^{20} +36.10^\circ$ in $CHCl_3$, $+25.3^\circ$ in C_6H_6 ; hydrolysis of this yielded only (II). Acetolysis with $HClO_4$ gave β -tetra-acetylglycuronic acid, and with H_2SO_4 [using (II)], glucose α -penta-acetate, m.p. 109—111°, was obtained. Hydrolysis of (III) with 5% HCl gave a 90% yield of 2:3:6-trimethylglucose, and with 1% MeOH-HCl, a 93% yield of 2:3:6-trimethylmethylglucoside. 2:3:4-Trimethylglucose was not detected. It is concluded that in the structure of (I), many α - and β -glucofuranoses (1:4) are linked, commencing with the α , at the first and fifth C. Two methods, the "alcohol" and the "enzyme," for the determination of (I) in "Bukuryo" are described. J. N. A.

"Bukuryo," sclerotia of *Pachyma Hoelen*, Rumph. VII. Production of tetra-acetylglycuronic acid by acetolysis of β -pachyman in the presence of perchloric acid. K. TAKEDA (J. Agric. Chem. Soc. Japan, 1934, 10, 1010—1013).—Two *acetates* were obtained: (a), m.p. 83—86°, $[\alpha]_D^{20} +9.56^\circ$ in $CHCl_3$, $+8.47^\circ$ in C_6H_6 , (b) $C_{14}H_{18}O_{11}$, m.p. 103—107°, $[\alpha]_D^{20} +65.6^\circ$ in C_6H_6 , $+66.2^\circ$ in $CHCl_3$, $+60.9^\circ$ in MeOH. (b) is probably tetra-acetylglycuronic acid and hydrolysis gave a syrup which yielded an *osazone*, $C_{18}H_{20}O_5N_4$, m.p. 167—174°. J. N. A.

Hydrolysis of cellulose and its oligosaccharides. K. FREUDENBERG and G. BLONQUIST (Ber., 1935, 68, [B], 2070—2082).—New data are recorded for $[M]$ for cellotriose (I) and cellotetraose (II) and the velocities of hydrolysis of cellobiose (III), (I), (II), and cellulose (IV) are measured in 51% H_2SO_4 , the changes being followed polarimetrically and by iodometric determination of liberated $\cdot CHO$. The hypothesis that from (I) onwards each unit with a terminal union reacts according to k , with all other unions according to k_n , is a suitable basis for calculation, but is an approximation, and it appears probable that the hydrolysis of (IV) and its oligosaccharides (V) is precisely similar to the fission of the polypeptides of glycine and, in a measure, to the cracking of hydrocarbons. The evidence that the

(V) contain only one type of structure, that of (III), from which a straight chain leads to the polysaccharide, which is thus an extrapolation of (V), is as follows. Methylcellobiose (VI) is hydrolysed to 1 mol. of tri- (VII) and 1 mol. of tetra- (VIII) -methylglucose. Methylcellotriose (IX) yields 2 mols. of (VII) and 1 mol. of (VIII), whereas methylcellotetraose gives 3 mols. of (VII) and 1 mol. of (VIII), and methylcellulose many mols. of (VII) and one of (VIII). (VII), (VIII), (III), (VI), and (IX) have been completely synthesised and their structure has been elucidated. $[M]$ from (III) onwards changes almost additively by the val. of one intermediate section for (I), of two sections for (II), and so on. $[M]$ of this intermediate section is nearly $[M]$ of the unit of (IV). The yield of (III) leads to the conclusion that the biose union alone is constitution-chemically and configuratively present in (IV). The course of the hydrolysis of (I), (II), and (IV) can be adequately explained by the hypothesis that all unions are of a single type, that of (III). Evaluation of the graphs obtained polarimetrically shows that all unions are sterically similar. H. W.

Action of ethylene oxide on cellulose. I. N. I. NIKITIN and T. I. RUDNEVA (J. Appl. Chem. Russ., 1935, 8, 1023—1032).—Bleached cotton-wool (I) and $(CH_2)_2O$ at 50° afford a product containing 1 $OH \cdot CH_2 \cdot CH_2 \cdot O \cdot (II)$ per 32 $C_6H_{10}O_5$ units; the proportion rises to 1:4—8 in presence of dil. alkalis, and attains a max. of 1:1.5 in presence of 18% NaOH or 35% KOH (50—60°; 15 min.). The products are much more readily hydrolysed and acetylated than is (I), but the velocity of benzoylation is not affected; they yield highly viscous solutions in NaOH, the viscosity rising with the no. of (II) introduced. R. T.

Celluloid formation. II. Effect of reaction medium on heterogeneous changes occurring in the fibrous state. M. WADANO, K. HESS, and C. TROGUS. III. Catalysed reactions in the fibrous state. Heterogeneous catalysis with a solid substrate and liquid catalyst. M. WADANO, C. TROGUS, and K. HESS. IV. Production of celluloid from cellulose nitrate and *l*- or *dl*-camphor. K. HESS, C. TROGUS, and M. WADANO (Z. physikal. Chem., 1935, B, 30, 159—182, 183—231, 232—235; cf. A., 1932, 568).—II. The reaction between cellulose nitrate (I) and camphor in presence of aliphatic alcohols as solvents is complete at such low camphor concn. that it can be effected at room temp. The X-ray diagrams and analysis of the solid phase show the existence of two new compounds, camphor-cellulose nitrate II (II) and camphor-cellulose nitrate III (III), in addition to the camphor-cellulose nitrate I (IV) previously observed. It seems probable that (III) corresponds with hydro-cellulose and (II) and (IV) correspond with natural cellulose. The camphor concn. at which reaction starts to proceed into the interior of the micelles increases with the size of the alkyl radical. The fact that the nature of the reaction product and the relation between the amount of camphor taken up and the camphor concn. vary with the solvent is possibly due to the first stage of the reaction being formation of

a double compound between the solvent and (I). Aromatic hydrocarbons promote the reaction of (I) with camphor in varying degrees.

III. The reaction of (I) with camphor in benzene solution in presence of ketones and alcohols has been studied. The effect of these substances on the concn. of camphor required for complete reaction is due to catalysis, and the varying fine structure of the product is determined by processes which are superimposed on the sorption of camphor. COMe_2 and cyclohexanone are better catalysts than alcohols. For a camphor concn., c , of 30% the amount taken up passes through a max. with increasing COMe_2 concn., C , whilst for const. C the amount of camphor taken up rises towards a limit with increase in c . When c is moderate and C small the product is (IV). (II) is obtained when C is $\approx 1\%$. If C is $> 10\%$ and $c = 5-20\%$, the product is camphor-cellulose nitrate IV, which contains COMe_2 . The formation of the various compounds of camphor and (I) is irreversible, and it is in general impossible to transform one into another. The catalytic action of COMe_2 is attributed to its relatively rapid reaction with (I) to give a compound which reacts with camphor giving camphor-cellulose nitrate and re-forming COMe_2 . With increasing C the swelling of the (I) fibres passes through a max., then through a min. EtOH and MeOH act similarly to COMe_2 as catalysts. The presence of H_2O favours the formation of (II).

IV. The optical isomerides of camphor are identical in their behaviour towards (I). R. C.

Reaction mechanism: action of fused sodamide on mono-, di-, and tri-methylamines. H. S. FRY and W. V. CULP (Rec. trav. chim., 1935, 54, 838—846).—Analogy with the reaction $\text{RH}_n + n\text{NaOH} \rightarrow \text{R}(\text{ONa})_n + n\text{H}_2$ (A., 1928, 615) suggests the reaction $\text{RH}_n + n\text{NaNH}_2 \rightarrow \text{R}(\text{NHNa})_n + n\text{H}_2$. Summation of the expected reaction stages leads to the equation $\text{NH}_2\text{Me} + \text{NaNH}_2 \rightarrow \text{NaCN} + \text{NH}_3 + 2\text{H}_2$ for the interaction between NH_2Me and fused NaNH_2 (in excess) at 250° . Determination of the NH_2Me used (liberated from $\text{NH}_2\text{Me}\cdot\text{HCl}$ by dropwise addition of $10N\text{-NaOH}$), NaCN (Volhard), NH_3 (absorbed in an excess of $6N\text{-H}_2\text{SO}_4$), and H_2 (no other gaseous products formed), gives 94% agreement with this equation. Similarly the mechanism $\text{NHMe}_2 + 2\text{NaNH}_2 \rightarrow 2\text{NaCN} + \text{NH}_3 + 4\text{H}_2$ is verified to the extent of 97%, but the derived $\text{NMe}_3 + 3\text{NaNH}_2 \rightarrow 3\text{NaCN} + \text{NH}_3 + 6\text{H}_2$ is invalid, since NMe_3 does not react with fused NaNH_2 . It is suggested that the initial stage $\text{NMe}_2 + \text{NaNH}_2 \rightarrow [\text{NHMeR}_2, \text{NHNa}] \rightarrow \text{NHMeNa} + \text{NHR}_2$, occurs with NH_2Me ($\text{R}_2 = \text{H}_2$, $K_b = 5.0 \times 10^{-4}$) and NHMe_2 ($\text{R}_2 = \text{MeH}$, $K_b = 5.4 \times 10^{-4}$), but not with the more weakly basic NMe_3 ($\text{R}_2 = \text{Me}_2$, $K_b = 5.9 \times 10^{-5}$). J. W. B.

Thermal decomposition of triethylamine.—See this vol., 33.

Trichlorohydroxy-aliphatic amines. F. D. CHATTAWAY and P. WITHERINGTON (J.C.S., 1935, 1623—1624).— $\gamma\gamma\gamma$ -Trichloro- α -amino- β -hydroxypropane, m.p. 123° [oxalate, m.p. 220° (decomp.); sulphate, m.p. 255° (decomp)]; Ac derivative, m.p. 154° ; Ac_2 derivative, m.p. 99°], is obtained from the hydrochloride (I), m.p. 235° (decomp.), which is pre-

pared by the reduction (Sn-HCl) of $\gamma\gamma\gamma$ -trichloro- α -nitro- β -hydroxypropane. Similarly $\gamma\gamma\delta$ -trichloro- α -amino- β -hydroxy- n -pentane, m.p. 141° (darkening) [hydrochloride (II), m.p. about 231° (decomp.); oxalate, m.p. 232° (decomp.); sulphate, m.p. $235-240^\circ$ (decomp.); Ac derivative, m.p. 109° ; Ac_2 derivative, m.p. 136°], is obtained from the corresponding NO_2 -compound. (I) with KCN yields $\gamma\gamma\gamma$ -trichloro- β -hydroxy- n -propylcarbamide, m.p. 175° , and (II) similarly yields $\gamma\gamma\delta$ -trichloro- β -hydroxy- n -amylcarbamide, m.p. 175° . F. N. W.

Introduction of halogen or thiocyanate into organic compounds by means of dichloropentamethylenetetramine. M. V. LICHOSCHERSTOV and T. D. ALDOSCHIN (J. Gen. Chem. Russ., 1935, 5, 981—985).—The reaction $(\text{CH}_2)_5\text{N}_4\text{Cl}_2 + 2\text{MX} + 2\text{HR} \rightarrow 2\text{RX} + 2\text{MCl} + (\text{CH}_2)_5\text{N}_4\text{H}_2$ ($\text{M} = \text{K}, \text{Na}$; $\text{X} = \text{halogen}$ or CNS ; $\text{R} = \text{aryl radical}$) is of general application, and affords high yields of relatively pure products in cases in which the ordinary methods do not do so (nitrophenols). R. T.

(A) **Action of N -sulphuric acid and N -sodium hydroxide on glycine.** (B) **Interaction of glycine and glycyglycine with nicotine.** I. S. JATTSCHNIKOV (J. Gen. Chem. Russ., 1935, 5, 967—969, 970—971).—(A) Formol-titratable N diminishes immediately after addition of glycine (I) to $N\text{-H}_2\text{SO}_4$, to attain a min. val. after 3 days, and then rises to a const. val. after 30 days at room temp. $N\text{-NaOH}$ exerts a similar action, the min. val. being attained after 28 days. The phenomena are ascribed to trans-formation of anhydride, peptide, or polymeride.

(B) (I) and glycyglycine combine with nicotine in presence of CH_2O . R. T.

Determination of the sum of glycine and serine. S. RAPOPORT (Biochem. Z., 1935, 281, 30—36).—The sum of the amounts of these acids (e.g., in protein hydrolysates) is determined, after removal of dicarboxylic NH_2 -acids, by deamination with NaNO_2 and oxidation (to $\text{H}_2\text{C}_2\text{O}_4$) of the product with $0.1N$ alkaline KMnO_4 . The results are slightly $>$ those obtained by other methods except with caseinogen, with which the vals. are much higher. At 120° in 5 hr. serine (I) is converted by $\text{HI} + \text{P}$ into alanine (II), which is then determined by the method of Kendall *et al.* (A., 1931, 246), but this procedure gives inaccurate results when preformed (II) is present. Glycic acid is colorimetrically determined with the help of the blue colour produced on addition of conc. H_2SO_4 and naphthoresorcinol, and hence (I) and glycine can be separately determined in sericin, the vals. being 8.71 and 1.69%, respectively. W. McC.

Carbamido-acid and hydantoin of arginine. W. R. BOON and W. ROBSON (Biochem. J., 1935, 29, 2573—2575).—Arginine on warming in aq. solution with KCNO gave carbamidoarginine, m.p. 172° , passing in warm acid solution into arginine-hydantoin, m.p. 100° . H. D.

Conversion of arginine into citrulline. K. DIRR and H. SPATH (Z. physiol. Chem., 1935, 237, 121—130; cf. A., 1934, 993).—The hydrochloride ($1\text{H}_2\text{O}$), m.p. 155° (decomp.), $[\alpha]_D^{25} + 13.0^\circ$, of arginine-amide (I) [picrate, m.p. 220° (decomp.)] obtained from

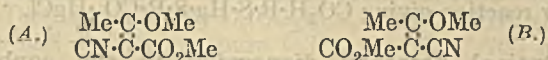
the Me ester in MeOH and NH_3 , and the *hydrochloride* ($1\text{H}_2\text{O}$), decomp. 260° , of α -monobenzoylarginine-amide (II) yield no citrulline (III) on hydrolysis and are not attacked by arginase (IV). Together with (I) *arginine-diketopiperazine*, decomp. 316° , is obtained. *Dibenzoylarginine Me ester hydrochloride* has m.p. 171° . (I) and (II) yield the Bz_3 derivative of (I), m.p. 245° , which gives a 10% yield of the corresponding Bz_3 derivative (V), m.p. 220° , of (II) on hydrolysis with conc. HCl at room temp., a substance, m.p. 178° , probably an inactive form of (V), being produced (sometimes) at the same time. Hot acid hydrolysis of (V) gives BzOH , NH_3 , ornithine, and proline, but no (III) or $\text{CO}(\text{NH}_2)_2$. CH_2N_2 with α -benzoylcitrulline gives the *Me ester*, decomp. about 120° , and NH_3 converts the ester into the corresponding *amide* (VI), m.p. about 140° . Benzoylation of (VI) gives (V). It seems that in the biological conversion of arginine (VII) into (III) by deimidase and (IV) the attack on the guanidine residue must be preceded by blocking of the CO_2H . W. McC.

Preparation of ornithine, ornithuric acid, and α -benzoylornithine. W. R. BOON and W. ROBSON (Biochem. J., 1935, 29, 2684—2688).—Improved methods (yields in brackets) for the prep. of the following are described: ornithuric acid (I) [68.5%] from arginine hydrochloride and [nearly theoretical] from carbamido-arginine (II); ornithine hydrochloride [nearly theoretical] from (II); and benzoylornithine [76%] from (I). J. N. A.

Relationships between acidity and tautomerism. IV. Effect of the cyano-group. F. ARNDT, H. SCHOLZ, and E. FROBEL (Annalen, 1935, 521, 95—121).—The behaviour of a series of CN-compounds towards FeCl_3 , Br, and CH_2N_2 shows that the acidifying action of CN exceeds that of any other simple C-containing substituent and approximates to that of SO_2 . CN shows electromeric action in the form of "enotropic effect" and as conjugation partner; in both respects it is considerably inferior to keto-CO, but superior to ester CO. $\text{CH}\cdot\text{CN}$ can therefore pass into $\text{C}\cdot\text{C}\cdot\text{NH}$, but a conjugation partner is necessary, which, as always, must not precede CN in the sequence of electromeric activity. A second CN, ester CO, or, in certain circumstances, NO_2 can function as conjugation partner for the enimisation of CN. In addition, the prototropic expenditure of energy must be greatly decreased by strong acidification of the central CH to render enimisation possible. Hence it does not occur with $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ or $\text{CH}_2(\text{CN})_2$. In combination with keto-CO, CN behaves essentially as conjugation partner. The enimine group behaves towards FeCl_3 , Br, and CH_2N_2 similarly to the enol group and can, if it occurs, have a more or less considerable share of the empirical activity of the corresponding dissolved compound. With regard to acidifying action (inductive effort) and electromeric effect the sequences of substituents are, respectively, $\text{NO}_2 > \text{SO}_2\text{OR} > \text{SO}_2\text{R} > \text{CN} > \text{CO}_2\text{R} > \text{CH}\cdot\text{O} > \text{CR}\cdot\text{O}$ and $\text{CH}\cdot\text{O} > \text{CR}\cdot\text{O} > \text{ON} > \text{CO}_2\text{R} > \text{NO}_2$.

Application of the Br titration method to the following compounds gives variable and non-reproducible results which frequently depend greatly on temp.

and solvent; the underlying reasons are fully discussed. Absorption of Br in some measure, however, invariably goes hand in hand with occurrence of a colour with FeCl_3 . $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ gives a red colour with FeCl_3 and immediately decolorises Br in MeOH, but not in CHCl_3 . With CH_2N_2 in Et_2O at -50° it yields two substances, m.p. 76° and $97\text{--}98^\circ$,



probably A and B, since the former passes into the latter when heated for some time at 130° and each forms the same compound with NH_3 . The enimine or ester OH groups do not participate in the change. *p*-Toluenesulphonylacetonitrile (I), m.p. $147\text{--}148^\circ$, does not react with Br or FeCl_3 ; in absence of catalyst it does not react with CH_2N_2 , but after liberal addition of MeOH it slowly affords α -*p*-toluenesulphonylpropionitrile, m.p. 60° (corresponding amide, m.p. 168°), and the compound $\begin{array}{c} \text{N}\cdot\text{NMe} \\ \text{N}\text{---}\text{CH} \end{array} > \text{C}\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Me}$, m.p. 162° .

Its acidity is therefore due solely to CH_2 . *Me p*-toluenesulphonylcyanoacetate, m.p. $79\text{--}80^\circ$, from the Na derivative of (I) and ClCO_2Me , shows marked reaction with FeCl_3 and decolorisation of Br; with CH_2N_2 it yields the substance $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{C}(\text{CN})\cdot\text{C}(\text{NMe})$, m.p. $125\text{--}127^\circ$, and *Me α -cyano- α -p-toluenesulphonylpropionate*, m.p. 101° . The solid substance is therefore $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Me}$, and passes in solution completely or preponderatingly into the enimine form. *α -Cyano- α -p-toluenesulphonylacetone*, m.p. $122\text{--}123^\circ$, from the Na derivative of (I) and AcCl in cold Et_2O , gives a moderate FeCl_3 reaction, and immediately decolorises Br in EtOH or CHCl_3 . In solution in Et_2O it is converted exclusively into the *enol ether*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{C}(\text{CN})\cdot\text{CMe}\cdot\text{OMe}$, m.p. 124° , whereas the solid when treated with $\text{CH}_2\text{N}_2\text{--Et}_2\text{O}$ affords also *α -acetyl- α -p-toluenesulphonylpropionitrile*, m.p. $150\text{--}151^\circ$. *N*-Methylation is not observed. The solid substance is $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{CHAc}\cdot\text{CN}$ and is partly enolised but not eniminated in solution. $\text{CH}_2(\text{CN})_2$ does not react with Br or FeCl_3 or with CH_2N_2 in presence of MeOH. *p*-Toluenesulphonylmalononitrile, m.p. $101\text{--}102^\circ$ after softening at 93° , from the Na compound of (I) and CNBr , gives considerable FeCl_3 reaction and immediately decolorises Br in EtOH or CHCl_3 . With CH_2N_2 at -50° it yields small amounts of *p*-toluenesulphonylmethylmalononitrile, m.p. 103° , whereas under the customary conditions some *N*-methylation is observed. Hence the solid is $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{CH}(\text{CN})_2$ and becomes eniminated in solution. *Me dicyanoacetate*, m.p. 65° , gives strong FeCl_3 reaction and decolorises Br. With CH_2N_2 at -50° it gives a non-cryst. product with 6.3% NMe and 12.0% OMe (of which 10.9% is present as CO_2Me). *$\alpha\alpha$ -Dicyanoacetone*, m.p. 141° , from $\text{CHNa}(\text{CN})_2$ and AcCl [*p*-nitrophenylhydrazone, m.p. 144° (decomp.)], gives a marked FeCl_3 reaction and immediately decolorises a little Br. *O*-Methylation predominates with CH_2N_2 , but some *N*-methylation is observed. An ethereal solution of $\text{CH}(\text{CN})_3$ gives an intense FeCl_3 reaction and absorbs much Br. The product formed with CH_2N_2 gives about half the calc. NMe val., showing that NH is formed and resembles enolic OH in behaviour towards FeCl_3 . H. W.

Determination of thiol and disulphide compounds, with special reference to cysteine and cystine. III. Reaction between thiol compounds and mercuric chloride. K. SHINOHARA (J. Biol. Chem., 1935, 141, 435—442).—Cysteine or $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ reacts rapidly with HgCl_2 at p_{H} 5, giving a mercaptide of the type $\text{Hg}(\text{S}\cdot\text{R}\cdot\text{CO}_2\text{H})_2$, followed by a slow reaction giving $\text{CO}_2\text{H}\cdot\text{R}\cdot\text{S}\cdot\text{Hg}\cdot\text{S}\cdot\text{R}\cdot\text{CO}_2\cdot\text{HgCl}$.

F. A. A.

Optical rotatory dispersion in the carbohydrate group. VI. Amide rotation rule. T. L. HARRIS, E. L. HIRST, and C. E. WOOD (J.C.S., 1935, 1658—1662; cf. A., 1935, 568).—The rotatory dispersion of *d*-dimethoxysuccinamide, *d*-dimethoxysuccinmethylamide, and 1:2:3:5-trimethylarabonamide (all obeying the amide rule) is controlled by the induced dissymmetry, and can be represented by a one-term Drude-Natanson equation. Similar examination of 4:6-dimethylmannonamide, which obeys the amide rule in EtOH but not in H_2O , shows that special stereochemical arrangements of the substituent groups may give rise to an induced activity opposite in sign to that of the normal amide. Data for various λ for the above compounds and for *Me d-dimethoxysuccinate*, b.p. $120^\circ/12$ mm., with H_2O and EtOH as solvents are given.

F. N. W.

Action of magnesium phenyl bromide on α -bromobutyrdimethylamide. S. P. TI (Bull. Soc. chim., 1935, [v], 2, 1799—1800; cf. A., 1931, 1279).—The reaction products of MgPhBr and α -bromobutyrdimethylamide, b.p. 123 — $124^\circ/17$ mm., are butyrdimethylamide, *crotondimethylamide* (impure), b.p. about 200° , and a little COPhPr^{r} and β -dimethylamino- α -diphenylbutanol, m.p. 58° [picrate, m.p. 155° ; perchlorate, m.p. 182° ; Ac derivative (picrate, m.p. 138°)].

H. G. M.

Reactions of sulphuryl diamide (sulphamide). F. C. WOOD (Nature, 1935, 136, 837).—*Dixanthyl sulphamide*, m.p. 182 — 184° , is obtained by adding a solution of xanthhydrol (I) in EtOH to one of sulphamide in aq. AcOH. Condensation products have also been obtained with (I) and *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$, m.p. 209° , *m*- $\text{C}_6\text{H}_4(\text{SO}_2\cdot\text{NH}_2)_2$, m.p. 170° , and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NH}_2$, m.p. 198° . These general reactions can be used for the determination of sulphamides and sulphonamides.

L. S. T.

Determination of glutamine in presence of asparagine. H. B. VICKERY, G. W. PUCHER, H. E. CLARK, A. C. CHIBNALL, and R. G. WESTALL (Biochem. J., 1935, 29, 2710—2720).—The amide group is completely hydrolysed when glutamine (I) is heated at 100° for 2 hr. at p_{H} 6.5. The increase in $\text{NH}_2\text{-N}$ that occurs gives the amount of (I) $\text{NH}_2\text{-N}$ in the extract of the plant tissue. The decrease in $\text{NH}_2\text{-N}$ of an extract on hydrolysis under these conditions is a valuable qual. criterion of the presence of (I). Interference from asparagine is negligible, for it requires heating for 3 hr. at 100° with *N*- H_2SO_4 , whilst the effect of $\text{CO}(\text{NH}_2)_2$ and allantoin can be easily detected. Data on the stability of (I) with regard to temp. and p_{H} are given. The chief products of hydrolysis of (I) at essentially neutral reaction are NH_3 and pyrrolidonecarboxylic acid.

J. N. A.

Dicyanodiamide. F. CHASTELLAIN (Helv. Chim. Acta, 1935, 18, 1287—1302).—Hydrolysis of dicyanodiamide (I) with a slight excess of acid at 50 — 80° gives a quant. yield of guanylcarbamide (II), but with insufficient acid further hydrolysis to $\text{NH}\cdot\text{C}(\text{NH}_2)_2$ occurs. Hydrolysis of (I) with 1% NaOH at 100° has been quantitatively studied by determination of the NH_3 evolved (cf. B., 1926, 505), $\text{CO}(\text{NH}_2)_2$ (Fosse), $\text{NH}_2\cdot\text{CN}$ (Perotti), and unchanged (I). The increase in the NH_3 evolved is rapid during the first 2 hr. and thereafter becomes linear with time. The amount of NH_3 evolved is equally dependent on the concn. of (I) and of NaOH, and is the same whether the mol. ratio (I)/NaOH (*r*) is *a* or $1/a$. The $\text{CO}(\text{NH}_2)_2$ formed [only slightly increased by excess of NaOH, but greatly increased by increasing the mol. proportion of (I)] increases to a max. at about 3 hr. and then decreases linearly with time. The sum $\text{NH}_3\text{-N} + \text{CO}(\text{NH}_2)_2\text{-N}$ increases to a const. val. for any particular val. of *r*, and this const. val. itself increases from 16.5% of total N when $r=5$ to 60% when $r=0.5$, and then remains approx. const. to $r=0.2$. The initial stage is the depolymerisation of (I) to $\text{NH}_2\cdot\text{CN}$, which reaches max. concn. after < 1 hr., and disappears after 5 hr. ($r=1$), and no (I) could be detected after 9 hr. During the first ten hr. only $\text{CO}(\text{NH}_2)_2$ is hydrolysed, hydrolysis of melamine [formed from (I) and $\text{NH}_2\cdot\text{CN}$] to (finally) $(\text{HCNO})_3$ requiring more drastic conditions. No (II), $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CN}$, or $\text{NH}(\text{CO}\cdot\text{NH}_2)_2$ could be detected in the alkaline hydrolysis. These and earlier results are discussed and it is concluded that (I) is tautomeric,

$$\text{NH}\cdot\text{C}\left\langle\begin{array}{c} \text{NH} \\ \text{NH} \end{array}\right\rangle\text{C}\cdot\text{NH} \rightleftharpoons \text{NH}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}\cdot\text{CN}$$

existing solely as the former in alkaline and neutral solution and probably in the solid state, and as the latter in acid solution.

J. W. B.

Photochemical and thermal decomposition of azomethane.—See this vol., 37.

Iron-cyanogen compounds. VI. Action of oxalates on the blue iron-cyanogen compounds. M. KOHN (Monatsh., 1935, 66, 393—405; cf. A., 1924, i, 21).—Sol. and ordinary Prussian-blue (I) dissolve completely in $\text{K}_2\text{C}_2\text{O}_4$ with formation of $\text{K}_3\text{F}_2(\text{C}_2\text{O}_4)_3$ and $\text{K}_4\text{Fe}(\text{CN})_6$; Turnbull's blue (II) is mainly but not completely sol., leaving a residue of white $\text{Fe}_3\text{Fe}(\text{CN})_6$. The action of H_2O_2 on a mixture of $3\text{FeSO}_4 + 2\text{K}_3\text{Fe}(\text{CN})_6$ [(II)], whereby complete reaction should lead to $\text{OH}\cdot\text{Fe}^{\text{III}}[\text{Fe}^{\text{III}}\text{Fe}(\text{CN})_6]_2$, or on a mixture of $2\text{FeSO}_4 + \text{K}_4\text{Fe}(\text{CN})_6$ which similarly should give $(\text{OH})_2\text{Fe}^{\text{III}}[\text{Fe}(\text{CN})_6]$ gives in each case blue preps. of insol. basic (I), which are converted by $\text{K}_2\text{C}_2\text{O}_4$ into $\text{Fe}(\text{OH})_3$ in theoretical amount, $\text{K}_4\text{Fe}(\text{CN})_6$, and $\text{K}_3\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3$. Oxidation of a mixture of FeSO_4 and $\text{K}_4\text{Fe}(\text{CN})_6$ by H_2O_2 affords a basic (I), colloiddally sol. in H_2O , which when treated with $\text{K}_2\text{C}_2\text{O}_4$ gives $\text{K}_3\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3$, $\text{K}_4\text{Fe}(\text{CN})_6$, and considerably more $\text{Fe}(\text{OH})_3$ than is expected from theory, since the unused $\text{K}_4\text{Fe}(\text{CN})_6$ is oxidised to $\text{K}_3\text{Fe}(\text{CN})_6$ and the OH' thus liberated is consumed by the blue ppt. For this reason basic (I) results from sol. (I) by the action of H_2O_2 in presence of excess of $\text{K}_4\text{Fe}(\text{CN})_6$. Basic (I) is not formed in appreciable amount from sol. (I) under the influence of H_2O_2 .

(I) is transformed by KHC_2O_4 into a colloidal, blue solution and, if large amounts of KHC_2O_4 are used, also converted into $\text{H}_4\text{Fe}(\text{CN})_6$ and $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3$, whereby pale yellowish-green solutions which are sensitive to light result.

H. W.

Dihydroxides of tertiary arsines, arsonium derivatives, and their salts. G. A. RAZUVAEV, V. S. MALINOVSKI, and D. A. GODINA (J. Gen. Chem. Russ., 1935, 5, 721—727).— AsMe_3 in Et_2O and HNO_3 yield the *mononitrate*, m.p. 127° , of $\text{AsMe}_3(\text{OH})_2$; the free hydroxide readily eliminates H_2O to yield AsMe_3O . AsMe_4I affords $\text{AsMe}_4\cdot\text{NO}_3$, m.p. $268-270^\circ$, with AgNO_3 , and $\text{AsMe}_4\cdot\text{OH}$ with AgOH . The following compounds have been prepared analogously: AsPhMe_2O , m.p. $157-161^\circ$, $\text{OH}\cdot\text{AsPhMe}_2\cdot\text{NO}_3$, m.p. $149-150^\circ$, $\text{AsPhMe}_3\cdot\text{OH}$, m.p. $106-116^\circ$ (*nitrate*, m.p. $195-196^\circ$), $\text{AsPh}_2\text{Me}(\text{OH})_2$ (*nitrate*, m.p. $106-107^\circ$), $\text{AsPh}_2\text{Me}_2\text{I}$, m.p. $211-213^\circ$, $\text{AsPh}_2\text{Me}_2\cdot\text{OH}$, m.p. $120-135^\circ$ (*nitrate*, m.p. $149-151^\circ$), $\text{AsPh}_3\text{Me}\cdot\text{NO}_3$, m.p. 100° , $(\text{AsPh}_3\cdot\text{OH})_2\text{SO}$, m.p. 195° , AsR_2Me , b.p. $170^\circ/20\text{ mm.}$, $\text{AsR}_2\text{Me}_2\text{I}$, m.p. $186-187^\circ$, $\text{AsR}_2\text{Me}\cdot\text{OH}$ (*nitrate*, m.p. 147°) (R=cyclohexyl).

R. T.

Preparation of germanium alkyl or phenyl trihalides, RGeX_3 , and of germanium methylene hexachloride. A. TCHAKIRIAN and M. LEWINSOHN (Compt. rend., 1935, 201, 835—837).—Good yields of GeRX_3 are obtained by heating $\text{Cs}[\text{GeCl}_3]$ (A., 1931, 322) with alkyl or aryl halides (iodides best). Thus at 110° EtI affords GeEtCl_3 (60% yield) and PhI at 250° gives GePhCl_3 (80%). With CH_2I_2 at 200° is obtained *germanium methylene hexachloride*, b.p. $110^\circ/18\text{ mm.}$ (80%). Hydrolysis of these affords MeGeO_2H and *germanomalic acid*, $\text{CH}_2(\text{GeO}_2\text{H})_2$, reconverted into the chlorides by conc. HCl .

J. W. B.

Preparation of lead diethyl dichloride. A. J. JAKUBOVITSCH and I. PETROV (J. pr. Chem., 1935, [ii], 144, 67—68).—Passage of HCl into a solution of PbEt_4 in PhMe at 90° leads to mixtures of PbEt_2Cl_2 and PbCl_2 , the composition of which varies with the duration of the action (cf. Gilman *et al.*, A., 1933, 900). Grüttner's method (A., 1916, i, 799) is trustworthy.

H. W.

Dimethylcyclohexanes. O. MILLER (Bull. Soc. chim. Belg., 1935, 44, 513—522; cf. A., 1933, 815).—Hydrogenation of *p*-xylene in AcOH with a Pt-black catalyst at room temp. gives mainly *cis*-, m.p. -91.6° , b.p. $124.59^\circ/760\text{ mm.}$, and a little *trans*-1:4-dimethylcyclohexane, m.p. -37.2° , b.p. $119.63^\circ/760\text{ mm.}$, separated by repeated fractional distillation. At 200° (and without AcOH) the latter is the chief product. With a $\text{Ni-Al}_2\text{O}_3$ catalyst at 180° the *trans*-isomeride is mainly formed together with some methylcyclohexane (I). Similarly hydrogenation of *m*-xylene yields *cis*-, m.p. -100° , b.p. $124.9^\circ/760\text{ mm.}$, and *trans*-1:3-dimethylcyclohexane, m.p. -79.4° , b.p. $120.40^\circ/760\text{ mm.}$, the latter being the chief product both at 20° and at 180° . With a $\text{Ni-Al}_2\text{O}_3$ catalyst some (I) is also formed. In each case the *trans*-configuration has been assigned to the more volatile isomeride. 1:1-Dimethylcyclohexane, m.p. -34.1° , b.p. $119.8^\circ/760\text{ mm.}$ (A., 1932, 372), is most readily obtained by hydrogenation of dimethyl-

dihydroresorcinol in EtOAc with an active Pt catalyst. The *d*, *n*, and γ of these compounds are recorded.

H. G. M.

Constituents of the unsaponifiable fraction of wheat-germ oil. Vitamin-E.—See A., 1935, 1551.

The hydrocarbon C_6D_6 . H. ERLÉNMEYER and H. LOBECK (Helv. Chim. Acta., 1935, 18, 1464—1466).—Distillation of dry $\text{C}_6(\text{CO}_2)_6\text{Ca}_3$ with $\text{Ca}(\text{OD})_2$ (from Ca and D_2O) gives pure C_6D_6 , b.p. $79.4^\circ/760\text{ mm.}$, m.p. 6.8° (cf. Wilson, A., 1935, 1198).

J. W. B.

Fluorinated chlorobenzenes. H. S. BOOTH, H. M. ELSEY, and P. E. BURCHFIELD (J. Amer. Chem. Soc., 1935, 57, 2064—2065).—The prep. of *m*-chlorofluorobenzene, b.p. $127.6^\circ/760\text{ mm.}$, m.p. $<-78^\circ$, and 2:4:6-trichlorofluorobenzene, b.p. $208.4^\circ/760\text{ mm.}$, m.p. 11.2° , is described. V.p. of these compounds at $0-130^\circ$ have been measured.

E. S. H.

Iodoxy-group and its relations. I. MASSON, E. RACE, and (in part) F. E. POUNDER (J.C.S., 1935, 1669—1679).— PhIO_2 (I) (modified prep.) is not identical with *diphenyliodonium periodate*, m.p. 129° (decomp.); it is quantitatively nitrated (methods described) to *m*- $\text{IO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, m.p. 37.9° , is amphoteric, and yields the following salts: *sulphate*, m.p. 127° (decomp.), *perchlorate*, explosive decomp. at room temp., *nitrate*, and *phosphate*. With cold aq. NaOH , (I) first reacts as an acid of apparent $K 10^{-10.4}$, forming a *phenyliodoxylyate* (II) ($\text{PhIO}_2 + \text{OH}' = \text{PhIO}_2\cdot\text{OH}'$) which rapidly gives NaIO_3 and *Ph₂IO·OH* (III) or *Ph₂I(OH)₃* [*Ac* derivative (IV), m.p. 114° (decomp.); *carbonate*, amorphous]; with aq. alkali at 100° , (I) or (III) yields the iodate and C_6H_6 . This and other evidence shows the $\cdot\text{IO}_2$ to be a *m*-directing, strongly cationoid dipole. Structures are suggested for (I), (II), and (IV).

F. N. W.

Nitration of hydrocarbons by nitrogen peroxide in the gaseous phase, with and without the action of ultra-violet light. P. P. SCHORIGIN and A. V. TOPTSCHEV (J. Gen. Chem. Russ., 1935, 5, 549—554).— PhMe and NO_2 at 14° afford $\text{CH}_2\text{Ph}\cdot\text{NO}$ and $\text{C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$; the yields of both are increased by ultra-violet light, and fall with rise in temp. The yields of NO_2 -derivatives of C_6H_6 and *cyclo*- and *n*-hexane are unaffected by ultra-violet light, whence it is concluded that this influences only those substrates capable of tautomeric change.

R. T.

Benzotrifluoride and its halogenated derivatives. H. S. BOOTH, H. M. ELSEY, and P. E. BURCHFIELD (J. Amer. Chem. Soc., 1935, 57, 2066—2069).—The prep. of CPhF_3 from CPhCl_3 and SbF_3 is described. The following compounds have been prepared: *m*-, b.p. 100.9° , m.p. -81.5° , and *p*- $\text{C}_6\text{H}_4\text{F}\cdot\text{CF}_3$, b.p. 102.8° , m.p. -41.7° ; *o*-, b.p. 152.8° , m.p. -7.4° to -7.6° , *m*-, b.p. 138.4° , m.p. -55.4° , and *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CF}_3$, b.p. 139.3° , m.p. -34.0° ; 3:4- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{CF}_3$, b.p. 173.5° , m.p. -12.3° to -12.5° .

E. S. H.

Condensations of alcohols with aromatic hydrocarbons in presence of aluminium chloride. II. Condensation of secondary alcohols with benzene and toluene. I. TZUKERVANIK and K. TOKAREVA (J. Gen. Chem. Russ., 1935, 5, 764—766).—

C_6H_6 and $Pr^{\beta}OH$ in presence of $AlCl_3$ afford $PhPr^{\beta}$ and $C_6H_5Pr^{\beta}$, b.p. 205—210°; with $PhMe$ the product is $p-C_6H_4MePr^{\beta}$, and with $Bu^{\beta}OH$, $PhBu^{\beta}$ and $C_6H_5MeBu^{\beta}$ are obtained. The reaction is $ROH + AlCl_3 \rightarrow AlCl_2 \cdot OR$ (I) + HCl ; (I) + $C_6H_6 \rightarrow PhR + AlCl_2 \cdot OH$. R. T.

Influence of structure on the polymerisation of substituted styrenes. P. P. SOUORIGIN and N. V. SOHORIGINA (J. Gen. Chem. Russ., 1935, 5, 555—561).—The polymeride of *o*-tolylethylene is more elastic than is that of styrene, whilst those of *m*- and *p*-tolyl- and 1-naphthyl-ethylene are less so. R. T.

Optical rotation of phenylethylmethyldecylmethane [α -phenyl- γ -methylundecane]. P. A. LEVENE and S. A. HARRIS (J. Biol. Chem., 1935, 111, 735—738).— $l-CH_2Ph \cdot CH_2 \cdot CHMe \cdot CH_2 \cdot MgBr$ and $C_9H_{13} \cdot CHO$ give α -phenyl- γ -methylundecan- ϵ -ol, b.p. 183—184°/5 mm., $[\alpha]_D^{20} -2.64^\circ$, converted by cold HI into the iodide, which, when hydrogenated (Raney Ni) in ligroin-MeOH-NaOH, affords α -phenyl- γ -methylundecane, b.p. 143—145°/2 mm., $[\alpha]_D^{20} -1.12^\circ$, and thence (H_2 -PtO₂; AcOH-EtOAc) α -cyclohexyl- γ -methylundecane, b.p. 147°/3 mm., $[\alpha]_D^{20} -0.44^\circ$. The contribution of C_6H_{11} to $[M]$ is much < that of Pr^{β} in this series. $[\alpha]$ are max. vals. for the homogeneous liquids. R. S. C.

Laws of substitution in the sulphonation of naphthalene and its derivatives. V. N. UFINITZEV (J. Gen. Chem. Russ., 1935, 5, 653—660).—Substitution takes place according to the same laws as for C_6H_6 , on the assumption that $C_{10}H_8$ exists in three tautomeric forms, containing two aromatic nuclei, or one aromatic and one hydroaromatic nucleus. R. T.

Nitration of 1-ethylnaphthalene. G. LEVY (Compt. rend., 1935, 201, 900—902).— $1-C_{10}H_7Et$ when nitrated (cf. A., 1933, 57) gives an inseparable mixture of isomerides, reduced (Fe-AcOH) to 4-ethyl- α -naphthylamine, an oil (Ac derivative, m.p. 148.5°; hydrochloride), the sulphate of which with 1% H_2SO_4 at 200° gives 4-ethyl- α -naphthol (cf. A., 1933, 1287). J. L. D.

Methylethynaphthalenes. III. Synthesis of 2-methyl-6-ethylnaphthalene. O. BRUNNER and F. GROF (Monatsh., 1935, 66, 433—437).—Application of Reformatski's method to $p-C_6H_4Et \cdot CHO$ and $CHMeBr \cdot CO_2Et$ leads to *Et* α -methyl-*p*-ethylcinnamate, b.p. 159—160°/11 mm., reduced by Na and EtOH to γ -*p*-ethylphenyl- β -methylpropanol (I), b.p. 140°/10 mm. (I) is transformed successively into γ -*p*-ethylphenyl- β -methyl-*n*-propyl bromide, b.p. 141—142°/10 mm., and the corresponding nitrile, which is hydrolysed by boiling 10% KOH-EtOH to γ -*p*-ethylphenyl- β -methyl-*n*-butyric acid, b.p. 185—187°/10 mm. The acid and conc. H_2SO_4 at 100° afford 4-keto-2-methyl-6-ethyl-1:2:3:4-tetrahydronaphthalene, b.p. 143—148°/11 mm., reduced (Clemmensen) to 2-methyl-6-ethyl-1:2:3:4-tetrahydronaphthalene, b.p. 140—145°/10 mm., dehydrogenated by S at 270—300° to 2-methyl-6-ethylnaphthalene, b.p. 145—150°/11 mm. (picrate, m.p. 100—101°; styphnate, m.p. 138—139°). H. W.

Sulphonation of naphthalene. I. Determination of the relative proportions of naphthalene-

1- and 2-sulphonic acids. R. LANTZ (Bull. Soc. chim., 1935, [v], 2, 1913—1932).—Under closely defined conditions $1-C_{10}H_7 \cdot SO_3H$ (I) is brominated with loss of SO_3H to an insol. substance which is determined by CrO_3 -oxidation (cf. B., 1932, 590), whilst $2-C_{10}H_7 \cdot SO_3H$ (II) is brominated without loss of SO_3H and remains sol., thus permitting the determination of (I) and (II) in mixtures. H. G. M.

Substitution in polycyclic systems. I. Nitration of fluorene and 9-bromofluorene. S. V. ANANTAKRISHNAN and E. D. HUGHES (J.C.S., 1935, 1607—1609).—Nitration of fluorene (cf. A., 1930, 1425) yields 2:5- and 2:7-dinitrofluorene, m.p. 205—300° (decomp.) (lit. 269° and 334°). Mild nitration (HNO_3 in Ac_2O ; 1 hr.; 0°) of 9-bromofluorene (I) gives 9-bromo-2-nitrofluorene (II); more vigorous treatment (2 hr. at 0°, followed by 15 hr. at room temp.) gives 9-bromo-2:5- (III), m.p. 199°, and -2:7-dinitrofluorene (IV), m.p. 255° (decomp.). Nitration of (I) in AcOH yields (IV) and 7-bromo-2-nitrofluorenone (?), whilst oxidation ($Na_2Cr_2O_7$ in AcOH) of (II), (III), and (IV) gives 2-nitro-, 2:5- and 2:7-dinitrofluorenone, respectively. (III) and (IV) are also obtained by nitration (HNO_3 in Ac_2O) of (II). F. N. W.

Influence of poles and polar linkings on the course pursued by elimination reactions. XXIII. Stable derivatives of the tercovalent carbon compound of Ingold and Jessop. E. D. HUGHES and K. I. KURIYAN (J.C.S., 1935, 1609—1611).—9-Bromo-2-nitrofluorene with Me_2S in $MeNO_2$ yields 2-nitrofluorenyl-9-dimethylsulphonium bromide (I), m.p. 130° (decomp.). (I) or the corresponding picrate, m.p. 185° (decomp.), with alkali in H_2O , EtOH, or $COMe_2$ yields dimethylsulphonium 9-2-nitrofluorenylidide, m.p. 300°, which decomposes in boiling $MeNO_2$ solution forming 2:2'-dinitrobisdi-phenylene-ethylene (II), with liberation of Me_2S . (II) is oxidised ($Na_2Cr_2O_7$ -AcOH) to 2-nitrofluorenone. Nitration [HNO_3 (d 1.5) at -15°] of fluorenyl-9-dimethylsulphonium picrate yields 2:7-dinitrofluorenyl-9-dimethylsulphonium picrate (III), m.p. 180° (decomp.), converted by aq. alkali into dimethylsulphonium 9-2:7-dinitrofluorenylidide, which with $HBr \cdot COMe_2$ yields 2:7-dinitrofluorenyl-9-dimethylsulphonium bromide (IV), m.p. about 230°, and when boiled in $MeNO_2$ gives 2:2':7:7'-tetranitrobisdi-phenylene-ethylene (V), m.p. >300°. (III) when refluxed with $HBr \cdot AcOH$ (30 min.) gives 9-bromo-2:7-dinitrofluorene (VI), whilst (IV) with CrO_3 -AcOH yields 2:7-dinitrofluorenone and when heated alone forms (VI) with liberation of Me_2S . (V) is oxidised to 2:7-dinitrofluorenone. Me_2Se and 9-bromofluorene in $MeNO_2$ give fluorenyl-9-dimethylselenonium bromide, m.p. 134—135° (corresponding picrate, m.p. 143°). F. N. W.

Compounds related to the sterols, bile acids, and oestrogen-producing hormones. VII. A. COHEN, J. W. COOK, and C. L. HEWITT (J.C.S., 1935, 1633—1637).—2-Methyl-1-allyl-3:4-dihydrophenanthrene (I) (picrate, m.p. 75—76°) is obtained from $CH_2=CH \cdot CH_2 \cdot MgBr$ and 1-keto-2-methyl-1:2:3:4-tetrahydrophenanthrene (II) (modified prep.). 2-Methyl-1-*n*-propylphenanthrene, m.p. 65° [picrate, m.p.

121.5—122°; $s\text{-C}_6\text{H}_3(\text{NO}_2)_3$ complex, m.p. 131°, is obtained from (I) either by heating with Se (320°, 15 hr.) or by heating in saturated HCl-AcOH solution (100°, 1 hr.). 2-Methyl-1- Δ^7 -butenyl-3 : 4-dihydrophenanthrene, b.p. 155—160°/0.3 mm. (picrate, m.p. 77—78°), contaminated with 2-methyl-3 : 4-dihydrophenanthrene results from the interaction of (II) and $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{MgBr}$, and when cyclised with $\text{H}_2\text{SO}_4\text{-AcOH}$ (1 : 20) (100°, 2.25 hr.) yields principally methylhexahydrochrysene. 1-(β -5-Tetraylethyl)cyclohexanol, b.p. 175—180°/0.4 mm. (3 : 5-dinitrobenzoate, m.p. 124—125°), obtained by the interaction of cyclohexanone and Mg β -5-tetraylethyl chloride, yields 1-(β -5'-tetraylethyl)- Δ^1 -cyclohexene (III), b.p. 140—150°/0.05 mm., when heated with KHSO_4 (160—170°, 1 hr.). (III) when cyclised with AlCl_3 (0°, 7.5 hr.) gives a mixture of dodecahydrochrysene, which is partly hydrogenated (300—310°, 14 hr., Se) to *s*-octahydrochrysene, m.p. 136—138° (picrate, m.p. 139—140°), and a hydrocarbon, b.p. 123—130°, which is dehydrogenated (Pt-black; 300—320°, 3 hr.) to 4 : 5-benzhydrindene-1-spirocyclohexane, m.p. 56—57° (picrate, m.p. 125—126°). F. N. W.

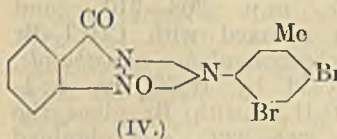
The alleged dihydrophenylbenzamidine. A. KIRSSANOV and I. IVASTCHENKO (Bull. Soc. chim., 1935, [v], 2, 1944—1950).—Contrary to the views of Bernthsen *et al.* (A., 1880, 639) no dihydrophenylbenzamidine (I) is obtained when phenylbenzamidine (II) (improved prep.) is reduced by Na-Hg, the only products being PhCHO, NH_2Ph , $\text{NPh}\cdot\text{CH}_2\text{Ph}$, $\text{CH}_2\text{Ph}\cdot\text{NH}_2$, and unchanged (II). The product regarded by Bernthsen as (I) is considered to be purified (II). (I) has therefore never been prepared.

H. G. M.

Reactivity of halogen compounds. III, IV.—See A., 1935, 1465.

Derivatives of 6-bromo- and 4 : 6-dibromo-*m*-toluidine. G. D. PARKES and E. D'A. BURNEY (J.C.S., 1935, 1619—1621).—The following *m*-toluidines, prepared by suitable modifications of ordinary methods, are described : *o*'-, m.p. 146°, *m*'-, m.p. 114°, and *p*'-nitrobenz-, m.p. 148°; benz-6-bromo-, m.p. 123° (lit. 98°); *o*'-, m.p. 163°, *m*'-, m.p. 185.5°, and *p*'-nitrobenz-6-bromo-, m.p. 258°; benz-4 : 6-dibromo-, m.p. 131°; *o*'-, m.p. 203°, *m*'-, m.p. 207°, and *p*'-nitrobenz-4 : 6-dibromo-, m.p. 182.5°. 6-Bromo-, m.p. 191°, and 4 : 6-dibromo-*m*-tolylcarbamide, m.p. 218°, are obtained from the appropriate toluidine, KCNO, and warm 0.5*N*-HCl. $\text{CO}(\text{NH}_2)_2$ when heated with excess of the appropriate base yields *s*-bis-6-bromo-, m.p. 276°, and 6-bis-4 : 6-dibromo-*m*-tolylcarbamide, m.p. 297°. 6-Bromo-, m.p. 143°, and 4 : 6-dibromo-*m*-tolueneazo- β -naphthol, m.p. 193°, were prepared from the appropriate diazotised base and $\beta\text{-C}_{10}\text{H}_7\text{OH}\cdot 2\text{N}\cdot\text{NaOH}$. The following were prepared from the appropriate aldehyde and 6-bromo-*m*-tolylhydrazine hydrochloride obtained by reduction of diazotised 6-bromo-*m*-toluidine with $\text{SnCl}_2\text{-HCl}$: benzaldehyde-, m.p. 154°; *o*-, m.p. 175.5°, *m*- (I), m.p. 188°, and *p*-nitrobenzaldehyde-6-bromo-*m*-tolylhydrazone, m.p. 171.5°. The following were prepared by similar methods: benzaldehyde-, m.p. 109°; *o*-, m.p. 180°, *m*- (II), m.p. 204°, and *p*-nitrobenzaldehyde-4 : 6-dibromo-*m*-tolylhydrazone, m.p. 221°. *m*-

Nitrobenzaldehyde-*m*-tolylhydrazone with Br-AcOH affords α -bromo-*m*-nitrobenzaldehyde-4 : 6-dibromo-*m*-tolylhydrazone, m.p. 191°, also obtained by bromination of (I) and (II). α -Bromobenzaldehyde-, m.p. 122°, and α -bromo-*o*-nitrobenzaldehyde-4 : 6-dibromo-*m*-tolylhydrazone (III), m.p. 151°, were similarly prepared. α -Bromo-*p*-nitrobenzaldehyde-4 : 6-dibromo-*m*-tolylhydrazone when warmed with $\text{EtOH}\cdot\text{H}_2\text{O}\cdot\text{NH}_3$ yields *p*-nitrobenzenyl-4 : 6-dibromo-*m*-tolylhydrazidine, m.p. 207°. The corresponding *m*- NO_2 -compound, similarly prepared, has m.p. 155°. (III) when warmed with just sufficient EtOH for dissolution yields 3-keto-1 : 3-endo-4' : 6'-dibromo-*m*-tolylimino-1 : 2-dihydro-1 : 2-benzisodiazole 1-oxide (IV), which explodes at 126°. H. G. M.



Synthesis and chemical properties of α -ethylenic carbimides, $\text{R}\cdot\text{CH}\cdot\text{CR}'\cdot\text{N}\cdot\text{C}\cdot\text{O}$. J. HOCH (Compt. rend., 1935, 201, 733—735).—*N*-Carbethoxyketimines (A., 1935, 1483) under reduced pressure in presence of kieselguhr at 400° afford carbimides. The following are prepared: δ - Δ^7 -heptenyl-, b.p. 55—56°/17 mm., $\Delta^{1:2}$ -cyclohexenyl- (I), b.p. 61—63°/18 mm., 2-methyl- $\Delta^{1:2}$ -cyclohexenyl-, b.p. 73—74°/18 mm., α -phenylvinyl-, b.p. 99°/25 mm., and α -phenyl- Δ^{α} -propenyl-carbimide, b.p. 110—112°/18 mm. They decolorise Br rapidly and with NH_2Ph in anhyd. Et₂O afford phenylcarbimides, m.p. 102°, 197°, 170°, 142°, and 185°, respectively, which are easily decomposed by dil. HCl into ketones and $\text{NPh}\cdot\text{CO}\cdot\text{NH}_2$. (I) with NH_3 gives $\Delta^{1:2}$ -cyclohexenylcarbamide, m.p. 144°, with N_2H_4 , hydrazine- $\alpha\beta$ -dicarboxydicyclohexenylamide, m.p. 186°, and with NPhMe , *N*-cyclohexenyl-*N*'-phenylmethylcarbamide, m.p. 88°. With EtOH, $\text{Pr}^{\beta}\text{OH}$, and PhOH, (I) affords Et, b.p. 148—149°/26 mm., Pr^{β} , b.p. 147°/23 mm., and Ph $\Delta^{1:2}$ -cyclohexenylcarbamate, m.p. 106—107°, respectively, and with $\text{CPh}_2\cdot\text{NH}$, *N*-cyclohexenyl-*N*'-diphenylmethylenecarbamide, m.p. 119°. J. L. D.

Rearrangement of thiocyanates into thiocarbimides. E. BERGMANN (J.C.S., 1935, 1361—1362). If the change $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{SCN} \rightarrow \text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{N}\cdot\text{C}\cdot\text{S}$ proceeds by attachment of N to terminal C and rupture between CH_2 and S, cinnamyl thiocyanate (I), m.p. 68° (prepared from $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\text{Br}$ and KSCN), should when heated in vac. give $\text{CHPh}(\text{NCS})\cdot\text{CH}\cdot\text{CH}_2$; actually cinnamylthiocarbimide (II), b.p. 162°/12 mm., is formed. The structure of (I) is proved by hydrogenation to γ -phenylpropyl thiocyanate, b.p. 180°/30 mm., also obtained from $\text{CH}_2\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{Br}$ (III) and NH_4SCN ; that of (II) by reaction with NH_2Ph to form *s*-phenylcinnamylthiocarbamide, m.p. 119°, also obtained from $\text{NPh}\cdot\text{C}\cdot\text{S}$ and $\text{CH}_2\text{Ph}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{NH}_2$ (IV); and that of (IV) confirmed by hydrogenating the phthalimide, from which it is prepared, to phthal- γ -phenylpropylimide, m.p. 61°, also obtained from (III), and thus excluding the alternative structure $\text{NH}_2\cdot\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2$.

E. W. W.

Substitution in arylsulphon-1- and -2-naphthalides. R. CONSDEN and J. KENYON (J.C.S., 1935,

1591—1596).—*m*-Nitrobenzenesulphon-1-naphthalide (I), m.p. 162—164° [obtained from α -C₁₀H₇NH₂ and *m*-NO₂·C₆H₄·SO₂Cl (II)], is nitrated (a) by AcOH-conc. HNO₃ giving 2:4-dinitro-1-*m*-nitrobenzenesulphon-naphthalide, m.p. 185—188° [hydrolysed by conc. H₂SO₄ to 1:2:4-C₁₀H₅(NH₂)(NO₂)₂], and (b) by ice-cold fuming HNO₃, and (c) by AcOH-fuming HNO₃ on the water-bath giving the 2:4:5-(NO₂)₃-derivative, m.p. 215° (decomp.) (C₅H₅N salt, m.p. 170—175°), also obtained from 5-nitro-1-*m*-nitrobenzenesulphon-naphthalide, m.p. 208—210°, and AcOH-HNO₃. (I) when refluxed with CHCl₃-Br gives 4-bromo-1-*m*-nitrobenzenesulphon-naphthalide, m.p. 174—176° (hydrolysed by H₂SO₄ to 4:1-C₁₀H₆Br·NH₂), and in C₅H₅N with Br gives the 2:4-Br₂-derivative, m.p. 232—233°, also obtained from 2:4:1-C₁₀H₅Br₂·NH₂ (improved prep.) and (II). 4-Nitro-1-*p*-toluenesulphon-naphthalide with Br in C₅H₅N (but not CHCl₃) yields its 2-Br-derivative, m.p. 193—195°, hydrolysed to 2:4:1-C₁₀H₅Br(NO₂)·NH₂. *p*-Toluenesulphon-1-naphthalide with AcOH-conc. HNO₃ affords its 2:4-(NO₂)₂- and 2-NO₂-derivative, m.p. 154°, hydrolysed to 1:2-C₁₀H₆(NH₂)·NO₂. Nitration of 2:4-dinitro- α -naphthol with fuming HNO₃ (with or without AcOH) yields the 2:4:5- and 2:4:7-(NO₂)₃-derivatives in the ratio of about 5:2. *p*-Toluenesulphon-2-naphthalide (III) with Br-CHCl₃ yields its 1-Br-derivative, 1:3:2-C₁₀H₅Br₂·NH₂ when refluxed (2 hr.) with EtOH-conc. HCl granulated Sn affords 3-bromo- β -naphthylamine, m.p. 173° (*Ac* derivative, m.p. 177°), the *p*-toluenesulphonyl derivative, m.p. 127—129°, of which is nitrated in AcOH to 3-bromo-1-nitro-2-*p*-toluenesulphon-naphthalide, m.p. 237—239° (decomp.), also obtained from the appropriate nitro-compound with C₅H₅N-Br, reduced (Sn-HCl or Zn-AcOH) to 3-bromo-2-*p*-toluenesulphonyl-1:2-naphthylenediamine, m.p. 185°, and hydrolysed (ice-cold H₂SO₄) to 3-bromo-1-nitro- β -naphthylamine (IV), m.p. 105° (*Ac* derivative, m.p. 136°). This with boiling *N*-NaOH affords 3-bromo-1-nitro- β -naphthol, m.p. 131° (decomp.). (IV) is reduced with Sn-HCl to 3-bromo-1:2-naphthylenediamine, m.p. 85°, which with benzil in hot EtOH gives a quinoxaline derivative, m.p. 195—199°. 1:6-Dinitro-2-*p*-toluenesulphon-naphthalide with Br-C₅H₅N gives its 3-Br-derivative, m.p. 228—231° (decomp.), hydrolysed to 3-bromo-1:6-dinitro- β -naphthylamine, m.p. 238—241° [*Ac* derivative, m.p. 273—277° (decomp.)]. (III) in C₅H₅N with I, ICl, or ICl₂ affords 1-iodo-2-*p*-toluenesulphon-naphthalide, m.p. 126—127°, from which the base could not be obtained owing to its instability (cf. J.C.S., 1885, 47, 520), and which when warmed with AcOH-NaNO₂ during 3 hr. affords the corresponding 1-NO₂-derivative. The following were obtained by similar methods: 3-iodo-2-*p*-toluenesulphonamidodiphenyl, m.p. 114—115°; 3-iodo-4-*p*-toluenesulphonamidodiphenyl, m.p. 109—115°; 2-iodo-*p*-toluenesulphon-*p*-toluidide, m.p. 127—123°.

H. G. M.

Ditolyl series. IV. Separation of *dl*-6-bromo-6'-amino-2:2'-dimethyldiphenyl into its optical antipodes. A. ANGELETTI [in part with C. MIGLIARDI] (Gazzetta, 1935, 65, 819—823).—For the prep. of 6-bromo-6'-nitro-2:2'-dimethyldiphenyl (I),

the diazotisation of the 6-NH₂-compound is best effected in HBr. (I) is reduced (SnCl₂) to *dl*-6-bromo-6'-amino-2:2'-dimethyldiphenyl (II), m.p. 77—78°, which is resolved by *d*-tartaric acid into the *l*- (III), m.p. 77—78°, [α]_D²⁰ -5.32°, and *d*-, m.p. 77—78°, [α]_D²⁰ +5.04°, forms. (II) is converted into *dl*-, m.p. 109—110°, and (III) into *l*-, m.p. 109—110°, [α]_D²⁰ -6.2°, -6:6'-dibromo-2:2'-dimethyldiphenyl. E. W. W.

Alkylated ethylenediamine derivatives. IV. Reaction between α - β -bis(benzylideneamino)-ethane, phenylcarbimide, and water. J. VAN ALPHEN (Rec. trav. chim., 1935, 54, 885—887; cf. A., 1935, 1118).—Interaction of equimol. proportions of PhNCO and (·CH₂·N·CHPh)₂ (I) in moist Et₂O affords *s*-phenyl- β -benzylideneaminoethylcarbamide (II), hydrolysed by dil. HCl to β -(γ -phenylcarbamido)-ethylamine (*Bz* derivative, m.p. 210°), and reduced (Na-EtOH) to the hydrochloride of benzyl- β -(γ -phenylcarbamido)ethylamine (*Bz* derivative, m.p. 160°). With an excess of PhNCO (I) gives 2-keto-3:4-diphenyl-1- β -(γ -phenylcarbamido)ethyl-1:3-diazacyclobutane, NPh<math display="block">\begin{array}{c} \text{CHPh} \\ \diagup \quad \diagdown \\ \text{CO} \end{array}\text{N}\cdot\text{C}_2\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{NPh}, m.p. 208° (decomp.) [also by action of PhNCO on (II)], hydrolysed by boiling dil. HCl to PhCHO and NPh·CO·NHR, and reduced (Na-EtOH) to NPh·CO·NHR·CH₂Ph (R=C₂H₄·NH·CO·NPh).

J. W. B.

Preparation of *m*- and *p*-phenylenediethylamine and benzohexamethyleneimine from the three phenylenediacetonitriles. P. RUGGLI, B. B. BUSSEMAKER, W. MÜLLER, and A. STAUB (Helv. Chim. Acta, 1935, 18, 1388—1395).—Reduction of *m*- and *p*-phenylenediacetonitrile, in EtOH saturated with NH₃, with H₂-Ni at 90—100°/70 atm. affords, respectively, *m*- [dihydrochloride + H₂O, m.p. 300—302° (block); platinichloride, m.p. 242° (decomp.); Bz₂ derivative, m.p. 181°], and *p*-phenylene- β β' -diethylamine, b.p. 130°/3 mm., m.p. 36° (dihydrochloride; platinichloride; picrate, decomp. 246°; Ac₂, m.p. 210°, and Bz₂, m.p. 225°, derivatives). Similar reduction of *o*-phenylenediacetonitrile gives *s*-homotetrahydroisoquinoline (von Braun *et al.*, A., 1926, 178) (*Bz*, m.p. 100°, and *Ac*, m.p. 70°, derivatives). A mechanism is suggested.

J. W. B.

Interaction between aromatic diamines and ethyl acetoacetate. O. G. BACKEBERG (J.C.S., 1935, 1568—1570).—Primary aromatic diamines with CH₂Ac·CO₂Et (I) yield β -phenylaminocrotonic esters and no acetoacetylides. *m*-C₆H₄(NH₂)₂ when heated with (I) on the water-bath (2 hr.), or when heated to 200° and rapidly poured into boiling (I), yields *Et m*-phenylenebis- β -aminocrotonate. These reactants, however, when heated under seal gave 5- or 7-amino-2-hydroxylepidine (cf. A., 1898, i, 450). *m*-Aminoacetanilide and (I) when heated on the water-bath yield *Et* β -3-acetamidophenylaminocrotonate, m.p. 92°. *p*-C₆H₄(NH₂)₂ when heated to 200° and poured into boiling (I), or when heated with (I) on the water-bath (2 hr.) or at 150° (½ hr.) [but not at 170° (4 hr.)], yields *Et p*-phenylenebis- β -aminocrotonate, m.p. 135° (cf. A., 1887, 247) (insol. in NaOH-H₂O; gives dark red coloration with FeCl₃-EtOH). By similar methods *p*-C₆H₄(NH₂)·NHAc

and (I) yield *Et* β -4-acetamidophenylaminocrotonate, m.p. 185° (hydrolysed by boiling MeOH), but when heated under seal at 140° for 5 hr. affords some p -C₆H₄(NHAc)₂. Dianisidine when refluxed with (I) in MeOH yields *Et* 3:3'-dimethoxydiphenylene-4:4'-bis- β -aminocrotonate, m.p. 132—134°. Similarly tolidine and (I) afford *Et* 3:3'-dimethyldiphenylene-4:4'-bis- β -aminocrotonate, m.p. 129—130°, whilst benzidine and (I) give a little *Et* diphenylene-4:4'-bis- β -aminocrotonate, m.p. 99.5—100°, and mainly a double compound (NH₂·C₆H₄·C₆H₄·NHX)₂, NHX·C₆H₄·C₆H₄·NHX (X = CMe·CH·CO₂Et), m.p. 134° (cf. A., 1899, i, 366), which, although readily dissociated, could not be separated into its components, and with C₆H₅-Ac₂O gave *Et* 4-acetamidodiphenyl-4'- β -aminocrotonate, m.p. 201°, readily hydrolysed to monoacetylbenzidine.

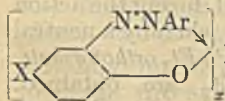
H. G. M.

Reduction of azoxy-compounds in relation to that of diazonium derivatives. D. BIGIARI and C. ALBANESE (Gazzetta, 1935, 65, 773—788).—NaHSnO₂ reacts at once with p -C₆H₄Me·N₂·OH and p -OMe·C₆H₄·N₂·OH, but KHSnO₂ only very slowly with the o -isomerides, or with 2:5-C₆H₂Me₃·N₂·OH. NaHSnO₂ reduces dimethylaminoazoxybenzene slowly to dimethylaminoazobenzene, and pp' -dihydroxyazoxybenzene to azophenol. Azoxybenzene, and the α - and β -forms of its p -NH₂-, p -Br-, p -OH-, p -CO₂H-, p -Me, p -OEt-, and oo' -Me₂ derivatives, are reduced by NaHSnO₂ with varying ease to azo-compounds. Na₃AsO₃ does not reduce α - or β -benzeneazoxyphenol; these are, however, reduced by FeSO₄, as is p -OH·C₆H₄·N₂·Ph, which gives NH₂Ph and p -NH₂·C₆H₄·OH. A new test for small amounts of isodiazio-compounds in solution is to dip filter-paper into the latter, to which AcOH and β -C₁₀H₇·OH or *R*-salt are added; the paper removed and exposed to the air develops a red stain. This reaction is given only very slowly by phenylnitroamine; the last, and its NO-derivative, are reduced to isodiazio-compounds fairly rapidly by NaHSnO₂, but only very slowly by Na₃AsO₃.

E. W. W.

The azo-group as a chelating group. I.

Metallic derivatives of o -hydroxyazo-compounds. (MISS) M. ELKINS and L. HUNTER (J.C.S., 1935, 1598—1600).—The following Cu^{II}, Ni, and Co^{III} salts of some o -monohydroxyazo-compounds are described. They are insol. in H₂O, sparingly sol. in polar solvents, readily sol. in non-polar solvents, and are chelated. They have the annexed structure, in which



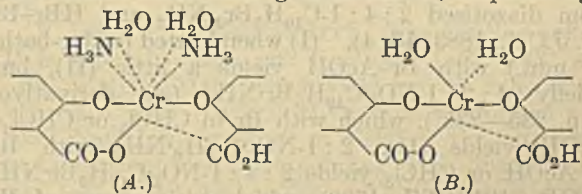
the arrangement of the aryl groups about the azo-group is *trans*. Decomp. of the metallic

complexes by cold acid always regenerates the original azo-compound, and this supports the view that all stable azo-compounds are *trans*. *Cu*, m.p. 230°, *Ni*, m.p. 216°, and *Co* 3-benzeneazo- p -tolylloxide, m.p. 202°; *Cu*, m.p. 242°, *Ni*, m.p. 242—243°, and *Co* 3- p' -tolueneazo- p -tolylloxide, m.p. 200—201°; *Cu*, m.p. 221°, *Ni*, m.p. 214° (impure), and *Co* 3- m' -tolueneazo- p -tolylloxide, m.p. 187°; *Cu*, m.p. 243°, *Ni*, decomp. 295—310° (impure), and *Co* 2:4-bisbenzeneazophenoxide, m.p. 180—185°; *Cu*, m.p. 295°, *Ni*, m.p. 290° (dark green; gives brown solutions in C₆H₆, PhMe, and CHCl₃), and

Co 1-benzeneazo- β -naphthoxide, m.p. 221°; *Cu*, m.p. 237°, *Ni*, m.p. 293° (olive-green; gives brown solutions in C₆H₆, PhMe, and CHCl₃), and *Co* 2-benzeneazo- α -naphthoxide, m.p. 199°. No metallic derivatives could be obtained from p -hydroxyazo-compounds, as chelation is impossible. H. G. M.

Azo-dyes and their intermediates. XVI. Reactions of tetrazo-compounds of the benzene and naphthalene series. *peri*-Disazo-dyes. III. P. RUGGLI and E. CASPAR (Helv. Chim. Acta, 1935, 18, 1414—1420).— m -Xylylene-4:6-diamine hydrochloride (improved prep.) with NaNO₂·HBF₄ at -10° gives the *bisdiazonium borofluoride*, which couples with 6:2-C₁₀H₆Br·OH in NaOAc-AcOH to give m -xylylene-4:6-bisazo-6'-bromo- β -naphthol, is converted by CuSO₄·KCN at 0° into 4:6-dimethylisophthalodinitrile, and by SH·CH₂·CO₂H into the unstable *bisazo-compound*, C₆H₂Me₂(N:N·S·CH₂·CO₂H)₂, which decomposes in H₂O to give m -xylylene-4:6-dithioglycollic acid. Similarly 1:8-C₁₀H₆(NH₂)₂ affords its *bisdiazonium borofluoride*, which couples with (I) to give *naphthylene-1:8-bisazo-6'-bromo- β -naphthol*. J. W. B.

Chromium compounds from salicylic acid-azo-dyes and from o -methoxybenzoic acid. K. BRASS and W. WITTENBERGER (Ber., 1935, 68, [B], 1905—1912).—Introduction of Cr into salicylic acid-azo-dyes can be effected by Cr alum, but not by K₂Cr₂O₇ unless a reducing agent such as OH·CHMe·CO₂H is present. The azo-dyes from o -OH·C₆H₄·CO₂H and m -NO₂·C₆H₄·NH₂ (I), NH₂Ph, o -C₆H₄Me·NH₂, and benzidine, respectively, are converted into the corresponding lakes by heating their solutions, after neutralisation with NaOH, with Cr alum (Cr:dye:Na::1:1:1). In the lakes, dye:Cr:H₂O=2:1:2. They are stable at 130°, and Cr can be removed from them by boiling AcOH, leaving the homogeneous dye acid. H₂O cannot be directly determined in them with accuracy, and attempts to displace it by NH₃ lead to adducts in which 2NH₃ is very firmly retained. These and the lakes are therefore formulated according to A and B, respectively:



Repetition of the work of Morgan *et al.* (A., 1924, i, 1359) shows that (I) prepared under their conditions contains unchanged dye, after removal of which the residue has the same composition as that obtained by the authors' method. Methylation of (I) is not effected with Me₂SO₄ or ethylation with EtBr, and coupling of o -OMe·C₆H₄·CO₂H with m -NO₂·C₆H₄·N₂Cl does not lead to the methylated dye. In a simpler case the action of Cr alum on o -OMe·C₆H₄·CO₂H affords the compound OH·Cr(O·CO·C₆H₄·OMe)₂·H₂O, suggesting the analogous structure OH·Cr(O·CO·C₆H₄·OH)₂·H₂O for Barbieri's chromisalicylic acid. Similar structures can be assigned to the lakes, but their difficult solubility in alkali is hard to explain. H. W.

Oxidation of hydrohalides of phenylhydrazine in presence of copper salts. A. B. BRUKEV and L. S. SOBOROVSKI (J. Gen. Chem. Russ., 1935, 5, 1024—1028).— $\text{NPh}\cdot\text{NH}_2$ in aq. HCl and CuCl_2 form the compound $\text{NHPh}\cdot\text{NH}_2\cdot\text{HCl}\cdot\text{CuCl}$, decomp. at 150° , converted by excess of Cu^{II} or by atm. O_2 into PhCl and N_2 . When F is taken in place of Cl in the above reaction the sole products are C_6H_6 and N_2 . R. T.

Aryldiazonium chloride-heavy metal chloride double salts and the preparation of organo-tin compounds through diazo-compounds. A. N. NESMEJANOV, K. A. KOZESCHKOV, and V. A. KLIMOVA [with, in part, N. K. GIPP] (Ber., 1935, 68, [B], 1877—1883).—The synthesis of organo-mercury substances from diazonium compounds (A., 1929, 711) is an example of a general reaction, $(\text{RN}_2\text{Cl})_m\text{XCl}_2 + 2m/p\text{M}^{(p)} = \text{R}_m\text{X}^{(m)}\text{Cl}_{n-m} + m\text{N}_2 + 2m/p\text{M}^{(p)}\text{Cl}_p$. Double salts are obtained by mixing cold solutions of the heavy metal chloride (ZnCl_2 , CdCl_2 , SnCl_4 , PbCl_4 , PtCl_4 , TiCl_3 , BiCl_3 , FeCl_3 , AuCl_3) in HCl ($d=1.19$) and the requisite aryldiazonium chloride ($\text{Ph}\cdot$, o -, m -, and p - $\text{C}_6\text{H}_4\text{Me}\cdot$, p - $\text{OH}\cdot\text{C}_6\text{H}_4\cdot$, p - $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot$, o -, m -, and p - $\text{C}_6\text{H}_4\text{Cl}\cdot$, p - $\text{C}_6\text{H}_4\text{Br}\cdot$, p - $\text{C}_6\text{H}_4\text{I}\cdot$, o -, m -, and p - $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot$) in about 5*N*- HCl . For details the original must be consulted. Decomp. of $(\text{RN}_2\text{Cl})_2\text{SnCl}_4$ is effected by its gradual addition to a well-stirred suspension of the metallic powder in the solvent heated at the requisite temp. The best solvent is usually EtOAc at its b.p. Sn powder is more effective than Zn dust or Cu powder. The sole organo-metallic product is SnR_2Cl_2 except when $\text{R} = o\text{-CO}_2\text{Me}\cdot\text{C}_6\text{H}_4\cdot$. Small yields of PbPh_3Cl and PbPh_2O are obtained by decomp. of $(\text{RN}_2\text{Cl})_2\text{PbCl}_4$. H. W.

Action of bromine on 2- and 4-nitro- α -naphthylamines. R. CONSDEN and J. KENYON (J.C.S., 1935, 1596—1597).— $4:1\text{-NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$ (I) with Br in CHCl_3 yields $2:4$ -dibromo-1-naphthalenediazoperbromide (II), decomp. $128\text{—}136^\circ$ according to rate of heating, but no HBr . (II) is converted into $1:2:4\text{-C}_{10}\text{H}_5\text{Br}_3$ when heated, treated with $\text{C}_2\text{H}_5\text{N}$, or boiled with Ac_2O or AcOH , and was also obtained from diazotised $2:4:1\text{-C}_{10}\text{H}_5\text{Br}_2\cdot\text{NH}_2$ and $\text{HBr}\text{-Br}$ (cf. J.C.S., 1883, 43, 4). (I) when heated (water-bath, 30 min.) with $\text{Br}\text{-AcOH}$ yields a little (II), but chiefly $4:2:1\text{-NO}_2\cdot\text{C}_{10}\text{H}_5\text{Br}\cdot\text{NH}_2$ (*Ac* derivative, m.p. $235\text{—}236^\circ$), which with Br in CHCl_3 or $\text{CHCl}_3\text{-AcOH}$ yields (II). $2:1\text{-NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$ with Br in AcOH or CHCl_3 yields $2:4:1\text{-NO}_2\cdot\text{C}_{10}\text{H}_5\text{Br}\cdot\text{NH}_2$ (J.C.S., 1910, 97, 1709), which with excess of Br yields (II). o - and $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ with Br yield Br -derivatives and no diazo-perbromides. H. G. M.

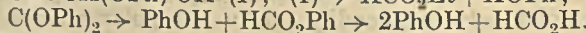
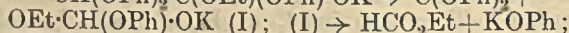
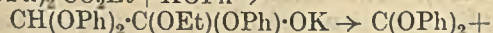
Alkylation of phenols. I. TZUKERVANIK and Z. NAZAROVA (J. Gen. Chem. Russ., 1935, 5, 767—770).—Amylene hydrate, PhOH , and AlCl_3 in light petroleum yield a mixture of amyphenol and $\text{C}_5\text{H}_{11}\text{Ph}$. PhOH and $\text{Bu}^\gamma\text{OH}$ yield chiefly $\text{C}_6\text{H}_4\text{Bu}^\gamma\text{OH}$, together with PhBu^γ and $\text{C}_6\text{H}_4\text{Bu}^\gamma_2$, in amounts increasing with the relative amount of AlCl_3 present. PhOH and $\text{Bu}^\delta\text{OH}$ under similar conditions yield chiefly $\text{C}_6\text{H}_4\text{Bu}^\delta\text{OBu}^\delta$, b.p. 230° , together with $\text{C}_6\text{H}_4\text{Bu}^\delta\text{OH}$ and PhBu^δ ; PhOH and $\text{Pr}^\delta\text{OH}$ give similarly $\text{C}_6\text{H}_4\text{Pr}^\delta\text{OPr}^\delta$, b.p. 232° , $\text{C}_6\text{H}_4\text{Pr}^\delta\text{OH}$ (I), and PhBr^δ , whilst $\text{Pr}^\delta\text{OH}$

and PhOMe afford chiefly o - and $p\text{-C}_6\text{H}_4\text{Pr}^\delta\text{OMe}$, together with $\text{C}_6\text{H}_3\text{Pr}^\delta\text{OMe}$ and (I). R. T.

Action of isobutylene on phenyl methyl ethers, and the structure of *tert*-butylphenyl methyl ethers. B. M. DUBININ (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 263—266).—The substance obtained from isobutylene and $p\text{-C}_6\text{H}_4\text{Me}\text{-OMe}$ (A., 1933, 60) is *3-tert*-butyl-*p*-tolyl Me ether, since it is also obtained from $\text{Bu}^\gamma\text{Br}$ and $1:4:3\text{-C}_6\text{H}_3\text{Me(OMe)MgBr}$ (cf. A., 1894, i, 449). Nitration affords the 5-NO_2 -derivative, m.p. $93\text{--}5^\circ$, and then $1:3:5:4\text{-C}_6\text{H}_2\text{Me(NO}_2)_2\text{OMe}$ by elimination of the Bu^γ . The Bu^γ groups in the Bu^γ_1 (I) and Bu^γ_2 (II) derivatives of $1:3\text{-C}_6\text{H}_4(\text{OMe})_2$ are given the 4 and 4:6 positions, respectively, since nitration of (I) affords *4-nitro-6-tert-butylresorcinol Me_2 ether* (III), m.p. $99\text{—}100^\circ$, and then $4:6:1:3\text{-C}_6\text{H}_2(\text{NO}_2)_2(\text{OMe})_2$; (II) also affords (III). The blue colour produced in the prep. of (III) from (I), but not from (II), is due to the presence of a free position *p* to an OMe in (I) (cf. A., 1920, i, 37; 1921, i, 240; 1922, i, 135).

P. G. C.

Compounds of bivalent carbon. XI. Carbon monoxide acetal fission of esters and amides of diphenoxyacetic acid during chemical reactions. XII. Thermal carbon monoxide acetal fission of diphenoxyacetic acid and its derivatives. XIII. Diphenoxymethylchloride (formyl chloride diphenyl acetal) and its transformation into tetraphenoxyethylene (dicarbon monoxide tetraphenyl acetal). H. SCHEIBLER and M. DEPNER (Ber., 1935, 68, [B], 2136—2143, 2144—2151, 2151—2153).—XI. *Ph diphenoxyacetate*, m.p. 95° , could not be obtained by heating $\text{CH}(\text{OPh})_2\text{CO}\cdot\text{NH}_2$ with PhOH or $\text{CH}(\text{OPh})_2\text{CO}_2\text{Et}$ with PhOAc , but is readily prepared by the successive action of SOCl_2 and PhOH on the acid in $\text{Et}_2\text{O}\text{-C}_6\text{H}_5\text{N}$. It is converted by excess of NaOEt in boiling C_6H_6 into HCO_2Et , $\text{CH}(\text{OPh})_2\text{CO}_2\text{Et}$, and $\text{C}(\text{OPh})_2\text{C}(\text{OEt})_2$, whereas $\text{CH}(\text{OPh})_2\text{CO}_2\text{Et}$ and KOPh in boiling C_6H_6 afford HCO_2Et and (after treatment of the non-volatile portion with H_2O) HCO_2H and PhOH , whilst in boiling EtOH the products are HCO_2H and $\text{CH}(\text{OPh})_2\text{CO}_2\text{H}$. The change is therefore:
 $\text{CH}(\text{OPh})_2\text{CO}_2\text{Et} + \text{KOPh} \rightarrow$



The CO acetal fission is also observed during the action of $\text{NEt}_2\cdot\text{MgBr}$ on $\text{CH}(\text{OPh})_2\text{CO}_2\text{Et}$, whereby a neutral product, b.p. $85^\circ/15\text{ mm.}$, possibly *Ph Et_2 orthoformate*, and, probably, $\text{CH}(\text{OPh})_2\text{CO}\cdot\text{NEt}_2$ are obtained. Higher yields of these compounds are obtained when the reaction product is heated with EtOH at 150° , whereby PhOEt is also produced.

$\text{CH}(\text{OPh})_2\text{CO}_2\text{Ph}$ is much more stable than the Et ester, but in C_6H_6 at 150° gives HCO_2H and PhOH (? HCO_2Ph). Only elimination of PhOH is observed by the action of $\text{NEt}_2\cdot\text{MgBr}$ on *diphenoxyacetyl diethylamide*, m.p. 137° [from $\text{CH}(\text{OPh})_2\text{CO}_2\text{Et}$ and NHEt_2 in EtOH at 100°].

XII. $\text{CH}(\text{OPh})_2\text{CO}_2\text{H}$ passes at 120° into CO , CO_2 , HCO_2Ph , Ph_2CO_3 , and, probably, *diphenoxymaleic anhydride*, m.p. 153° ; CO acetal fission has only a

subordinate part in the change. $\text{CH}(\text{OPh})_2 \cdot \text{CO}_2\text{Et}$ is comparatively thermostable, but the following thermolabile derivatives have been examined. *Diphenoxyacetyl chloride* (II), obtained by cautious treatment of the acid with SOCl_2 in C_6H_6 , passes at $170\text{--}180^\circ$ into CO and $\text{CHCl}(\text{OPh})_2$, probably with intermediate production of $\text{C}(\text{OPh})_2$ and HCOCl . *Acetic diphenoxyacetic anhydride* [attempted prep. from (II) and AgOAc or from AcCl and $\text{CH}(\text{OPh})_2 \cdot \text{CO}_2\text{Ag}$] is decomposed in Et_2O into AcOH and $\text{C}(\text{OPh})_2 \cdot \text{CO}$. (II) and NaN_3 in C_6H_6 give NaCl , $\text{C}(\text{OPh})_2 \cdot \text{CO}$, and N_3H . $\text{CH}(\text{OPh})_2 \cdot \text{CO}_2\text{Ph}$ is produced by the action of Ag_2O (II) in C_6H_6 , PhOH , resulting from hydrolysis, reacting with $\text{C}(\text{OPh})_2 \cdot \text{CO}$ or unchanged $\text{CH}(\text{OPh})_2 \cdot \text{COCl}$. $\text{C}(\text{OPh})_2 \cdot \text{CO}$ does not appear to be changed intermediately by the action of $\text{CH}(\text{OPh})_2 \cdot \text{COCl}$ on PhOH in presence of $\text{C}_5\text{H}_5\text{N}$. Elimination of HCl from $\text{CH}(\text{OPh})_2 \cdot \text{COCl}$ occurs under the influence of $p\text{-OH} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{NPh}$, whereby the compound $\text{C}_{12}\text{H}_{11}\text{ON}_2\text{Cl}$ separates and, on exposure to moisture, $\text{CH}(\text{OPh})_2 \cdot \text{CO}_2\text{H}$ is formed, presumably from $\text{C}(\text{OPh})_2 \cdot \text{CO}$. *Triphenylmethyl diphenoxyacetate*, m.p. 112° , from $\text{CH}(\text{OPh})_2 \cdot \text{CO}_2\text{Ag}$ and CPh_3Cl in anhyd. Et_2O , decomposes at 160° /high vac. into CO_2 , CHPh_3 , and $\text{C}(\text{OPh})_2$.

XIII. Treatment of $\text{CHCl}(\text{OPh})_2$ with CNaPh_3 in Et_2O under N_2 leads to CHPh_3 and $\alpha\beta\beta$ -*tetraphenoxymethylene* (dicarbon monoxide Ph_4 acetal), m.p. 168° , which readily reduces alkaline KMnO_4 , unites energetically with Br in CHCl_3 , and is converted by 30% HBr in AcOH into $\text{CH}(\text{OPh})_2 \cdot \text{CO}_2\text{Ph}$. H. W.

Ester enolates and ketal acetals. XIX. *Diphenylketen diphenylacetal*, and *phenyldiphenylvinyl ether*. H. SCHEIBLER and M. DEPNER (Ber., 1935, 68, [B], 2154—2157).— $\text{CH}(\text{OPh})_2 \cdot \text{CO}_2\text{Et}$ is transformed by MgPhBr in Et_2O into α -*hydroxy- β -diphenoxy- α -diphenylethane* (*hydroxydiphenylacetaldehyde Ph_2 acetal*) (I), m.p. 103° , converted by SOCl_2 in Et_2O - $\text{C}_5\text{H}_5\text{N}$ into α -*chloro- β -diphenoxy- α -diphenylethane* (II), decomp. $>100^\circ$. (II) is transformed by C_6H_6 -quinoline, less advantageously by Ag_2CO_3 , AgCN , or $\text{Hg}(\text{CN})_2$, into α -*diphenoxy- β -diphenylethane* (*diphenylketen Ph_2 acetal*) (III), b.p. $185^\circ/0.5$ mm., m.p. 112° , also obtained from (I), P_2O_5 , and NET_3 in C_6H_6 at 150° . (III) is hydrolysed by EtOH - HCl to PhOH and $\text{CHPh}_2 \cdot \text{CO}_2\text{Et}$, and by HBr - AcOH to *Ph diphenylacetate*, m.p. 65° , also obtained with $\text{C}_6\text{H}_5\text{Br}_3 \cdot \text{OH}$ from (III) and Br in CCl_4 . (II) with MgPhBr in Et_2O or with Zn dust and $\text{C}_5\text{H}_5\text{N}$ affords α -*diphenylvinyl Ph ether*, m.p. 60° . H. W.

Behaviour of bromine derivatives of guaiacol towards nitrating agents. L. C. RAIFORD and R. E. SILKER (Proc. Iowa Acad. Sci., 1934, 41, 171).—4 : 5 : 6-Tribromoguaiacol could not be nitrated, either with HNO_2 (cf. Zincke, A., 1900, i, 545) or with HNO_3 . The Ac and Bz derivatives, with fuming HNO_3 at room temp., give 4 : 5 : 6-tribromo-3-nitro-2-methoxyphenyl acetate and *m*-nitrobenzoate, respectively. CH. ABS. (r)

Metallic derivatives of 2-nitroso-5-methoxy- and of 3-chloro-2-nitroso-5-methoxy-phenol. H. H. HODGSON and W. E. BATTY (J.C.S., 1935, 1617—1619).—2-Nitroso-5-methoxyphenol (I) exists in

the NO-form in C_6H_6 and in the quinoneoxime form in EtOH , whereas its 3-Cl-derivative (II) is always in the NO-form and is highly chelated, being sparingly sol. in H_2O and readily sol. in C_6H_6 . The following salts of (I) ($\text{X}=\text{C}_7\text{H}_6\text{O}_3\text{N}$) and (II) ($\text{Y}=\text{C}_7\text{H}_5\text{O}_3\text{NCl}$) are described; they are sol. in org. solvents (C_6H_6 and CHCl_3) and probably are co-ordination compounds: HgX_2 , m.p. 201° ; HgY_2 ; AlXCl_2 ; AlYCl_2 ; SnXCl_3 , m.p. 147° ; SnYCl_3 ; $\text{Fe}(\text{OH})\text{X}_2$; FeX_3 ; $\text{Fe}(\text{OH})\text{Y}_2$; FeY_3 ; CoX_3 ; CoY_3 ; NiX_2 ; NiY_2 ; and the following double compounds with salicylaldehyde (=S): NaX,S ; NaY,S ; KX,S ; and KY,S . The following salts are insol. in org. solvents and probably are normal salts (non-co-ordinated): NaX ; NaY ; KX ; KY ; AgX ; AgY ; ZnX_2 ; ZnY_2 ; CdX_2 ; CdY_2 ; PbX_2 ; PbY_2 ; MnX_2 ; MnY_2 ; UO_2X_2 ; UO_2Y_2 . The Ag and Hg salts of 2-nitroso-3-ethoxyphenol described by Kietaihl (A., 1899, i, 343) are really those of 2-nitroso-5-ethoxyphenol. Wool mordanted with Fe^{II} salts is dyed bluish-green with nitrosophenol solutions: the colour lake is decolorised by acids, restored by NH_3 , and destroyed by SnCl_2 . H. G. M.

Dimorphism of trinitroresorcinol, bromobenzylhydrazine, and benzaldehyde-*p*-nitrophenylhydrazine.—See this vol., 16.

Diaryls and their derivatives. IV. Oxidation of β -naphthol-6-sulphonic acid and 2 : 6-dihydroxynaphthalene. V. Optical activity of 2 : 2'-dihydroxy-1 : 1'-dinaphthylsulphonic acids. I. S. JOFFE (J. Gen. Chem. Russ., 1935, 5, 877—885, 950—955).—IV [with S. G. KUZNETZOV]. 2 : 2'-Dihydroxy-1 : 1'-dinaphthyl-6 : 6'-disulphonic acid (I), obtained in 90% yield from $\text{Na}\beta$ -naphthol-6-sulphonate and aq. FeCl_3 ($20\text{--}25^\circ$; 20 days), yields 2 : 2'-dihydroxy-1 : 1'-dinaphthyl when heated with H_2SO_4 ($170\text{--}180^\circ$; 12 hr.), and 2 : 6 : 2' : 6'-tetrahydroxy-1 : 1'-dinaphthyl (II), m.p. $318\text{--}320^\circ$, when heated with KOH ($320\text{--}330^\circ$; 15 min.). (II) may also be obtained from dil. aq. 2 : 6- $\text{C}_{10}\text{H}_6(\text{OH})_2$ and FeCl_3 at room temp.; excess of FeCl_3 leads to the production of the corresponding octahydroxytetra-naphthyl. (II) in aq. NaOAc and $p\text{-NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2\text{Cl}$ yield the 5-*p*-nitrobenzeneazo-derivative, m.p. $179\text{--}183^\circ$.

V. [with I. V. GRATSCHEV]. The brucine salt of (I) is separable into two fractions, $[\alpha]_D^{20} -43^\circ$ and -65° in 50% EtOH , which yield two Na salts of (I), $[\alpha]_D^{20} -154^\circ$ and $+166^\circ$ in H_2O , when hydrolysed with 0.05*N*- NaOH in presence of CHCl_3 ; the analogous products from the corresponding 7 : 7'-disulphonate have $[\alpha]_D^{20} -312^\circ$ and $+259^\circ$. The free acids do not exhibit optical activity, and both the acids and their salts readily racemise in aq. solution. R. T.

Application of the Raman effect to the *cis-trans* isomerism of methylcyclohexanols.—See this vol., 11.

Benzyl formate. R. HOLTZ (J. Appl. Chem. Russ., 1935, 8, 1014—1015).— $\text{CH}_2\text{Ph} \cdot \text{OH}$ and HCO_2H (21% excess) at the b.p. of the mixture, and in presence of sufficient CaCl_2 to bind the H_2O produced, afford $\text{HCO}_2 \cdot \text{CH}_2\text{Ph}$ in 91% yield, and of high purity.

R. T.

Synthesis of β -phenylbutyl alcohol. S. P. LAGEREV (J. Gen. Chem. Russ., 1935, 5, 515—516).—

Mg, CH_2PhI , and EtCHO afford β -phenylbutyl alcohol, b.p. 124—127°/25 mm. (benzoate, m.p. 115—116°), which with HBr in Et_2O yields the bromide, b.p. 112°/15 mm. R. T.

Semipinacolic deamination of β -amino- p -tolyl- and α -anisyl- α -phenylpropanol. Exclusive preferential migration of phenyl. M. TIFFENEAU, J. LÉVY, and E. DITZ (Bull. Soc. chim., 1935, [v], 2, 1871—1876).—Treatment of the α - and β -forms of p - $\text{C}_6\text{H}_4\text{Me}\cdot\text{CPh}(\text{OH})\cdot\text{CHMe}\cdot\text{NH}_2$ in AcOH with $\text{NaNO}_2\text{-H}_2\text{O}$ yields p -tolyl α -phenylethyl ketone, m.p. 43° (semicarbazone, m.p. 148°), also obtained by methylation of p - $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$. Similarly the α -form of p - $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CPh}(\text{OH})\cdot\text{CHMe}\cdot\text{NH}_2$ in AcOH and $\text{NaNO}_2\text{-H}_2\text{O}$ yield p -anisyl α -phenylethyl ketone, m.p. 55° (cf. lit.), also obtained by methylation of p - $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$. In each case only the Ph has migrated during deamination. H. G. M.

Formation of a single diastereoisomeride in the action of organo-magnesium derivatives on amino-ketones. M. TIFFENEAU, J. LÉVY, and E. DITZ (Bull. Soc. chim., 1935, [v], 2, 1848—1855; cf. A., 1930, 470).—The action of MgRBr on ketones $\text{R}'\cdot\text{CO}\cdot\text{CHMe}\cdot\text{NH}_2$ (I) (R different from R') which have an asymmetric C adjacent to the CO gives rise to only one of the two possible diastereoisomeric products. The other is obtained by inverting the order in which the substituents are attached to the new asymmetric centre. A further example is given (cf. loc. cit.). p -Tolyl α -aminoethyl ketone and $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{MgBr}$ (II) yield solely β -amino- α - p -tolyl- α -anisylpropanol, m.p. 90° (hydrochloride, m.p. 260°; picrate, m.p. 217°); the corresponding β -compound, m.p. 84° (hydrochloride, m.p. 242°; picrate, m.p. 197°), is obtained from anisyl α -aminoethyl ketone and p - $\text{C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$. (II) and ω -aminoacetophenone (which contains no asymmetric C) give the same β -amino- α -phenyl- α -anisylethanol, m.p. 100°, as do ω -amino- p -methoxyacetophenone and MgPhBr . An improved method is described for the prep. of the oximino-ketones which on reduction yield the ketones (I). These exist only as hydrochlorides, the free bases cyclising to the corresponding dihydropyrazines. H. G. M.

Deamination of α -amino- β -phenylpropan- β -ol and α -amino- β -phenylbutan- β -ol. Exclusive preferential migration of phenyl. M. TIFFENEAU and H. CAHNMANN (Bull. Soc. chim., 1935, [v], 2, 1876—1882).— $\text{OH}\cdot\text{CPhMe}\cdot\text{CH}_2\cdot\text{NH}_2$ [prepared from $\text{COPh}\cdot\text{CH}_2\cdot\text{NH}_2$ and MgMeI , and together with some β -phenylallylamine, b.p. 90—92°/14 mm. (hydrochloride, m.p. 143—144°; methiodide, m.p. 160°), also obtained from N -methyl- β -phenylallylamine), by reduction with Na-EtOH of $\text{OH}\cdot\text{CPhMe}\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$, obtained from $\text{COPh}\cdot\text{CH}\cdot\text{NOH}$] is deaminated by $\text{AcOH-H}_2\text{O-NaNO}_2$ to $\text{CH}_2\text{Ph}\cdot\text{COMe}$. Similarly $\text{OH}\cdot\text{CPhEt}\cdot\text{CH}_2\cdot\text{NH}_2$, b.p. 137—146°/15 mm. [hydrochloride, m.p. 184.5—185°; prepared, together with some β -phenyl- Δ^8 -butenylamine, b.p. 110—115°/15 mm. [hydrochloride, m.p. 166.5—167° (corr.)], by reduction of the product obtained from $\text{COPh}\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$ and MgEtBr], is deaminated by $\text{AcOH-H}_2\text{O-NaNO}_2$ to $\text{CH}_2\text{Ph}\cdot\text{COEt}$ [semicarbazone,

m.p. 156.5—157° (cf. lit.)]. In each case only the Ph has migrated during the deamination. H. G. M.

Action of magnesium phenyl bromide on d -dibenzoylglyceraldehyde. Formation of a single diastereoisomeride: α - d -dibenzoylphenylglycerol. M. TIFFENEAU, I. S. NEUBERG-RABINOVITCH, and H. CAHNMANN (Bull. Soc. chim., 1935, [v], 2, 1866—1871).— d -Dibenzoylglyceraldehyde and MgPhBr (1 mol.) give a single d -dibenzoylphenylglycerol (laevorotatory), which with BzCl and $\text{C}_5\text{H}_5\text{N}$ gives solely laevorotatory α - d -tribenzoylphenylglycerol, m.p. 147°, converted into α - d -phenylglycerol, m.p. 105—106° (corr.), $[\alpha]_{\text{D}}^{19.5} + 21.1^\circ$ and $[\alpha]_{\text{D}}^{19.5} + 18.4^\circ$ in H_2O . H. G. M.

Cubebin. VII. [Criticism of] a new structural formula proposed for cubebin. VIII. Identity of cubebinolide with hinokinin. E. MAMELI (Gazzetta, 1935, 65, 877—885, 886—888).—VII. The objections of Ginzberg *et al.* (A., 1934, 302) to the formula proposed (A., 1913, i, 47; 1922, i, 347) for cubebin (I), and their new formula, are criticised and the earlier structure is upheld.

VIII. Cubebinolide (*loc. cit.*) is identical with the hinokinin (II) of Yoshiki and Ishiguro (J. Pharm. Soc. Japan, 1933, 53, 11); properties and derivatives are compared. The extraction of (II) from the conifer *Chamaecyparis obtusa*, Sieb. and Zucc., shows that the occurrence of (I) and its derivatives is not restricted to the angiosperms. E. W. W.

"Plane-radial" compounds. I. Hexahydroxymethylbenzene and its derivatives. II. Hexathiomethylbenzene and its thioethers. H. J. BACKER (Rec. trav. chim., 1935, 54, 833—837, 905—915).—I. $\text{C}_6(\text{CH}_2\text{Br})_6$ (I) (A., 1935, 1487) is converted by boiling $\text{KOAc-Ac}_2\text{O}$ into the Ac_6 derivative, m.p. 163°, hydrolysed by KOH-EtOH to hexahydroxymethylbenzene, m.p. 310—311° (crystallographic data) {hexanitrate, m.p. 176.5° (decomp.); hexapropionate, m.p. 90—100° [from (I)- $\text{EtCO}_2\text{Na}-(\text{EtCO})_2\text{O}$]; Me_6 , m.p. 100°, Et_6 , m.p. 93°, and Ph_6+2PhMe , and solvent-free, m.p. 223°, ethers [all from (I) by the action of NaOR-ROH]}. II. Interaction of $\text{C}_6(\text{CH}_2\text{Br})_6$ and $\text{CS}(\text{NH}_2)_2$ in EtOH affords hexaisothiocabamidomethylbenzene, decomp. 290°, as its hydrobromide, m.p. 250° (decomp.), hydrolysed by NaOH to hexathiomethylbenzene, m.p. 225—226° [$\text{Na}+36\text{H}_2\text{O}$, and $\text{Pb}+3\text{H}_2\text{O}$, salts: Me_6 , m.p. 220—222°; Et_6 , m.p. 131°; Pr_6 , m.p. 55.5°; Pr^{β}_6 , m.p. 232—232.5°; Bu^{α}_6 , m.p. 34—34.5°; Bu^{β}_6 , m.p. 94°; sec.- Bu_6 , m.p. 172°; Bu^{γ}_6 , m.p. 304° (decomp.); ($n\text{-C}_5\text{H}_{11}$) $_6$, m.p. 25.5—26°; (CMe_2Et) $_6$, m.p. 295°; ($n\text{-C}_6\text{H}_{13}$) $_6$, m.p. 11.5—12°; Ph_6+PhMe and solvent-free, m.p. 191—192°; ($p\text{-C}_6\text{H}_4\text{Me}$) $_6$, m.p. 183—184°; ($p\text{-C}_6\text{H}_4\text{Cl}$) $_6$, m.p. 179—180°; ($p\text{-C}_6\text{H}_4\text{Bu}^{\gamma}$) $_6$, m.p. 182—183°, and (CH_2Ph) $_6+\text{PhMe}$, m.p. 148°, thioether, all formed by the action of NaOEt-RSH on $\text{C}_6(\text{CH}_2\text{Br})_6$]. The close packing of branched-chain alkyl groups greatly raises the m.p., and with the n -alkyl thioethers, the m.p. is lower the longer is the normal C chain. Crystallographic data (TERPSTRA) are given for some of the above compounds. J. W. B.

Action of carbonyl chloride, chloromethyl chloroformates and carbonates on cholesterol.

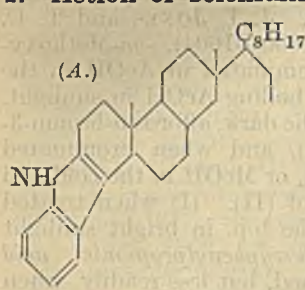
A. KLING and M. ROUILLY (Compt. rend., 1935, 201, 782—784; cf. A., 1934, 216).—Cholesterol in warm CHCl_3 reacts with COCl_2 to give a *chlorocarbonate* (I), m.p. 114°. ClCO_2Me does not react; $\text{ClCO}_2\text{CH}_2\text{Cl}$, $\text{ClCO}_2\text{CHCl}_2$, and $\text{ClCO}_2\text{CCl}_3$ give a highly unstable product, *cholesteryl dichloromethyl carbonate*, m.p. 85°, and *cholesteryl CCl_3 carbonate*, m.p. 107°, respectively. $\text{CO}(\text{O}\cdot\text{CCl}_3)_2$ similarly affords (I) (cf. A., 1920, i, 805). This reaction may account for the toxicity of these substances when inhaled.

J. L. D.

Hydrogenation under the action of selenium.

I. Action of selenium on cholesterol at 230°.

C. DORÉE and V. A. PETROV (J.C.S., 1935, 1391—1393).—After 10 hr., cholesterol is partly converted by Se at 230° into cholestanone (I) (*semicarbazone*, m.p. 234—238°), with small quantities of cholestanol and cholestenone; after 25 hr., 10% of (I) is formed.



With $\text{NPh}\cdot\text{NH}_2$ in AcOH , (I) forms a *tetrahydrocarbazole* derivative, m.p. 180—181° (*picrate*, m.p. 209—210°), which from ease of formation and surface film area probably has the angular structure (A).

E. W. W.

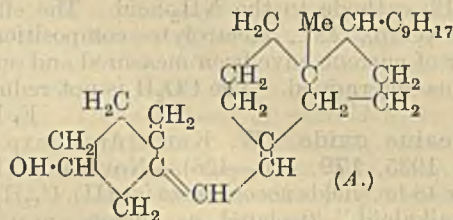
Sitostanol and stigmastanol. B. E. BENGTSSON (Z. physiol. Chem., 1935, 237, 46—51).—The probability of the identity of ordinary dihydrostosterol with tetrahydrostigmasterol is advanced. "Ordinary" and γ -sitostane can be differentiated by their mixed m.p. with stigmastane. Fucostanol is not identical with stigmastanol (cf. A., 1934, 1347).

F. O. H.

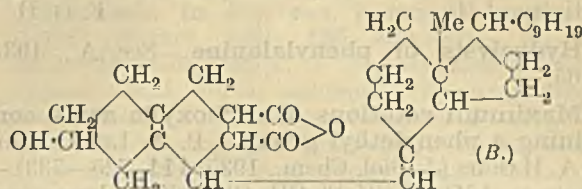
Phytosterol of wheat-germ oil.—See A., 1935, 1551.

Constitution of vitamin- D_2 . A. WINDAUS and W. THIELE (Annalen, 1935, 521, 160—175).—Treatment of calciferyl acetate with maleic anhydride in boiling C_6H_6 affords an *adduct*, m.p. (indef.) 189—196°, hydrolysed and then converted by CH_2N_2 into α -*calciferyl acetate Me_2 maleate* (I), m.p. 141°, $[\alpha]_D^{20} +170.8^\circ$ in CHCl_3 , which absorbs 2 O when titrated with BzO_2H . The filtrates from (I) when treated with $\text{KOH}\text{-MeOH}$ give a sparingly sol. *K* salt, from which AcOH liberates β -*calciferol-maleic acid* (II), m.p. 196° (decomp.), the *Me* ester, m.p. 67—68°, of which is converted by Ac_2O into β -*calciferyl acetate Me_2 maleate*, m.p. 94—95°, $[\alpha]_D^{20} -158.3^\circ$ in CHCl_3 , which absorbs 3 O from BzO_2H . The adducts can be distilled in a vac. without decomp. Hydrogenation (Pd in COMe_2) of (I) gives the H_2 -derivative (III), m.p. 112°, $[\alpha]_D^{20} +167.8^\circ$ in CHCl_3 , which absorbs 1.16—1.33 O and is further reduced (Pt in AcOH) to the H_4 -compound. Similarly (II) gives a H_2 -derivative, m.p. 193° (decomp.) [β -*dihydrocalciferyl acetate Me_2 maleate* (IV), m.p. 86—86.5°, $[\alpha]_D^{19} -144.7^\circ$ in CHCl_3 , which absorbs 2 O from BzO_2H], and a non-cryst. H_4 -derivative, converted by acetylation and methylation into β -*tetrahydrocalciferyl acetate Me_2 maleate*, m.p. 122°, $[\alpha]_D^{19} -51.5^\circ$ in CHCl_3 , which absorbs Br but is only slowly attacked by O_3 .

Ozonisation of (III) or (IV) in CHCl_3 followed by reductive or oxidative fission of the ozonide yields a



ketone, $\text{C}_{10}\text{H}_{34}\text{O}$ (*semicarbazone*, m.p. 225°; *oxime*, m.p. 129.5°). Hydrolysis of (I) gives α -*calciferol-*



maleic acid, m.p. 146—147° (decomp.), dehydrogenated by Pd-C at 330—340° to C_{10}H_8 , and β - $\text{C}_{10}\text{H}_7\text{-CO}_2\text{H}$, and by Se at 280—325° to 2:3- $\text{C}_{10}\text{H}_6\text{Me}_2$. The structures A and B are therefore assigned to calciferol and the H_2 -adduct, respectively.

H. W.

Reaction of carboxylic acid chlorides with metallic hydrides. O. NEUNHOEFFER and F. NERDEL (J. pr. Chem., 1935, [ii], 144, 63—66; cf. Wohl *et al.*, A., 1912, i, 161).—Freshly prepared CuH is red to chocolate-brown, and even when moist with Et_2O cannot be handled without some danger, whereas the aged product is black and almost non-dangerous. Its complete purification from compounds of P is extremely difficult. Interaction of CuH and BzCl in presence of Et_2O in an inert atm. affords EtOBz in widely varying yield, but no PhCHO . Since in presence of C_6H_6 or *cyclohexane* in place of Et_2O there is no formation of EtOBz , its production must be ascribed to fission of Et_2O . Reaction between CuH and acid chloride is accompanied by evolution of H_2 . Since the amount thus liberated + that evolved on subsequent addition of HCl equals the total H present, it follows that none is expended in reduction. Since CuH is very sensitive to Cl' , the BzCl used is first shaken with CaCO_3 and a trace of $\text{C}_2\text{H}_5\text{N}$ is added to accelerate the change; under these conditions CuH is almost completely stable to BzCl , and evolution of H_2 does not occur until HCl is added. CaH_2 and LiH are more stable than CuH . AcCl , $\text{CHPh}\cdot\text{CH}\cdot\text{COCl}$, and adipyl chloride behave similarly to BzCl .

H. W.

Nitration of benzoic and toluic acids. A. GIACALONE (Gazzetta, 1935, 65, 840—844).—Nitration at 0—5° of *m*-toluic acid (20 g.) with KNO_3 in H_2SO_4 gives 4-nitro- (12 g.) and 2-nitro- (6 g.) without 6-nitro-*m*-toluic acid. Similar nitration of BzOH and of *o*- and *p*-toluic acid gives products more readily purified than those obtained in the usual manner.

E. W. W.

Effect of substituents on organic reactions.—See A., 1935, 1465.

Electrolytic preparation of anthranilic acid. J. W. SHIPLEY and J. M. CALHOUN (Canad. J. Res.,

1935, 13, B, 123—132).— o -NO₂·C₆H₄·CO₂H is reduced electrolytically (92% yield) in EtOH-H₂SO₄ with a Pb cathode to the NH₂-acid. The effects of varying temp., c.d., electrolyte composition, and quantity of current have been measured and optimum conditions determined. The CO₂H is not reduced.

F. R. S.

Novocaine oxide. W. KEIL (Arch. exp. Path. Pharm., 1935, 179, 425—426).—Novocaine (I) with H₂O₂ for 48 hr. yields *novocaine oxide* (II), C₁₂H₂₂O₄N₂, a "genalkaloid" (isolated as *picrate*, m.p. 172°). In its anæsthetic actions on the rabbit's cornea and human skin, (II) has respectively 50 and 25% of the activity of (I).

F. O. H.

Hydrolysis of phenylalanine.—See A., 1935, 1465.

Maximum rotations of carboxylic acids containing a phenylethyl group. P. A. LEVENE and S. A. HARRIS (J. Biol. Chem., 1935, 114, 725—733).—The max. $[M]_D$ of CH₂Ph·CH₂·CHMeEt is determined and that of related compounds calc. In the series, CH₂Ph·CH₂·CHMe·[CH₂]_n·CO₂H, there is periodic fluctuation of $[M]$ as n increases from 0 to 3. γ -Phenyl- α -methylbutyric acid, resolved by the cinchonidine salt in COMe₂, has $[\alpha]_D^{20}$ -28.75°. α -Phenyl- γ -methylpentane, from (a) the alcohol and cold HI, followed by H₂-Raney Ni in 10% NaOH-MeOH, or (b) *l*-C₅H₁₁·MgBr and PhCHO, has $[\alpha]_D^{25}$ -5.52°. ζ -Phenyl- δ -methylhexoic acid, b.p. 152—154° (or 162°)/1 mm., $[\alpha]_D^{25}$ -1.60°, is obtained from (a) CH₂Ph·CH₂·CHMe·[CH₂]₂·MgBr and CO₂, or (b) CH₂Ph·CH₂·CHMe·CH₂Br and CH₂(CO₂Et)₂, and leads to the *Et* ester, b.p. 122°/5 mm., $[\alpha]_D^{25}$ -3.71°, and ζ -phenyl- δ -methylhexan-2-ol, b.p. 155°/10 mm., $[\alpha]_D^{25}$ -5.27°. CH₂Ph·CH₂·CHMe·[CH₂]₃·MgBr and CO₂ give ζ -phenyl- δ -methylheptoic acid, b.p. 172°/2.5 mm., $[\alpha]_D^{25}$ -3.27°. Hydrogenation (PtO₂) in AcOH affords ϵ -cyclohexyl- γ -methylhexoic acid, b.p. 180°/10 mm., $[\alpha]_D^{25}$ -1.18°, and ζ -cyclohexyl- δ -methylheptoic acid, b.p. 136—140°/0.3 mm., $[\alpha]_D^{25}$ -1.41°. $[\alpha]$ are max. vals. for the homogeneous liquids.

R. S. C.

Catalytic hydrogenation of ethyl cinnamate under pressure. S. P. LAGEREV (J. Gen. Chem. Russ., 1935, 5, 517—518).—Et cinnamate yields CH₂Ph·CH₂·CO₂Et, but not δ -phenylbutyl alcohol, when heated with H₂ (12 hr.; 250°/220 atm.) in presence of Cr-Cu catalyst in an Fe autoclave. R. T.

Steric factor in organic chemical reactions.

I. Influence of esterification on mode of addition of bromine to β -phenylpropionic acid. P. R. AYYAR (J. Indian Inst. Sci., 1935, 18, A, 123—127).—Addition of Br to CPh₂·CO₂H (I) at 0° in the dark affords *cis*- and *trans*-CPhBr·CBr·CO₂H in the ratio 3 : 2, whereas at 0—25° in diffused daylight the ratio is 2 : 1. Using the Me ester of (I), the ratios under the above conditions are 1 : 2 and 1 : 3, respectively.

P. G. C.

Synthesis of a methyloctahydrophenanthrene-carboxylic acid and of 4-methylphenanthrene. G. DARZENS and A. LÉVY (Compt. rend., 1935, 201, 730—733).— β -Chloromethyltetrahydronaphthalene (cf. A., 1931, 208) with CHNa(CO₂Et)₂ gives *Et*₂ tetrahydronaphthylmethylmalonate, b.p. 179°/1.5

mm. (the acid, m.p. 123°, loses CO₂ in vac. at 170° to give β -tetrahydronaphthylpropionic acid, m.p. 127°), the Na derivative of which affords (cf. A., 1935, 975) an *allyl* derivative, b.p. 189—190°/2 mm. [acid, an oil, which loses CO₂ in vac. at 170—180° to give β -tetrahydronaphthyl- α -allylpropionic acid (I), an oil]. (I) with AcOH-H₂SO₄ at 50° gives a lactone, b.p. 187°/2 mm., and 4-methyloctahydrophenanthrene-2-carboxylic acid, m.p. 148—149°, which with Se at 300—350° gives 4-methylphenanthrene, m.p. 116° (cf. A., 1931, 1282; 1932, 608). J. L. D.

Addition of halogens to unsaturated acids and esters. V. Bromination of *m*-methoxycinnamic acid and its ethyl ester. J. I. JONES and T. C. JAMES (J.C.S., 1935, 1600—1604).—*m*-Methoxycinnamic acid (I) when brominated in AcOH in the dark (cf. A., 1928, 519), in boiling AcOH in sunlight, or in CCl₄ or CHCl₃ at 0° in the dark, affords 6-bromo-3-methoxycinnamic acid (II), and when brominated in boiling MeOH in sunlight, or MeOH in the cold and dark, yields the Me ester of (II). (I) when treated with Br and dry CCl₄ at the b.p. in bright sunlight yields $\alpha\beta$ -dibromo- β -3-methoxyphenylpropionic acid (III), m.p. 167°, also obtained, but less readily, when (I) is brominated in CCl₄ in the cold in sunlight, or in boiling CS₂. Bromination of (I) in boiling CHCl₃ in sunlight gives a mixture consisting mainly of (II). (III) is unaffected by boiling EtOH, and is oxidised by KMnO₄ to *m*-OMe·C₆H₄·CO₂H (IV). Bromination of the Et ester of (I) in AcOH or CHCl₃ in the cold and dark gives only the Et ester of (II), but in CCl₄ in strong sunlight gives the *Et* ester, m.p. 58°, of (III). (II) in boiling CCl₄ with Br in strong sunlight yields $\alpha\beta$ -dibromo- β -6-bromo-3-methoxyphenylpropionic acid, m.p. 163°, also obtained by bromination of (III). (III) with KOH-EtOH affords α -bromo-*m*-methoxycinnamic acid (V), m.p. 122° (A., 1934, 72), and α -bromo-*m*-methoxyallocinnamic acid, m.p. 91°, separated by means of their Ba salts and also obtained by removal of HBr from the ester of (III). The *allo*-acid, when kept in the solid state or in CCl₄ solution, in strong sunlight, or when heated during several hr. at 150°, is converted into (V). (V) when boiled with KOH-EtOH during 4 hr. yields *m*-methoxyphenylpropionic acid, m.p. 109°, which with K₂CO₃-I-KI-H₂O affords $\alpha\beta$ -di-iodo-*m*-methoxycinnamic acid, m.p. 142°, and is hydrogenated (colloidal Pd "protected" by Na protalbate) to *m*-methoxyallocinnamic acid (VI), m.p. 109—110°, converted on long exposure to sunlight into (I). (VI) with CHCl₃-Br in the cold and dark affords 6-bromo-3-methoxyallocinnamic acid, m.p. 133°, oxidised by KMnO₄ to (IV). H. G. M.

Preparation of fluorinated arylamides [of 2 : 3-hydroxynaphthoic acid].—See B., 1935, 1132.

Reaction of Grignard reagents with some succinic anhydrides. C. WEIZMANN, (MRS.) O. BLUM-BERGMANN, and F. BERGMANN (J.C.S., 1935, 1370—1371).—(·CH₂CO)₂O treated with the Mg derivative of 1- or 2-C₁₀H₇Br yields β -(1- or β -(2-naphthoyl)propionic acid. Phenylsuccinic anhydride with MgPhBr and with the Mg derivative of 1-C₁₀H₇Br gives $\alpha\gamma\gamma$ -triphenyl-, m.p. 162°, and α -phenyl- $\gamma\gamma$ -di-(1-naphthyl)-*n*-butyrolactone, m.p. 211°, the last being accompanied by an acid, reduced to a

substance, b.p. 265—270°/1.4 mm. 3-Phenyl- Δ^4 -tetrahydrophthalic anhydride and MgPhBr form an acid product, and a triphenyltetrahydrophthalide, 2-(diphenylmethylol)-6-phenyl- Δ^4 -tetrahydrobenzoic acid lactone, m.p. 227°. E. W. W.

Hydrolysis of cyclopentanedicarboxylic esters.

—See A., 1935, 1465.

Configurations of the Δ^2 -tetrahydro- and hexahydro-terephthalic acids. W. H. MILLS and G. H. KEATS (J.C.S., 1935, 1373—1375).—“Fumaroid” Δ^2 -tetrahydroterephthalic acid (I), m.p. 228° (*Me*₂ ester, m.p. 11°, b.p. 152—154°/30 mm.), is resolved into optical antimerides, and is thus the *trans*-form. The *brucine* salt, $[\alpha]_{D}^{16}$ -117°, gives 1-*trans*- Δ^2 -tetrahydroterephthalic acid, m.p. 222°, $[\alpha]_{D}^{16}$ -279°; an impure *d*-acid, $[\alpha]_{D}^{16}$ +132°, is also obtained. The “maleinoid” form, m.p. 161°, is not resolvable, and must be the *cis*-acid (II) (*Me*₂ ester, b.p. 148°/30 mm.). (I) and (II) are hydrogenated (Pt) to *trans*- and *cis*-hexahydroterephthalic acid, respectively, m.p. 309° and 167°; the conclusions of Malachowski *et al.* (A., 1934, 1350) are thus confirmed. The primary and secondary dissociation consts. of (I) and (II) at 22° are: (I), K_1 1.18×10^{-4} , K_2 1.19×10^{-5} ; (II), K_1 0.82×10^{-4} , K_2 0.81×10^{-5} . The vals. of K_1/K_2 indicate that the distance between dissociating H atom and negative charge on $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_{10} \cdot \text{CO}_2^-$ is approx. 8.2 Å. in both (I) and (II) (cf. A., 1931, 1126); this is in agreement with models.

E. W. W.

Grignard reactions with phthalic anhydride.

C. WEIZMANN, E. BERGMANN, and F. BERGMANN (J.C.S., 1935, 1367—1370).—*o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ and its derivatives, including 4-methoxyphthalic anhydride, m.p. 97°, b.p. 202°/25 mm. (obtained from 4-hydroxyphthalic anhydride, b.p. 250—255°/24 mm., prepared from the acid, and CH_3N_2), react with MgRBr to form derivatives of *o*- $\text{C}_6\text{H}_4(\text{COR}) \cdot \text{CO}_2\text{H}$ and of *o*- $\text{C}_6\text{H}_4(\text{CR}_2\text{OH}) \cdot \text{CO}_2\text{H}$ or its lactone. The following are new: *o*- β -Naphthoylbenzoic acid, m.p. 128° (decomp.) (as hydrate), 168° (anhyd.); *di*- β -naphthoylphthalide; *o*-(6-methoxy-2-naphthoyl)-, m.p. 166°, *o*-9-phenanthroyl-, m.p. 174—175°, 4(5?)-methoxy-2-benzoyl-, m.p. 167°, 4(5?)-methoxy-2- α -naphthoyl-, m.p. 196°, and tetrachloro-*o*-4-anisoyl-, m.p. 186—187°, -benzoic acid; tetrachloro-*di*-4-bromophenylphthalide, m.p. 144—145° (decomp.); and 2- α - (I), m.p. 228—229°, and 2- β -naphthoyl-, m.p. 240°, and 2-4'-methoxybenzoyl-, m.p. 234°, -3-naphthoic acid. With AlCl_3 and NaCl, *o*- α -naphthoylbenzoic acid yields naphthacenequinone, new m.p. 276°. In H_2SO_4 , (I) condenses to 1 : 2 : 6 : 7-dibenzanthraquinone, m.p. 227°.

E. W. W.

Synthesis of rotenone and its derivatives.

VII. Tetrahydro tubaic acid. A. ROBERTSON and G. L. RUSBY (J.C.S., 1935, 1371—1373).—A new synthesis of tetrahydro tubaic acid (I), of which the Ac_2 derivative, new m.p. 140—141°, is obtained by oxidation (KMnO_4) of the Ac_2 derivative, m.p. 47.5°, of tetrahydro tuba-aldehyde (2 : 4-dihydroxy-3-isoamylbenzaldehyde) (II), m.p. 112.5° (semicarbazone, m.p. 198°), (II) being prepared $[\text{Zn}(\text{CN})_2]$ from tetrahydro tubanol (A., 1933, 1169). The orientation of (I) is established by converting (II) ($\text{MeI}-\text{K}_2\text{CO}_3$ in Ac_2O)

into 2-hydroxy-4-methoxy-3-isoamylbenzaldehyde, b.p. 180°/15 mm. (semicarbazone, m.p. 193°), since this condenses with ω -methoxyacetoveratone to 3 : 7 : 3' : 4'-tetramethoxy-8-isoamylflavylum chloride (ferrichloride, m.p. 131—132°); (III) is acetylated, oxidised, and deacetylated to 2-hydroxy-4-methoxy-3-isoamylbenzoic acid. The azlactone of asaraldehyde (A., 1932, 860) is converted by NaOH, SO_2 , and HCl into 2 : 4 : 5-trimethoxyphenylpyruvic acid, m.p. 198°, of which the *oxime* treated with Ac_2O yields 2 : 4 : 5-trimethoxyphenylacetonitrile, m.p. 85°, hydrolysed to the -acetic acid, new m.p. (hydrate) 81°, (anhyd.) 106°.

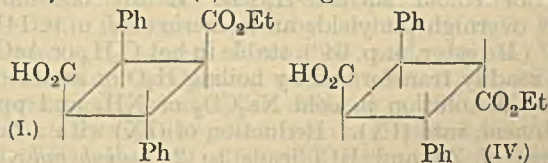
E. W. W.

Synthesis in the sex hormone group. A.

COHEN (Nature, 1935, 136, 869—870; A., 1935, 752).—At room temp., 1-vinylnaphthalene readily combines with maleic anhydride (I) giving dihydrophenanthrene-1 : 2-dicarboxylic anhydride (II), m.p. 186—189° (decomp.); dehydrogenated (Pt-black; 300°) to phenanthrene-1 : 2-dicarboxylic anhydride, m.p. 310° (corr.) (Fieser *et al.*, *ibid.*, 1495). Dehydration 6-methoxy-1-naphthylethyl alcohol yields 1-vinyl-6-methoxynaphthalene, m.p. 41—42° (picrate, m.p. 114.5°), which combines with (I) forming the OMe-derivative of (II), m.p. 171—175° (decomp.) This is dehydrogenated by Pt-black at 280—300° to 7-methoxyphenanthrene-1 : 2-dicarboxylic anhydride, m.p. 260° (corr.). L. S. T.

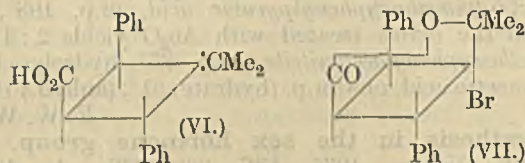
Diphenylmalonic acid. H. J. MORSMAN (Helv. Chim. Acta, 1935, 18, 1466—1468).—Prolonged shaking with H_2O converts $\text{CPh}_2(\text{COCl})_2$ into cryst. diphenylmalonic acid, m.p. indefinite owing to rapid loss of CO_2 to give $\text{CHPh}_2 \cdot \text{CO}_2\text{H}$. J. W. B.

Degradation of γ -truxillic acid to a diphenylcyclobutanemonocarboxylic acid. XVIII. R. STOERMER and H. STROH [with, in part, H. ALBERT]. Unique position of ϵ -truxillic acid; truxillocketones. XIX. R. STOERMER and K. CRUSE. Semitruxonic acids of the truxillic acid series and the missing truxone, *peri*-truxone. XX. R. STOERMER and F. MÖLLER (Ber., 1935, 68, [B], 2102—2111, 2117—2124, 2125—2134).—XVIII. The degradation of γ -truxillic acid without contraction of the ring is effected through the stages: $>\text{CH} \cdot \text{CO}_2\text{H} \rightarrow >\text{CH} \cdot \text{CMe}_2 \cdot \text{OH} \rightarrow >\text{C} \cdot \text{CMe}_2 \rightarrow >\text{CO}$. Treatment of Et H γ -truxillate (I) with MgMeI affords 3 ϵ -*hydr*-



oxyisopropyl-2 ϵ -4'-diphenylcyclobutane-1 ϵ -carboxylic acid (II), m.p. 198° (*Me*, m.p. 102—103°, and *Et*, m.p. 77—78°, ester). Similar treatment of the Et_2 ester leads to 1 ϵ : 3 ϵ -*di*- α -hydroxyisopropyl-2 ϵ : 4'-diphenylcyclobutane (tetramethyl- γ -truxilldiol), m.p. 127—128°, with the lactone (III), m.p. 148°, and ester of (II) into which they are converted by hydrolysis. Under similar conditions, Et H α -truxillate (IV), m.p. 171°, best obtained by partial esterification of the corresponding acid, is transformed into 3 ϵ - α -hydroxyisopropyl-2 ϵ : 4'-diphenylcyclobutane-1 ϵ -carboxylic acid (V), m.p. 174—175° (*Me* ester, m.p.

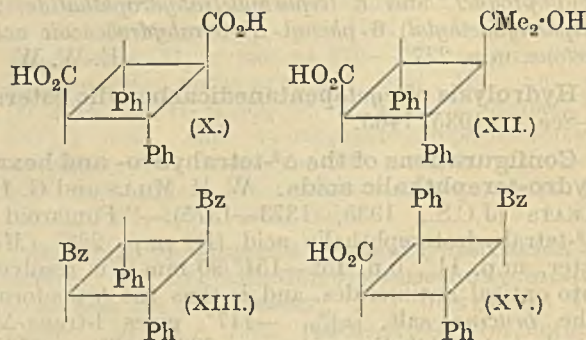
81—82°). (I), Mg, and EtBr give 3^c- α -hydroxy- α -ethyl-*n*-propyl-2^c:4'-diphenylcyclobutane-1'-carboxylic acid, m.p. 216—217° (*Me* ester, m.p. 141°); 3^c- α -hydroxy- α -ethyl-*n*-propyl-2^c:4'-diphenylcyclobutane-1'-carboxylic acid has m.p. 151° (*Me* ester, m.p. 97—98°). Treatment of (II), (III), or (V) with AcOH at 210° yields 3-isopropylidene-2^c:4'-diphenylcyclobutane-1'-carboxylic acid (VI), m.p. 143—144°



(sparingly sol. *Na* salt), best obtained by passing HCl rapidly through a solution of (II) in boiling conc. HCl. It is thus established that there is no alteration in the spatial distribution of the other groups around the cyclobutane ring. Bromination of (VI) in CHCl₃ affords a single, saturated bromolactone [probably (VII)], m.p. 157—158°, which is not debrominated in acid or neutral solution, but with Zn and AcOH or Al—Hg yields small amounts of (VI) and is converted by red P and HI (*d* 1.5) into a Br-free lactone, m.p. 161—162°, probably formed by ring fission, and an acid, C₂₀H₂₁O₂I, m.p. 210—211° (*Na* salt); treatment of it with alkali gives a CO-acid, an unsaturated acid, and a OH-lactone of unexplained structure. Treatment of the diol with AcOH at 210° yields 1:3-diisopropylidene-2^c:4'-diphenylcyclobutane, b.p. 202°/11 mm., ozonised to (?) isopropylidenediphenylcyclobutanone, m.p. 106—109°. Proof that the acid (VI) contains a semicyclic double linking is afforded by the production of COMe₂ after ozonisation. The ozonide decomposes very rapidly in CHCl₃, AcOH, or EtOAc, and when treated with alkali gives phenylbenzylsuccinic acid (VIII), m.p. 183—184° (*Me*, ester, m.p. 125°). If ozonisation is effected in EtOAc and the product is immediately catalytically hydrogenated, diphenylcyclobutanonecarboxylic acid (IX), m.p. 98° (*Me* ester, m.p. 72°; *p*-nitrophenylhydrazone, m.p. 184°), is almost quantitatively obtained; it appears unsaturated towards KMnO₄ and reduces ammoniacal Ag solution, but does not give the Angeli—Rimini test or colour fuchsin—H₂SO₃. If the ozonide is kept overnight, it yields an isomeric acid, m.p. 141—142° (*Me* ester, m.p. 64°), stable in hot C₆H₆ or AcOH, but readily transformed by boiling H₂O or aq. media, or by dissolution in cold Na₂CO₃ or NH₃ and pptn. with acid, into (IX). Reduction of (IX) with a large excess of Zn and HCl leads to 2:4-diphenylcyclobutane-1-carboxylic acid, m.p. 111—112° (anilide, m.p. 165—166°).

XIX. ϵ -Truxillic acid (X) is converted by boiling Ac₂O into the polymeric ϵ -anhydride, transformed by warm NH₂Ph into a mixture of (X), its dianilide, and anilic acid. Repeated distillation of (X) under 0.4 mm. yields *peri*- and γ -truxillic anhydride, thus affording the first instance of a change of the ϵ -configuration. *Me H* ϵ -truxillate (XI), m.p. 131° (*Na* and *Ca* salts), obtained by the action of HNO₂ on *Me* ϵ -truxillanilate or by half-hydrolysis of Me₂ ϵ -truxillate, passes when heated into MeCl and CHPh:CH·CO₂H.

It is considered therefore that monomeric ϵ -truxillic anhydride cannot exist. Interaction of MgMeI and

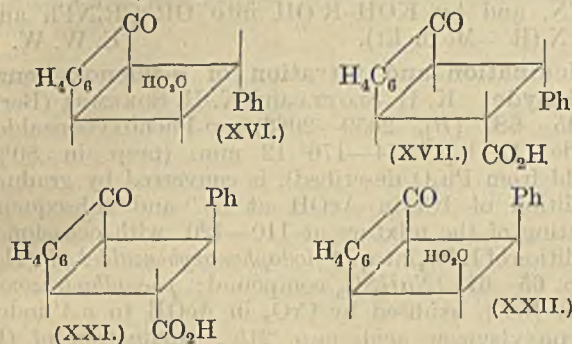


(XI) gives comparatively very large quantities of ϵ -tetramethyltruxilldiol, m.p. 146°, and 3^c- α -hydroxy-isopropyl-2^c:4'-diphenylcyclobutane-1'-carboxylic acid (XII), m.p. 145° (*Ca* salt), which gives CHPh:CH·CO₂H and a non-cryst., non-hydrolysable substance of high b.p. when its dehydration is attempted by the methods used for the γ -acid (see above). Unexpectedly, treatment of (XI) with MgPhBr leads to (X) and 1^c:3^c-dibenzoyl-2^c:4'-diphenylcyclobutane (XIII), m.p. 207—208°, which passes when heated with KOH—EtOH and NH₂OH, but not with KOH—EtOH only, into an isomeric truxillketone, m.p. 222°; both ketones yield Ph styryl ketone when cautiously distilled under atm. pressure.

Treatment of γ -truxillic anhydride (XIV) with AlCl₃ in C₆H₆ at 100° gives 3^c-benzoyl-2^c:4'-diphenylcyclobutane-1'-carboxylic acid (XV), m.p. 227° [sparingly sol. *Na* and NH₄ salts; phenylhydrazone, m.p. 100° (much decomp. with production of lactam); *Me*, m.p. 169°, and *Et*, m.p. 162°, ester], which is depolymerised when heated or treated with conc. H₂SO₄ to CHPh:CH·CO₂H and CHPh:CHBz. The corresponding chloride, m.p. 150—152°, is transformed by AlCl₃ and C₆H₆ into much non-cryst. matter and a substance, m.p. 92—93°. The behaviour of (XIV) towards AlCl₃ and C₆H₆ depends greatly on the quality of the AlCl₃, temp., and duration of action. With somewhat weathered AlCl₃, a truxillketone, m.p. 77—78°, and a substance (C₁₁H₆O₂)_n, m.p. 195° (possibly Stobbe's truxillketone *D*), are obtained in small yield.

XX. Treatment of γ -truxillic acid with HCl and cold MeOH gives the *Me H* ester (very sparingly sol. *Na* salt), converted by SOCl₂ in boiling C₆H₆ into the corresponding chloride, m.p. about 86°, which is transformed by AlCl₃ in CS₂ into *Me* γ -truxonate. The latter is hydrolysed by KOH—EtOH to γ -truxonic acid (XVI), m.p. 152° (*Me* ester, m.p. 127—128°; oxime, m.p. 207°; amide, m.p. 236—237°; phenylhydrazone, m.p. 225°). *Me H* α -truxillate, m.p. 195° (very sparingly sol. *Na* salt), is similarly transformed through the chloride into *Me* α -truxonate, m.p. 186°, hydrolysed by alkali to (XVI), but by boiling AcOH containing a little H₂SO₄ and H₂O to α -truxonic acid (XVII), m.p. 216° (sparingly sol. *Na*, *Ca*, and NH₄ salts; phenylhydrazone, m.p. 239°), converted by SOCl₂ in C₆H₆, and thence by AlCl₃ in CS₂, into α -truxone. *peri*-Truxillic anhydride, m.p. 287°, is best obtained by heating the γ -anhydride under N₂ at about 280°, and converting the crude product by NH₃—EtOH into

peri-truxillamic acid (XVIII), m.p. 256.5° (decomp. in sealed capillary) (NH_4 salt), which is boiled in



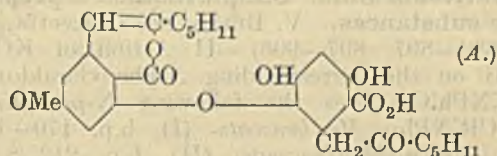
AcOH or treated with HNO_2 in AcOH. It is transformed by CH_2N_2 in $C_2H_4(OH)_2$ into *Me H peri-truxillamate*, m.p. 197—198°, which with HNO_2 in AcOH affords homogeneous *Me H peri-truxillate*. Treatment of (XVIII) with conc. NH_3 at 110° gives unimol. *peri-truxillamide*, m.p. 237°, and *epitruxill-b-amic acid* (XIX), m.p. 263°, whereas with boiling 10% NaOH it yields *epitruxillic acid*, m.p. 286°. With CH_2N_2 in MeOH (XIX) gives *Me epitruxillamate*, m.p. 228°, transformed by HNO_2 in AcOH into *Me H epitruxillate*, m.p. 204.5°, identical with that obtained by half-hydrolysis of Me_2 *epitruxillate*. The isomeric *b-ester* (XX), m.p. 141° (sparingly sol. *Na* salt), is obtained by saturating a suspension of the *epi-acid* in MeOH at 20° with HCl. (XX) is converted by $SOCl_2$ and thence by the Friedel-Crafts reaction into *Me epitruxonate*, m.p. 106—107, smoothly hydrolysed by KOH-MeOH to *epitruxonic acid* (XXI), m.p. 160° [*oxime*, m.p. 260° (decomp.)]. *peri-Truxonic acid* (XXII), m.p. 221—224° [*phenylhydrazone*, m.p. 189° (indef.)], is obtained among other products by the action of $AlCl_3$ in CS_2 on *peri-truxillic anhydride* and is converted through the chloride into *peri-truxone*, m.p. 194°, transformed by $NHPh \cdot NH_2$ in AcOH into the *monophenylhydrazone*, m.p. 217°, and by $NHPh \cdot NH_2$ in N_2 at 150—160° into the *diphenylhydrazone*, m.p. about 280° (decomp.). Its isomerisation into α -truxone by conc. HCl at 180° could not be established definitely. H. W.

Phenylbenzylsuccinic acids. R. STOERMER and H. STROH (Ber., 1935, 68, [B], 2112—2116).— $Et_3 \alpha$ -phenyl- β -benzylethane- $\alpha\beta\beta$ -tricarboxylate, b.p. 232°/3 mm., m.p. 48°, from $CHPhBr \cdot CO_2Et$ and $CH_2Ph \cdot CH(CO_2Et)_2$, is hydrolysed by 18% HCl at 180—190° to phenylbenzylsuccinic acid (I), m.p. 176° (*Me* ester, m.p. 89—90°), whereas hydrolysis with AcOH and 50% H_2SO_4 at 120° leads to the isomeric *phenylbenzylsuccinic acid* (II), m.p. 183—184° (*Me* ester, m.p. 125°, identical with that obtained by degradation of diphenylcyclobutanonecarboxylic acid obtained from α - or γ -truxillic acid (preceding abstract). Short treatment of (II) with boiling $AcCl$ leads to the corresponding *anhydride*, m.p. 92°, whereas (I) with warm $AcCl$ affords a non-cryst. mixture of anhydrides converted by H_2O into a mixture of (I) and (II). Boiling Ac_2O containing NaOAc converts either acid into *phenylbenzylangelic-lactone* (III), $CH_2Ph \cdot CH \cdot CO \cdot O \cdot CPh \cdot CMe$, m.p. 96°, hydro-

lysed by KOH-MeOH to β -phenyl- α -benzyl-lævulic acid, m.p. 120—121° (*Me* ester, m.p. 81—82°), transformed by $NHPh \cdot NH_2$ in AcOH into 2:5-diphenyl-4-benzyl-6-methylpyridazin-3-one, m.p. 148—149°, and oxidised by NaOBr to (I). The change is therefore $CO_2H \cdot CH(CH_2Ph) \cdot CHPh \cdot CO_2H \rightarrow CO_2H \cdot CH(CH_2Ph) \cdot CPhAc \cdot CO_2H \rightarrow CO_2H \cdot CH(CH_2Ph) \cdot CHPhAc \rightarrow$ (III). This view is supported by the observation that whereas $CH_2Ph \cdot CH_2 \cdot CO_2H$ is stable towards boiling Ac_2O containing NaOAc, $CH_2Ph \cdot CO_2H$ is converted into $CH_2Ph \cdot COMe$ in very good yield. H. W.

Oxidation of bisphenylpyruvic [α -hydroxy- γ -keto- β -phenyl- α -benzylglutaric] acid. J. JARROUSSE (Compt. rend., 1935, 201, 676—677).—Bisphenylpyruvic acid with $KMnO_4$ in alkali at 0° affords $\alpha\gamma$ -diketo- $\beta\delta$ -diphenylvaleric acid, which easily loses CO_2 to give β -keto- $\alpha\gamma$ -diphenylbutaldehyde, m.p. 114° [*semicarbazone*, m.p. 200° (decomp.)], oxidised by I in presence of Na_2CO_3 to a substance, m.p. 190° (decomp.). J. L. D.

Lichen substances. LIX. Non-existence of γ -collatolic acid. LX. Microphylllic acid and its fission products. LXI. Olivetoric acid. III. Y. ASAHINA and F. FUJIKAWA (Ber., 1935, 68, [B], 2020—2021, 2022—2025, 2026—2028).—LIX (cf. A., 1933, 713).— α -Collatolic acid (I) in moderately conc. $NaHCO_3$ solution is slowly converted into β -collatolic acid (II). (II) is not a natural product, but is formed during the alkaline hydrolysis of *Me* α -collatolate. *Me* β -collatolate, m.p. 75°, is formed by the restricted action of CH_2N_2 on (II), whereas prolonged action gives the *Me* ester *Me*₂ ether (III), m.p. 114°, also obtained similarly from (I). γ -Collatolic acid is (II) more or less contaminated with (I), since homogeneous (II) can be isolated therefrom by crystallisation from C_6H_6 , and treatment of it with an excess of CH_2N_2 gives (III). (II) has therefore structure A.



LX (cf. A., 1935, 490). Microphylllic acid (IV), m.p. 116°, is transformed by boiling HCO_2H into olivetonide (V) and olivetonide *p*-Me ether (VI). (IV) and Ac_2O containing a little conc. H_2SO_4 afford *anhydrodiacetylmicrophylllic acid*, m.p. 98°. Hydrolysis of (IV) with 11% NaOH gives (VI) and *olivetonic acid* (VII), m.p. 159—160° (*Me* ester, m.p. 85—86°), also obtained by the action of KOH on (V). (IV) is decomposed by excess of CH_2N_2 , but treatment with Ag_2O and MeI gives *Me microphyllate Me*₂ ether (VIII), m.p. 89—90°, hydrolysed by boiling 95% HCO_2H to *olivetonide Me*₂ ether, m.p. 94° [also obtained by treatment of (VI) with Ag_2O and MeI], and *olivetonide o*-Me ether, m.p. 146—147°, converted by CH_2N_2 into (VIII). The following derivatives of (V) and (VII) are described: *p*-acetylolivetonide, m.p. 55°, and its *o*-Me ether, m.p. 84°, obtained by means of Ag_2O and MeI; *diacetylolivetonide*, m.p. 59°; *o*-acetylolivetonide *p*-Me ether, m.p. 60—61°;

olivetic acid *p*-, m.p. 94—95°, and *o*-Me ether, m.p. 119—120°; Me olivetate Me ether, m.p. 80°.

LXI. Extraction of the thalli of *Parmelia olivetorum*, Nyl, with Et₂O and treatment of the extract with NaHCO₃ yields (?) chloroatranorin and olivetoric acid, m.p. 150—151°. The latter is converted by cautious treatment with CH₃N₂ into the Me ester, m.p. 134°, and by Ag₂O and MeI into Me olivetorate Me₂ ether, m.p. 4—7.5°, alkaline hydrolysis of which affords olivetonic acid Me₂ ether, m.p. 92°, and olivetolcarboxylic acid *o*-Me ether, m.p. 105°. H. W.

Bile acids. XLVII. Preparation of the compound C₂₄H₃₀O₁₀N₂ (bilianic acid series). M. SCHENCK (*Z. physiol. Chem.*, 1935, 237, 105—112).—The ketolactamtricarboxylic acid, C₂₄H₃₅O₈N (A., 1931, 841), purified by KMnO₄ in aq. Na₂CO₃, yields with 57% HNO₃ the compound C₂₄H₃₀O₁₀N₂ (I), which with hot 90% H₂SO₄ affords the "β-acid," C₂₄H₃₀O₁₀N₂, decomp. 203° (A., 1930, 1435), and with hot HCl, the aminoamide, C₂₄H₃₈O₁₁N₂. The data support a lactamamide rather than the aminonitrile structure for (I) (cf. A., 1932, 742).

F. O. H.

Cannizzaro reaction. C. D. NENITZESCU and I. GAVAT (*Bul. Soc. Chim. România*, 1934, 16, [A], 42—46).—The velocity of the Cannizzaro reaction with PhCHO in 80% MeOH at 20° is greatly increased by increase in the concn. of KOH from 0.5*N* to 4.6*N* and slightly (catalytically) by Cu at 50°. NMe₃·Et·OH effects the reaction, but Na₂CO₃ and Na₂HPO₄ do not. Equimol. mixtures of PhCHO with CH₂O or OMe·C₆H₄·CHO give both pairs of acids and alcohols. A large excess of CH₂O gives almost exclusively HCO₂H and the aromatic alcohol (CH₂Ph·OH, OMe·C₆H₄·CH₂·OH, or *m*-NO₂·C₆H₄·CH₂·OH).

R. S. C.

Nitrones. A new transposition reaction. II. III. Transformation [of oximes] into cyano-derivatives of anils. Simple method of preparing these substances. V. BELLAVITA (*Gazzetta*, 1935, 65, 889—897, 897—906).—II. Action of KCN in MeOH on the corresponding *N*-phenylalaldoximes, CHR·NPh·O, gives the following *N*-phenylimides, OMe·CR·NPh. Me benzoate- (I), b.p. 170—175°/9 mm., Me *p*-chlorobenzoate- (II), b.p. 212°/8 mm. (obtained from *N*-phenyl-*p*-chlorobenzaldoxime, m.p. 153—154°), Me anisate- (III), b.p. 212°/8.5 mm.; Me cinnamate- (IV), m.p. 70°, Me piperonylate-, b.p. 227°/7 mm., and Me piperonylacrylate-, b.p. 242°/5 mm., -*N*-phenylimides. These are hydrolysed to the ester (or acid), and aniline; (I) to (IV) also give the anilide.

III. *N*-Phenylbenzaldoxime triturated with KCN in MeOH at room temp. yields ω-cyanobenzaldanil, CN·CPh·NPh, m.p. 73.5°, an intermediate compound of the reaction described in the preceding abstract. The following are prepared similarly. ω-Cyano-*p*-chlorobenzaldanil, m.p. 108° (converted by KOH·EtOH into Et *p*-chlorobenzoate-*N*-phenylimide, b.p. 190—192°/10 mm.); ω-cyano-*o*-, -*m*-, and -*p*-nitrobenzaldanil, m.p. 105—106°, 101—102°, and 126.5°, respectively; ω-cyanosalicylaldanil, m.p. 96°; ω-cyanocinnamaldanil, m.p. 73—74°; ω-cyanoanisaldanil, m.p. 119°; ω-cyanopiperonaldanil, m.p. 139—140°;

and ω-cyanopiperonylacaldanil, m.p. 160—161°. These compounds are converted by acid into NH₂Ph and R·CN, and by KOH·R'OH into OR'·CR·NPh and KCN (R' = Me or Et).

E. W. W.

Iodination and nitration of *p*-phenoxybenzaldehyde. K. H. SLOTTA and K. H. SOREMBÄ (*Ber.*, 1935, 68, [B], 2059—2066).—*p*-Phenoxybenzaldehyde (I), b.p. 174—176°/12 mm. (prep. in 80% yield from Ph₂O described), is converted by gradual addition of ICl in AcOH at 50° and subsequent heating of the mixture at 110—120° with occasional addition of HIO₃ into *p*-4'-iodophenoxybenzaldehyde (II), m.p. 65—67° (NaHSO₃ compound; phenylhydrazone, m.p. 150°), oxidised by CrO₃ in AcOH to *p*-4'-iodophenoxybenzoic acid, m.p. 215°. Iodination of (I) could not be effected with I+HIO₃ in aq. EtOH and (II) is not formed by treatment of *p*-C₆H₄I·OPh with AlCl₃, HCl, and HCN. Nitration of (II) with conc. H₂SO₄-HNO₃ (*d* 1.41) gives a complex mixture of products, whereas addition of (II) to HNO₃ (*d* 1.410) at 15° affords *p*-4'-nitrophenoxybenzaldehyde, m.p. 107—108° (phenylhydrazone, m.p. 160°), also obtained with *p*-2'-nitrophenoxybenzaldehyde, m.p. 84—86°, from *p*-C₆H₄Cl·NO₂ and *p*-OH·C₆H₄·CHO. Under defined conditions (I) is transformed by H₂SO₄-HNO₃ into 3':2':4'-trinitro-4-phenoxybenzaldehyde (III), m.p. 169° (phenylhydrazone, m.p. 190—192°), also obtained by nitration of 2':4'-dinitro-4-phenoxybenzaldehyde; its constitution follows from its non-identity with 2':4':6'-trinitro-4-phenoxybenzaldehyde, m.p. 128° (phenylhydrazone, m.p. 225°), derived from picryl chloride and *p*-OH·C₆H₄·CHO. Oxidation of (III) with CrO₃ in AcOH affords 3':2':4'-trinitro-4-phenoxybenzoic acid, m.p. 205—207°, converted by NaOH into 2:4-(NO₂)₂C₆H₃·OH and 3-nitro-4-hydroxybenzoic acid.

H. W.

Synthesis of polyterpenoid compounds. II. J. W. COOK and C. A. LAWRENCE (*J.C.S.*, 1935, 1637—1638; cf. A., 1935, 756).—β-Δ¹-cyclohexenylethyl bromide (improved prep.) when heated (water-bath; 120 hr.) with CHK(CO₂Et)₂ in C₆H₆ affords Et β-(Δ¹-cyclohexenylethyl)malonate, b.p. 148°/1—1.5 mm., hydrolysed to the acid, m.p. 123—124°, which when heated at 180° for ¼ hr. and distilled in vac. yields γ-Δ¹-cyclohexenylbutyric acid, b.p. 122—125°/0.8 mm. (*p*-phenylphenacyl ester, m.p. 79.5—81°). This was converted into the acid chloride which with CS₂-SnCl₄ at -7° to -10° yields Δ^{9:10}-α-octalone (A., 1933, 704).

H. G. M.

Nitro- and bromonitro-derivatives of *p*-aminoacetophenone. C. W. RAADSVELD (*Rec. trav. chim.*, 1935, 54, 813—827).—With HNO₃ (*d* 1.52) at -15° to -20° *p*-C₆H₄Ac·NHAc affords its 3-NO₂ and 3:5-(NO₂)₂-derivatives, but with HNO₃-Ac₂O at 0° a 90% yield of the 3-NO₂-compound (I) is obtained. With HNO₃-H₂SO₄ at 100° picric acid is the only product isolated. Me *p*-acetylphenylcarbamate, m.p. 162° [obtained from *p*-C₆H₄Ac·NH₂ (II) and ClCO₂Me·Na₂CO₃ in boiling Et₂O], with HNO₃ (*d* 1.45) gives its 2-NO₂-derivative (III), m.p. 107°, but with HNO₃ (*d* 1.52) at 0° the 2:6-(NO₂)₂-derivative (IV), m.p. 213°, is obtained. Et *p*-acetylphenylcarbamate, m.p. 159°, and its 2-NO₂- (V), m.p. 111°, and 2:6-(NO₂)₂-derivative (VI), m.p. 176°, are similarly obtained.

If the nitration products of these carbamates are heated to 50° before pouring on ice, *substances*, m.p. 200° and 135°, respectively (from the Me ester), and m.p. 153° and 113° (Et ester), are obtained. Nitration of *N*-4-acetylphenyl-*N'*-ethylcarbamide, m.p. 157° [from (II) and EtNCO in dry C₆H₆ at 100°] with HNO₃ (*d* 1.45) at 0° affords *N*-(2-nitro-4-acetyl)-*N'*-nitro-*N'*-ethylcarbamide, C₆H₄Ac(NO₂)·NH·CO·NEt·NO₂ (VII), m.p. 91°, whereas HNO₃ (*d* 1.52) gives the corresponding 2 : 6-NO₂-nitroamine (VIII), m.p. 120° (decomp.), converted by the appropriate ROH, respectively, into carbamates. Hydrolysis of (VII) with boiling aq. COMe₂, of (III) or (V) with conc. H₂SO₄ at 100°, or of (I) with boiling 6*N*-HCl, affords 3-nitro-4-aminoacetophenone (VIII), the 3 : 5-(NO₂)₂-derivative, m.p. 176° (*Ac* derivative, m.p. 222°; cf. above), being obtained similarly from (IV) or (VI). Bromination of *p*-C₆H₄Ac·NHAc gives the 3-Br-compound, hydrolysed by 6*N*-HCl to the hydrochloride, decomp. < 100° (Raiford *et al.*, A., 1928, 303, give m.p. 155–156°), of 3-bromo-4-aminoacetophenone, but with Br–AcOH at 100° the *ω*-Br-compound is obtained. *p*-C₆H₄Ac·NH₂ with CH₂Br·COCl–AcOH–NaOAc at 0° gives *p*-bromoacetamidoacetophenone, m.p. 157°. With HNO₃ (*d* 1.52) at –10° to –15°, 3-bromo-4-acetamidoacetophenone gives its 5-NO₂-derivative, m.p. 203°, hydrolysed (conc. H₂SO₄ or 6*N*-HCl in presence of EtOH) to 3-bromo-5-nitro-4-aminoacetophenone, m.p. 181°, also obtained by the action of Br–AcOH on (VIII). The structures of these derivatives are confirmed by elimination of the NH₂ group after diazotisation, to give known CPhMe derivatives.

J. W. B.

Derivatives of *p*-aminoacetophenone. C. W. RAADSVELD (Rec. trav. chim., 1935, 54, 827–832).—Condensation of *p*-C₆H₄Ac·NH₂ (I) with the appropriate carbimide affords *p*-acetylphenylcarbamide, m.p. 183° (lit., m.p. 148°), *s*-*p*-acetylphenylphenyl-, m.p. 195°, and *s*-*p*-acetylphenyl-*α*-naphthylcarbamide, m.p. 209°. With PhNCS a *substance*, m.p. 195° (not the thiocarbamide), is obtained. Condensation of (I) with the appropriate aromatic compound containing reactive Cl affords *p*-(2 : 4-dinitroanilino)-, m.p. 192° (lit., m.p. 185°), *p*-(2 : 4 : 6-trinitroanilino)-, and *p*-(2 : 4-dinitro-*α*-naphthylamino)-, m.p. 162°, *acetophenone*. With CO(NH₂)₂ at 200–215° (I) gives a *substance*, decomp. 280° (block), and, with CS₂–EtOH–KOH, a yellow *substance*, m.p. 230–235°. The following ketazines (with N₂H₄, H₂SO₄) and phenylhydrazones are prepared: the *ketazine* of 3-nitro-4-amino-, m.p. 350° (*phenylhydrazone*, m.p. 135–138°); 3-nitro-4-acetamido-, m.p. 270° (*phenylhydrazone*, m.p. 160°); 3 : 5-dinitro-4-amino-, m.p. 345° (*phenylhydrazone*, m.p. 245°); 3-bromo-4-acetamido-, m.p. 80°; 5-bromo-3-nitro-4-amino-, m.p. 315° (*phenylhydrazone*, m.p. 80°); and 5-bromo-3-nitro-4-acetamido-, m.p. > 350°, *acetophenone*.

J. W. B.

Bromination of cholestanone and coprostanone; Δ^{1:2}-cholesten-3-one. A. BUTENANDT and A. WOLFF (Ber., 1935, 68, [B], 2091–2094).—The action of 1 mol. of Br on 3-keto-compounds of the sterol group results preferentially in substitution at C₂ or C₄ according as the initial ketone belongs to

the dihydrocholesterol (*allo* or *trans*) or the coprosterol (*cis*) series. Treatment of coprostanone with Br in AcOH containing traces of HBr gives 4-bromocoprostanone, m.p. 110–111°, converted by boiling anhyd. C₅H₅N into cholestenone, m.p. 79–80° (yield 30%). Under similar conditions, cholestanone affords 2-bromocholestanone, m.p. 169–170° (apparently not homogeneous), largely resinified by boiling quinoline and transformed by boiling anhyd. C₅H₅N into a *compound*, m.p. > 300°. It is converted by AcOH–KOAc at 200° into Δ^{1:2}-cholesten-2-one, m.p. 111–112°, [α]_D²⁰ –32.1° in EtOH (*oxime*, m.p. 146–147°). H. W.

Substituted unsaturated cyclic ketones. A. COHEN and J. W. COOK (J.C.S., 1935, 1570–1572).—Unsaturated cyclic ketones are obtained by elimination of HCl from nitrosochlorides and hydrolysis of the resulting oximes. 1-β-Phenylethyl-Δ¹-cyclohexene nitrosochloride, m.p. 139–140° (lit. 118–119°), when boiled with C₅H₅N for 2.5 hr. yields 2-β-phenylethyl-Δ²-cyclohexenoneoxime, m.p. 118–120°, hydrolysed by boiling 6*N*-H₂SO₄ to the *ketone*, b.p. 125–130°/0.7 mm. (*semicarbazone*, m.p. 188–190°). Similarly 1-(β-1'-naphthylethyl)-Δ¹-cyclopentene nitrosochloride, m.p. 108–110° (obtained from the cyclopentene, AcOH, Et₃O, amyl nitrite, and HCl), when boiled with C₅H₅N for 5 min. affords 2-(β-1'-naphthylethyl)-Δ²-cyclopentenoneoxime, m.p. 106.5–107.5°, hydrolysed to the *ketone*, b.p. 165–167°/0.3 mm. (*semicarbazone*, m.p. 226–227°), which gave no castrous response when injected into ovariectomised mice. All attempts to cyclise these ketones failed.

H. G. M.

Benzanthrone derivatives. III. Autoxidisable dihydrobenzanthrone. E. CLAR (Ber., 1935, 68, [B], 2066–2070; cf. A., 1932, 1134).—Benzanthrone (I) is reduced by Zn dust in boiling AcOH to dihydrobenzanthrone (II), m.p. 150–152° when rapidly heated under CO₂ in a sealed capillary, which is very sensitive to air, adds 2 O in xylene, immediately decolorises 2 Br, and becomes disproportioned by strong acids or weak bases or when heated at 150° to (I) and 9-hydroxy-1 : 10-trimethylenephenanthrene. Oxidation is accelerated by light and occurs most rapidly in AcOH, but then requires only 1.6 O. A peroxide could not be isolated, but the solutions retain peroxidic properties. Apparently in xylene the active O is imparted to the hydrocarbon and does not further affect unaltered (II), whereas in AcOH H₂O₂ is formed which transforms (II) into (I). (II) gives an *acetate*, m.p. 159–161° in sealed capillary filled with CO₂. The intermediate occurrence of an orange colour during the reduction of (I) indicates the possible formation of a H₁-derivative similar to that, m.p. 120–125° in sealed tube under CO₂, obtained by mixing equimol. amounts of (I) and (II) in hot AcOH under CO₂. Bz-1-Bromodihydrobenzanthrone has m.p. 167° (decomp.). H. W.

Condensation of phthalic anhydride with *s*-octahydrophenanthrene. E. DE B. BARNETT, N. F. GOODWAY, and C. A. LAWRENCE (J.C.S., 1935, 1684).—*s*-Octahydrophenanthrene and *o*-C₆H₄(CO)₂O with AlCl₃ in C₂H₂Cl₄ yield *o*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrophenanthroylbenzoic acid (I), m.p. 200°.

Similarly the corresponding 4':5'-dichloro-octahydro-phenanthrolylbenzoic acid, m.p. 276° (decomp.), is obtained from 4:5-dichlorophthalic anhydride, but the product from 3:6-dichlorophthalic anhydride could not be crystallised. (I) when heated (water-bath) during 15 hr. with activated Zn dust, NaOH, and $\text{NH}_3\text{-H}_2\text{O}$ yields ω -1:2:3:4:5:6:7:8-octahydrophenanthryl-*o*-toluic acid, m.p. 192°, cyclised by cold, conc. H_2SO_4 to octahydro-1:2:3:4-dibenzanthrone (II), m.p. 200°, converted by $\text{Ac}_2\text{O-C}_5\text{H}_5\text{N}$ into octahydro-1:2:3:4-dibenzanthranyl acetate, m.p. 214°. (II) is oxidised by boiling $\text{CrO}_3\text{-AcOH-H}_2\text{O}$ to octahydro-1:2:3:4-dibenzanthraquinone (III), m.p. 234°, and when boiled (3 hr.) with activated Zn dust, EtOH, H_2O , and KOH is reduced to octahydro-1:2:3:4-dibenzanthracene, m.p. 129°. Attempts to dehydrogenate this with Se, and (III) with Br, failed to yield any pure products. H. G. M.

Carvacrol. V. Benzyl ethers of acylated methylisopropylphenols. H. JOHN and P. BEETZ (J. pr. Chem., 1935, 144, 49—53).—The following ethers are obtained in about 85% yield by the action of CH_2PhCl or $p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Cl}$ on the K salt of the requisite phenol: *p*-acetothymyl CH_2Ph , m.p. 71°, and *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2$, m.p. 104°, ether; *p*-propiothymyl CH_2Ph , m.p. 64°, and *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2$, m.p. 110°, ether; *p*-butyrothymyl CH_2Ph , m.p. 47°, and *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2$, m.p. 91°, ether; *p*-isovalerothymyl CH_2Ph , m.p. 40°, and *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2$, m.p. 84°, ether; *p*-benzoylthymyl *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2$ ether, m.p. 91°, *p*-acetocarvacryl CH_2Ph , m.p. 64°, and *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2$, m.p. 114°, ether; *p*-propiocarvacryl *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2$ ether, m.p. 128°. Glyceryl α -*p*-acetothymyl ether, m.p. 109°, from *p*-acetothymol, $\text{OH}\cdot\text{CH}_2(\text{CH}_2\text{Cl})_2$, and KOH-EtOH, and glyceryl α -*p*-nitro-*p*-acetylthymyl ether, m.p. 95°, are described. H. W.

Action of organo-magnesium compounds on adiponitrile. A. COMPERE (Bull. Soc. chim. Belg., 1935, 44, 523—526).—Adiponitrile with MgEtBr and Et_2O yields C_8H_{16} , 1-imino-2-cyanocyclopentane, and decane- γ -dione; with MgPhBr it gives $\text{COPh}\cdot[\text{CH}_2]_4\cdot\text{COPh}$ and a little Ph_2 , and with $\text{CH}_2\text{Ph}\cdot\text{MgBr}$ it gives α -*p*-diphenyloctane- β - γ -dione, m.p. 72° (disemicarbazone, m.p. 210°). H. G. M.

7-Hydroxy-1-keto-1:2:3:4-tetrahydrophenanthrene. A. BUTENANDT and G. SCHRAMM (Ber., 1935, 68, [B], 2083—2091).—Unlike 1-keto-1:2:3:4-tetrahydrophenanthrene, 7-hydroxy-1-keto-1:2:3:4-tetrahydrophenanthrene (I) is physiologically inactive according to the Allen-Doisy method. 1:6- $\text{NH}_2\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{H}$ is heated with KOH at 250—310° and the product is treated with cold Ac_2O , thus giving 1:6- $\text{NHAc}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$, m.p. 214°, in 36% yield. It is converted by $\text{Me}_2\text{SO-NaOH}$ into 1:6- $\text{NHAc}\cdot\text{C}_{10}\text{H}_6\cdot\text{OMe}$, m.p. 140°, hydrolysed by HCl-EtOH to 6-methoxy- α -naphthylamine (II), m.p. 74° [hydrochloride, m.p. 205—220° (decomp.)], whence 6-methoxy- α -naphthonitrile, m.p. 79°. Treatment of (II) in the usual manner but at the lowest possible temp. gives 1:6- $\text{C}_{10}\text{H}_6\cdot\text{I}\cdot\text{OMe}$ (in 55% yield), the Grignard compound from which is transformed by $\text{CHO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ or $\text{CHO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{MgI}$ into γ -6-methoxy-1-naphthylbutenoic acid, m.p. 156° [*Me*

ester (III), m.p. 60°]. γ -Hydroxy- γ -6-methoxy-1-naphthyl-*n*-butyric acid and the corresponding lactone, m.p. 114°, are obtained as by-products. Hydrogenation of (III) in AcOH (Pt or Pd) and hydrolysis of the product gives γ -6-methoxy-1-naphthyl-*n*-butyric acid, m.p. 149°, cyclised by SnCl_4 at 105° to 7-methoxy-1-keto-1:2:3:4-tetrahydrophenanthrene, m.p. 101°, which with HBr (*d* 1.48) in boiling AcOH yields (I), m.p. 232° (slight decomp.) (*Bz* derivative, m.p. 212°). *Et succinaldehyde semicarbazone* has m.p. 133°. H. W.

Manufacture of polynuclear cyclic ketones.—See B., 1935, 1133.

Sex hormone. VIII. Preparation of testosterone by use of mixed esters. L. RUZICKA, A. WETTSTEIN, and H. KÄGL. **IX. *trans*- Δ^4 -Dehydroandrosterone and the preparation of *trans*- Δ^5 -dehydroandrosterone from stigmaterol.** L. RUZICKA, W. FISCHER, and J. MEYER. **X. Preparation of 17-methyltestosterone and other androstene and androstene derivatives. Relationship between chemical constitution and male hormone activity.** L. RUZICKA, M. W. GOLDBERG, and H. R. ROSENBERG (Helv. Chim. Acta, 1935, 18, 1478—1482, 1483—1487, 1487—1498).—VIII. With $\text{BzCl-C}_5\text{H}_5\text{N}$ *trans*- Δ^5 -androstene-3:17-diol 3-monoacetate (A., 1935, 1371) gives its 17-benzoate, m.p. 180—182°, hydrolysed by KOH-MeOH at room temp. to the -3:17-diol 17-mono-benzoate, m.p. 220.5—222°. Addition of Br-AcOH, followed by oxidation with CrO_3 -90% AcOH, and debromination of the product with NaI-EtOH- C_6H_6 and 2% Na_2SO_3 gives the 17-mono-benzoate, m.p. 194—196° (corr.), of 17-hydroxy- Δ^4 -androstene-3-one (testosterone), which is obtained by hydrolysis with 2% KOH-MeOH.

IX. *trans*- Δ^5 -Dehydroandrosterone (I) (A., 1935, 1125) in Et_2O with EtOH saturated with HCl at 0° gives its hydrochloride, m.p. 156—157°, converted by KOAc-EtOH into *trans*- Δ^4 -dehydroandrosterone, m.p. 128.5—130° [rather less active than (I)]. Oxidation of stigmateryl acetate (hydrobromide, m.p. 160.5—161.5°) by bromination, CrO_3 , and debromination (as for cholesteryl acetate) also gives (I). Stigmaterol with an excess of HCl-Et₂O gives its hydrochloride (*Ac* derivative, m.p. 183—183.5°).

X. (I) (semicarbazone, m.p. 267°) with MgMeI or MgEtI affords, respectively, *trans*- Δ^5 -17-methyl- (II), m.p. 204°, and -17-ethyl-androstene-3:17-diol, m.p. 173°. (II) is converted by bromination, oxidation with CrO_3 , and debromination with Zn into 17-hydroxy-17-methyl- Δ^4 -androstene-3-one (17-methyl-testosterone), m.p. 163—164°. Oxidation of methyl-androstanediol (A., 1935, 1125) with $\text{CrO}_3\text{-AcOH}$, gives 17-hydroxy-17-methyl-androstan-3-one, m.p. 192—193° (semicarbazone, m.p. 235—236°). Reduction of *trans*-androstene-3-hydroxy- α -allocholan-17-one (III) (semicarbazone, m.p. 282—283°) with $\text{H}_2\text{-PtO}_2$ in AcOH and hydrolysis (some acetate formed) gives *trans*-androstane-3:17-diol, m.p. 168° (*Ac*, derivative, m.p. 127—128°). With MgMeI or MgEtI (III) gives, respectively, *trans*-17-methyl-, m.p. 211—212°, and -17-ethyl-androstane-3:17-diol (IV), m.p. 204—205°. Oxidation of (IV) with CrO_3 -

AcOH affords 17-hydroxy-17-ethylandrostan-3-one, m.p. 137—138°. Androsterone and MgEtI afford cis-17-ethylandrostan-3:17-diol, m.p. 143—144°. The relationship between physiological activity (on the basis of both the cock's comb and rat tests) and (a) the *cis*- or *trans*-configuration, or the presence of a double linking at C₅, or (b) the nature and configuration of substituents at C₃ and C₁₇, for these and other known androstane derivatives, is summarised and discussed.

J. W. B.

Sexual hormones and related substances. V. *epi*Dihydrocinchol and its oxidation to 3-*epi*-hydroxyætiolcholan-17-one (androsterone). W. DIRSCHERL (Z. physiol. Chem., 1935, 237, 52—56).—Oxidation of dihydrocinchol (I) (from hydrolysis of acetyldihydrocinchol; A., 1935, 1242) by CrO₃ yields dihydrocinchone, m.p. 163° (all m.p. corr.), [α]_D²⁵ +42° in CHCl₃, which on reduction (Pt-H₂) affords *epidihydrocinchol* (II), m.p. 206°, [α]_D²⁵ +26° in CHCl₃ [obtained directly from (I) by reduction with NaOEt at 215° and subsequent isolation as digitonide]. Oxidation of the *Ac* derivative, m.p. 90°, [α]_D²⁵ +28.4° to +29.4° in CHCl₃, of (II) with CrO₃ yields 3-*epiacetoxyætiolcholan*-17-one, the *semicarbazone*, m.p. 284—285°, of which is converted by AcOH-HCl followed by hydrolysis into 3-*epi*hydroxyætiolcholan-17-one (cf. *ibid.*; A., 1934, 1221).

F. O. H.

Dehydroandrosterone. A. BUTENANDT, H. DANNENBAUM, G. HANISCH, and H. KUDSZUS (Z. physiol. Chem., 1935, 237, 57—74).—Dehydroandrosterone (I) (A., 1935, 413, 1125) [benzoate, m.p. 250° (all m.p. uncorr.); acetate, m.p. 168—169°, [α]_D²⁵ +3.9° in EtOH; oxime, m.p. 188—191°; semicarbazone, decomp. 262—264°] exists in polymorphic modifications, e.g., m.p. 137—138° and 180°, the latter showing marked depression on irradiation by arc or sun-light. All forms have [α]_D²⁵ +10.9°±0.7° in EtOH. (I) is separated from the CHCl₃-sol. unsaponifiable matter of men's urine by pptn. with digitonin; this yields a cryst. mixture from which cholesterol and, by means of the semicarbazone, (I) are isolated. Treatment of (I) with MeOH-HCl, pptn. by digitonin, etc. affords the chloroketone, C₁₉H₂₇OCl (A., 1935, 413), also prepared by treating (I) with SOCl₂ in presence of dry CaCO₂ and Et₂O. Hydrogenation (Pd-CaCO₃) of (I) in MeOH yields *isoandrosterone* (A., 1935, 1033). Cholesteryl acetate in AcOH treated with Br followed by CrO₃ yields, on debromination etc., 2.78% of (I) and 3-hydroxy-Δ^{5:6}-cholenic acid, m.p. 224° (cf. A., 1935, 1125) (3-OAc-acid, m.p. 181°, and its *Me* ester, m.p. 156—157°). Similarly 3-hydroxy-Δ⁵-bisorcholenic acid (A., 1933, 1290) was prepared from stigmastanol. Both (I) and its acetate have approx. $\frac{1}{3}$ the activity of androsterone by the cock's-comb assay; the benzoate is much less active than (I).

F. O. H.

Androstenedione. Genesis of reproductory hormones. A. BUTENANDT and H. KUDSZUS (Z. physiol. Chem., 1935, 237, 75—88).—Dehydroandrosterone (I) (cf. preceding abstract) with Br and CrO₃ yields a product which on debromination (Zn) affords Δ⁴-androstene-3:17-dione (II), m.p. 173—174°, [α]_D²⁵ +185°, absorption max. at 235 mμ [*di-*

oxime, m.p. 143° (uncorr.)] (cf. A., 1935, 1125, 1242). (II) has no sp. progesterone activity, whilst the cock's-comb test indicates a ratio of activities for (I), (II), and androstanediol (A., 1935, 1033) of 1:3:9 (cf. A., 1935, 1285). (II), unlike related compounds, is more active by the "capon unit" than the "mouse unit." The physiological activity of (II) appears to be especially of a "male" character; its relation to other sex hormones and its possible conversion into testosterone (A., 1935, 1370) and, by loss of CH₄, into œstrone are discussed.

F. O. H.

Testosterone. Conversion of dehydroandrosterone into androstenediol and testosterone. Preparation of testosterone from cholesterol. A. BUTENANDT and G. HANISCH (Z. physiol. Chem., 1935, 237, 89—97).—Testosterone (I) (A., 1935, 1033) is identical with Δ⁴-androsten-17-ol-3-one (*ibid.*, 1370), and hence can be synthesised from cholesterol. Growth of cocks' combs indicates that the ratio of activities of (I), androstanediol, and androsterone is approx. 6:2:1. (I) has also a much greater action on the genital organs of male rats.

F. O. H.

Catalytic hydrogenation of progesterone. A. BUTENANDT and G. FLEISCHER (Ber., 1935, 68, [B], 2094—2097).—Hydrogenation of progesterone (PtO₂ in AcOH) gives a mixture of diols (I) oxidised by CrO₃ in AcOH to *allopregandione* and *pregnandione*. Similar reduction of pregnen-3-ol-20-one affords (I) almost exclusively. In acid solution, therefore, the compounds behave as expected from their constitutions. Contrary to Slotta *et al.* (A., 1935, 128), there is no evidence of the production of a new diketone, m.p. 188°.

H. W.

New members of the androsterone group. A. BUTENANDT, K. TSCHERNING, and G. HANISCH (Ber., 1935, 68, [B], 2097—2102).—*iso*Androsterone (I) is reduced by Na and Pr^oOH or by Al-Hg to *isoandrostanediol* (II) [*alloætiolcholan*-3:17-diol], m.p. 164°, [α]_D²⁵ +4.2° (*diacetate*, m.p. 123—124°), which does not yield a sparingly sol., additive compound with digitonin and which somewhat exceeds (I) in physiological activity. *iso*Androstanediol diacetate is partly hydrolysed and the monoacetate is oxidised by CrO₃ to androstan-17-ol-3-one acetate, the semicarbazone of which is hydrolysed to *androstan-17-ol-3-one* (III) [*alloætiolcholan-17-ol-3-one*], m.p. 178°, [α]_D²⁵ +32.4° in EtOH (*acetate*, m.p. 157°; *oxime*, m.p. 209°), also obtained, together with (II), by hydrogenation (Pd sponge in Et₂O) of testosterone (IV). Physiologically (III) is more active than androsterone. Reduction of (IV) with Al(OPr^o)₃ affords Δ^{4:5}-androstene-3:17-diol, m.p. 155.5°, which gives a yellow colour with C(NO₂)₄, a violet colour with CCl₃-CO₂H, and an additive compound with digitonin; it has little physiological activity.

H. W.

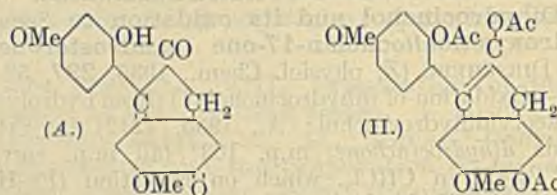
Examination of products obtained in the preparation of ketones by the Friedel-Crafts reaction from acid chlorides and ethers of phenols. Synthesis of ketones of the naphthalene series. P. E. POPOV (J. Gen. Chem. Russ., 1935, 5, 986—992).—*o*-C₁₀H₇-OMe and AcCl in CS₂ with AlCl₃ afford chiefly 1-methoxy-4-acetylnaphthalene, to-

gether with 2:4-diacetyl- α -naphthol, m.p. 139—140°, also obtained from 4-acetyl- α -naphthol as above. Under analogous conditions, α -C₁₀H₇·OEt and BzCl yield chiefly 1-ethoxy-4-benzoylnaphthalene, together with 4-benzoyl-, m.p. 164—165°, and 2:4-dibenzoyl- α -naphthol, m.p. 138—139°. 2-Acetyl- α -naphthol and BzCl with AlCl₃ afford 4-benzoyl-2-acetyl- α -naphthol, m.p. 131—132°. R. T.

2:6-Dibenzoylquinol. O. DISCHENDORFER and A. VERDINO (Monatsh., 1935, 66, 255—285).—Doebner and Wolff's reaction product from *p*-C₆H₄(OH)₂ and BzCl (A., 1879, 638) is not, as regarded by Bogert and Howells (A., 1930, 477), 2:5-dibenzoylquinol (I) (cf. this vol., 82), but 2:6-dibenzoylquinol (II), as is shown by synthesis. The formation of (II) rather than (I) is in any case to be expected. (I) is prepared by Doebner's method. It is oxidised by alkaline KMnO₄ to BzOH, the absence of C₆H₄(CO₂H)₂ showing the absence of condensed rings. It gives Ac₂, m.p. 146°, and *x*-Br-, m.p. 140—141°, derivatives, and a Me₁ ether (III), new m.p. 101° (*Ac* derivative, m.p. 105°), and is oxidised by the method of Bogert (*loc. cit.*) to 2:6-dibenzoylbenzoquinone (IV), new m.p. 162°. To establish that the second Bz in (II) is not attached to a C of the first Bz, COPh₂, BzCl, and AlCl₃ were heated at 190—200°, and gave 1:3-C₆H₄Bz₂ and some 1:3:5-C₆H₃Bz₃. Attempted synthesis from *m*-C₆H₄(CO₂H)₂ failed. 5-Nitrosophthalic acid was converted into the chloride, and this by C₆H₆ and AlCl₃ in CS₂ into 5-nitro-1:3-dibenzoylbenzene, m.p. 130°. This is reduced by Na in MeOH to 3:5:3':5'-tetrabenzoylazoxybenzene, m.p. 202° to a cloudy liquid, clearing at 219°, and by SnCl₂ in AcOH to 3:5-dibenzoylaniline (V), m.p. 129—130° [hydrochloride, m.p. about 185°; sulphate; Ac, m.p. 147°, and Bz, m.p. 152—153°, derivatives; 2:4:6-Br₃-derivative, m.p. 235° (*Ac* derivative, m.p. 215°)]. The benzylidene derivative, m.p. 124°, of (V) is converted by HNO₃ into 2:4(or 2:6)-dinitro-3:5-dibenzoylaniline, m.p. 197°. Diazotisation of (V) yields 3:5-dibenzoylphenol (VI), m.p. 135° (*Ac* derivative, m.p. 138—139°; 2:4:6-Br₃-derivative, m.p. 216°). Attempts to isolate the 4-NO₂-derivative of (VI) having failed, (VI) was oxidised by K₂S₂O₈ [which converts *o*-cresotic acid into 2:5-dihydroxy-3-methylbenzoic acid (Ac₂ derivative, m.p. 150°)], and gave a very small quantity of (IV), identical with that obtained from (I). As additional evidence, 2-hydroxy-5-methoxybenzophenone was condensed with benzoïn to 5-methoxy-7-benzoyl-2:3-diphenylcoumarone (VII), m.p. 155°, together with 2-hydroxy-5-methoxy-4(or 6)-desylbenzophenone, m.p. 232° (decomp.) (*Ac* derivative, m.p. 168°). Oxidation (CrO₃) of (VII) gives (III), identical with that from (I). Thus the structure of (I) is established, and the other compounds described by Bogert (*loc. cit.*) are 2:6-dibenzoylquinol Me₂ ether, 2-anilino-3:5-dibenzoylquinol, and the triacetate of 2-hydroxy-3:5-dibenzoylquinol; the views of Bogert (*loc. cit.*) on the structure of Koznievski and Marchleviski's "Pechmann dye" now lose their foundation. E. W. W.

Quinoid oxidation products in the brazilin series. T. PFEIFFER and P. SCHNEIDER [with, in

part, H. KOB] (J. pr. Chem., 1935, [ii], 144, 54—62).—The main product of the oxidation of trimethyldeoxybrazilin is the colourless trimethylbrazilone, but small amounts of a red quinone (I), C₁₇H₁₄O₅, m.p. 241° (yellow *Ac* derivative, m.p. 158—160°; violet monoxime), are also produced. The colour, solubility in KOH-EtOH with transient green colour, and degradation by H₂O₂ to 2-hydroxy-4-methoxybenzoic acid establish the constitution *A* for it, thus supporting Robinson's formulation of brazileïn. Reductive acetylation (Ac₂O-NaOAc-Zn dust) of



(I) leads to the substance (II), m.p. 139°, the structure assigned to which is supported by the observation that 2-phenylindan-1-one is smoothly converted into an *Ac* derivative, C₆H₄ $\left\langle \begin{array}{c} \text{CH}_2 \\ \text{C}(\text{OAc}) \end{array} \right\rangle$ CPh, m.p. 109—110°, into which it is readily re-converted by hydrolysis with 30% KOH-MeOH. Bromotrimethyldeoxybrazilin (Pfeiffer *et al.*, A., 1934, 780) is similarly oxidised to a *Br*-quinone, C₁₇H₁₃O₅Br, m.p. 215° (*Ac* derivative, m.p. 208—210°). H. W.

Reaction of glyoxal with dimethyldihydroresorcinol. A. REZEK (Bull. Soc. Chim. Yougoslav., 1935, 6, 115—120).—Methone and glyoxal in EtOH-Et₂O at the b.p. in presence of P₂O₅ yield $\alpha\alpha\beta\beta$ -tetra-(2-hydroxy-6-keto-4:4-dimethyl-3:4:5:6-tetrahydrophenyl)ethane, m.p. 235—236°. R. T.

Diene synthesis. B. A. ARBUZOV, E. P. SALMINA, and O. M. SCHAFSCHINSKAJA (Trans. Butlerov Inst. Chem. Tech. Kazan, 1934, No. 2, 9—18).—Condensation could not be effected of maleic anhydride with 1-vinylnaphthalene (I) at 100° or with Ph₂ at 170—215°, or between benzoquinone and Ph₂. Citraconic anhydride did not react with CPh₂:CH₂ at 150°. During the prep. of (I) by the method of Tiffeneau and Daudel (A., 1908, i, 972), α -1-naphthyl-ethyl alcohol, m.p. 64°, b.p. 170—175°/35—40 mm., was obtained. CH. ABS. (r)

Halochromism of 5-benzoyl-1:4-naphthaquinol. R. SCHOLL, J. DONAT, and S. HASS (Ber., 1935, 68, [B], 2034—2039).—5-Benzoyl-1:4-naphthaquinol (I) does not resemble 1-benzoylanthraquinone and -anthraquinol in yielding halochromic salts of a furan derivative when treated with Al powder in conc. H₂SO₄, but nevertheless forms strongly halochromic salts. 5-Benzoyl-1:4-naphthaquinone, m.p. 152°, obtained in 25% yield by oxidation of 1-C₁₀H₇Bz in AcOH by CrO₃ at low temp., is reduced by SnCl₂ in EtOH to (I), m.p. 194—196°. With HClO₄ in COMe₂ (I) yields a violet-blue, lustrous perchlorate C₁₇H₁₂O₃·HClO₄, from which it is regenerated in 90% yield by treatment with H₂O and COMe₂ containing NaOAc. The less definite hydrochloride, sulphate, and mol. compound with SnCl₄ are described, all blue crystals with metallic lustre. Oxidation of 1-benzoyl-2-methylnaphthalene affords 5-benzoyl-6-

methyl-1:4-naphthaquinone, m.p. 146°, whilst *1-benzoyl-2:6-dimethylnaphthalene*, m.p. 83—84° (whence *5-benzoyl-2:6-dimethyl-1:4-naphthaquinone*, m.p. 169°), is obtained from $2:6\text{-C}_{10}\text{H}_6\text{Me}_2$, BzCl , and AlCl_3 in CS_2 .

[With A. KELLER.] $1:1':4:4'$ -Tetrahydroxy-2:2'-dinaphthyl and the corresponding diquinone in AcOH give the *quinhydrone*, $\text{C}_{20}\text{H}_{12}\text{O}_4$, decomp. about 200°. H. W.

Constitution of alkannin, shikonin, and alkan-
nan. H. BROCKMANN (Annalen, 1935, 521, 1—47). Alkannin (I) is *l*-2- α -hydroxy- δ -methyl- Δ^y -pentenylnaphthazarin; shikonin (II) is the *d*-form, mixed with 20% of the *dl*-form, which is named shikalkin. (I), m.p. 148°, $[\alpha]_{\text{D}}^{20} -167^\circ$ in C_6H_6 , -226° in CHCl_3 (3 active H; Bz_2 derivative, m.p. 174—175°), best extracted from the roots of *Alkanna tinctoria* by ligroin, contains < 0.1% of *alkannan* (III) [2-*isohexylnaphthazarin*], m.p. 97—98°, $[\alpha] 0^\circ$, from which it is separated by adsorption from C_6H_6 by kieselguhr. (I) is decomposed by long heating in Ac_2O , but can be crystallised therefrom, and with Ac_2O - NaOAc (short heating) or Ac_2O - $\text{C}_5\text{H}_5\text{N}$ gives the Ac_2 derivative (IV), m.p. 132°, $[\alpha]_{\text{D}}^{20} -110^\circ$ in C_6H_6 . With Zn - Ac_2O it gives a *substance*, $\text{C}_{20}\text{H}_{21}\text{O}_8$, m.p. 147°, $[\alpha] 0^\circ$, probably a mixture. (I) sublimes unchanged at 140—150°/0.001 mm., but at 200°/760 mm. gives H_2O and 5-methylquinizarin, m.p. 246—247°, which is readily obtained from diacetylnaphthazarin by condensation with piperylene in EtOH at 100° and aerial oxidation of the product in 2*N*- NaOH . When distilled with Zn dust, (I) gives 1- and 2-methylanthracene and C_{10}H_8 [which last proves the two-ring structure of (I)]. With KMnO_4 in aq. alkali or COMe_2 (I) gives only AcOH and maleic acid, and with O_3 in AcOH a product oxidised by KMnO_4 to 0.8 mol. of COMe_2 , which is obtained to the same extent from (I) by the Kuhn-Roth method, proving the presence of CMe_2 in (I). (IV) and O_3 in CHCl_3 give a little 3:6-dihydroxyphthalic acid, establishing the naphthazarin grouping in (I). (I) and 10% HCl - MeOH at room temp. (15—18 hr.) yield 2- α -methoxy- δ -methyl- Δ^y -pentenylnaphthazarin [*Me ether* of (I)] (V), m.p. 105°, sublimes at 140—150°/0.001 mm. (2 active H); complete racemisation occurs in this reaction, indicating the α -position of the aliphatic OH, which is confirmed by the sparing solubility of (I) in aq. Na_2CO_3 . The *dl*- α -*Et*, m.p. 83°, and *Pr*^a *ether*, m.p. 57—58°, are similarly prepared. Hydrogenation of (I) is very rapid at first [1 mol.; formation of the quinol, which is very rapidly oxidised by air to (I)], then slower (further 2 mols.), and thereafter still slower. The second stage in the reduction (PtO_2) in AcOH or other solvents gives (III) and other products. Intermediate reduction products could not be isolated. Hydrogenation of (V) is similar; absorption of 3 mols. gives (III), but at the 2 mol. stage some *dihydroalkannin Me ether* [2- α -methoxy- δ -methyl-*n*-amylnaphthazarin], m.p. 50—51°, is obtained. This ether with KMnO_4 gives α -methyl- ϵ -methyl-*n*-hexoic acid (VI), the presence of which in the products is proved by formation of δ -methylvaleraldehyde (VII) (2:4-dinitrophenylhydrazone, m.p. 95°) therefrom by distillation with PbO_2 and dil. H_3PO_4 .

The α -position of the OH is thus proved. (VI), b.p. 123—124°/10 mm. ($p\text{-C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{CH}_2$ ester, m.p. 74—75°), is synthesised from NaOMe and *Me* α -bromo- ϵ -methyl-*n*-hexoate, b.p. 88—90°/10 mm., obtained by Br and red P at 100°; when mixed with other acids, it cannot be detected by conversion into (VII) by distillation with Cu , but the PbO_2 - H_3PO_4 method is effective.

(III), m.p. 99°, sublimes at 120—140°/0.001 mm. (2 active H; Ac_2 derivative, m.p. 99—101°), gives only 0.23 mol. of COMe_2 (Kuhn-Roth), with Ac_2O - Zn gives 1:4:5:8-tetra-acetoxy-2- δ -methyl-*n*-amylnaphthalene, m.p. 170°, and with SnCl_2 the 1:4:5:8-(OH)₄-compound, m.p. 65—66° [oxidised by air to (III) (only)]; with KMnO_4 it gives ϵ -methyl-*n*-hexoic acid ($p\text{-C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{CH}_2$ ester, m.p. 75°). With acids other than HCl or with 2*N*- NaOH at 100° (I) yields *anhydroalkannin* [2- δ -methyl- Δ^y -pentadienylnaphthazarin], m.p. 155°, sublimes at 140—145°/0.001 mm. [gives 0.85 mol. of COMe_2 (Kuhn-Roth); 2 active H], which is hydrogenated (PtO_2) in AcOH to (III). With SnCl_4 in C_6H_6 or CHCl_3 (I) gives *cycloalkannin* [1:4:5-trihydroxy-8:8-dimethyl-5:6:7:8-tetrahydro-anthraquinone] (VIII), m.p. 79—80°, sublimes at 140—145°/0.001 mm., $[\alpha]_{\text{D}}^{20} -59.2^\circ$ in C_6H_6 .

(II), obtained by ligroin from the roots of *Lithospermum erythrorhizon*, has m.p. 143°, $[\alpha]_{\text{D}}^{20} +135^\circ$ in C_6H_6 , gives a product, m.p. 146—147°, only after sublimation and repeated crystallisation, is identical with (I) in absorption spectrum, is hydrogenated as is (I), gives the inactive *Me ether*, and with SnCl_2 affords the impure *isomeride* [*cycloshikonin*], m.p. 79—80°, $[\alpha]_{\text{D}}^{20} +51.2^\circ$ in C_6H_6 , of (VIII). The *racemate* of (VIII) has m.p. 86°. The relationship of (I) and (II) is proved by mixed m.p. determinations, which show a *racemate*, m.p. 148°, to be a stable compound. Absorption spectra and changes of colour with p_{H} are recorded. (I) and (II) have lower oxidation potentials than naphthazarin, in spite of the α -OH in the side chain, showing that they exist mainly in 5:8-dihydroxy-2-alkyl-1:4-quinone form with relatively little, if any, of the 6-alkyl form. M.p. are corr. R. S. C.

Some examples of substitution addition in the anthraquinone series. C. MARSCHALK (Bull. Soc. chim., 1935, [v], 2, 1809—1830).—*Na* quinizarin-2-sulphonate (I), Na_2CO_3 , KCN , and H_2O at 90° (30 min.) yield a dicyano-leuco-compound oxidised by $(\text{NH}_4)_2\text{S}_2\text{O}_8$ to 1:4-dihydroxy-2:3-dicyanoanthraquinone (II), m.p. > 300°, also obtained, but less readily, from quinizarin and conc. KCN . (II) on hydrolysis with 90% H_2SO_4 yields the *anhydride* of 1:4-dihydroxyanthraquinone-2:3-dicarboxylic acid (+ H_2O) (III), readily obtained from the anhydride and by oxidation of 1:4-dihydroxy-2:3-dimethylanthraquinone with H_2SO_4 - H_3BO_3 - NaNO_2 at 140—150° (8 hr.). This establishes the constitution of (III). (I) and NaOH - KCN at room temp. yield 1:4-dihydroxy-2-cyanoanthraquinone (IV), m.p. 228—229°, hydrolysed to the corresponding *amide*, m.p. > 300°, and acid (V). (IV) and Na_2SO_3 - H_2O at 80° yield 1:4-dihydroxy-3-cyanoanthraquinone-2-sulphonic acid (VI), also obtained from (I), Na_2CO_3 - KCN - H_2O , and air, and desulphonated to (IV) by

treatment with $\text{Na}_2\text{S}_2\text{O}_4$ followed by oxidation. Both (IV) and (VI) with alkaline KCN give (II). (III) is decarboxylated to (V) (a) when heated with $\text{H}_2\text{SO}_4\text{-H}_3\text{BO}_3$ at 200° , (b) when boiled with aq. NaOH, and (c) when treated below 4° during 1 hr. with $\text{Na}_2\text{CO}_3\text{-Na}_2\text{S}_2\text{O}_4\text{-H}_2\text{O}$ followed by oxidation with NaOH-air. Prolonged boiling with NaOH and treatment with excess of $\text{Na}_2\text{S}_2\text{O}_4$ at room temp. results in the loss of both CO_2H . (V), its amide and Et ester with KCN each yield products hydrolysed to (III), and Na quinizarin-2 : 6-disulphonate and KCN give a product which contains both S and N. Similarly 1-amino-4-hydroxyanthraquinone-2-sulphonic acid and the corresponding -3-sulphonic acid with KCN- $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$ at $90\text{--}95^\circ$ afford 1-amino-4-hydroxy-2 : 3-dicyanoanthraquinone, m.p. $< 300^\circ$, oxidised by $\text{H}_2\text{SO}_4\text{-MnO}_2$ to (II), and hydrolysed by H_2SO_4 at $140\text{--}150^\circ$ to 1-amino-4-hydroxyanthraquinone-2 : 3-dicarboxylic acid (anhydride). No reaction occurs with 1-amino-4-methoxyanthraquinone-2-sulphonic acid. cyclopentadiene reacts with (I) (with loss of SO_3H), (IV), (V), quinizarin, and naphthazarin in aq. alkaline sol., but not in org. solvents. These are not considered to be normal "diene" reactions. The colours and colour reactions of the foregoing products are described.

H. G. M.

Kinetics of sulphonation [of anthraquinone].—See A., 1935, 1465.

Turpentine oil. I. Laricinolic acid. F. TROST (Annali Chim. Appl., 1935, 25, 496—504).—From laricinolic acid (I), m.p. $146\text{--}147^\circ$ (block), $[\alpha]_{\text{D}}^{20}\text{--}48.5^\circ$ in EtOH (from larch turpentine) (A., 1900, i, 680), were prepared: Me ester; retene, m.p. 124° (picrate, m.p. 99°), by dehydrogenation by Se (A., 1928, 51); retenequinone, m.p. $196\text{--}197^\circ$ (A., 1885, 905); the abietic acid, m.p. $160\text{--}164^\circ$, of Steele (A., 1922, i, 739); various isomerides formed during distillation and by treatment with AcOH and HCl; the additive compound, m.p. $213.5\text{--}215^\circ$ of Me ester and maleic anhydride (A., 1932, 1254) and the derived anhydride-carboxylic acid, m.p. $227\text{--}228^\circ$ (ibid.). The relation of (I) (for which the name "laricinic acid" is proposed) to abietic acids is discussed.

F. O. H.

Synthesis of dl-piperitone (dl- Δ^1 -p-menthen-3-one). J. WALKER (J.C.S., 1935, 1585—1586).—Me β -chloroethyl ketone, Et α -isopropylacetoacetate, and NaOEt give Et Δ^1 -p-menthen-3-one-4-carboxylate, b.p. $155\text{--}165^\circ/16$ mm., hydrolysed (MeOH-KOH) to dl-piperitone, identical (oxime) with the racemised natural product.

F. R. S.

Synthesis of dl-fenchone. G. KOMPPA and A. KLAMI (Ber., 1935, 68, [B], 2001—2003).—dl-Camphenonic acid is converted by SOCl_2 into dl-camphenonyl chloride, b.p. $135\text{--}137^\circ/9$ mm., m.p. 33° , transformed by H_2 in xylene containing Pd-BaSO₄ at 150° into 1-ketofenchone (I), b.p. $127\text{--}128^\circ/18$ mm. (monosemicarbazone, m.p. 238° ; monoxime, m.p. $102\text{--}103^\circ$), which readily passes into a polymeride, m.p. 240° . Reduction of (I) in AcOH containing PtO₂-FeSO₄ gives dl-fenchone (II) and ω -hydroxyfenchone (III), b.p. $134\text{--}135^\circ/17$ mm. (oxime, m.p. 140°). (III) and PCl₅ in CHCl₃ afford ω -chlorofenchone, b.p. $121\text{--}123^\circ/18$ mm., from which

(II) is derived by treatment with Zn dust in boiling AcOH.

H. W.

Snitter's camphenilene. G. GRATTON and J. L. SIMONSEN (J.C.S., 1935, 1621—1623).—By elimination of HCl from camphenyl chloride, a hydrocarbon closely agreeing in physical properties with santene and Snitter's hydrocarbon (A., 1933, 1300) has been obtained. Oxidation (O₃) shows it to be not homogeneous and to consist mainly of santene, giving acidic products, CH₂O, a ketone, C₈H₁₂O [2 : 4-dinitrophenylhydrazone (I), m.p. $114\text{--}115^\circ$], and a hydrocarbon, C₉H₁₄, m.p. 42° (apocyclene). (I) differs from methylnorcamphor-2 : 4-dinitrophenylhydrazone, m.p. $116\text{--}117^\circ$. Snitter's hydrocarbon is probably mainly apocyclene.

F. R. S.

Transition in camphor and chemically related compounds.—See this vol., 12.

Caryophyllenes. III. G. R. RAMAGE and J. L. SIMONSEN (J.C.S., 1935, 1581—1584).—Ozonolysis of β -caryophyllene nitrosite in EtOAc-CCl₄ gives CH₂O and the α -dinitro-ketone, C₁₄H₂₂O₅N₂, m.p. 161.5° , $[\alpha]_{\text{D}}^{25}\text{--}33.6^\circ$ in CHCl₃ (phenylsemicarbazone, decomp. 224° ; 2 : 4-dinitrophenylhydrazone, decomp. 225°), and in AcOH forms an isomeric β -dinitro-ketone, decomp. 155° , easily converted into the α -form. The α -ketone and C₂H₅N yield a nitro-ketone, m.p. 69° , $[\alpha]_{\text{D}}^{25}\text{--}114^\circ$ in CHCl₃ (semicarbazone, m.p. $186\text{--}187^\circ$), oxidised (O₃) to a diketo-monocarboxylic acid, C₁₄H₂₁O₄, of which the Me ester, b.p. $194\text{--}195^\circ/15$ mm. (bis-2 : 4-dinitrophenylhydrazone, decomp. $108\text{--}110^\circ$), is identical with that obtained by Semmler and Mayer (A., 1912, i, 120). The constitution of the caryophyllenes is discussed.

F. R. S.

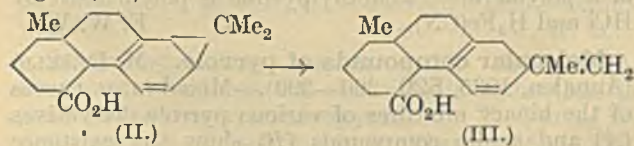
Constituents of natural phenolic resins. III. Synthesis of dehydro-"sulphite-liquors lactone" dimethyl ether and some observations on the structure of podophylotoxin. R. D. HAWORTH, T. RICHARDSON, and G. SHELDRIK (J.C.S., 1935, 1576—1581).—Et β -(3 : 4-dimethoxybenzoyl)propionate, m.p. $57\text{--}58^\circ$, with HCO₂Et gives Et β -(3 : 4-dimethoxybenzoyl)- β -hydroxymethylenepropionate, m.p. $114\text{--}116^\circ$, and with Et₂C₂O₄ forms Et β -(3 : 4-dimethoxybenzoyl)- Δ^2 -crotonolactone- γ -carboxylate, m.p. $154\text{--}156^\circ$, neither ester giving well-defined reduction products. β -3 : 4-Dimethoxybenzoyl- α -(3' : 4'-dimethoxybenzylidene)- β -methylenepropionic acid, m.p. $157\text{--}158^\circ$, obtained from the corresponding -propionic acid and aq. CH₂O, is converted (MeOH-HCl) into the lactone of the β -chloromethylpropionic acid, m.p. $183\text{--}184^\circ$ (which with MeOH gives the lactone of the β -methoxy-methylpropionic acid, m.p. 145°), and Me 6 : 7-dimethoxy-1-(3' : 4'-dimethoxyphenyl)-2-chloromethylnaphthalene-3-carboxylate, m.p. $176\text{--}177^\circ$, the corresponding acid (I), m.p. $244\text{--}245^\circ$, being cyclised to 4' : 5' : 6 : 7-tetramethoxybenzo-3 : 4-fluorene-1-carboxylic acid, m.p. $303\text{--}305^\circ$ (Me ester, m.p. $202\text{--}204^\circ$). (I) or its Me ester and NaOH give the lactone of 6 : 7-dimethoxy-1-(3' : 4'-dimethoxyphenyl)-2-hydroxymethylnaphthalene-3-carboxylic acid (dehydro-"sulphite-liquors lactone" Me₂ ether), m.p. $215\text{--}216^\circ$.

The Na salt of β -(3 : 4 : 5-trimethoxybenzoyl)propionic acid, m.p. $121\text{--}122^\circ$, obtained from Et 3 : 4 : 5-

trimethoxybenzoylacetate, $\text{CH}_3\text{Br}\cdot\text{CO}_2\text{Et}$, and NaOEt , with piperonal and Ac_2O forms the γ -lactone of β -(3:4:5-trimethoxybenzoyl)- α -(3':4'-methylene-dioxybenzylidene)-propionic acid, m.p. 161—162°, hydrolysed to the acid, m.p. 183—184°, which is converted into the β -methylene-propionic acid, m.p. 169—170°. A similar series of reactions leads to 6:7-methylenedioxy-1-(3':4':5'-trimethoxyphenyl)-2-chloromethylnaphthalene-3-carboxylic acid, m.p. > 300°, and the lactone of the 2-hydroxymethylnaphthalene-3-carboxylic acid (II), m.p. 288—289°. (II) differs from the lactone obtained from dehydroanhydro-piropodophyllin (III), and this is evidence in favour of the Borsche-Späh formula for podophyllotoxin. Oxidation (KMnO_4) of (II) gives 6:7-methylenedioxy-1-(3':4':5'-trimethoxyphenyl)naphthalene-2:3:dicarboxylic acid (anhydride, m.p. 299—300°; Me_2 ester, m.p. 206—207°), identical with the oxidation product of (III). F. R. S.

Complete deoxidation of resins by catalytic hydrogenation. H. I. WATERMAN, J. F. CLAUSEN, and A. J. TULLENERS (Rec. trav. chim., 1935, 54, 701—710).—Brown colophony resin, consisting chiefly of abietic acid (I), is completely freed from O when heated to about 400° with H_2 (initial pressure about 100 kg. per sq. cm.) in presence of a Mo or Ni catalyst. The temp. at which H_2 is mainly absorbed depends on the nature of the catalyst. The products are stable, partly aromatic, and free from olefines even when a low initial H_2 pressure (10 kg. per sq. cm.) is used. Two compounds, $\text{C}_{19}\text{H}_{34}$ and $\text{C}_{20}\text{H}_{36}$, closely related to (I) ($\text{C}_{20}\text{H}_{30}\text{O}_2$) in structure have been isolated. They were examined by the method of Waterman *et al.* (B., 1932, 536). H. G. M.

Resinic acids of *Pinus sylvestris* resin. I, II. P. S. PISCHTSCHIMUKA (J. Gen. Chem. Russ., 1935, 5, 738—751, 752—763).—I. The chief, if not only, acidic constituent of the fresh resin is $\text{C}_{19}\text{H}_{29}\text{CO}_2\text{H}$ (I), m.p. 138°, the following salts of which are described: MgR_2 , CaR_2 , BaR_2 , PbR_2 , m.p. 190°, CuR_2 , HgR_2 , $\text{NaR}\cdot 3\text{HR}$, $\text{CaR}_2\cdot 2\text{HR}$, m.p. 160°, $\text{BaR}_2\cdot 2\text{HR}$, m.p. 158° ($\text{R} = \text{C}_{19}\text{H}_{29}\text{CO}_2$). The acid from a 14-year-old sample of resin crystallised in hexagonal plates, $[\alpha]_D^{25} = -30.36^\circ$ in EtOH, which passed at 118° into lentiform crystals, m.p. 157°. $[\alpha]_D$ (in EtOH) of (I) changes from -61.7° to $+42.5^\circ$ when it is heated at 120° in CO_2 , and again changes to -32.7° at 145°. In xylene solution at 130° $[\alpha]_D$ approaches zero after 5 hr., and attains a max. val. of $+40^\circ$ after 24 hr., falling to $+30.8^\circ$ after 48 hr., whilst at 200° and 250° $[\alpha]_D$ tends to a const. val. of $+10^\circ$. The I val. of (I) corresponds with the presence of two ethylenic linkings. (I) is readily oxidised by atm. O_2 , but not by HNO_3 . It is suggested that abietic acid has the structure (II), readily changing to (III).



II. (I) and 33% HNO_3 or (I) in ligroin and conc. HNO_3 at 50—60° yield a dibasic acid (IV),

$\text{C}_{20}\text{H}_{22}\text{O}_5\text{N}_2$, sintering at 128°, which readily adsorbs org. vapours. Attempts at elucidating the structure of (IV) were not successful. R. T.

Sanguisorbigenin. T. MATSUKAWA (J. Pharm. Soc. Japan, 1934, 54, 965—979; cf. Kodako and Abe, A., 1934, 175).—Pure sanguisorbigenin (I), $\text{C}_{30}\text{H}_{46}\text{O}_2$ [monoacetate (II), m.p. 324°], has m.p. 275—276°, and contains one double linking. (I), with $\text{AcOH}\cdot\text{HCl}$, yields acetylsanguisorbigenin lactone, decomp. 323°, which is hydrolysed to the parent lactone, m.p. 301°. (II) and CrO_3 afford β - or δ -hydroxy-acetylsanguisorbigenin lactone, decomp. 268° (acetate, m.p. 287°), which contains a *tert.*-OH. When heated, (I) yields sanguisorbigenol, m.p. 206° (acetate, m.p. 185—186°), a triterpene alcohol. When oxidised with CrO_3 , (I) yields sanguisorbigenone, m.p. 159° and 229° (double m.p.) (monoxime, decomp. 281°). The *Me* ester (III), m.p. 207—209°, of (I) yields sanguisorbigenone *Me* ester, m.p. 216° (monoxime, decomp. 243°), on oxidation; hence the OH is *sec.* (I) is not hydrogenated with Pt-black. Methylation of (II) or acetylation of (III) affords acetylsanguisorbigenin *Me* ester, m.p. 243—245°. CH. ABS. (r)

Toad poisons. I. Dehydrogenation of cinobufagin by selenium. R. TSCHESCHE and H. A. OFFE (Ber., 1935, 68, [B], 1998—2000; cf. A., 1932, 397).—Dehydrogenation of cinobufagin (improved method of isolation from Ch'an Su) with Se at 270—330° gives very small amounts of methylcyclopentophenanthrene, thus proving the poison to have the ring system of the sterols and bile acids. H. W.

Constituents of red sandalwood. Homoptero-carpin. H. LEONHARDT and E. OECHLER (Arch. Pharm., 1935, 273, 447—452).—1-Dihydrohomoptero-carpin (modified prep.), m.p. 153—154°, $[\alpha]_D^{20} = -5.8^\circ$ (2:4-dinitrophenylhydrazone, decomp. 192°), with $\text{CrO}_3\text{-AcOH}$ or BzO_2H gives dihydrohomoptero-carpone (I), $\text{C}_{17}\text{H}_{16}\text{O}_5$, m.p. 178.5° [2:4-dinitro-, decomp. 258°, and *p*-nitro-phenylhydrazone, decomp. 148°; oxime, decomp. 225° (2:4-dinitrophenylhydrazone, decomp. 199°)]. (I) is a 1:4-quinone and with $\text{Zn-Ac}_2\text{O-NaOAc}$ yields a *quinol diacetate*, m.p. 122—123°, sol. only in hot NaOH . R. S. C.

Manchurian kaoliang.—See this vol., 124.

Acetylation of lignin. F. KOMAROV and G. FILMONOVA (J. Appl. Chem. Russ., 1935, 8, 1033—1042).— ≈ 5.6 — 6.6% of the OH-groups of sulphate lignin (I) are acetylated by treatment with Ac_2O in $\text{C}_5\text{H}_5\text{N}$, or with Ac_2O in AcOH in presence of catalysts (H_2SO_4 , ZnCl_2 , H_3PO_4) (18—20°; 90 min.) in absence of catalysts the latter reaction takes place only at the b.p. of the mixture. Decomp. of (I), or elimination of *Me* groups, does not occur during the above reactions. The products are sparingly sol. in org. solvents. R. T.

Hydrogenation of furfuraldehyde. I. G. ROBERTI (Annali Chim. Appl., 1935, 25, 530—540).—Reduction of furfuraldehyde to furfuryl alcohol (I) at $\approx 200^\circ$ and under pressures of H_2 of approx. 100 atm. with Ni, Cu, and Cu chromite (II) catalysts was investigated. With (II), an almost quant. formation of (I) occurs, but (II) rapidly loses its catalytic activity (cf. A., 1934, 1225). The influence of reagents

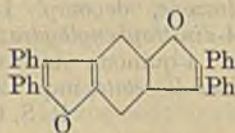
(e.g., CaO, AcOH) on the above hydrogenation catalysts is discussed. F. O. H.

Hydrolysis of phenyl furyl ketimine.—See this vol., 34.

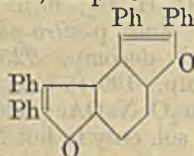
γ -Tetrahydropyranaldehyde. V. PRELOG and E. CERKOVNIKOV (Coll. Czech. Chem. Comm., 1935, 7, 430—435).—Catalytic reduction (poisoned Pd) of the chloride of γ -tetrahydropyran-carboxylic acid (I) affords γ -tetrahydropyranaldehyde (II), b.p. 74—77°/11 mm. (phenylhydrazone, m.p. 93—94°; 2:4-dinitrophenylhydrazone, m.p. 163°; semicarbazone, m.p. 191°), also obtained by heating the mixed Ba salts of (I) and HCO₂H. On keeping, (II) deposits a trimeride, m.p. 221°, depolymerised by heat. Condensation of (II) with rhodanine affords the substance, C₉H₁₁O₂NS₂, m.p. 254°, converted by aq. NaOH into β -4-tetrahydropyran-yl- α -thionpropionic acid, O<CH₂-CH₂>CH·CH₂·CS·CO₂H, m.p. 151—152°.

P. G. C.

Condensation of benzoin with quinol. O. DISCHENDORFER (Monatsh., 1935, 66, 201—217).—The alkali-sol. product obtained by Japp *et al.* (J.C.S., 1899, 75, 1035) by condensation of benzoin (I) with resorcinol (II) in H₂SO₄ is proved to be 5-hydroxy-2:3-diphenylcoumarone, new m.p. 163°, since its Bz derivative, m.p. 122°, is oxidised (CrO₃) to 2:5-dibenzoyloxybenzophenone, m.p. 118°, which is hydrolysed to 2-benzoylquinol. The alkali-insol. product, obtained by using excess of (I), is *s*-tetraphenyl-1:2:4:5-*p*-difuranobenzene (III) (cf. A., 1933, 1302), new m.p. 281° (cf. *loc. cit.*). (III) is oxidised (CrO₃) to the B₂ derivative, m.p. 220—221°, of 2:5-dibenzoylquinol, m.p. 203° (Ac₂ derivative, m.p. 209°), different from the compound to which Bogert and Howells (A., 1930, 477) incorrectly ascribe this structure (cf. this vol., 78). With Br in C₆H₆ at 100°, (III) yields a *meso*-Br₂-derivative, m.p. 384—388°,



(III.)



(IV.)

which is also obtained from (I) and 2:5-dibromoquinol in H₂SO₄, and is oxidised (CrO₃ in PhNO₂-AcOH) to the B₂ derivative, m.p. 317°, of 3:6-dibromo-2:5-dibenzoylquinol, m.p. 288° (decomp.). The position of Br is confirmed by oxidation (KMnO₄-NaOH), which gives BzOH, without the Br-acids which would result from a bromophenyl compound. A third product from (I) and (II), recovered from the mother-liquors, is *as*-tetraphenyl-1:2:4:5-*p*-difuranobenzene (IV) (cf. A., 1933, 1302), m.p. 264—265°; this is oxidised (CrO₃) to the B₂ derivative, m.p. 276°, of 2:3-dibenzoylquinol, m.p. 188°, which with N₂H₄·H₂O yields 5:8-dihydroxy-1:4-diphenylphthalazine, m.p. 315° (decomp.). E. W. W.

Configuration of dioxan and the *cis*- and *trans*-naphthadioxans. J. BÖESEKEN, F. TELLEGEN, and P. H. HENRIQUEZ (Rec. trav. chim., 1935, 54, 733—739).—The dipole moments, given in parentheses in Debye units, of the following compounds have been

measured with the apparatus previously described (cf. A., 1935, 598): dioxan (0.3); 2:3-dichloro-(I) (1.6), 2:3:5:6-tetrachloro-, m.p. 60° (0), m.p. 100° (1.85°), m.p. 144° (1.05), and 2:2:3:5:5:6-hexachloro-dioxan (0); thioxan (0.47); selenoxan (0.30); *cis*-, m.p. 111° (1.9), and *trans*-naphthadioxan, CH₂·O·CH·O·CH₂, m.p. 136° (0.72). These last two isomerides were obtained from (I) and glycol (II), and from glyoxal and (II), and correspond with the *cis*- and *trans*-decalins. The configuration of these compounds is discussed (cf. A., 1935, 15). H. G. M.

Unequal reactivity towards organometallic compounds of the carbonyl group in succinimide and in *N*-methylpyrrolidone. R. LUKEŠ and K. SMOLEK (Coll. Czech. Chem. Comm., 1935, 7, 476—481; cf. A., 1929, 576, 935; 1930, 1296).—Succinimide with CH₂Ph·MgCl in cold dry C₆H₆-Et₂O rapidly gives 2-benzyl-1-methyl-5-pyrrolone, whereas *N*-methylpyrrolidone with MgEtBr gives 1:2-dimethyl- Δ^2 -pyrroline only after many hr. The difference is explained in terms of the polarities of the mol. groupings. J. L. D.

Action of Grignard reagent on the amidogroup. VIII. Action of organo-magnesium compounds on ethyl 1-methyl-2-pyrrolone-5-acetate. R. LUKEŠ and J. PŘEUCIL (Coll. Czech. Chem. Comm., 1935, 7, 482—490; cf. A., 1932, 521).—Et 1-methyl-2-pyrrolone-5-acetate (I) with MeMgI in C₆H₆-Et₂O gives *Et* 1:2-dimethylpyrrole-5-acetate, b.p. 135—136°/20 mm. [the acid, m.p. 119.5° (decomp.)], is decarboxylated to give 1:2:5-trimethylpyrrole]. Similarly, with Mg *n*-hexyl bromide and MgPhBr, (I) yields *Et* 1-methyl-2-hexylpyrrole-5-acetate, b.p. 184—185°/21 mm. (*acid*, m.p. 89—91°, which when heated gives 5-hexyl-1:2-dimethylpyrrole, b.p. 171—172°/71 mm.), and *Et* 2-phenyl-1-methylpyrrole-5-acetate, b.p. 208—210°/18 mm. [*acid*, m.p. 157° (decomp.)], decarboxylated to 5-phenyl-1:2-dimethylpyrrole, m.p. 50—51°, respectively. In no case was a diketone isolated (cf. A., 1932, 621). MgRX does not attack the ·CO₂Et because this is probably in close electronic association with N. J. L. D.

Basic properties of pyrroles. P. PRATESI (Gazzetta, 1935, 65, 658—668).—When pyrroles form salts, the using of the unshared N electrons converts the aromatic into a conjugated olefinic structure, the stability of which is increased by substituents. Thus 2:3:4-trimethylpyrrole forms a *hydrochloride* and a *ferrocyanide*; 2:4-dimethyl-3-ethylpyrrole can be recovered from HCl solution (as can 2:3:5-trimethyl-4-ethylpyrrole), and forms a *ferrocyanide*; these salts are monomeric. The *ferrocyanide* of 1-methyl-2:5-diethylpyrrole is contaminated with that of a polymeride. 2-Methylpyrrole is polymerised by HCl and H₄Fe(CN)₆. E. W. W.

Molecular compounds of pyrrole. M. DEZELIĆ (Annalen, 1935, 520, 290—300).—Mixed m.-p. curves of the binary mixtures of various pyrrole derivatives (A) and acidic compounds (B) show the existence of the following compounds. Et 3-acetyl-2:4-dimethylpyrrole-5-carboxylate gives compounds with

$\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$, m.p. $85\cdot3^\circ$, PhOH , m.p. 93° , picric acid, m.p. $97\cdot8^\circ$, all of type *AB*, salicylic acid, *AB*, m.p. 107° , and AB_2 , m.p. 113° , *o*-, m.p. $108\cdot5^\circ$, *m*-, m.p. 139° , and $p\text{-C}_6\text{H}_4(\text{OH})_2$, m.p. 153° , all of type AB_2 . No compounds are formed with AcOH , BzOH , or succinic acid. Et 2 : 4-dimethylpyrrole-5-carboxylate gives a compound AB_2 , m.p. 100° , with picric acid (initial polymerisation to B_2), but not with $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$, BzOH , PhOH , salicylic acid, or *o*-, *m*-, or $p\text{-C}_6\text{H}_4(\text{OH})_2$. Et 3-aldehydro-2 : 4-dimethylpyrrole-5-carboxylate gives compounds with $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$, m.p. $74\cdot5^\circ$, salicylic acid, m.p. 135° , picric acid, m.p. 97° , and *o*-, m.p. 114° , and *m*- $\text{C}_6\text{H}_4(\text{OH})_2$, m.p. 111° , all of type *AB*, and of type AB_2 with $p\text{-C}_6\text{H}_4(\text{OH})_2$, m.p. 142° : no compound with BzOH . Et 4-aldehydro-2 : 5-dimethylpyrrole-3-carboxylate gives compounds with salicylic acid, *AB*, m.p. $111\cdot5^\circ$, and AB_2 , m.p. 111° , and *m*-, m.p. 98° , and $p\text{-C}_6\text{H}_4(\text{OH})_2$, m.p. $117\cdot5^\circ$ (type *AB*), but not with $o\text{-C}_6\text{H}_4(\text{OH})_2$. Constitutions are briefly discussed. J. W. B.

Yellow coloration produced by ultra-violet light on mixtures of pyridine with sugars, monohydric alcohols, and acetone. R. CANTIENI (Helv. Chim. Acta, 1935, 18, 1420—1427).—The relative effects of various concns. of the above-named substances on (a) the velocity of formation of the yellow colour, and (b) the fading of this yellow colour, produced by ultra-violet irradiation of $\text{C}_5\text{H}_5\text{N}$ have been investigated quantitatively by colorimetric comparison with 1 vol.-% solutions of $\text{C}_5\text{H}_5\text{N}$ in H_2O . The main conclusions are as follows: glucose, galactose, sucrose, and lactose accelerate colour formation and retard fading, but their effect is < that of fructose. Pure MeOH is almost without influence on colour formation, but has a greater retarding action on fading than has fructose. Pure EtOH retards colour formation, but the colour is more stable in EtOH than in MeOH. COMe_2 has a powerful inhibiting effect on colour formation. J. W. B.

4-Bromopyridine. J. P. WIBAUT, J. OVERHOFF, and H. GELDOF (Rec. trav. chim., 1935, 54, 807—812).—4-Hydroxypyridine with POBr_3 and PBr_5 at $130\text{--}140^\circ$ affords (together with some 2 : 4 : 6-tribromopyridine) 4-bromopyridine (I), b.p. $27\cdot5\text{--}30^\circ/0\cdot4$ mm., f.p. $0\text{--}1^\circ$, also obtained by the action of NaNO_2 -conc. HBr on 4-nitroaminopyridine (Koenigs *et al.*, A., 1924, i, 989), and characterised as its picrate, sinters $135\text{--}140^\circ$, m.p. 223° (decomp.), mercurichloride, darkens $130\text{--}140^\circ$, decomp. $> 270^\circ$, and platinichloride. (I) is very unstable and is converted in the dark at 0° , and even in Et_2O solution, into a yellowish-brown substance which may be 4-bromo-*N*-4'-pyridylpyridinium bromide (platinichloride, decomp. $> 325^\circ$; platinibromide; mercurichloride, m.p. approx. 221°). When heated with aq. NH_3 (*d* 0.9) at 200° , (I) is converted into 4-aminopyridine. J. W. B.

2-Aminopyridine series. III. 2-Salicylamidopyridine and its electrolytic reduction to 2-*o*-hydroxybenzylaminopyridine. K. FEIST, W. AWE, and W. VÖLKSEN (Arch. Pharm., 1935, 273, 476—478; cf. A., 1935, 92).—Electrolytic reduction of 2-salicylamidopyridine in $\text{EtOH}\text{--}\text{H}_2\text{SO}_4$ gives

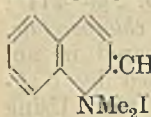
2-*o*-hydroxybenzylaminopyridine, m.p. 105° (picrate, m.p. $185\text{--}186^\circ$), thus proving the structure of the amide. Similar reduction of 2-pyridylphthalimide causes fission. R. S. C.

Hydroxyquinolines. I. Iodo-derivatives of 8-hydroxyquinoline. F. PIRRONE and A. CHERUBINO (Gazzetta, 1935, 65, 743—754).—An extended account of work previously published (A., 1934, 418). 5-Iodo-8-hydroxyquinoline (I), new m.p. $125\text{--}127^\circ$ (picrate, new m.p. $170\text{--}172^\circ$; sulphate, new m.p. $209\text{--}211^\circ$; 1-MeI derivative, new m.p. $134\text{--}137^\circ$; chloroacetate, m.p. $157\text{--}158^\circ$; Co salt), when prepared in aq. EtOH, using I and KI, is accompanied by 5 : 7-di-iodo-8-hydroxyquinoline, m.p. $185\text{--}187^\circ$. Using I in EtOH in presence of NaOAc, only (I) is formed. E. W. W.

Absorption spectra in relation to the constitution of derivatives of isatin and carbostyryl. R. G. AULT, E. L. HIRST, and R. A. MORTON (J.C.S., 1935, 1653—1657).—Absorption spectra of isatin (I) and derivatives have been measured under rigidly controlled conditions, and show that (I) and its *O*- and *N*-ethers all possess similar spectra. There is sufficient difference between the spectra of the lactam and lactim derivatives in the hydroxyquinoline series to permit the use of absorption spectra in structural determinations. (I) and CH_2N_2 yield 3-hydroxy-, m.p. 360° , and 3-methoxy-quinoline, m.p. 191° . *N*-Methylisatin and CH_2N_2 give 3-methoxy-1-methylquinoline, m.p. 42° , and *O*-methylisatin forms 3-hydroxy-2-methoxyquinoline, m.p. $83\text{--}84^\circ$. F. R. S.

***p*-Dimethylaminobenzylidenequinaldine. Action of chromophoric and auxochrome groups.** H. RUPE, H. HAGENBACH, and A. COLLIN (Helv. Chim. Acta, 1935, 18, 1395—1413).—The following salts of 2-*p*-dimethylaminostyrylquinoline (I), m.p. $183\cdot5\text{--}184\cdot5^\circ$ (Noelting *et al.*, A., 1906, i, 886; Pfeiffer *et al.*, A., 1925, i, 411, give m.p. $177\text{--}179^\circ$), are prepared pure: colourless dihydrochloride; bluish-violet monohydrochloride, m.p. $239\text{--}240^\circ$; almost colourless diperchlorate; reddish-violet monopercchlorate, m.p. $229\text{--}230^\circ$ (decomp.), and monopicrate, m.p. $167\text{--}168^\circ$. With MeI in MeOH at 100° (I) gives a mixture of a pale yellow methiodide, $\text{C}_9\text{H}_6\text{N}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_3\text{I}$ (II), decomp. $250\text{--}251^\circ$, synthesised by condensation of *p*-aldehydophenyltrimethylammonium iodide, m.p. 144° (decomp.), and quinaldine in EtOH-piperidine, and a bluish-red methiodide, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_9\text{H}_6\text{NMeI}$ (III), m.p. $253\text{--}254^\circ$ (decomp.), synthesised from quinaldine methiodide and *p*- $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ (IV). With 1 mol. of Me_2SO_4 in H_2O (I) gives red 2-*p*-dimethylaminostyrylquinoline methosulphate, m.p. $242\text{--}243^\circ$ (decomp.), of type (III), synthesised from 2-methylquinoline methosulphate, m.p. $223\text{--}224^\circ$ (decomp.), and (IV), whereas condensation of *p*-dimethylaminobenzaldehyde methosulphate, m.p. 154° , and quinaldine give the colourless β -2-quinolylstyryltrimethylammonium methosulphate, m.p. $201\cdot5\text{--}202\cdot5^\circ$ (decomp.), of type (II). With 2 mols. of Me_2SO_4 (I) gives its colourless dimethosulphate, m.p. $252\text{--}253^\circ$ (decomp.). Thus salts of type (II) and the bis-quaternary salts are colourless, and those of type (III) are coloured.

Reduction of (I) with H_2-Ni in $EtOAc-EtOH$ first saturates the ethylenic linking and yields, finally, 2- β -*p*-dimethylaminophenylethyl-1 : 2 : 3 : 4-tetrahydroquinoline, m.p. 68—68.5° (dihydrochloride, m.p. 210—211°; diperchlorate, m.p. 157—158°; dimethiodide, m.p. 158—159°; *NO*-, m.p. 90.5—91°, and *Bz*, m.p. 120.5—121.5°, derivatives). With $MgPhBr$ in Et_2O (I) affords a 1 : 4-adduct, 2-(β -*p*-dimethylaminophenyl- β -phenylethylidene)-1 : 2-dihydroquinoline (V), m.p. 125° [dihydrochloride; diperchlorate, m.p. 192—194°



(decomp.); methiodide, m.p. 125—126° (decomp.); *NO*-derivative, m.p. 195—196° (decomp.); *N*-methyl dimethiodide (annexed formula), m.p. 206—208° (decomp.); and *N*-methyl diperchlorate, m.p. 216—217° (decomp.), and a substance, m.p. 194.5° [perchlorate, m.p. 207—208°; dimethiodide, m.p. 196—197° (decomp.)], which is not isomeric with (V), and gives no *NO*- or *Bz* derivative. The relationship of colour to constitution is discussed. J. W. B.

Reaction products of indoles with diazo-esters. R. W. JACKSON and R. H. MANSKE (Canad. J. Res., 1935, 13, B, 170—174).—Addition of $CHN_2 \cdot CO_2Et$ and indole gives, after hydrolysis, indolyl-3-acetic acid (I), and indylene-1 : 3-diacetic acid, m.p. 242°, hydrolysed to 3-methylindolyl-1-acetic acid, m.p. 178°. Indole and Et_2 diazosuccinate similarly form indolyl-3-succinic acid, m.p. 199°. No substitution occurs in position 2. Hydrolysis of Et_2 β -cyanopropionacetal to the acid, and further hydrolysis (HCl) to the semialdehyde of succinic acid, followed by condensation with $NHPh \cdot NH_2$ and treatment with H_2SO_4 , leads by the Fischer synthesis to (I). F. R. S.

Colour and constitution of indole derivatives. C. TOFFOLI (Gazzetta, 1935, 65, 647—658).—Theoretical. The colour, and changes of colour on salt-formation, of various indoles, e.g., *o*-3-(2-methylindolyl)phenyl 3-(2-methylindolyl) ketone (A., 1934, 1110), and α -3 : 3'-di-indolyl- and -3-indolyl-3'-indolidene-ethane (*ibid.*, 1113), are discussed on the basis of the Bonino model for pyrrole (A., 1933, 886), and of Burawoy's theories (A., 1931, 144, 544; 1932, 791). Salt-formation disturbs the aromatic character of indoles, and introduces chromophoric conjugated systems. E. W. W.

Preparation and properties of mesochloroacridine and acridone, and their derivatives. N. S. DROZDOV and N. S. LEZNOVA (J. Gen. Chem. Russ., 1935, 5, 690—700).—Mesochloroacridine (I) yields acridone (II), together with the hydrochloride (III) of a double salt of (I) and (II), when boiled with dil. HCl; (III) readily decomposes in aq. NH_3 or boiling H_2O to yield (II). 4'-Methoxydiphenylamine-2-carboxylic acid and excess of $POCl_3$ in xylene yield 5-chloro-3-methoxyacridine (IV), m.p. 154°, the hydrochloride of which is obtained by boiling with dil. HCl; with a limited amount of $POCl_3$ the product is 3-methoxyacridone. 5-Chloro-1-nitro-7-methoxyacridine (V), m.p. 226°, and its hydrochloride are prepared analogously. *o*- $C_6H_4Cl \cdot CO_2H$, 4-nitro-2-aminoanisole, KOH, and CuO in *iso*- $C_5H_{11} \cdot OH$ (140°; 10 hr.)

give 5'-nitro-2'-methoxydiphenylamine-2-carboxylic acid (VI), m.p. 234°, from which 4-nitro-1-methoxyacridone (VII), m.p. 281° (decomp.), may be prepared by heating with conc. H_2SO_4 or with $POCl_3$. On chlorination, (VII) yields the corresponding 5-chloroacridine (VIII), m.p. 173° (hydrochloride), also obtained directly from (VI) and excess of $POCl_3$. 4-Chloro-4'-methoxydiphenylamine-2-carboxylic acid, m.p. 189°, prepared from 3 : 6-dichlorobenzoic acid, *p*-anisidine, KOH, and CuO in glycerol (140°; 10 hr.), affords similarly 1-chloro-7-methoxyacridone, m.p. > 300° and 1 : 5-dichloro-7-methoxyacridine (IX), m.p. 205—206° (hydrochloride). The hydrochlorides of (IV) and (IX) are hydrolysed when boiled with dil. HCl, under which conditions those of (V) and (VIII) are converted into the corresponding acridones. The above observations do not support the view that acridol is an intermediate stage in the conversion of mesochloroacridines into acridones. R. T.

Antimalarial drugs. Syntheses in the acridine series. J. C. FELDMAN and E. L. KOPELOVITSCH (Arch. Pharm., 1935, 273, 488—495).—2 : 5- $C_6H_3Cl_2 \cdot CO_2H$ (prepared from *o*- $C_6H_4Me \cdot NO_2$ by way of 5-chloro-*o*-toluidine and 2 : 5- $C_6H_3MeCl_2$) with *p*- $OMe \cdot C_6H_4 \cdot NH_2$, K_2CO_3 , and a little Cu in *iso*- $C_5H_{11} \cdot OH$ at 130—135° gives 5-chloro-2-*p*-anisylaminobenzoic acid, m.p. 185—186°, converted by $POCl_3$ at 100—123° into 5 : 7-dichloro-3-methoxyacridine, m.p. 203—204°, which with $NH_2 \cdot CHMe \cdot [CH_2]_3 \cdot NEt_2$ yields 7-chloro-5- δ -diethylamino- α -methyl-*n*-butylamino-, m.p. 221—222°, and with $NH_2 \cdot [CH_2]_3 \cdot NEt_2$ 7-chloro-5- γ -diethylaminopropyl-3-methoxyacridine dihydrochloride, m.p. 246—247°. $C_6H_3MeCl_2$ with Cl_2-Fe gives a mixture, m.p. 80—81°, $C_6H_3MeCl_2$, converted by HNO_3 into a mixture of 2 : 4 : 6- and 2 : 4 : 5- $C_6H_2Cl_3 \cdot CO_2H$ (I). (I) leads to 4 : 5-dichloro-2-*p*-anisylaminobenzoic acid, m.p. 233—234°, 5 : 7 : 8-trichloro-3-methoxyacridine, m.p. 192—193°, and 7 : 8-dichloro-5- δ -diethylamino- α -methylbutylaminoacridine dihydrochloride, m.p. 236—237°. The three acridine bases are less effective antimalarials than is acrichine (atebrine). R. S. C.

3-Phenyl-1- β -phenylethylpyrazol-5-one. E. VOTOČEK and O. WICHTERLE (Coll. Czech. Chem. Comm., 1935, 7, 388—391).—3-Phenyl-1- β -phenylethylpyrazol-5-one (I), m.p. 145.5° (methiodide, m.p. 174—175°), is obtained from $CH_2Ph \cdot CH_2 \cdot NH \cdot NH_2$ and $COPh \cdot CH_2 \cdot CO_2Et$. (I) with $NaNO_2-HCl$ affords a *NO*-derivative, m.p. 138—139°, converted by $Zn-AcOH$ into the compound $RH \cdot N \cdot R' \left(R = CH_2Ph \cdot CH_2 \cdot N \begin{matrix} \diagup N=CPh \\ \diagdown CO \cdot C \end{matrix} \right)$ m.p. 165°, and an *NH_2*-derivative (not isolated) of (I). P. G. C.

Asymmetric platinum atom. VII. A new type of optically active compound. H. REIHLEN, G. SEIPEL, and E. WEINBRENNER (Annalen, 1935, 520, 256—269).—Dichloro-*l*-phenylethylenediamine-platinum (I) (A., 1935, 1132) boiled with 2 : 2'-dipyridyl affords dipyridyl-*l*-phenylethylenediamineplatinum chloride (II) + $2H_2O$ and + $3H_2O$, $[M]_D^{20} + 90^\circ$ (platinochloride), which is a racemate of the active Pt centre [denoted by (\pm)Pt]. With dil. HNO_3-NaNO_3 it gives the (\pm)Pt nitrate, partly separated by shaking

with H_2O at $10-15^\circ$ into the less sol., stable (+)Pt nitrate (III), $[M]_D + 115^\circ$, $[\Delta Pt]_D + 25^\circ$, whereas the mother-liquor affords only the racemate from the readily racemized (-)Pt salt. With 1 mol. of Na *d*-bromocamphor- π -sulphonate (IV) in H_2O , (II) gives the (\pm)Pt *d*-bromocamphor- π -sulphonate chloride $+ 3H_2O$, $[M]_D + 363^\circ$ ($273^\circ + 90^\circ$), but the gelatinous (\pm)Pt *di-d*-bromocamphor- π -sulphonate, $[M]_D + 622^\circ$, obtained by evaporation of (II) with 2 mols. of (IV), slowly affords crystals of the (+)Pt *d*-bromocamphor- π -sulphonate chloride (V) $+ 3H_2O$, $[M]_D + 392^\circ$, $[\Delta Pt]_D + 25^\circ$ to 29° , converted by dil. HNO_3-NaNO_3 into (III). The mother-liquor of (V) with (IV) gives the (-)Pt *di-d*-bromocamphor- π -sulphonate $+ 2H_2O$, $[M]_D + 604^\circ$, $[\Delta Pt]_D - 32^\circ$. *o*-Phenanthroline (VI) with K_2PtCl_4 in hot H_2O affords dichloro-*o*-phenanthrolineplatinum, converted by $l-NH_2 \cdot CHPh \cdot CH_2 \cdot NH_2$ into *o*-phenanthroline-1-phenylethylenediamineplatinum chloride $+ 2H_2O$, $[M]_D + 121^\circ$ [also from (I) and (VI)] (nitrate, $[M]_D + 119^\circ$; platinochloride; *di-d*-bromocamphor- π -sulphonate $+ 2H_2O$, $[M]_D + 666^\circ \pm 10^\circ$). Similarly dichloroethylenediamineplatinum with (I) affords 1-phenylethylenediamine-ethylenediamineplatinum chloride, partly separated by crystallisation into fractions of $[M]_D + 134^\circ$ and $+ 120^\circ$, whence are obtained the iodide, $[M]_D + 139^\circ$ and $+ 110.5^\circ$ (pure, $[M]_D + 125^\circ$, the *d*-compound, $[M]_D - 125^\circ$, also being obtained), perchlorate, $[M]_D + 110^\circ$ and $+ 142^\circ$, and iodide perchlorate, $[M]_D + 142^\circ$. Thus

in the spirans of type $\left[\begin{array}{c} A \\ \vdots \\ B \end{array} : Pt : \begin{array}{c} D \\ \vdots \\ D \end{array} \right] X_2$, either the four

N are not in the same plane as the Pt, or the four Pt-N linkings are not equiv. All $[M]_D$ vals. are in H_2O .

J. W. B.

Preparation of 2:2'-diquinolyl by catalytic dehydrogenation of quinoline. J. P. WIBAULT, H. D. T. WILLINK, jun., and W. E. NEUWENHUIS (Rec. trav. chim., 1935, 54, 804-807).—Dehydrogenation of quinoline (I) by heating at $325-335^\circ$ with a Ni- Al_2O_3 catalyst affords 2:2'-diquinolyl [15% yield, calc. on (I) consumed]. Very poor yields are also obtained using 0.5% of an I catalyst, but with 2.0% I complete decomp. results.

J. W. B.

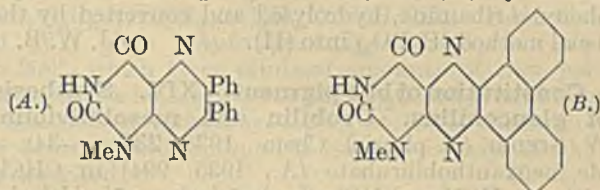
Decolorisation of indigotin by alkyl- and aryl-sulphinic acids. M. BAZLEN and F. SCHOLTZ (Ber., 1935, 68, [B], 2045).—Indigotin becomes decolorised when heated at 180° in glycerol with the Zn or Na salts of $MeSO_2H$, $EtSO_2H$, $PhSO_2H$, 1- or 2- $C_{10}H_7 \cdot SO_2H$; the free acids cannot be used, since they become decomposed at temp. below that at which reducing action is developed. The colour returns when the solution is cooled and shaken with air. *p*- $C_6H_4Me \cdot SO_2H$, *o*- $NH_2 \cdot C_6H_4 \cdot SO_2H$, benzanthrone-*Bz*-1-sulphinic acid, and anthraquinone-2-sulphinic acid behave similarly.

H. W.

Manufacture of conversion products of N-nitroamines etc. [benztriazoles].—See B., 1935, 1132.

Fluorescence of derivatives of pyrimidine, purine, and pyrimidazine. H. VON EULER, K. M. BRANDT, and G. NEUMÜLLER (Biochem. Z., 1935, 281, 206-214).—The fluorescence (substance and solution) of alloxazine (I), 6:7-dimethoxy- (I) and

4:5-diamino-3-methyluracil (II), diisobarbituric acid (III) and its oxidised form (IV), diuracilpyridazine, the azine (A), m.p. $268-269^\circ$ [from (II) by heating



in CO_2 at $190-200^\circ$ for 45 min. with Bz_2], the azine (B), m.p. $> 330^\circ$ [from (II) by boiling in AcOH for 20-30 min. with phenanthraquinone], dioxindole (V), and acridine has been examined, p_{Hf} -fluorescence curves being given for (I)-(V).

W. McC.

Crystalline hypoxanthine. H. STEUDEL (Z. physiol. Chem., 1935, 236, 228-229).—Pure crystalline hypoxanthine (I) (prisms) is obtained from the sulphate after conversion into the compound with NH_3 , and pure crystalline hypoxanthine (II) (rhombic plates) from the hydrochloride, in both cases by treatment with $NaOAc$. The crystalline form attributed by Horbaczewski (A., 1898, i, 50) to (I) is that of (II).

W. McC.

Flavin syntheses. VIII. Synthesis of 6-methyl-9-1-d-ribitylisoalloxazine and other synthetic investigations in the flavin series. P. KARRER and F. M. STRONG (Helv. Chim. Acta, 1935, 18, 1343-1351).—4-Nitro-*m*-toluidine (improved prep.) with $ClCO_2Et$ in $CHCl_3$ gives its carbethoxy-derivative, m.p. $51-52^\circ$, reduced (H_2-PtO_2) to 3-carbethoxyamino-*p*-toluidine, m.p. 120° , converted successively by usual methods (cf. A., 1934, 1134) into 2-carbethoxyamino-*p*-tolyl-*d*-ribamine, m.p. 153° , and 6-methyl-9-*d*-riboflavin (I), m.p. 282° , $[\alpha]_D^{25} - 84.6^\circ$ in 0.05*N*- $NaOH$. 6-Nitro-2:4-dimethylaniline (by hydrolysis of its Ac derivative, m.p. 176.5° ; lit., m.p. 172°) with $ClCO_2Et$ gives a poor yield of its carbethoxy-derivative, m.p. 135° (lit., $125-126^\circ$), which is best obtained by the action of conc. $H_2SO_4-HNO_3$ (*d* 1.40) at -5° on Et 2:4-dimethylphenylcarbamate, and is reduced (H_2-Pt) to the 6- NH_2 -compound, m.p. 99.5° , from which 2-carbethoxyamino-3:5-dimethylphenyl-*d*-ribamine, m.p. 139° , is obtained. Alkaline hydrolysis of this gives only 1-*d*-ribityl-2-hydroxy-4:6-dimethylbenzimidazole, m.p. 248° . (I) exhibits good growth-promoting efficiency in $10-20 \times 10^{-6}$ g. daily doses.

J. W. B.

Synthesis of lactoflavins. P. KARRER, B. BECKER, F. BENZ, P. FREI, H. SALOMON, and K. SCHÖPP (Helv. Chim. Acta, 1935, 18, 1435-1448).—In part a historical résumé of flavin syntheses. Details are given for the prep. of *d*-ribose (I) (270 g.) from *d*-arabinose (3 kg.) by the method used by Austin *et al.* (A., 1934, 759) for *l*-ribose. The production of $NH_2 \cdot C_6H_4Me_2 \cdot NH \cdot CH_2 \cdot [CH \cdot OH]_3 \cdot CH_2 \cdot OH$ by catalytic reduction of $NO_2 \cdot C_6H_4Me_2 \cdot N \cdot CH \cdot [CH \cdot OH]_3 \cdot CH_2 \cdot OH$ (Kuhn *et al.*, A., 1935, 1382) is disputed, since these authors describe the condensation of 5-nitro-4-amino-*o*-xylene only with *l*-arabinose and not with *d*-ribose. The synthesis of 6:7-dimethyl-9-*d*-riboflavin (II), in good yield, by the following reaction sequence is detailed: *m*-xylene \rightarrow 4- NO_2 \rightarrow 4- NH_2 \rightarrow 4- $NH \cdot CO_2Et$ -derivative \rightarrow 4-carbethoxyamino-5-nitro-

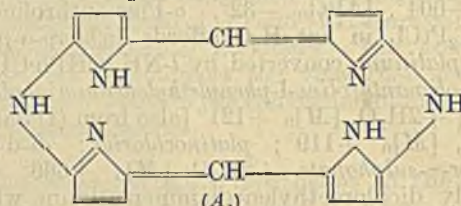
o-xylene, reduced to the 5-NH₂-compound, which condenses with (I) to give, after catalytic reduction of the product, 2-carbethoxyamino-4:5-dimethylphenyl-*d*-ribamine, hydrolysed and converted by the usual method (H₃BO₃) into (II). J. W. B.

Constitution of bile pigment. XIV. Synthesis of glaucobilins. Urobilin and mesobiliviolin. W. SIEDEL (*Z. physiol. Chem.*, 1935, 237, 8—34).—Me neoxanthobilirubate (A., 1935, 994) in CHCl₃ with dry HCN and HCl affords 5-hydroxy-5'-aldehydo-3':4'-dimethyl-3-ethyl-4'-β-carbomethoxyethylpyrromethene, m.p. 205.5° (all m.p. corr.), hydrolysed to the corresponding acid (I), m.p. 257°. Similarly Me isoneoxanthobilirubate (II) gives 5-methoxy-5'-aldehydo-3':3'-dimethyl-4-ethyl-4'-β-carbomethoxy-methylpyrromethene, m.p. 218—220° [corresponding acid (III), m.p. 273°]. 5-Bromo-3:3'-dimethyl-4-ethyl-4'-β-carbomethoxyethylpyrromethene hydrobromide (A., 1935, 632) yields (cf. A., 1933, 404) 5-methoxy-3:3'-dimethyl-4-ethyl-4'-β-carboxyethylpyrromethene, m.p. 160.5—161.5° [*Me* ester, m.p. 76°, from CH₂N₂ and isoneoxanthobilirubic acid (IV) *Me* ether]. Ferrobilin IX α-Me₂ ester in CHCl₃ treated with 2*N*-NaOH affords "analytical" glaucobilin IX α-Me₂ ester (V), m.p. 232°, identical (by optical and physical characteristics) with the synthetic product, m.p. 232—234° [formed by refluxing (I)+(IV) in MeOH with HBr], and giving no depression of m.p. with isoglaucobilin IX α-Me₂ ester, m.p. 232° [from (III)+neoxanthobilirubic acid (VI)]. Similarly (I)+(IV) refluxed in MeOH with HCl affords glaucobilin IX α, m.p. 316.3° (decomp.), showing no depression with the analytical compound, m.p. 318° (decomp.). (I)+(IV) heated in AcOH with 2*N*-HCl in presence of FeCl₃ yields ferrobilin IX α, m.p. 265° (recryst. from COMe₂-AcOH, m.p. 270°) showing no depression with the analytical compound, m.p. 265°; a similar identity holds for the Me₂ ester (VII), m.p. 264°. Glaucobilin XIII α-Me₂ ester (VIII), m.p. 246—247°, prepared by heating (I)+(VI) in MeOH with HBr, differs from (V) in solubility, but has similar optical properties, whilst depression of the mixed m.p. is small (approx. 1°). Treatment of mesobilirubin XIII in AcOH with FeCl₃ followed by dry HCl yields ferrobilin XIII α, m.p. 275° [Me₂ ester, m.p. 282.5°, showing no depression with (VII)]. (IV) heated with HCO₂H and Ac₂O followed by MeOH-HCl affords glaucobilin III α-Me₂ ester, m.p. 238.5°, showing small (approx. 2°) and marked (approx. 13°) depressions with (V) and (VIII), respectively. Equiv. amounts of (I) and (IV) *Me* ether heated in AcOH yield 1'-hydroxy-8'-methoxy-1:3:6:7-tetramethyl-2:8-diethyl-4:5-di-(β-carboxyethyl)bilin [Me ether of (V)]. Equiv. amounts of (I) and isoneobilirubic acid in MeOH heated with HBr give mesobiliviolin (IX), which yields a violet CHCl₃ solution (absorption max. at 575 mμ) turned blue by HCl (560, 607 mμ), and a blue solution fluorescing red (630 mμ) with EtOH-Zn(OAc)₂. Condensation in presence of HBr of aldehydeoneobilirubic acid and (IV) in MeOH yields mesobilirhodin (X), which gives a red CHCl₃ solution (575 mμ) turned violet by HCl (496, 557, 605 mμ) and a greenish-brown fluorescent (510 mμ) solution with EtOH-Zn(OAc)₂. Chromatographic analysis of

(IX) prepared by oxidation (FeCl₃) of mesobilirubinogen indicates the presence of (X). The bearing of the data on the structure of bile pigments is discussed.

F. O. H.

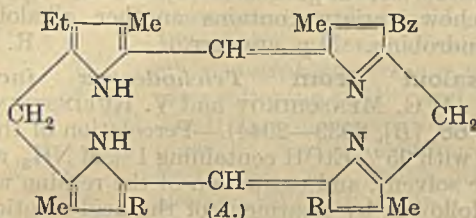
Synthesis of di-iminoporphyrins. I. H. FISCHER, H. HABERLAND, and A. MÜLLER (*Annalen*, 1935, 521, 122—128).—Prolonged contact of 5:5'-dibromo-4:4'-dimethyl-3:3'-di-β-carboxyethylpyrromethene hydrobromide (I) with 25% NH₃ at room temp gives βδ-di-iminocoprophyrin II (II) (cf. A), m.p. 398—400° (ill-defined *Cu* salt; *Me*₄ ester, m.p. 250°, and its *Cu* salt, m.p. 312°). In spite of some doubt due to spectrochemical evidence, the structure A with 2 NH in place of 2 CH is preferred to a con-



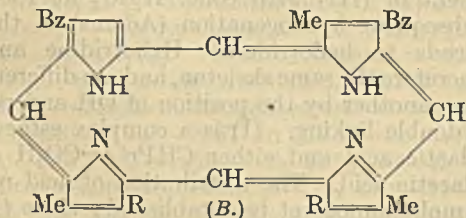
stitution with 2 N, since the substance has an enhanced acid no. in comparison with coproporphyrin and does not give a hydrobromide or hydrochloride. Also there is no evidence of dehydrogenation during or subsequent to the synthesis, and (I) with NH₂Me or NH₂Et gives substances spectroscopically similar to (II). H. W.

Synthesis of benzoylporphyrins. H. FISCHER and K. HANSEN (*Annalen*, 1935, 521, 128—156).—Attempts, by the introduction of heavy residue, are described to determine whether the stability of the chlorophyll mol., apart from the influence of the complex metal, is due to the involved isocyclic ring system. 2:3-Dimethylpyrrole is converted by CH₂N₂·CO₂Et and *Cu* powder into *Et* 2:3-dimethylpyrrole-5-acetate, b.p. 142°/16 mm., hydrolysed and decarboxylated to 2:3:4-trimethylpyrrole. *Et* 2-methyl-3-ethylpyrrole-5-acetate, b.p. 143°/14 mm., is obtained similarly. Saturation of a solution of 2-methyl-3-ethylpyrrole and anhyd. HCN in Et₂O with HCl and subsequent hydrolysis of the imine hydrochloride affords 2-methyl-3-ethylpyrrole-5-aldehyde (I), m.p. 109° (corresponding aldazine, m.p. 162°). *Et* 2:5-dimethylpyrrole-3-carboxylate, BzCl, and AlCl₃ in CS₂ give *Et* 4-benzoyl-2:5-dimethylpyrrole-3-carboxylate, m.p. 135°. *Et* 3-benzoyl-2:4-dimethylpyrrole-5-carboxylate is hydrolysed to 3-benzoyl-2:4-dimethylpyrrole-5-carboxylic acid, m.p. 194° (decomp.), which passes at 200° into 3-benzoyl-2:4-dimethylpyrrole (II), m.p. 130°. 2:3-Dimethylpyrrole-5-aldehyde and (II) condense in EtOH containing HBr to 4-benzoyl-3':4:5:5'-tetramethylpyrromethene hydrobromide, m.p. 208° (decomp.), readily brominated in AcOH to 3-bromo-4'-benzoyl-3':4:5:5'-tetramethylpyrromethene hydrobromide, decomp. 193°; under similar conditions 4'-acetyl-3':4:5:5'-tetramethylpyrromethene hydrobromide, decomp. 212°, gives ill-defined products. The wide applicability of the method of condensation is illustrated by the prep. of 4'-benzoyl-3':5:5'-trimethyl-4-ethylpyrromethene hydrobromide, m.p. 224° (decomp.) (3-*Br*-derivative, decomp. 202°), from 2-methyl-3-ethylpyrrole-5-aldehyde and (II), of 4'-acetyl-3':5:5'-

trimethyl-4-ethylpyrromethane hydrobromide, m.p. 214° (decomp.), from (I) and 3-acetyl-2:4-dimethylpyrrole, of 4'-benzoyl-3:3':4:5:5'-pentamethylpyrromethene hydrobromide, m.p. 224° (decomp.), from (II) and 2:3:4-trimethylpyrrole-5-aldehyde, of 4'-benzoyl-3:3':5:5'-tetramethyl-4-ethylpyrromethene hydrobromide (III), m.p. 211° (decomp.), from 2:4-dimethyl-3-ethylpyrrole-5-aldehyde and (II), of 4'-benzoyl-3:3':5:5'-tetramethylpyrromethene hydrobromide, m.p. 189° (decomp.) (corresponding 4-Br-derivative which becomes discoloured at about 210°), and of 4'-benzoyl-3:3':5:5'-trimethyl-4-β-carboxyethylpyrromethene hydrobromide, m.p. 204° (decomp.) (corresponding 5-Br-derivative, which has no defined m.p.). If (II) is heated with 95% HCO₂H and 48% HBr is then added, 4:4'-dibenzoyl-3:3':5:5'-tetramethylpyrromethene hydrobromide (IV), decomp. 225°, is obtained, also prepared in AcOH or from Et 3-aldehyde-2:4-dimethylpyrrole-5-carboxylate and (II). 4:4'-Dibenzoyl-3:3':5:5'-tetramethylpyrromethene, m.p. 209°, is very stable. Addition of an intimate mixture of (III), 5:5'-dibromo-4:4'-dimethyl-3:3'-di-β-carboxyethylpyrromethene hydrobromide, and



(·CH₂·CO₂H)₂ to boiling (·CH₂·CO₂H) gives, after treatment of the product with CH₂N₂, small amounts of 4-benzoyl-2:3:5:8-tetramethyl-1-ethyl-6:7-di-β-carbomethoxyethylporphyrin (cf. A; R=·[CH₂]₂·CO₂H), m.p. 263° (corr.), and mesoporphyrin 13, thus establishing the formation of cryptopyrrole-methene as intermediate product. Analogous treatment of (IV) and 5:5'-dibromo-4:4'-dimethyl-3:3'-di-β-carboxyethylpyrromethene hydrobromide leads to 1:4-dibenzoyl-2:3:5:8-tetramethyl-6:7-di-β-carbomethoxyethylporphyrin [dibenzoyldeuteroporphyrin Me₂ ether 13]

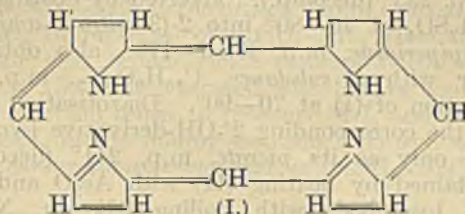


(cf. B: R=·[CH₂]₂·CO₂Me), m.p. 252° (corr.), which with Fe(OAc)₂ and NaCl in boiling AcOH affords the compound C₄₆H₄₀O₆N₄FeCl, m.p. about 290°; products, m.p. 183.5° (corr.) and 257° (corr.), respectively, are also obtained in the synthesis, which gives poor yields. Dibenzoyledeuteroporphyrin 5 is described.

Treatment of pyrrohaemin ester with Bz₂O and SnBr₄ at 70° leads to benzoylpyrrohaemin Me ester 5 (V), m.p. 313° (corr.), less readily obtained by use of SnCl₄; the corresponding free acid (VI) has m.p. > 320°. Treatment of (V) with AcOH, Fe(OAc)₂, and NaCl in boiling CHCl₃ affords benzoylpyrrohaemin Me ester, C₃₉H₃₈O₃N₄FeCl. (V) and Cu(OAc)₂ in

C₅H₅N-AcOH give the Cu salt, C₃₉H₃₈O₃N₄Cu. Benzoylpyrrohaemin oxime has m.p. 224°, but reaction is not observed with the acid and p-NO₂-C₆H₄·NH·NH₂ or NH₂·CO·NH·NH₂. Reduction of (VI) gives α-hydroxybenzylpyrrohaemin, m.p. > 300°, which gives minimal amounts of new porphyrins with boiling Ac₂O or (EtCO)₂O and pyrrohaemin when treated with conc. H₂SO₄ at 100°. Reduction of benzoylpyrrohaemin with Na and isoamyl alcohol is described. H. W.

Porphyrins. XXXV. Synthesis of porphyrin. H. FISCHER and W. GLEIM (Annalen, 1935, 521, 157—160).—Slow addition of pyrrole-2-aldehyde in EtOH



to boiling HCO₂H followed by protracted ebullition of the mixture gives very small amount of porphyrin (I), which darkens above 360° and blackens at 400°, and, in dioxan, closely resembles spectroscopically deoxoatioporphyrin. The Cu and Fe salts have been examined spectroscopically. H. W.

Optical absorption of porphyrins. III.—See this vol., 8.

Fluorescence spectra of chlorophyll pigments.—See this vol., 125.

Optical activity of hæmoglobin and its derivatives.—See this vol., 92.

Mechanism of oxidation of o-toluenesulphonamide to saccharin. O. J. MAGIDSON and I. G. ZILBERG (J. Gen. Chem. Russ., 1935, 5, 920—923).—o-C₆H₄Me·SO₂·NH₂ (I) in Ac₂O and CrO₃ at -5° to 30° yield o-C₆H₄Me·SO₂·NHAc, m.p. 132—134°, a substance (II), m.p. 174—176° (probably OAc·CH₂·C₆H₄·SO₂·NHAc), and a substance (III), m.p. 103—105°; in presence of H₂SO₄ acetsaccharin is obtained in addition to the above products. (II) and (III) yield saccharin (IV) when oxidised with KMnO₄, and (II) is probably an intermediate in the oxidation of (I) to (IV). R. T.

Fission of ketosulphidocarboxylic acids. II. Aryl selenohalides. VI. O. BEHAGEL and W. MÜLLER (Ber., 1935, 68, [B], 2164—2166; cf. A., 1935, 1237, 1257).—3-Keto-2:3-dihydro-1:4-benzoselenazine (I), C₆H₄Se<math display="block">\begin{array}{l} \text{Se-CH}_2 \\ \text{NH-CO} \end{array}, m.p. 182°, obtained by reduction of o-nitrophenylselenolacetic acid, is converted by Br in CHCl₃ into 1:1-dibromo-3-keto-2:3-dihydro-1:4-benzoselenazine (II), m.p. 211°, which loses HBr in boiling PhMe giving 2-bromo-3-keto-2:3-dihydro-1:4-benzoselenazine (III), m.p. 213—214°. Analogously 1:1-dichloro-3-keto-2:3-dihydro-1:4-benzoselenazine (IV), m.p. 222°, affords 2-chloro-3-keto-2:3-dihydro-1:4-benzoselenazine, m.p. 228°. Boiling H₂O transforms (II) or (IV) into the corresponding oxide, m.p. (indef.) 160°. (III) condenses

with $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ in feebly acid solution to the acid, $\text{C}_8\text{H}_7\text{Sc} > \text{CH}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, m.p. 209—210°, hydrolysed by alkali to (I), H_2S , and $\text{H}_2\text{C}_2\text{O}_4$.

H. W.

Amidation with sodium and potassium amides on α - and α' -aminoanabasine. IV. Nitration of α' -aminoanabasine. M. M. KATZNELSON and M. I. KABATSCHNIK (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 169—172).—2-(2'-Amino-5'-pyridyl)piperidine (I), m.p. 109° (α' -aminoanabasine; A., 1935, 223), with HNO_3 (d 1.4)— H_2SO_4 at 0° affords the 2'-nitroamine isolated as its sulphate + H_2O and anhyd. (II), m.p. 233° (decomp.), converted by heating with conc. H_2SO_4 at 70—80° into 2-(3'-nitro-2'-amino-5'-pyridyl)piperidine, m.p. 178.5—179°, also obtained, together with a substance, $\text{C}_{10}\text{H}_9\text{O}_6\text{N}_3$, m.p. 70°, by nitration of (I) at 70—90°. Diazotisation of (I) affords the corresponding 2'-OH-derivative (Na salt) isolated only as its picrate, m.p. 241° (decomp.), also obtained by heating (II) with Ac_2O and subsequent hydrolysis with boiling 5% aq. NaOH. [Note: the m.p. of the 3'- and 5'-pyridyl compounds (*loc. cit.*) should be interchanged; that of the former is 89.5—90°.]

J. W. B.

Cactus alkaloids. XV. Separation of the Anhalonium bases. E. SPÄTH and F. BECKE (Monatsh., 1935, 66, 327—336).—Mescal buttons are extracted with pure EtOH at room temp. and, after removal of solvent, the extract is dissolved in H_2O , treated with excess of KOH, and exhaustively extracted with pure Et_2O . The extract is shaken with conc. KOH. The combined alkaline solutions are neutralised, rendered slightly alkaline with K_2CO_3 , and extracted with Et_2O , thus giving all the phenolic alkaloids with small amounts of non-basic compounds. From them anhalamine is first separated as the hydrochloride. The free bases are isolated from the mother-liquors from this salt, distilled in a high vac., and pellotine is pptd. as the hydrochloride from their solution in EtOH— Et_2O . The residual mixture of bases give a cryst. perchlorate which is not homogeneous. Treatment of the bases with Et_2O separates them into the sparingly sol. anhalonidine and anhalidine [N-methylanhalamine]. From the non-phenolic bases the bulk of the mescaline is first separated as the sulphate from H_2O ; from the mother-liquors anhalonine is isolated as the sparingly sol. hydrochloride. Anhalinine [O-methylanhalamine] is also isolated, whilst the final mother-liquors afford lophophorine, separated as the picrate.

H. W.

Alkaloids of Papaver types. I. Alkaloids of P. armeniacum and P. orientale. R. KONOVALOVA, S. JUNUSOV, and A. OREKHOV (Ber., 1935, 68, [B], 2158—2163).—Percolation with $\text{C}_2\text{H}_4\text{Cl}_2$ of the air-dried foliage of *P. orientale* which has been moistened with 10% NH_3 leads to the isolation of thebaine and oripavine, $\text{C}_{18}\text{H}_{21}\text{O}_3\text{N}$, m.p. 200—201°. [α]_D -211.8° in CHCl_3 (hydrochloride, m.p. 244—245°; methiodide, m.p. 207—208°), which dissolves in 10% NaOH giving a cryst. Na salt. It appears to be $\text{C}_{18}\text{H}_{12}\text{O}(\text{NMe})(\text{OMe})\cdot\text{OH}$. The presence of isothebaine could not be detected. Similar treatment of *P. armeniacum* yields arnepavine (I), $\text{C}_{19}\text{H}_{23}\text{O}_3\text{N}$,

m.p. 148—149° (or, + H_2O , m.p. about 100°), [α]_D -118.7° in CHCl_3 (hydrochloride, m.p. 151—152°; sparingly sol. oxalate, m.p. 211—212°; methiodide, m.p. 199—200°), which contains NMe, 2 OMe, and OH. (I) is transformed by MeI and NaOMe in boiling MeOH into O-methylarnepavine methiodide, m.p. 120—122°. Treatment of (I) in CHCl_3 with ClCO_2Et and NaOH gives an optically inactive oil, indicating that (I) may be a tetrahydroisoquinoline derivative.

H. W.

Alkaloid of chin-shih-hu. K. K. CHEN and H. L. CHEN (J. Biol. Chem., 1935, 111, 653—658).—Chin-shih-hu from Szechuan contains 0.52% of alkaloids, mainly dendrobine (modified isolation), $\text{C}_{16}\text{H}_{25}\text{O}_2\text{N}$, m.p. 135°, [α]_D²⁰ -52° in EtOH [hydrochloride, m.p. 193°, [α]_D²⁰ -40.3°; hydrobromide, m.p. 259—259.5°, [α]_D²⁰ -34.3°; hydriodide, m.p. 284—284.5°, [α]_D²⁰ -29°; nitrate, m.p. 198.5—199°, [α]_D²⁰ -30.2°; sulphate, m.p. 178°, [α]_D²⁰ -36.7°; oxalate, m.p. 137—138°, [α]_D²⁰ -50.8°; picrate, m.p. 210° (decomp.); flavianate, decomp. 212°; methiodide, m.p. 246°, [α]_D²⁰ -28.8° in EtOH; aurichloride, m.p. 183—184°; platinichloride, m.p. 283°. [α] are in H_2O]. The Kweichow variety contains another alkaloid, but no dendrobine. M.p. are corr.

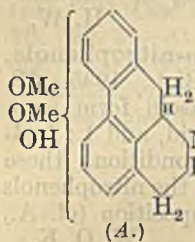
R. S. C.

Alkaloid from Trichodesma incanum D.C. I. G. MENSCHIKOV and V. RUBINSTEIN (Ber., 1935, 68, [B], 2039—2044).—Percolation of the dried plant with 95% EtOH containing 1% of NH_3 , removal of the solvent, and extraction of the residue with dil. HCl followed by treatment of the acid solution with NH_3 and CHCl_3 yields trichodesmine (I), $\text{C}_{18}\text{H}_{27}\text{O}_6\text{N}$, m.p. 160—161° (decomp.), [α]_D +38° in EtOH [methiodide, m.p. 202° (decomp.)], which does not react with cold HNO_2 , and hence contains tert.-N. Hydrolysis of (I) with 10% NaOH at 100° affords COMeBu^β, r-lactic acid, and trichodesmidine (II), $\text{C}_8\text{H}_{13}\text{O}_2\text{N}$, m.p. 117—118.5°, [α]_D +50° in MeOH (picrate, m.p. 142—143.5°), not identical with heliotridine. Hydrogenation of (II) readily affords the saturated hydroxytrichodesmidane (III), $\text{C}_8\text{H}_{15}\text{ON}$, m.p. 92—94° [picrate, m.p. 211.5—212.5° (decomp.)]. Treatment of (III) with conc. H_2SO_4 at 165—170° and subsequent hydrogenation (Adams) of the product leads to heliotridane. Heliotridine and (II) have therefore the same skeleton, and are differentiated from one another by the position of OH and possibly of the double linking. (I) is a complex ester of (II) and r-lactic acid and either $\text{CHPr}^\beta\text{Ac}\cdot\text{CO}_2\text{H}$ or isovalerylacetic acid. The distribution of acid residues in the mol. cannot yet be established; since (I) does not give a colour with FeCl_3 , it is probable that lactic acid esterifies the enolic OH of the tautomeric form of the β -CO-acid.

H. W.

Sinomenine. XLIV. Tuduranine, a new alkaloid from Sinomenium acutum. K. GOTO (Annalen, 1935, 521, 175—184).—The mother-liquors from the extraction of sinomenine give the sparingly sol. tuduranine hydrochloride (I), $\text{C}_{18}\text{H}_{19}\text{O}_3\text{N}\cdot\text{HCl}$, m.p. 286° (decomp.), [α]_D²⁵ -148° in $\text{H}_2\text{O} + \text{MeOH}$, from which the poorly cryst. tuduranine (II), m.p. about 125° after softening at 105°, is isolated. (II) contains 2 OMe, but no CH_2O , is freely sol. in alkali, but gives a feeble FeCl_3 or diazo-reaction. The presence of

1 OH is established by the isolation of *diacetyltuduranine*, m.p. 170°, $[\alpha]_D^{25}$ -321.71° in MeOH, which does not combine with MeI, and is hydrolysed to *N-acetyltuduranine*, m.p. 277°, $[\alpha]_D^{25}$ -395.24° in MeOH-CHCl₃, whence *N-acetyltuduranine Me ether*, m.p. 189°, $[\alpha]_D^{25}$ -400.17° in CHCl₃. (II) and MeI in MeOH afford *N-methyltuduranine methiodide* (III), m.p. 224°. (II) gives a characteristic, fuchsin-red colour with CH₂O-H₂SO₄. Spectroscopically, (I) is closely similar to morphothebaine Me₂ ether (III). The Hofmann degradation of *N-methyltuduranine Me ether methiodide*, m.p. 219°, however, affords successively *de-N-dimethyltuduranine Me ether (methiodide)*, m.p. 279° and *trimethoxyvinylphenanthrene*, m.p. 93.5°, with NMe₃; the positions of the 3 OMe in the ether do not therefore coincide with those in (III) or *isothebaine Me ether*. (I) is transformed by NaOH and Et₂SO₄ followed by KI into *N-ethyltuduranine Et ether ethiodide*, m.p. 238°, $[\alpha]_D^{25}$ -112.47° in CHCl₃ (with some *N-diethyltuduranine Et ether ethiodide*, m.p. 163—164°), converted by the successive action of NaOH and EtI into *de-N-diethyltuduranine Et ether ethiodide*, m.p. 164°, $[\alpha]_D^{25}$ $\pm 0^\circ$ (corresponding *hydriodide*, m.p. 163—164°), whence *dimethoxyethoxyvinylphenanthrene*, m.p. 148° after softening at 110°, and NEt₃. The Hofmann degradation of (III) gives *de-N-dimethyltuduranine (methiodide)*, m.p. 259°, whence a compound, C₁₈H₁₆O₃, m.p. 292—294°. Oxidation of (II) with



KMnO₄ gives very small amounts of an acid, m.p. about 263°, but no hemipinic or *metahemipinic* acid. The structure *A* is therefore assigned to (II). H. W.

Sinomenine. XLII. (+)- and (-)-**Bromothebenone.** K. GOTO, M. OGAWA, and J. SAITO (Bull. Chem. Soc. Japan, 1935, 10, 481—482; cf. A., 1935, 1138).—Dihydrode-*N*-methylmethoxydihydrosinomenine (I) and Br-AcOH give the (+)-1-*Br*-derivative (II), m.p. 192°, $[\alpha]_D^{17}$ $+61.6^\circ$ in CHCl₃ [*hydrobromide*, m.p. 257° (decomp.); *methiodide*, m.p. 273°]. The methiodide of (I) and 25% KOH give (-)-1-*bromothebenone* (III), m.p. 70°, $[\alpha]_D^{17}$ -22.67° in CHCl₃. 1-Bromodemethoxydihydrosinomenine methiodide and 15% NaOH give 1-*bromode-N-methylmethoxydihydrosinomenine* (IV), m.p. 200—201°, $[\alpha]_D^{17}$ -8.67° in CHCl₃, the *methiodide*, decomp. 243°, of which with 11% NaOH affords (-)-1-*bromodehydrothebenone* (V), m.p. 145°, $[\alpha]_D^{17}$ -186.8° in CHCl₃. (-)-*Dehydrosinomenine* and Br-AcOH yield (-)-*iso-9-* or *-10-bromodehydrothebenone* (VI), m.p. 125—133°, $[\alpha]_D^{17}$ -113.3° in CHCl₃. The *stereoisomerides* are prepared from thebainone and admixture gives the *dl-bases*, (II), m.p. 175—177°, (III), m.p. 191—193°, (IV), m.p. 189—192°, (V), m.p. 159—162°, and (VI), m.p. 156—158°. R. S. C.

Bitter principles of the Colombo root. III. K. FEIST, E. KUNTZ, and R. BRACHVOGEL (Annalen, 1935, 521, 184—188; cf. A., 1935, 1245).—The discrepancies between the authors' observations and those of Wessely *et al.* (*ibid.*, 1432) are due to the use by the latter of insufficiently purified material. Columbin is very sensitive to alkali, and attempts to

methylate it by KOH-*p*-C₆H₄Me-SO₃Me lead to *carboxyiso-V-columbin*, m.p. 194—195° (decomp.).

H. W.

Alkaloids of *Duboisia Hopwoodii*.—See this vol., 125.

Alkaloids of European *Lycopodium* species.—See this vol., 125.

Influence of air on solutions of salvarsan derivatives.—See this vol., 32.

Arsenical derivatives of carbazole. S. M. SCHERLIN and A. J. BERLIN (J. Gen. Chem. Russ., 1935, 5, 938—942).—Diazotised 3-aminocarbazole and Na₃AsO₃ in presence of CuSO₄-NH₃ yield *carbazyl-3-arsinic acid*, which yields *carbazyl-3-dichloroarsine* (I), m.p. 150°, when treated with SO₂ in conc. HCl-EtOH at room temp. in presence of I₂ and carbazole and AsCl₃ in the boiling solution. (I) and aq. NH₃ afford *carbazyl-3-arsinous acid*, m.p. 267—269°.

R. T.

Action of alkyl iodides on heterocyclic organic arsenic compounds. I. V. S. MALINOVSKI (J. Gen. Chem. Russ., 1935, 5, 510—514).—The Cl of 5-chloro- and 5-chloro-10-acetyl-5:10-dihydrophenarsazine, chlorophenoxarsine, and diphenylenechlorarsine in replaced by I when the compounds are heated with MeI, EtI, or *iso*-C₅H₁₁I in sealed tubes, products containing As^v not being formed. 5:10-Dihydrophenarsazine oxide and MeI (6 hr.; 90°) afford an unidentified *product*, C₁₄H₁₅NAsI₂, m.p. 138—142°, containing As^v, whilst EtI and *iso*-C₅H₁₁I yield 5-iodo-5:10-dihydrophenarsazine. 5-Acetyl-5:10-dihydrophenarsazine and MeI give 5-methyl-5:10-dihydrophenarsazine methiodide. R. T.

Hydroxy-derivatives of 5-alkyl(aryl)-5:10-dihydrophenarsazine. II. Synthesis and properties of monohydroxy-5-R-5-R'-5:10-dihydrophenarsazine. III. Synthesis of derivatives of the betaine type. G. A. RAZUVAIEV and V. S. MALINOVSKI (J. Gen. Chem. Russ., 1935, 5, 570—574, 575—579).—II [with A. F. SHIGATSCHEV and Z. I. AZARCHI]. The methiodides of 5-alkyl(aryl)-dihydrophenarsazines yield the following hydroxides and nitrates with AgOH and AgNO₃, respectively: *monohydroxide* of 5:5-*dimethyl*-, m.p. 242° [*nitrate* (I), m.p. 258°; *NO*₂-*derivative* (II)], of 5-*phenyl-5-methyl*-, m.p. 202—204° [*nitrate*, m.p. 210°; *NO*₂-*derivative* (III), m.p. 120—124°], and of 5-*methyl-5-isoamyl-5:10-dihydrophenarsazine*, m.p. not given (*nitrate*, m.p. 191—193°). Attempts to reduce the NO₂ of (II) and (III) resulted in its elimination.

III [with S. E. ARKINA]. 5-Methyl-5:10-dihydrophenarsazine and CH₂Cl-CO₂H in C₆H₆ at 90° yield 5-*chloro-5-methyl-5:10-dihydrophenarsazinoacetic acid* (IV), m.p. 237—238° [*Et ester* (V), m.p. 198°; *nitrate*, m.p. 179°; *platinichloride*, m.p. 138—140°; *picrate*, m.p. 199°]; the analogous 5-*Et derivative*, m.p. 201—204° (*nitrate*, m.p. 170°), is obtained similarly. (IV) or (V) afford an *anhydride* (VI), m.p. 199—203°, of the betaine type, when heated with aq. NaOH. The *dinitro-derivative* of (VI), m.p. 163—165° obtained from (IV) and HNO₃, yields (VI) when reduced with Fe(OH)₂ in aq. NaOH. R. T.

with $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ in feebly acid solution to the acid, $\text{C}_6\text{H}_4\cdot\text{Se}\begin{matrix} \diagup \\ \text{NH-CO} \end{matrix}\text{CH}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, m.p. 209—210°, hydrolysed by alkali to (I), H_2S , and $\text{H}_2\text{C}_2\text{O}_4$.

H. W.

Amidation with sodium and potassium amides on α - and α' -aminoanabasine. IV. Nitration of α' -aminoanabasine. M. M. KATZNELSON and M. I. KABATSCHIK (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 169—172).—2-(2'-Amino-5'-pyridyl)piperidine (I), m.p. 109° (α' -aminoanabasine; A., 1935, 223), with HNO_3 (*d* 1.4)— H_2SO_4 at 0° affords the 2'-nitroamine isolated as its *sulphate*+ H_2O and anhyd. (II), m.p. 233° (decomp.), converted by heating with conc. H_2SO_4 at 70—80° into 2-(3'-nitro-2'-amino-5'-pyridyl)piperidine, m.p. 178.5—179°, also obtained, together with a *substance*, $\text{C}_{10}\text{H}_9\text{O}_6\text{N}_3$, m.p. 70°, by nitration of (I) at 70—90°. Diazotisation of (I) affords the corresponding 2'-OH-derivative (*Na* salt) isolated only as its *picrate*, m.p. 241° (decomp.), also obtained by heating (II) with Ac_2O and subsequent hydrolysis with boiling 5% aq. NaOH . [Note: the m.p. of the 3'- and 5'-pyridyl compounds (*loc. cit.*) should be interchanged; that of the former is 89.5—90°.]

J. W. B.

Cactus alkaloids. XV. Separation of the Anhalonium bases. E. SPATH and F. BECKE (Monatsh., 1935, 66, 327—336).—Mescal buttons are extracted with pure EtOH at room temp. and, after removal of solvent, the extract is dissolved in H_2O , treated with excess of KOH , and exhaustively extracted with pure Et_2O . The extract is shaken with conc. KOH . The combined alkaline solutions are neutralised, rendered slightly alkaline with K_2CO_3 , and extracted with Et_2O , thus giving all the phenolic alkaloids with small amounts of non-basic compounds. From them anhalamine is first separated as the hydrochloride. The free bases are isolated from the mother-liquors from this salt, distilled in a high vac., and pelletine is pptd. as the hydrochloride from their solution in $\text{EtOH}\text{-Et}_2\text{O}$. The residual mixture of bases give a *cryst. perchlorate* which is not homogeneous. Treatment of the bases with Et_2O separates them into the sparingly sol. anhalonidine and *anhalidine* [*N*-methylanhalamine]. From the non-phenolic bases the bulk of the mescaline is first separated as the *sulphate* from H_2O ; from the mother-liquors anhalonine is isolated as the sparingly sol. hydrochloride. Anhalinine [*O*-methylanhalamine] is also isolated, whilst the final mother-liquors afford lophophorine, separated as the *picrate*.

H. W.

Alkaloids of Papaver types. I. Alkaloids of *P. armeniacum* and *P. orientale*. R. KONOVALOVA, S. JUNUSSOV, and A. OREKHOV (Ber., 1935, 68, [B], 2158—2163).—Percolation with $\text{C}_2\text{H}_5\text{Cl}_2$ of the air-dried foliage of *P. orientale* which has been moistened with 10% NH_3 leads to the isolation of thebaine and *oripavine*, $\text{C}_{18}\text{H}_{21}\text{O}_3\text{N}$, m.p. 200—201°, $[\alpha]_D^{20}$ -211.8° in CHCl_3 (*hydrochloride*, m.p. 244—245°; *methiodide*, m.p. 207—208°), which dissolves in 10% NaOH giving a *cryst. Na* salt. It appears to be $\text{C}_{16}\text{H}_{12}\text{O}(\text{NMe})(\text{OMe})\text{-OH}$. The presence of *isothebaine* could not be detected. Similar treatment of *P. armeniacum* yields *armepavine* (I), $\text{C}_{19}\text{H}_{23}\text{O}_3\text{N}$,

m.p. 148—149° (or, + H_2O , m.p. about 100°), $[\alpha]_D^{20}$ -118.7° in CHCl_3 (*hydrochloride*, m.p. 151—152°; sparingly sol. *oxalate*, m.p. 211—212°; *methiodide*, m.p. 199—200°), which contains *NMe*, 2 *OMe*, and *OH*. (I) is transformed by *MeI* and *NaOMe* in boiling MeOH into *O-methylarmepavine methiodide*, m.p. 120—122°. Treatment of (I) in CHCl_3 with ClCO_2Et and NaOH gives an optically inactive oil, indicating that (I) may be a tetrahydroisoquinoline derivative.

H. W.

Alkaloid of chin-shih-hu. K. K. CHEN and H. L. CHEN (J. Biol. Chem., 1935, 111, 653—658).—Chin-shih-hu from Szechuan contains 0.52% of alkaloids, mainly dendrobine (modified isolation), $\text{C}_{16}\text{H}_{25}\text{O}_2\text{N}$, m.p. 135°, $[\alpha]_D^{20}$ -52° in EtOH [*hydrochloride*, m.p. 193°, $[\alpha]_D^{20}$ -40.3°; *hydrobromide*, m.p. 259—259.5°, $[\alpha]_D^{20}$ -34.3°; *hydriodide*, m.p. 284—284.5°, $[\alpha]_D^{20}$ -29°; *nitrate*, m.p. 198.5—199°, $[\alpha]_D^{20}$ -30.2°; *sulphate*, m.p. 178°, $[\alpha]_D^{20}$ -36.7°; *oxalate*, m.p. 137—138°, $[\alpha]_D^{20}$ -50.8°; *picrate*, m.p. 210° (decomp.); *flavianate*, decomp. 212°; *methiodide*, m.p. 246°, $[\alpha]_D^{20}$ -28.8° in EtOH ; *aurichloride*, m.p. 183—184°; *platinichloride*, m.p. 283°. $[\alpha]$ are in H_2O]. The Kweichow variety contains another alkaloid, but no dendrobine. M.p. are *corr.*

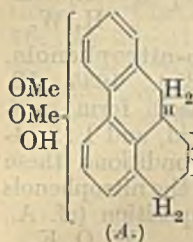
R. S. C.

Alkaloid from *Trichodesma incanum* D. C. I. G. MENSCHIKOV and V. RUBINSTEIN (Ber., 1935, 68, [B], 2039—2044).—Percolation of the dried plant with 95% EtOH containing 1% of NH_3 , removal of the solvent, and extraction of the residue with dil. HCl followed by treatment of the acid solution with NH_3 and CHCl_3 yields *trichodesmine* (I), $\text{C}_{18}\text{H}_{27}\text{O}_6\text{N}$, m.p. 160—161° (decomp.), $[\alpha]_D^{20}$ +38° in EtOH [*methiodide*, m.p. 202° (decomp.)], which does not react with cold HNO_2 , and hence contains *tert.-N*. Hydrolysis of (I) with 10% NaOH at 100° affords *COMeBu* ^{β} , *r*-lactic acid, and *trichodesmidine* (II), $\text{C}_8\text{H}_{13}\text{O}_2\text{N}$, m.p. 117—118.5°, $[\alpha]_D^{20}$ +50° in MeOH (*picrate*, m.p. 142—143.5°), not identical with *heliotridine*. Hydrogenation of (II) readily affords the saturated *hydroxytrichodesmidane* (III), $\text{C}_8\text{H}_{15}\text{ON}$, m.p. 92—94° [*picrate*, m.p. 211.5—212.5° (decomp.)]. Treatment of (III) with conc. H_2SO_4 at 165—170° and subsequent hydrogenation (Adams) of the product leads to *heliotridane*. *Heliotridine* and (II) have therefore the same skeleton, and are differentiated from one another by the position of *OH* and possibly of the double linking. (I) is a complex ester of (II) and *r*-lactic acid and either $\text{CHPr}^\beta\text{Ac}\cdot\text{CO}_2\text{H}$ or *iso*-valerylacetic acid. The distribution of acid residues in the mol. cannot yet be established; since (I) does not give a colour with FeCl_3 it is probable that lactic acid esterifies the enolic *OH* of the tautomeric form of the β -CO-acid.

H. W.

Sinomenine. XLIV. Tuduranine, a new alkaloid from *Sinomenium acutum*. K. GOTO (Annalen, 1935, 521, 175—184).—The mother-liquors from the extraction of sinomenine give the sparingly sol. *tuduranine hydrochloride* (I), $\text{C}_{18}\text{H}_{19}\text{O}_3\text{N}\cdot\text{HCl}$, m.p. 286° (decomp.), $[\alpha]_D^{20}$ -148° in $\text{H}_2\text{O}+\text{MeOH}$, from which the poorly *cryst. tuduranine* (II), m.p. about 125° after softening at 105°, is isolated. (II) contains 2 *OMe*, but no CH_2O_2 ; is freely sol. in alkali, but gives a feeble FeCl_3 or diazo-reaction. The presence of

1 OH is established by the isolation of *diacetyltuduranine*, m.p. 170°, $[\alpha]_D^{25} - 321.71^\circ$ in MeOH, which does not combine with MeI, and is hydrolysed to *N-acetyltuduranine*, m.p. 277°, $[\alpha]_D^{25} - 395.24^\circ$ in MeOH-CHCl₃, whence *N-acetyltuduranine Me ether*, m.p. 189°, $[\alpha]_D^{25} - 400.17^\circ$ in CHCl₃. (II) and MeI in MeOH afford *N-methyltuduranine methiodide* (III), m.p. 224°. (II) gives a characteristic, fuchsin-red colour with CH₂O-H₂SO₄. Spectroscopically, (I) is closely similar to morphothebaine Me₂ ether (III). The Hofmann degradation of *N-methyltuduranine Me ether methiodide*, m.p. 219°, however, affords successively *de-N-dimethyltuduranine Me ether (methiodide)*, m.p. 279° and *trimethoxyvinylphenanthrene*, m.p. 93.5°, with NMe₃; the positions of the 3 OMe in the ether do not therefore coincide with those in (III) or *isothebaine Me ether*. (I) is transformed by NaOH and Et₂SO₄ followed by KI into *N-ethyltuduranine Et ether ethiodide*, m.p. 238°, $[\alpha]_D^{25} - 112.47^\circ$ in CHCl₃ (with some *N-diethyltuduranine Et ether ethiodide*, m.p. 163—164°), converted by the successive action of NaOH and EtI into *de-N-diethyltuduranine Et ether ethiodide*, m.p. 164°, $[\alpha]_D \pm 0^\circ$ (corresponding *hydriodide*, m.p. 163—164°), whence *dimethoxy-ethoxyvinylphenanthrene*, m.p. 148° after softening at 110°, and NEt₃. The Hofmann degradation of (III) gives *de-N-dimethyltuduranine (methiodide)*, m.p. 259°, whence a compound, C₁₈H₁₆O₃, m.p. 292—294°. Oxidation of (II) with



KMnO₄ gives very small amounts of an acid, m.p. about 263°, but no hemipinic or *metahemipinic* acid. The structure A is therefore assigned to (II). H. W.

Sinomenine. XLII. (+)- and (-)-**Bromothebenone.** K. GOTO, M. OGAWA, and J. SAITO (Bull. Chem. Soc. Japan, 1935, 10, 481—482; cf. A., 1935, 1138).—Dihydrode-*N*-methylmethoxydihydrosinomenine (I) and Br-AcOH give the (+)-1-*Br*-derivative (II), m.p. 192°, $[\alpha]_D^{25} + 61.6^\circ$ in CHCl₃ [*hydrobromide*, m.p. 257° (decomp.); *methiodide*, m.p. 273°]. The methiodide of (I) and 25% KOH give (-)-1-*bromothebenone* (III), m.p. 70°, $[\alpha]_D^{25} - 22.67^\circ$ in CHCl₃. 1-Bromodemethoxydihydrosinomenine methiodide and 15% NaOH give 1-*bromode-N-methylmethoxydihydrosinomenine* (IV), m.p. 200—201°, $[\alpha]_D^{25} - 8.67^\circ$ in CHCl₃, the *methiodide*, decomp. 243°, of which with 11% NaOH affords (-)-1-*bromodehydrothebenone* (V), m.p. 145°, $[\alpha]_D^{25} - 186.8^\circ$ in CHCl₃. (-)-Dehydrosinomenine and Br-AcOH yield (-)-*iso-9-* or -*10-bromodehydrothebenone* (VI), m.p. 125—133°, $[\alpha]_D^{25} - 113.3^\circ$ in CHCl₃. The *stereoisomerides* are prepared from thebainone and admixture gives the *dl-bases*, (II), m.p. 175—177°, (III), m.p. 191—193°, (IV), m.p. 189—192°, (V), m.p. 159—162°, and (VI), m.p. 156—158°. R. S. C.

Bitter principles of the *Colombo* root. III. K. FEIST, E. KUNTZ, and R. BRACHVOGEL (Annalen, 1935, 521, 184—188; cf. A., 1935, 1245).—The discrepancies between the authors' observations and those of Wessely *et al.* (*ibid.*, 1432) are due to the use by the latter of insufficiently purified material. Columbin is very sensitive to alkali, and attempts to

methylate it by KOH-*p*-C₆H₄Me·SO₃Me lead to *carboxyiso-V-columbin*, m.p. 194—195° (decomp.).

H. W.

Alkaloids of *Duboisia Hopwoodii*.—See this vol., 125.

Alkaloids of European *Lycopodium* species.—See this vol., 125.

Influence of air on solutions of salvarsan derivatives.—See this vol., 32.

Arsenical derivatives of carbazole. S. M. SCHERLIN and A. J. BERLIN (J. Gen. Chem. Russ., 1935, 5, 938—942).—Diazotised 3-aminocarbazole and Na₃AsO₃ in presence of CuSO₄·NH₃ yield *carbazyl-3-arsinic acid*, which yields *carbazyl-3-dichloroarsine* (I), m.p. 150°, when treated with SO₂ in conc. HCl-EtOH at room temp. in presence of I, and carbazole and AsCl₃ in the boiling solution. (I) and aq. NH₃ afford *carbazyl-3-arsinous acid*, m.p. 267—269°.

R. T.

Action of alkyl iodides on heterocyclic organic arsenic compounds. I. V. S. MALINOVSKI (J. Gen. Chem. Russ., 1935, 5, 510—514).—The Cl of 5-chloro- and 5-chloro-10-acetyl-5:10-dihydrophenarsazine, chlorophenoxarsine, and diphenylenechloroarsine in replaced by I when the compounds are heated with MeI, EtI, or *iso*-C₅H₁₁I in sealed tubes, products containing As^V not being formed. 5:10-Dihydrophenarsazine oxide and MeI (6 hr.; 90°) afford an unidentified product, C₁₄H₁₅NAsI₂, m.p. 138—142°, containing As^V, whilst EtI and *iso*-C₅H₁₁I yield 5-iodo-5:10-dihydrophenarsazine. 5-Acetyl-5:10-dihydrophenarsazine and MeI give 5-methyl-5:10-dihydrophenarsazine methiodide.

R. T.

Hydroxy-derivatives of 5-alkyl(aryl)-5:10-dihydrophenarsazine. II. Synthesis and properties of monohydroxy-5-*R*-5-*R'*-5:10-dihydrophenarsazine. III. Synthesis of derivatives of the betaine type. G. A. RAZUVAIEV and V. S. MALINOVSKI (J. Gen. Chem. Russ., 1935, 5, 570—574, 575—579).—II [with A. F. SHIGATSKH and Z. I. AZARCH]. The methiodides of 5-alkyl(aryl)-dihydrophenarsazines yield the following hydroxides and nitrates with AgOH and AgNO₃, respectively: *monohydroxide* of 5:5-*dimethyl-*, m.p. 242° [*nitrate* (I), m.p. 258°; *NO₂-derivative* (II)], of 5-*phenyl-5-methyl-*, m.p. 202—204° [*nitrate*, m.p. 210°; *NO₂-derivative* (III), m.p. 120—124°], and of 5-*methyl-5-isoamyl-5:10-dihydrophenarsazine*, m.p. not given (*nitrate*, m.p. 191—193°). Attempts to reduce the NO₂ of (II) and (III) resulted in its elimination.

III [with S. E. ARKINA]. 5-Methyl-5:10-dihydrophenarsazine and CH₂Cl·CO₂H in C₆H₆ at 90° yield 5-*chloro-5-methyl-5:10-dihydrophenarsazinoacetic acid* (IV), m.p. 237—238° [*Et ester* (V), m.p. 198°; *nitrate*, m.p. 179°; *platinichloride*, m.p. 138—140°; *picrate*, m.p. 199°]; the analogous 5-*Et* derivative, m.p. 201—204° (*nitrate*, m.p. 170°), is obtained similarly. (IV) or (V) afford an *anhydride* (VI), m.p. 199—203°, of the betaine type, when heated with aq. NaOH. The *dinitro-derivative* of (VI), m.p. 163—165° obtained from (IV) and HNO₃, yields (VI) when reduced with Fe(OH)₂ in aq. NaOH.

R. T.

Formaldehyde, alcohol, and acetone titrations. Addendum. G. M. RICHARDSON (Proc. Roy. Soc., 1935, B, 119, 85—86; cf. A., 1934, 634).—In the titration of substances containing several acidic or basic groups the initial and end-points must be clearly defined.
E. A. H. R.

Determination of reducing sugars.—See this vol., 126.

Potentiometric determination of polypeptides and amino-acids. E. W. BALSON, G. A. EARWICKER, and A. LAWSON (Biochem. J., 1935, 29, 2700—2704).—Titration of mixtures of NH_2 -acids and polypeptides is carried out in 90% aq. EtOH: the degree of separation is discussed. As the p_{H} of the end-point for some mixtures varies over a range of 2 units depending on the proportions of the constituents, a potentiometric titration is used with a special method of differential plotting. J. N. A.

Determination of benzene by the Pulfrich step-photometer.—See this vol., 126.

Determination of toluidines in aqueous solution. D. CISMARU (Bul. Soc. Chim. România, 1934, 16, [A], 37—41).—Aq. *o*-, *m*-, or *p*-toluidine, CuSO_4 , and 0.1N- NH_4CNS give quantitatively salts, $[\text{CuB}_2](\text{SCN})_2$. The base is determined by filtration and titration of the excess of NH_4CNS in the filtrate.
R. S. C.

Spectrographic determination of phenol.—See this vol., 126.

Photo-electric determination of salicylic acid. P. F. BECH (Dansk Tidsskr. Farm., 1935, 9, 289—302).—The depth of colour of the Fe-salicylic acid complex in aq. solution is measured photo-electrically with a previously calibrated apparatus. Improvements in the author's earlier method are described (Farm. Tidende, 1933, 446). The effects of excess of salicylic acid and EtOH and of varying p_{H} have been investigated. Reproducible results are obtainable so long as Fe^{+++} is in excess, $[\text{EtOH}] \gtrsim 8\%$, and $p_{\text{H}} \leq 2.2$.
M. H. M. A.

Acid-base titration in alcohol-water mixtures.

III. Titration of alkaloids and alkaloid salts.

H. BAGGESGAARD-RASMUSSEN and F. REIMERS (Dansk Tidsskr. Farm., 1935, 9, 253—288; cf. A., 1934, 160).—The acidity consts. P_{K} for narcotine, papaverine, strychnine, morphine, codeine, brucine, cocaine, procaine, quinine, emetine, cinchonine, atropine, and ephedrine in 50% and 75% aq. EtOH have been determined colorimetrically and electrometrically, and the variation of P_{K} with $[\text{EtOH}]$ is compared with that of indicator end-points. Most alkaloids lie on the border of practicable titration in 50% EtOH, but titration of alkaloid salts with bases is more accurate in aq. EtOH than in H_2O .
J. A. S.

Biochemistry.

Gravimetric method for determining oxygen consumption in man. J. P. HETTWER (J. Lab. Clin. Med., 1935, 20, 499—506).
CH. ABS. (*p*)

Respiration apparatus for small animals. S. BELÁK and A. ILLÉNYI (Biochem. Z., 1935, 281, 27—29).
W. McC.

Oxygen saturation of human arterial blood. K. MATTHES (Arch. exp. Path. Pharm., 1935, 179, 698—711).—Continuous photo-electric recording (cf. A., 1934, 1377) indicates variations in arterial O_2 saturation during inspiration of O_2 -rich air, hyperventilation, respiratory failure, speaking, singing, etc. During the respiratory pause there is a fall in O_2 saturation, the rate of which is a function of alveolar vol. The exact respiratory vol. being known, determinations of this rate for resting men during a series of respiratory pauses give the vol. of residual air and total capacity of the lungs. Tension, consumption, and velocity of transport of O_2 during relaxation after heavy work are discussed.
F. O. H.

Thermochemistry of the oxygen-hæmoglobin reaction. I. Direct measurements of the heat of reaction under various conditions. F. J. W. ROUGHTON (Biochem. J., 1935, 29, 2604—2621).—The heat of reaction (Q) of hæmoglobin (I) with O_2 is measured by shaking the solution of (I) with O_2 in one Thermos flask and determining the temp. difference between this and another flask containing the same amount of fluid. Q is independent of the degree of O_2 saturation of the blood, and is practically

the same in whole and laked blood and in purified (I) solutions. Q increases with increasing p_{H} , due partly to the difference between the Q for ionised (I) and that for non-ionised (I), and partly to secondary ionic reactions.
H. D.

Time course of heat effects in rapid chemical changes. I. Apparatus and methods. II. Reactions of hæmoglobin with oxygen and carbon monoxide. J. B. BATEMAN and F. J. W. ROUGHTON (Biochem. J., 1935, 29, 2622—2638).—The earlier apparatus for measuring the heat effects in rapid chemical changes (A., 1930, 426) is modified so that the method will follow to within 1—2% the time course of the heat effects over a period of 0—0.01 sec. in which the total temp. change is $< 0.01^\circ$. The method is applied to the reaction of hæmoglobin (I) with O_2 and CO. With O_2 the liberation of heat is complete within 0.008 sec., and with CO in approx. 0.05 sec. The half-reaction times for (I) with O_2 and CO were 0.002 and 0.010 sec., respectively, in ordinary solutions of (I); in the intact corpuscles the times were 0.007 and 0.016 sec., respectively. The reaction rates as determined in this way agree with those obtained by Millikan's optical technique (A., 1934, 383). It is concluded that the primary combination of (I) with O_2 or CO is not followed by any secondary reactions of appreciable heat effect.
H. D.

Action of some guanidine derivatives on constituents of blood. K. TACHIBANA (Folia Pharm. acol. Japon., 1935, 19, 365—376).—Decamethylene-

pentamethylene-, and cyclohexyl-guanidine had no effect on red cells in rabbits, but increased pseudo-eosinophile and blood platelets when low concns. were used. Higher concns. hindered leucocyte formation. CH. ABS. (p)

Normal hæmatological standards. E. E. OS-GOOD (Arch. Int. Med., 1935, 56, 849—863).—From examinations of > 500 healthy persons of both sexes and of ages between 4 and 30, average vals. have been obtained for the erythrocyte, reticulocyte, and leucocyte counts, the hæmoglobin content and coeff., cell vol., vol. coeff., the colour, vol., and saturation indices, and sedimentation rate. H. G. R.

Oxidation of hæmoglobin to methæmoglobin by oxygen. II. Relation between rate of oxidation and partial pressure of oxygen. J. BROOKS (Proc. Roy. Soc., 1935, B, 118, 560—577).—The rate of oxidation of hæmoglobin (I) to methæmoglobin at p_H 5.69 and 30° is unimol. with respect to the (I) concn. With varying O_2 partial pressures (p) the rate is a max. at $p=20$ mm., being \propto the reduced (I) concn. and to $p/(1+bp)$. The rate-determining step is not the selective action of O_2 with any of the intermediate compounds of (I) and O_2 , and the effect of O_2 appears to be threefold: (i) the determination of the concn. of the other reactant, (ii) oxidation of compounds containing Fe^{++} , (iii) an inhibiting effect on the oxidation. There is evidence of the presence of another inhibitor. F. A. A.

Photochemical oxidation of hæmoglobin. F. G. LENNOX (Austral. J. Exp. Biol., 1935, 13, 193—196).—The photochemical conversion of hæmoglobin into methæmoglobin is accelerated by KI and NH_4I . Free I is without effect either in presence or absence of KI. W. O. K.

Optical activity of hæmoglobin and of derivatives: sulphur content. S. SIMONOVITS and G. BALASSA (Biochem. Z., 1935, 281, 186—197; cf. A., 1931, 857).—Horse-blood hæmoglobin (I) exists in two forms containing, respectively, 0.43 and 0.49% of S, the CO compounds of these having $[\alpha]_{680}^{20}$ +11.6° and +12.3° in H_2O , respectively (in 0.1% aq. $NaHCO_3$ the val. is independent of the concn.). Horse oxyhæmoglobin (II) once cryst. has $[\alpha]_{680}^{20}$ about +14.4° and $[\alpha]_{670}^{20}$ about +12.4° in H_2O (1%), the vals. decreasing as the dilution increases. Repeated recrystallisation causes these vals. to decrease and the max. absorption of the transmitted light to increase. CO-(I) from cattle has $[\alpha]_{680}^{20}$ +7.9° in H_2O (1%). Horse-(I) once cryst. and reduced with $Na_2S_2O_4$ has $[\alpha]_{680}^{20}$ about +28.3° in H_2O (5%). The S content of (II) is not altered by recrystallisation. W. McC.

Osmotic equilibria of hæmocyanin in a gravitational field. J. ROCHE, A. ROCHE, G. S. ADAIR, and M. E. ADAIR (Biochem. J., 1935, 29, 2576—2587).—Hæmocyanin (I), prepared from the blood of *Helix pomatia*, *Carcinus moenas*, and *Octopus vulgaris*, is placed in $M/15$ -phosphate buffer solution in a collodion sac, and the pressure attained at equilibrium with a similar buffer solution measured. Samples of the solution are withdrawn from different depths and protein is determined refractometrically.

The ratio of concns. at 1 cm. distance apart varied between 1.004 and 1.019. The osmotic pressures of the (I) solutions are calc., correcting for variation in concn. with height in the sac; estimates of the mol. wts. of the (I) obtained from the three sources are comparable with those obtained by Svedberg (A., 1933, 171). H. D.

State of phenol added to blood. G. BARAC (Compt. rend. Soc. Biol., 1935, 120, 522—523).—PhOH can be recovered completely from blood by deproteinisation with CCl_3CO_2H , and is therefore not destroyed by the red corpuscles. It is distributed equally between the plasma and the corpuscles. Plasma-PhOH is not partly bound to the lipins, since it is separated completely from these by ultrafiltration. R. N. C.

Plasma-lipins of normal men at different ages. I. H. PAGE, E. KIRK, W. H. LEWIS, jun., W. R. THOMPSON, and D. D. VAN SLYKE (J. Biol. Chem., 1935, 111, 613—639).—Free and ester cholesterol, neutral fat, and total lipins were determined in the plasma, and frequency distribution curves were plotted. The individual vals. and their relative magnitudes showed no dependence on the age of the subject. There is an approx. reciprocal relationship between the amounts of cholesteryl esters and neutral fats in the lipin mixtures. The vals. are compared with those obtained by other workers. H. D.

Influence of harmine on blood-sugar picture in rabbits. K. TACHIBANA (Folia Pharmacol. Japon., 1935, 19, 346—354).—Harmine (2—50 mg. per kg.) causes a marked hyperglycæmia. This action is inhibited by ergotamine, yohimbine, or by double splanchnicotomy, is increased by small doses of pilocarpine, and is opposed by insulin. CH. ABS. (p)

Residual carbon of blood in relation to sensitisation and anaphylactic shock. F. DIEHL (Arch. exp. Path. Pharm., 1935, 179, 670—677).—The total blood-residual C compounds (I) (i.e., not pptd. by, e.g., phosphotungstic acid) increase on sensitisation of dogs by injection of horse-serum. This increase is restricted to the "known" (I) [e.g., sugar (II), lactic acid (III), total phenols, and NH_2-N , urea-N, and glyoxaline derivatives], the "unknown" (I) remaining unchanged. The marked increase in (I) produced by subsequent anaphylactic shock is mainly restricted to unknown (I). The changes in (II), (III), and hydrolysable reducing substances indicate that carbohydrate metabolism is involved. F. O. H.

Blood modifications provoked by subcutaneous injection of glucose. G. DELRUE and P. HOLLEBEKE (Compt. rend. Soc. Biol., 1935, 120, 529—530).—Subcutaneous injection of glucose in the rabbit increases total proteins; the increase of globulins is > that of serines, and the serine-globulin ratio falls. Cl and total bases show decreases of the same order. Creatine and PO_4''' are increased. R. N. C.

Precipitation of serum-proteins with chloroform. A. GRÖNWALL (Biochem. Z., 1935, 282, 85—87).—The extent of pptn. of proteins from human serum by mixtures (3:1) of $CHCl_3$ and $C_3H_{11}OH$

varies greatly with $[H^+]$, max. being observed at p_H 4.3, 6.5, 8.4—8.7, and 9.4. W. McC.

Form of the micelles of the stroma-proteins. G. BOEHM (Biochem. Z., 1935, 282, 32—46; cf. A., 1932, 121).—A method for separating the proteins of the stroma of red blood-corpuscles (calf) from the hæmoglobin is described. The product is sol. in salt solutions of p_H 6.5—7.1. The solutions exhibit streaming double refraction and contain thread-like micelles (length-width ratio several thousand to 1). Since the space requirements of the micelles are very great, concs. > 3—4% cannot be obtained without production of gels. It follows that the stroma-protein of the erythrocytes is not conc. in a membrane, but extends throughout their interior. W. McC.

Blood-amino-nitrogen in health and disease. A. SIMON and B. ZEMPLÉN (Arch. exp. Path. Pharm., 1935, 179, 712—716).—The NH_2-N contents of whole blood, corpuscles, and plasma (before and after hæmolysis) of 21 normal and 44 diseased persons are tabulated and discussed. F. O. H.

Significance of post-operative rises in blood-non-protein-nitrogen. H. A. DEROW (New England J. Med., 1935, 212, 509—511).—In patients with normal renal function the increases may result from an oliguria, increased destruction of body-protein, or post-renal anuria. CH. ABS. (p)

State of combination of residual nitrogen [in blood-serum] in experimental uranium poisoning. M. JACOBY (Biochem. Z., 1935, 281, 198—199; cf. A., 1934, 558).—In rabbits the proportion of urea-N in the residual N of blood-serum increases following subcutaneous administration of $UO_2(NO_3)_2$. W. McC.

True and apparent creatine and creatinine of blood and urine. H. BOHN, A. FRIEDSAM, and F. HAHN (Zentr. inn. Med., 1935, No. 22, 465—473).—For determination of true creatine (I) alone, hydrolysis of the blood filtrate or urine must take place at a moderate temp. (60°) in presence of HCl. The true val. for blood-(I) in health is about 33% of the usually accepted val. In high blood pressure associated with paleness, the true blood-(I) is reduced. The results of Linneweh (Klin. Woch., 1934, 13, 589) indicate that preformed blood-creatinine is not entirely composed of pseudo-creatinine. NUTR. ABS. (m)

Does creatinine occur in normal blood? F. LINNEWEH (Klin. Woch., 1935, 14, 293—294).—Creatinine (I) can be detected in normal blood, extracted, and purified by adsorption on Lloyd's reagent. (I) excretion is therefore probably due to the removal of (I) from the blood by the kidneys, rather than to formation from creatine (II). The adsorbate from blood contains no substance that interferes with (I) determination, since Et_2O extraction does not reduce the (I) val., and supplementary (I) is not formed from (II) during the process. R. N. C.

Occurrence of acetylcholine in blood. R. AMMON (Klin. Woch., 1934, 13, 1472).—The acetylcholine-like effect of blood or urine, with or without eserine (I), on leech-muscle is not considered to be due to acetylcholine (II), since hæmolysed blood without

(I) contracts the uneserinated muscle, and this action is not inhibited by atropine or destroyed by treating the blood or urine with NaOH. Types of blood in which corpuscular $K >$ serum- K show a (II)-like action when hæmolysed. R. N. C.

Total and reduced glutathione compared with oxygen content and capacity in the blood of pregnant and non-pregnant women. F. W. OBERST and E. B. WOODS (Proc. Iowa Acad. Sci., 1934, 41, 166—167).—No relationship was apparent between the O_2 content and O_2 capacity of blood and the concn. of total or reduced glutathione (I). Vals. were similar in pregnant and non-pregnant women. Added (I) disappeared more rapidly from blood than from H_2O at 38°. Disappearance from blood was accelerated by NaF. CH. ABS. (p)

Azotæmia and chloræmia *in vitro*. J. LOISELEUR (Compt. rend. Soc. Biol., 1935, 120, 605—608).—Addition of urea (I) to blood *in vitro* causes a movement of Cl from the corpuscles to the plasma \propto the (I) added. Glycylglycine causes a movement of Cl into the corpuscles. R. N. C.

Azotæmia and chloræmia in course of histolysis. J. LOISELEUR (Compt. rend. Soc. Biol., 1935, 120, 675—678).—The corpuscular/plasma-Cl ratio in the blood depends on p_H , and is also influenced by the release of N compounds into the blood-stream from cell histolysis. It is inversely \propto the urea-N/total residual N ratio, and consequently falls on injection of peptone. Total blood-Cl falls in azotæmia, the fall being \propto the no. of mols. of N compounds. R. N. C.

Blood-iodine; a new chemical method. D. R. McCULLAGH (Cleveland Clin. Quart., 1935, 2, No. 1, 15—37).—Variations in blood-I under varying conditions are examined by the author's method (A., 1934, 1397). CH. ABS. (p)

Effect of age on the plasma-calcium content of men. E. KIRK, W. H. LEWIS, jun., and W. R. THOMPSON (J. Biol. Chem., 1935, 111, 641—642).—The plasma-Ca of normal adult men was independent of their ages. H. D.

Iron in the blood. Comparison of values for hæmoglobin determined by the Newcomer method and calculated from the iron content. H. W. JOSEPHS (Bull. Johns Hopkins Hosp., 1934, 56, 50—56).—Calc. vals. were the higher in most cases. CH. ABS. (p)

Spectrographic micro-method for detection of pathological lead in peripheral blood. H. BLUMBERG and T. F. MCN. SCOTT (Bull. Johns Hopkins Hosp., 1935, 56, 32—36).—A pathological finding is indicated when the Pb line 2833 Å. is detectable on the plate without the use of a lens. 0.1 c.c. of blood is examined. CH. ABS. (p)

Blood chemistry of swine. II. Blood changes following ingestion of glucose. D. F. EVELETH and M. W. EVELETH (J. Biol. Chem., 1935, 111, 753—756; cf. A., 1934, 543).—Feeding of glucose to fasting swine increases the serum-Mg and $H_2C_2O_4$, and decreases the inorg. PO_4''' and Ca. Ingestion of H_2O alone decreases the serum-sugar, Ca, Mg, $H_2C_2O_4$, and inorg. PO_4''' . J. N. A.

Sodium, potassium, calcium, and inorganic phosphate of blood during prolonged fasting. D. TORRISI (Arch. Fisiol., 1935, 34, 259).—In the serum of dogs and rabbits, during prolonged fasting, there is a progressive decrease in Na to \leq 21% of normal. The other elements show irregular and minor changes.

NUTR. ABS. (m)

Distribution of different fractions of acid-soluble phosphorus in the blood of dogs during intermediary metabolism, as observed on an empty stomach after introduction of glucose and radon. A. A. ARAPOVA (Ann. Roentgenol. Radiol. U.S.S.R., 1934, 13, 338—351).—Fractions of ortho- and pyro-phosphates and sol. and insol. phosphoric esters occur in blood-vessels. No creatininephosphoric acid is found in blood. The sol. ester fraction (I) is the most changed in its passage through organs, and also after introduction of glucose. Introduction of Rn increases (I) in arterial blood and in eliminations of the kidney.

CH. ABS. (p)

Conductivity of blood in the wave-length region 6—25 m. F. GRAUL (Ann. Physik, 1935, [v], 24, 326—348).—The conductivity of ox, pig, and human blood shows no change with frequency between $\lambda\lambda$ 6 and 20 m.; at 20—25 m. it decreases, but the effect is detectable only with centrifuged blood. Its variation at 13.6 m. with time of centrifuging and with the low-frequency conductivity is in accord with theory.

J. W. S.

Effect of pressure on the hydrogen-ion concentration of blood: use of glass electrodes. A. THIEL and H. GEMSA (Biochem. Z., 1935, 282, 146—156).—At 37°, no change in the p_H of cattle blood occurred when it was subjected to N_2 pressures up to 100 atm.

W. McC.

Amphibian metamorphosis. X. Hydrogen-ion concentration of the blood of anuran larvæ during involution. O. M. HELFF (Biol. Bull., 1932, 63, 405—418).—Blood- p_H shows a steady decline (7.50 \rightarrow 7.18) in progressive stages of metamorphosis.

CH. ABS. (p)

Calcium salts and blood coagulation. J. MATUSEVICH (Semana med., 1935, 1, 1021—1024).—Oral administration of $CaCl_2$ has no action, but Ca lactate + NH_4Cl shows a considerable effect with a max. after 8 days. Injected $CaCl_2$ + Ca gluconate is effective in 2—4 hr., with a return to normal after 24 hr.

CH. ABS. (p)

Acceleration of blood coagulation by acidic substances, especially pectin. O. RIESSER [with A. NAGEL] (Arch. exp. Path. Pharm., 1935, 179, 748—760).—Oral and parenteral administration of pectin (I) to rabbits accelerates the rate of coagulation, the effect persisting for 4—5 hr. Galacturonic and lactic acids, $AcOH$, and, in small intravenous doses, HCl have a similar action. Intramuscular injection of the neutral salts, *in-vitro* addition of the acids, or injection of (I)-activated blood [in which (I) is not detectable] into other animals has no effect. The mechanism of the phenomenon is discussed.

F. O. H.

Determination of velocity of blood coagulation. O. RIESSER and A. NAGEL (Arch. exp. Path. Pharm.,

1935, 179, 743—747).—The blood is introduced into a capillary tube, kept at const. temp., and the course of coagulation followed by its movements in response to unilateral pressure. Rabbits' blood (ear) gave vals. of 3—3.5 min. for the initiation and 4—5 min. for the completion of coagulation.

F. O. H.

Absence of correlation between lacto-gelification and protein disequilibrium of blood-serum. G. LEFROU and L. AUFFRET (Compt. rend. Soc. Biol., 1935, 120, 614—616).—There is no evidence of correlation between the time of lacto-gelification and the degree of protein disequilibrium.

R. N. C.

Hæmostatic effect of ascorbic acid in hæmaturia. A. KORÁNYI and A. BENTSÁTH (Orvosi Hetilap, 1935, 79, 378—379).—In some, but not in all, cases the hæmostatic action was accompanied by changes in composition of protein fractions in blood-plasma.

CH. ABS. (p)

Effect of Röntgen rays on the appearance of complement-fixing bodies in the blood. I. P. MISCHTSCHENKO and M. M. FOMENKO (Ann. Roentgenol. Radiol. U.S.S.R., 1934, 13, 327—336).—Complement-fixing bodies appeared in blood following X-irradiation.

CH. ABS. (p)

"Serum sickness" in rabbits following the intravenous injection of various foreign sera: relation to precipitins. D. KHORAZO (J. Immunol., 1933, 25, 113—120).—No differences in the rate of precipitin formation or disappearance of injected antigen from the blood could be associated with "serum sickness."

CH. ABS. (p)

Precipitin reaction between type III pneumococcus polysaccharide and homologous antibody. II. Conditions for quantitative precipitation of antibody in horse sera. III. Theory of the reaction mechanism. M. HEIDELBERGER and F. E. KENDALL (J. Exp. Med., 1935, 61, 559—562; cf. A., 1930, 1608).—II. The customary immunological procedure (2 hr. at 37° and overnight in oil) does not permit establishment of equilibrium, or max. pptn. of antibody-N. Analysis should be carried out at 0° and materials kept cold for \leq 24 hr. The chemical method for determining antibody is an accurate measure and does not include non-sp protein.

III. Antibody solutions and sera probably contain $>$ one antibody reactive with S III. The reaction between the sp. polysaccharide and homologous antibody is represented as a bimol. reaction, followed by a series of competing bimol. reactions dependent on the relative proportions of the components.

CH. ABS. (p)

Anaphylactogenic properties of milk. Immunochemistry of the purified proteins and antigenic changes resulting from heat and acidification. B. RATNER and H. L. GRUEHL (Amer. J. Dis. Children, 1935, 49, 287—306).—Casein and lactalbumin fractions of milk-proteins retain antigenic characteristics after drying, acidification, superheating, or evaporation. The whey fraction shows a marked loss of antigenic properties after evaporation or superheating. Loss of antigenic

properties of heated milk is due to coagulation of whey proteins. CH. ABS. (p)

Anaphylactogenic properties of malted sugars and maize-syrup. B. RATNER and H. L. GRUEHL (Amer. J. Dis. Children, 1935, 49, 307—317).—Allergy to carbohydrate food is due to added protein constituents rather than to the carbohydrate itself. Malt extracts and the barley-malts from which they are derived are highly anaphylactogenic and react specifically with hordein. Maize-syrups and pure "dextrimaltose" sugars are not anaphylactogenic. Addition of wheat germ or dried milk to non-anaphylactogenic converts them into active substances.

CH. ABS. (p)

Protein reaction for the more definite identification of blood-stains. V. TUMA (Chem. Listy, 1935, 29, 313—316).—Agglutination and pptn. reactions serve to distinguish dried human from animal blood-stains, and to determine the serological group to which the blood belongs. R. T.

Test for occult blood, especially in urine. W. J. STONE and G. T. BURKE (J. Amer. Med. Assoc., 1934, 102, 1549—1550).—The sediment from 15 c.c. of centrifuged urine is treated with 2 drops of a 1% solution of tolidine in MeOH and 3 drops of a 1:1 mixture of AcOH and H₂O₂. A greenish-blue colour lasting 1 min. develops in the presence of 100 blood-cells per c.c. of sediment. CH. ABS. (p)

Determination of calcium and phosphate content of bones. C. K. DEISCHER and W. M. McNABB (Analyst, 1935, 60, 750—751).—Ca is pptd. as CaC₂O₄, which is titrated with KMnO₄. P is pptd. as NH₄ phosphomolybdate, which is dissolved in excess of standard NaOH. The excess of NaOH is titrated with HCl. J. S. A.

Fluorine content of bones and teeth. R. KLEMENT (Ber., 1935, 68, [B], 2012—2019).—Examination of the bones and teeth of many animals leads to the following mean vals. for F in the inorg. matter: land mammals, 0.05%; sea mammals, 0.55%; land birds, 0.11%; sea birds, 0.32%; fresh-H₂O fish, 0.03%; sea-H₂O fish, 0.43%. The differences between land and sea animals are attributed to the F content of sea-H₂O exceeding that of fresh H₂O. F replaces OH in the hydroxyapatite (I) of bones and teeth with formation of mixed crystals to a greater extent with sea than with land animals; this is still more marked in fossil bones. The hardness of tooth enamel is explained by a small content of org. matter which causes a greater development of the crystallites of (I). F is probably without biological significance. H. W.

Lipin content of the jelly of Wharton. E. M. BOYD (J. Biol. Chem., 1935, 111, 667—669).—The mean lipin content of the jelly is 0.209%, which is < that of any other body-tissue. This agrees with Bloor's hypothesis that tissues of low physiological activity have a low lipin content. E. A. H. R.

Lipins. I. Amounts of lecithin, total and free cholesterol, and cholesteryl ester in the organs of guinea-pigs fed on a vitamin-C-free diet and the ratio among these lipins. II. Relationship between oxidation in the animal body and the

lipin contents of various organs. S. HONGO (Sei-i-Kwai Med. J., 1934, 53, No. 5, 1—22, 23—28).—I. On a dry-wt. basis organs of scorbutic guinea-pigs contained more lecithin (I) (notably in testicles, muscle, and kidney, but not liver and lungs) and more free cholesterol (II) (especially lungs, intestine, and kidneys) than normal animals. Intestine and kidneys have more total (II). The ratio of (I):(II) in intestine, kidney, and muscle is smaller in scorbutic animals.

II. Increased oxidation in rabbits injected with thyroideum is generally associated with a decrease in fat acids (III) and other lipins in various organs. In muscle (III) increased. In liver there is an increase in unidentified unsaponifiable substance without change in other lipins. Removal of thyroid increases (III) (except in the spleen) and other lipins without affecting the ratios in the various organs.

CH. ABS. (p)

Eel oil. I. Fatty acids. T. ONO (J. Agric. Chem. Soc. Japan, 1935, 11, 773—780).—The oil contains myristic, palmitic, and stearic acid, a saturated acid, m.p. 57—58°, probably the unsaturated acids, C₁₄H₂₆O₂, C₁₆H₃₀O₂, C₁₈H₃₄O₂, C₁₈H₃₂O₂ (iso-acid), C₁₆H₂₈O₂, C₂₀H₃₈O₂, C₂₂H₄₀O₂, and possibly C₁₆H₂₆O₂, C₂₀H₃₀O₂, and C₁₈H₂₄O₂. The Carr-Price reaction is negative and is very weak even with the liver extract. W. McC.

Renal threshold for glucose in man. J. W. SHERRILL and E. M. MacKAY (Arch. Int. Med., 1935, 56, 877—883).—The average vals. found for diabetics and normal persons were 149 and 128 mg. per 100 c.c., respectively. It is suggested that the "normal val." is misleading and a normal average should not be given. H. G. R.

Distribution of glycogen in the regions of the amphibian gastrula; micro-determination of glycogen. N. G. HEATLEY (Biochem. J., 1935, 29, 2568—2572).—Tissue is fixed in EtOH and digested with KOH; glycogen (I) is pptd. with EtOH, hydrolysed with acid, and the sugars formed are determined by the Linderström-Lang method (A., 1931, 1455). During gastrulation of the embryo of *Triton alpestris* the quantities of (I) are in the order: dorsal ectoderm > ventral ectoderm > yolk endoderm. During invagination there is a loss of approx. 35% of (I) in the invaginating cells. H. D.

Effects of repeated injections of glucose on the muscle-glycogen of the frog under normal conditions. A. MOSCHINI (Compt. rend. Soc. Biol., 1935, 120, 531—533).—Repeated injections of glucose (I) increase muscle-glycogen (II), the increase depending on the total amount of (I) given when (II) is low, but when (II) reaches high vals. the increases produced by further doses of (I) are smaller, until a steady max. is attained. R. N. C.

Effects of repeated injections of glucose on the muscle-glycogen of the frog, in different experimental states. A. MOSCHINI (Compt. rend. Soc. Biol., 1935, 120, 533—535).—Glucose (I) increases muscle-glycogen (II) in frogs with muscles atrophied by prolonged fasting, to the same extent as in normal frogs. Section of the sciatic nerve has no

immediate effect, but when degeneration of the foot muscles sets in, the amount of glycogen taken up is decreased. (II) falls after pancreatectomy, but (I) injections still cause deposition and mask this effect.

R. N. C.

(A) Determination of fermentable carbohydrates in rabbit liver. (B) Isolation of a reducing dextrin. C. B. PURVES (Quart. J. Exp. Physiol., 1935, 24, 383—389, 391—395).—(A) The fermentable carbohydrate in liver could not be accounted for (by 25%) as glycogen and free sugar. The presence of a polysaccharide insol. in 90% EtOH, sol. in 32% EtOH, and destroyed during the glycogen determination, is postulated.

(B) The fermentable carbohydrate isolated was probably a mixture of dextrans containing free Cu-reducing groups. CH. ABS. (p)

Colorimetric and iodometric determination of glutathione. K. UHLENBROOCK (Z. physiol. Chem., 1935, 236, 192—196; cf. A., 1935, 793; Fujita *et al.*, *ibid.*, 772).—For deproteinisation sulphosalicylic acid is much better than HPO_3 and KCN should be replaced by Na_2CO_3 in the method of Bierich *et al.* (A., 1933, 523), the apparatus of Lange (*ibid.*, 44) being used for measurement of the colour. Solutions should contain, per 100 c.c., 4.5—100 mg. of reduced glutathione (if < 4.5 mg. present larger vol. to be used). Results agree well with those obtained by titration with I for heart, muscle, lung, blood, brain, spinal cord, and spleen, but not for liver, kidney, and thymus. The last two contain substances which rapidly attack SH-compounds, and hence, with these organs, the colorimetric method cannot be applied. W. McC.

Bound water and phase equilibria in protein systems: ovalbumin and muscle. T. MORAN (Proc. Roy. Soc., 1935, B, 118, 548—559).—The bound H_2O of native (I) and denatured (II) ovalbumin at various temp. < 0° is dependent on the activity of H_2O . The chemically bound H_2O is approx. 0.26 g. per g. of protein for both (I) and (II), and for (I) the more loosely held H_2O is > for (II) at the higher activities. The bound H_2O of muscle at intermediate and high H_2O activities is approx. 0.40 g. per g. of dry solid. The eutectic temp. of muscle is about -37.5° . F. A. A.

Annelid muscle. I. Taurine in *Audouinia spirabranthus*, Moore. A. C. KURTZ and J. M. LUCK (J. Biol. Chem., 1935, 111, 577—584).—3% of taurine (I) was found in the muscle of *A. spirabranthus*, Moore, traces were found in *Nereis brandti*, and none in *Glycera rugosa*, *Lumbricus* sp., *Urechis caupe*, and *Phoronopsis harmeri*. The possible function of (I) in maintaining the osmotic pressure of the muscle is discussed. H. D.

Selenium in proteins from toxic foodstuffs. III. Removal of selenium from toxic protein hydrolysates. E. P. PAINTER and K. W. FRANKE (J. Biol. Chem., 1935, 111, 643—651).—The nature of the Se complex in toxic proteins is investigated. When the toxic proteins are hydrolysed, the Se may be extracted with BuOH. All the Se is completely pptd. by HgCl_2 , but only partly by phosphotungstic acid and by Cu and Ag salts. H. D.

Cryolysis, diffusion, and particle size. II. Investigations with myosin.—See this vol., 28.

Polysaccharoproteins. VI. State of glycogen in muscle. II. E. M. MISTKOVSKI, A. STILLER, and A. ZISMAN (Biochem. Z., 1935, 281, 231—237; cf. A., 1935, 1004).—Part of the glycogen (I) in the press-juice of rabbit, dog, and frog muscle exists irreversibly bound to myosin (II) and globulin-X (III). The amylase present degrades added (I) (at < the expected rate), but not the native bound (I), which also resists attack by ptyalin (IV). When the bound (I) is removed by alkaline hydrolysis it is attacked at the usual rate by amylase. The rate of hydrolysis of (I) by (IV) is reduced [extent of reduction \propto concn. of (II)] by adding (II), but appears to be increased by adding (III). W. McC.

Protamines. VI. (i) Acid hydrolysis of salmine. M. YAMAGAWA and T. NISHIZAWA (J. Imp. Fisheries Inst. Japan, 1934, 30, 97—115).—Salmine prepared from *Oncorhynchus keta* is identical with that from Rhine salmon. All $(\text{NH}_2)_1$ -acids are liberated by hydrolysis with $4N\text{-H}_2\text{SO}_4$ for 8 hr., leaving a residue of di- and tri-arginide. CH. ABS. (p)

Nature of the substance in fish meat which gives formaldehyde-like reactions. II. Squid (*Loligo bleekeri*, Keferstein) from Hokkaido. Y. HATTORI and T. HASELBE (J. Pharm. Soc. Japan, 1934, 54, 1081—1090).—The substance is identified as NMe_3O . CH. ABS. (p)

Nuclein metabolism. VI. Constitution of the nucleic acids. K. MAKINO (Z. physiol. Chem., 1935, 236, 201—207; cf. A., 1935, 1003).—Samples of yeast-nucleic acid (I) differ greatly in regard to the ease with which they are degraded by alkali, there being no relation between age of sample and ease of hydrolysis. The reaction of purified nucleosides with H_3BO_3 indicates that the deoxyribosides from thymus-nucleic acid (II) have the furan ring structure, and consequent changes are made in the proposed structural formulæ for (I) and (II). The criticisms of Klein *et al.* (*ibid.*, 510) are refuted. W. McC.

Adenine nucleotide in tissues. II. In heart muscle. K. LOHMANN and P. SCHUSTER (Biochem. Z., 1935, 282, 104—108; cf. A., 1934, 1020).—Most of the adenine nucleotide (I) of rapidly removed calves' hearts occurs as adenylypyrophosphoric acid. A small amount of (I) is isolated as adenosinediphosphoric acid and adenylic acid. W. McC.

Pigments of hair. H. ZWICKY and F. ALMASY (Biochem. Z., 1935, 281, 103—110).—Spectrophotometric examination of alkaline extracts of white, red, and black horse- and mule-hair indicate that, whilst two different pigments occur in the black hair (from different horses), one of them is indistinguishable from that which occurs in the red hair and in the hair from the darker parts of dappled horses. W. McC.

Pigments of the bull-frog retina. G. WALD (Nature, 1935, 136, 832—833).—The substances and processes found in the retina and pigment epithelium of *Rana catesbiana* are identical with those in species of frogs previously examined (A., 1934, 913). The retina contains varying amounts of retinene (I) and

vitamin-A (II). With SbCl_3 , (I) yields a sharp absorption band at 662—666 $\text{m}\mu$ and not at 655 $\text{m}\mu$. Dark-adapted retinas contain only a trace of (II), which can be extracted in the dark by benzene without injury to the visual purple. Light bleaches the latter to visual yellow, after which benzene extracts a large amount of (I). Destruction of the visual purple in the dark with CHCl_3 also liberates (I). Visual yellow thus appears to be simply free (I) (cf. *loc. cit.*). The (I) of bleached retinas is converted quantitatively into (II) by a thermal process in approx. 1 hr. in light or in darkness at 25°. In the isolated retina, (II) is the final product of the bleaching and fading reactions, but in the intact eye (II) is resynthesized to visual purple, thus completing the visual cycle.

L. S. T.

Carotenoids of *Rana esculenta*. O. BRUNNER and R. STEIN (Biochem. Z., 1935, 282, 47—50).—The liver, skin, fat glands, and ovaries contain β -carotene (I) and esterified lutein (II); the ovaries contain also free (II). About half of the total (I) and (II) occurs in the ovaries and about 25% in the liver. In liver, skin, and ovaries the contents of (I) and (II) are about equal, but the (II) content of the fat glands is much < the (I) content.

W. McC.

Visual purple. O. BRUNNER, E. BARONI, and W. KLEINAU (Z. physiol. Chem., 1935, 236, 257—262).— β -Carotene, obtained from the retina by extraction with MeOH, is adsorbed by Al_2O_3 . The light-absorption curve of the adsorbed material is similar, especially in the long-wave zone, to that of the visual purple. The retina contains no xanthophyll.

W. McC.

Accumulation of acid dyes in the silkworm by different tissues according to the route of application. P. P. GRASSE and L. LESPERON (Compt. rend., 1935, 201, 618—620).—Certain cells of the silkworm are stained by Congo-red, trypan-blue, trypan-red, and NH_4 carminate, but the results depend on whether the dyes are injected or administered orally.

W. O. K.

Progress of lactation in relation to the milk yield and the butter-fat percentage of milk produced by cows of the Shorthorn type. C. D. OXLEY (J. Dairy Res., 1935, 6, 113—120).—The standard error of the mean of observations of milk yields and % of butter-fat in milking records is determined. The time lag between the period of max. yield and min. % of butter-fat is discussed.

A. G. P.

Influence of diet on the antirachitic potency of cow's milk. B. H. THOMAS and C. Y. CANNON (Iowa Agric. Exp. Sta. Rept. on Agric. Res., 1934, 49).—Irradiated dried moulds may be used as a supplement to rations for increasing the vitamin-D content of milk. The response is most marked during the first few days of feeding and subsequently declines. The efficiency of transfer of -D from diet to milk is very low.

CH. ABS. (p)

Effect of diet on the milk: chemical modification and sensitisation to the alcohol test. L. ECHENIQUE and B. SUAREZ (Compt. rend. Soc. Biol., 1935, 120, 570—572).—*Xanthium cavanillense* is

non-toxic to cows, and when introduced into their diet provokes an increase in Ca in the milk; its withdrawal causes Ca to return to normal. The coagulation reaction with EtOH becomes positive when Ca is high. Milk that is coagulated by EtOH is not coagulated by boiling when the normal % of Ca in the ash is increased by 4.6.

R. N. C.

Effect of electrolytes on the synthesis of lactose. D. MICHLIN and T. FETISSOVA (Biochem. Z., 1935, 282, 26—31; cf. A., 1934, 1033).—The synthesis of lactose (I) in mammary gland is reversed when hydration of the tissue occurs. Added electrolytes ($\text{CaCl}_2 > \text{LiCl}, \text{NaCl}$) check hydration and prevent shifting of the equilibrium, hence increasing the amount of (I) produced or preventing reversal of the reaction. K_2SO_4 acts in the same way, but NH_4CNS and sometimes KCl check the synthesis. The synthesis is inhibited at p_{H} 9.5, but not at 4.8.

W. McC.

Mineral constituents in fresh and canned milk. A. J. HERMANO and S. CLARAVALL (Philippine J. Sci., 1935, 57, 323—328).—Ca, P, Fe, fat, protein, and lactose have been determined in fresh and canned samples of carabao's, goat's, and cow's milk.

H. G. R.

Cow's milk in Manchuria and Mongolia. IV. Non-protein nitrogenous substance. M. SUGIURA (J. Orient. Med., 1935, 22, 60).—Total N, non-protein-N, and protein in the milk from Manchu Mongol cows were < in milk from Japan, America, and Europe. Free NH_3 and urea showed considerable variations, but the uric acid and purine bases were const.

NUTR. ABS. (m)

Methylene-blue reduction test: its efficiency and interpretation under Philippine conditions. J. B. UICHANCO (Philippine J. Sci., 1935, 57, 295—319).—The test has been compared with the standard plate method on samples of carabao milk and is recommended for use with slight modification to suit local conditions.

H. G. R.

Determination of amylase in milk. M. MANICATIDE, BRATESCU, and M. POPA (Compt. rend. Soc. Biol., 1935, 120, 657—658).—Human colostrum contains 1024—2048 Wolgemuth units of amylase (I) per c.c., normal milk, 250 units (average). Cows' milk contains scarcely any (I). (I) is destroyed by boiling or pasteurisation.

R. N. C.

Extractives of peripheral lymph. S. ASAKUMA (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 136—137).— Et_2O -sol. matter in lymph from the popliteal gland and of blood-serum from leg veins of rabbits averaged 285.8 and 244.6 mg. per 100 g. of fluid, respectively.

CH. ABS. (p)

Hydrogen-ion concentration of peripheral lymph. M. ARAKI and G. Hōjō (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 132—134).—The p_{H} of lymph from the popliteal gland of rabbits (7.90) was lowered by injection of strychnine and increased by that of veratrine.

CH. ABS. (p)

Carbon dioxide content of lymph under different conditions. G. Hōjō (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 140—144).—Lymph- CO_2 increased when rabbits were fastened

immovably. Vals. for efferent lymph from the popliteal gland were similar for both sides; those for thoracic duct and intestinal lymph were markedly < that in the legs. Intravenous injection of KCN and injection of pilocarpine hydrochloride by the ear vein lowered the CO₂ content. Adrenaline had no action.

CH. ABS. (p)

Carbon dioxide content of peripheral lymph of rabbits. K. TSUJI (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 135).—Average vals. for efferent and afferent lymph were 44.33 and 46.64 c.c. per 100 parts (?), respectively.

CH. ABS. (p)

Sulphates in lymph. I. II. Sulphates in peripheral lymph after intravenous injection of aqueous phenol solution. S. MASUDA (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 22—24, 25—28).—I. Small amounts of SO₄'' occur in serous fluids, chyle, and blood. Only ethereal SO₄ (I) occurs in lymph. The (I) content in peripheral lymph is > that of chyle, and, in turn, > in blood.

II. Injection causes an increase in (I) content of the lymph.

CH. ABS. (p)

Lactic acid in peripheral lymph. Y. HŌJŌ (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 115—121).—Average vals. for efferent and afferent lymph were 0.795 and 0.673 mg. per 100 c.c., respectively. Vals. were decreased by injection of aq. NaF, NaI, or CH₂I·CO₂H.

CH. ABS. (p)

Lipase of peripheral lymph. K. ISHINO (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 48—52).—The lipase occurs in the inflowing and outflowing lymph of the popliteal gland, there being usually more in the outflow. It is not affected by neutral salts or by weakly acid or alkaline media.

CH. ABS. (p)

Total protein, globulin, and albumin fractions of peripheral lymph. B. NAKADA (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 112—114).—Vals. per 100 c.c. of lymph were: total protein, 2123 mg. in efferent and 1890 mg. in afferent lymph, globulin, 757 and 715, albumin, 1689 and 1599 mg., respectively.

CH. ABS. (p)

Autolysis of lymph. I. Reducing power. M. FUKUOKA (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 92—93).—The reducing power varied with the individual rabbit, reached a max. on the 2nd day of autolysis, and subsequently declined.

CH. ABS. (p)

Fibrin content of lymph. B. NAKADA (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 63—64).—Average vals. were 276.7 mg. of fibrin per 100 c.c. of efferent, and 261.1 mg. for afferent, lymph.

CH. ABS. (p)

Non-protein-nitrogen of vascular lymph. S. ASAKUMA (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 46—47).—The average non-protein-N content of lymph was 0.504 and of blood-serum, 0.513%.

CH. ABS. (p)

Resorption in the lymph passage. I. Resorption of yatoconin by subcutaneous application. II. Resorption of colloidal silver. III. Resorption of starch. M. KOSAKA (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 15—21,

80—89, 152—160).—I. Injection is immediately followed by an increase in wt. and in Ca and P contents in the lymph gland.

II. The Ag content of the gland increased rapidly to a max. and subsequently declined. Ag is soon resorbed in the lymph passage, but part remains stored in the gland.

III. Injected starch was detected in the gland up to 4 hr. after treatment. Resorption was complete in 5.5—6.0 hr. Reducing substances in glands after hydrolysis reached a max. soon after injection. The max. for reducing substances before hydrolysis was reached somewhat later.

CH. ABS. (p)

Lymph obtained by the "Brunnenlymph" method of Watanabe. Y. IWAKI (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 7—14).—Physical and chemical properties of the lymph are examined. Incoming lymph has the same physical properties as that from lymph glands.

CH. ABS. (p)

Decomposition of atropine in the peripheral lymph of the rabbit. S. KIRIYAMA (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 68—79).—Decomp. of atropine sulphate by lymph occurs at room temp. and at 37°, but not at low temp. Outflowing lymph was more active than inflowing lymph.

CH. ABS. (p)

Alteration of lymph after death of animal. Y. IWAKI (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 99—111).—Physical and chemical changes during 2 hr. after death are recorded.

CH. ABS. (p)

Lymph in experimental pneumonia. J. S. DAVIS, jun., and A. J. DELARIO (J. Lab. Clin. Med., 1935, 20, 460—467).—The increase in lactic acid (I) content of lymph and the decrease in CO₂ content tend to compensate for the loss of Cl'. The increase in (I) is the more important factor. The O₂ tension of lymph is > doubled by O₂ therapy.

CH. ABS. (p)

Relationship between sugar and urea contents of the blood and spinal fluid. J. N. CUMINGS and E. A. CARMICHAEL (Brain, 1934, 57, 338—347).—Levels of sugar and urea in lumbar fluid do not rise in association with the normal rise in the blood. Only in abnormal conditions does the ventricular fluid-sugar increase with a rise in blood-sugar.

CH. ABS. (p)

Proteolytic power of saliva. I. Proteolysis in saliva. II. Action of human saliva on proteins. P. FANTL and J. WEINMANN (Biochem. Z., 1935, 281, 37—41, 42—48).—I. The portion of human saliva which does not pass through filters contains enzymes which degrade the proteins of the saliva. The amount of enzymes present varies greatly from person to person, but remains almost const. in the individual.

II. Proteins (hen's egg, fibrin from human and horse blood) denatured by boiling or by pptn. at room temp. are not attacked by the enzymes of the saliva.

W. McC.

Significance of iron and copper in human bile. E. S. JUDD and T. J. DRY (J. Lab. Clin. Med., 1935, 20, 609—615).—The Fe content of liver

ranged from 0.031 to 1.68 and that of Cu from 0.063 to 1.07 mg. per 100 g. Cu is normally excreted by liver. Fe is secreted in bile and resorbed from the intestine.

CH. ABS. (*p*)

Microchemical study of human biliary calculi.

T. W. RAY (*J. Biol. Chem.*, 1935, 111, 689—697).—There is no essential difference in chemical composition chole between cholesterol-pigment-Ca stones and sterol-pigment stones.

E. A. H. R.

Concentration function of the gall-bladder: biliary glutathione. G. BALTACEANO and C. VASILIU (*Compt. rend. Soc. Biol.*, 1935, 120, 666—668).—The concn. of the glutathione in the vesical bile is > in the hepatic bile.

R. N. C.

Bile acids. XLVII. $C_{24}H_{36}O_{10}N_2$.—See this vol., 74.

Constituent of bile pigment. XIV.—See this vol., 86.

Gastric secretion. VI. Action of pilocarpine on the secretion of a transplanted gastric pouch without Auerbach's plexus. E. KLEIN (*Arch. Surgery*, 1935, 30, 277—283).—Pilocarpine hydrochloride (I) in 7-mg. doses stimulates secretion of free acid. Smaller doses stimulate pepsin secretion only. Atropine (1 mg.) inhibits secretion caused by (I) but not that produced by histamine.

CH. ABS. (*p*)

Copper content of urine of normal children. A. ROSS and I. M. RABINOWITCH (*J. Biol. Chem.*, 1935, 111, 803—805).—Cu is a const. constituent of urine and the amounts found ranged between 0.04 and 0.52 mg. per litre.

J. N. A.

Detection of dinitrophenol and its derivatives in urine. A. MEYER and H. DRUTEL (*Bull. Soc. Chim. biol.*, 1935, 17, 1455—1461).—Interference by skatole, which, like 2:4-dinitrophenol (I), gives a pink coloration in the Meyer test for (I), may be avoided by using $Hg(NO_2)_2$ as defecating agent and extracting (I) with Et_2O before reducing with Zn in AcOH.

A. L.

Urinary diastase. F. ECKARDT (*Deut. Arch. klin. Med.*, 1935, 177, 517—526).—Diastase, expressed as g. of starch hydrolysed by 1000 c.c. of urine at 37° in 3 hr., ranged from < 8 to > 600 (in adolescents 10—40, in old age < 8 to 20); the mean val. for all ages is about 20. The val. was uninfluenced by sex, but varied inversely with food consumption. Vals. in many different types of disease are given.

NUTR. ABS. (*m*)

Variations in urinary reducing substances of two normal dogs maintained on bread diets. E. P. LAUG and T. P. NASH, jun. (*J. Nutrition*, 1935, 10, 81—92; cf. A., 1935, 513).—Significant variations in the total, fermentable, non-fermentable, and hydrolysable reducing substances of urine are correlated with particular bread diets.

A. G. P.

Lipuria in dogs experimentally deprived of their dorso-lumbosacral marrow. H. HERMANN, J. DECHAUME, and J. VIAL (*Compt. rend. Soc. Biol.*, 1935, 120, 648—649).—Removal of the dorso-lumbosacral marrow induces an immediate increase in fat excretion, which disappears after 3—5 weeks, reappears after 3 months, and then persists. Et_2O extracts are

yellow when fresh, but extracts from urines of the first period of lipuria are decolorised by light; those from the second period are unaffected. The fat is free from N and P, and the acid contained in it is chiefly oleic acid.

R. N. C.

Biochemistry of allantoin. I. Effect of leucolysis on allantoin excretion. II. Amounts of allantoin in urine of various animals. III. Effect of thyroxine ingestion on allantoin excretion. T. MIYAHARA (*Sci-i-Kwai Med. J.*, 1934, 53, No. 8, 9—27, 28—41, 43—48).—I. When a leucopenia is produced in rabbits by injection of a phagolytic serum of goat, excretion of allantoin (I), uric acid (II), and total N (III) is increased. The ratios of (II):(III) and of (I):(III) also increase, whilst the uricolytic index is unchanged. The chief end-product of purine metabolism is (I) with (II) as intermediary.

II. Data are given for rabbit, guinea-pig, dog, pig, ox, rat, sheep, goat, and horse.

III. Injection of thyroxine (IV) increases the excretion of (III) and (I) and decreases that of (II). The uricolytic index is increased. (IV) increases the oxidation of (II) to (I).

CH. ABS. (*p*)

Action of colloidal substances on crystallisation, with reference to the problem of stone formation. S. VON KÜTHY (*Magyar orvosi Arch.*, 1934, 35, 289—297; *Chem. Zentr.*, 1935, i, 2209).—Urine and bile are to be considered as supersaturated solutions, in which normally crystallisation or concrement formation should begin, but the colloidal or surface-active substances of high mol. wt. exert a protective action. Model experiments with PbI_2 indicate the mechanism of this action of the colloids to be by selective adsorption in stages.

R. N. C.

Determination of lead in excreta and tissues. R. A. KEHOE (*Amer. J. Clin. Path.*, 1935, 5, 13—20).—Methods of prep. and ashing of samples are discussed and analytical methods are compared. For Pb in tissues spectrographic methods are the most satisfactory.

CH. ABS. (*p*)

Effect of external factors on perspiratio insensibilis. A. VAN HARREVELD, B. W. GRUTTERINK, and A. K. M. NOYONS (*Biochem. Z.*, 1935, 281, 1—26).—In man the phenomenon is practically unaffected by a $\pm 35\%$ change in the humidity and a change of temp. within the range 20—23.5° or by changes in the thickness of the clothing. Only after attainment of equilibrium are trustworthy results obtained. The val. varies greatly in the individual at different times with const. atm. conditions.

W. McC.

Changes in hydration of serum-colloids as a general feature of a disease. K. SCHULHOF (*Trans. Illinois State Acad. Sci.*, 1934, 27, 80).—Measurements of n and η of serum are utilised to assess the vol. occupied per g. of protein.

CH. ABS. (*p*)

Azotæmia and elevation of the alkaline reserve in course of anuria. R. HUGUENIN, R. TRUHAUT, and C. SANNIÉ (*Compt. rend. Soc. Biol.*, 1935, 120, 717—719).—Blood-urea (I) is increased and the alkaline reserve is lowered in anuria. $NaHCO_3$ increases the

alkaline reserve without affecting (I). Total Cl and the corpuscular/plasma-Cl ratio fall. R. N. C.

Influence of 3:5-di-iodotyrosine on experimental arteriosclerosis. A. OGATA, S. SANO, and K. MITSUI (J. Pharm. Soc. Japan, 1934, 54, 248—272).—The lipin content of blood was increased by feeding lanoline (I). Substitution of 3:5-di-iodotyrosine (II) hastened the restoration to normal lipin levels. The ratio of Et_2O extract to body-wt. for mice fed with (I) indicates the decrease in wt. following administration of (II) to result from a decline in lipin content. CH. ABS. (p)

Proteins of cancerous cells. C. ACHARD and M. PIETRE (Compt. rend., 1935, 201, 751—753; cf. A., 1935, 376).—Renal sarcomas of the ox and horse contain lipins (1.38—2.95%, largely cholesterol), globulins (2.6—4.2%) from which amides (0.48—0.67%) are isolated, and albumins (0.5—0.7%), which, although exhibiting the general properties of serum-albumins, possess a much smaller mol. (cf. A., 1933, 730). The residue insol. in H_2O affords myxoprotein. J. L. D.

Heavy water and tumour growth. W. H. WOGLON and L. A. WEBER (J. Amer. Med. Assoc., 1934, 102, 1289—1290).— D_2O had no effect on mouse sarcoma. CH. ABS. (p)

Phosphorus in the blood-plasma of hens suffering from sarcoma. F. PENTIMALI and G. SCHMIDT (Biochem. Z., 1935, 282, 62—73).—The amounts of total, lipid, and acid-sol. P in the plasma of hens suffering from Rous sarcoma are > those in healthy hen plasma (30% increase in total P). The plasma of the diseased (but not that of the healthy) hens contains protein-P possibly derived from the tumours, although plasma from the muscles, but not that from the tumours, loses acid-sol. P. W. McC.

Anomalous crystallisation of sodium chloride in normal and in sarcomatous blood-serum. V. KILIAN (Acta Cancerologica, 1934, 1, 22—28).—After dilution of serum with 0.9% NaCl and subsequent evaporation, the form of crystallisation of NaCl from samples from sarcomatous chicken differed from that from normal samples. CH. ABS. (p)

Enzymes in uterine cancer. II. Lipase and lecithinase. III. Esterase. IV. Invertase. V. Antitrypsin. K. NAKAHORI (Japan. J. Obstet. Gynecol., 1934, 17, 419—445; cf. A., 1935, 514).—The distribution of the enzymes in human uterine cancer tissues, lymphatic glands, mucosa, and muscular layers of the uterus is examined. CH. ABS. (p)

Influence of magnesium on growth of carcinoma, sarcoma, and melanoma in animals. K. SUIGURA and S. R. BENEDICT (Amer. J. Cancer, 1935, 23, 300—310).—Effects of varying levels of dietary Mg on the growths are examined. Neoplasms as well as normal tissue require definite amounts of Mg for growth. CH. ABS. (p)

Effect of intravenous injections of complex soluble salts of iron and ascorbic acid on tumours. F. ARLOING, A. MOREL, and A. JOSSE-AND (Compt. rend., 1935, 201, 745—747).—Clinical

results obtained in the treatment of cancers by injections of mixed complex Fe and Ca salts of ascorbic acid are better than when Fe-Na salts are used (cf. A., 1935, 1401). J. L. D.

Experimental tumours produced by decreased doses of coal tar. General action of the carcinogenic agent. L. M. SCHABAD (Acta Cancerologica, 1934, 1, 56—77).—The carcinogenicity of tar is due to a general rather than to a local action. CH. ABS. (p)

Effect of certain polycyclic hydrocarbons on the growth of the Jensen rat sarcoma. A. HADDOW (Nature, 1935, 136, 868—869).—Intra-peritoneal injections of colloidal preps. of 1:2:5:6-dibenzanthracene, 1:2-benzpyrene, 5:6-cyclopenteno-1:2-benzanthracene, and 1:2-benzanthracene, but not anthracene and phenanthrene, produce marked inhibition of growth of the implanted tumour in rats. Carcinogenic substances, like X-rays, may thus act primarily by producing a certain type of inhibition in the activity of the normal cell. L. S. T.

The Costa reaction (200 cases). R. H. KAMPMEIER (J. Lab. Clin. Med., 1935, 20, 531—538).—The ppt. formed in blood-serum by addition of procaine, Na citrate, and CH_2O occurred in 70% of cases with pulmonary tuberculosis and in 90% of cases with malignant tumour. None appeared in syphilis. CH. ABS. (p)

Calcium and inorganic phosphorus of blood-serum in dental caries. C. G. KERLEY, E. J. LORENZE, and E. R. GODFREY (J. Pediat., 1935, 6, 665—666).—Serum-Ca and -inorg. P were within normal limits. NUTR. ABS. (m)

Secretion of urine in diabetic coma. R. A. McCANCE and R. D. LAWRENCE (Quart. J. Med., 1935, 4, 53—79).—In diabetic coma there may occur disorganisation of renal function involving retention of urea, creatinine, and probably uric acid, of ketones, if present, and of sugar, if above the threshold. Urine may become acid ($p_{\text{H}} 5$); excretion of NH_3 and salt is normal. CH. ABS. (p)

Hæmochromatosis. I. Iron and sulphur content of the tissues. II. Results of spectrographic examination with special reference to copper and calcium. H. RAMAGE and J. H. SHELDON (Quart. J. Med., 1935, 4, 121—129).—I. In 5 patients with hæmochromatosis there was a uniform increase in the Fe content, distributed over all the tissues except the blood, brain, and colon. Organs such as the liver, pancreas, and salivary glands may have 50—100-fold increase. Enormous deposits occurred also in the lymph glands, thyroid, pituitary, choroid plexuses, and heart. The somatic muscles contain nearly as much Fe as the liver. The total Fe (calc.) of the body is 25—50 g. There was no general increase in S content. The moderate increase in S in the alimentary canal, omentum, pancreas, and adrenal glands is probably related to deposits of hæmofuscin.

II. Spectrographic examination showed a two- or three-fold increase in Cu in the liver and all tissues except the kidney, small intestine, and omentum.

An increase in Ca was general, but most evident in the liver, thyroid, striated muscles, and pancreas. Disturbance in the Na and K metabolism may have occurred, the concn. of these elements in the tissues usually deviating in reverse directions from the normal. The low Mn content of the liver is probably significant. No unusual elements were encountered.

NUTR. ABS. (*m*)

Alkalosis, a clinical problem. C. T. WAY and E. MUNTWYLER (*Ann. Intern. Med.*, 1935, 8, 818—824).—In cases of hypertension and renal disease with a slight or no increase in non-protein-N, the acid-base balance of blood may change with a tendency towards a lower Cl content. Administration of alkali should be controlled by blood acid-base analyses.

CH. ABS. (*p*)

Rôle of pressor substances in arterial hypertension. R. B. CAPPS, E. B. FERRIS, jun., F. H. L. TAYLOR, and S. WEISS (*Arch. Int. Med.*, 1935, 56, 864—876).—In hypertension the urinary pressor substance is \gt the normal, and appears to be a H₂O-sol. substance, acting centrally. COMc₂ extraction does not completely separate the pressor and depressor substances, but this fraction contains more pressor and less depressor material than the EtOH fraction.

H. G. R.

Calcium metabolism in idiopathic hypoparathyroidism. A. GOERNER and G. SAMUELSEN (*J. Amer. Med. Assoc.*, 1934, 102, 1001—1002).—The positive Ca balance in hypoparathyroidism was reduced by parathyroid extract. The increased excretion was by the urine.

CH. ABS. (*p*)

Goitre prophylaxis with iodised salt. R. D. McCURE (*Science*, 1935, 82, 370—371). L. S. T.

Malaria in Panama with reference to control with atebri and plasmoquin. W. H. W. KOMP and H. C. CLARK (*Amer. J. Trop. Med.*, 1935, 15, 131—154; cf. A., 1935, 1149).—Atebri and plasmoquin administered simultaneously enhance the toxic action of the latter. When given separately the desired effect is obtained with less toxicity.

CH. ABS. (*p*)

Muscle chemistry in myasthenia gravis, pseudohypertrophic muscular dystrophy, and myotonia. S. NEVIN (*Brain*, 1934, 57, 239—254).—The PO₄''' content of pathological muscle under various conditions is examined. A method for determining the partition of acid-sol. P between H₃PO₄, creatinephosphoric and adenosinetriphosphoric acids is described. Sol. carbohydrate phosphates are determined by difference. CH. ABS. (*p*)

Calcium and inorganic phosphorus in the blood-serum of emotionally unbalanced children. C. G. KERLEY, E. J. LORENZE, jun., and E. R. GODFREY (*N.Y. State J. Med.*, 1935, 35, 571—572).—Of 90 children 81 showed normal Ca vals. and 83 normal inorg. P vals. Exaggerated nervous symptoms were not more severe in children with low Ca vals. than in those with normal Ca and P vals.

NUTR. ABS. (*m*)

Renal damage following ingestion of a diet containing an excess of inorganic phosphate. E. N. MACKAY and J. OLIVER (*J. Exp. Med.*, 1935, 61, 319—333).—Permanent renal lesions were pro-

duced in rats by feedings an excess of K and Na phosphates or H₃PO₄. Removal of excess of PO₄''' does not restore normal structure. CH. ABS. (*p*)

Comparison of "yeast" milk and irradiated milk in the treatment of infantile rickets. E. T. WYMAN, R. C. ELEY, J. W. M. BUNKER, and R. HARRIS (*New England J. Med.*, 1935, 212, 257—262).—The two milks are equally effective.

CH. ABS. (*p*)

Nitrogen balance and oxidation process in experimental scurvy. II. Effect of reduced iron. L. D. KASCHEVNIK, S. A. EIDMANN, and J. B. FRIEDLAND (*Biochem. Z.*, 1935, 282, 56—61; cf. A., 1935, 888).—In guinea-pigs, daily oral administration of 10 mg. of reduced Fe prior to the onset of scurvy caused increase in N metabolism, stimulated subsequent urinary N excretion when scurvy had set in, and tended to decrease the O:N ratio. The Fe caused retention and deposition of fat during the course of the disease, but had no effect on the excretion of protein degradation products, there being retention of these when scurvy was developing and increased excretion when the disease was fully established. Subsequently, while the animals fasted, there was N retention.

W. McC.

Correlation of mineral metabolism and the vegetative nervous system in thyroid disease. J. KLEIN (*Ann. Int. Med.*, 1935, 8, 778—804).

CH. ABS. (*p*)

Interpretation of abnormal glucose-tolerance curves occurring in toxæmia in terms of liver function. S. SOSKIN, M. D. ALLWEISS, and I. A. MIRSKEY (*Arch. Int. Med.*, 1935, 56, 927—934).—Toxæmias cause abnormal glucose-tolerance curves through an interference with the homeostatic mechanism of the liver.

H. G. R.

Amino-acid content of the blood of the rabbit in tuberculous infection of the Yersin type. E. S. PANAYOTOPOULO (*Compt. rend. Soc. Biol.*, 1935, 120, 604—605).—NH₂-acids increase steadily until death. The increases are of the same order for avian and bovine infections.

R. N. C.

Tyrosine index of serum-polypeptides in the rabbit in the course of tuberculous infection of the Yersin type. E. S. PANAYOTOPOULO (*Compt. rend. Soc. Biol.*, 1935, 120, 695—696).—The tyrosine index increases steadily from the time of inoculation until death.

R. N. C.

Whooping-cough: diagnostic significance of blood counts. N. D. BEGG and M. F. COVENEY (*Lancet*, 1935, 229, 1113—1114). L. S. T.

Mathematical physics in metabolising systems with reference to lung cells. N. RASHEVSKY (*Physics*, 1935, 6, 117—119; cf. A., 1935, 1073).—Previous results are applied to glucose oxidation and glycolysis. The relative rates of the two reactions, when occurring simultaneously, determine whether the system will divide spontaneously or not. Rapidly-dividing cancer cells show abnormally high rates of glycolysis.

CH. ABS. (*p*)

Metabolism in children doing muscular work. I. Effect of racing on urinary constituents in



boys. I. NAKAGAWA and K. KAWAMO (Amer. J. Dis. Children, 1935, 49, 594—602).—Following a 1200-m. race some albuminuria and increased acidity occurred. NH_3 , creatine, and creatinine concns. were practically unchanged. P increased and total N decreased temporarily. The ratios, total N:urine vol., total P:urine vol., creatine:total N, and NH_3 :total N, were all increased. CH. ABS. (p)

Metabolism of injured tissue. H. DRUCKREY (Naturwiss., 1935, 23, 796—799).—Mechanical trauma, such as that sustained by cells in thin sections of tissue, produces a marked immediate rise in their metabolism followed by a slow fall. The rôle of tissue damage in producing the observed results of O_2 deficiency and also its possible significance in tumour metabolism are discussed. W. O. K.

Insect metabolism at temperatures below 0° . I. V. KOSHANTSCHIKOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 373—376).—The R.Q. of larvae of *Pyrausta nubilalis*, Hb., and of *Loxostege sticticalis*, L., indicate that metabolism at 0° is mainly concerned with carbohydrate, but at -6° and 20° fats and proteins become important. A. G. P.

Biological cell oxidation. A. BERTHO (Chem.-Ztg., 1935, 59, 953—957).—A review.

Metabolic oxidation and radiation. M. COPISAROW (Protoplasma, 1934, 21, 73—80).—Blood, urine, tissue extracts, and yeast exposed to atm. O_2 in the dark at 37° emit ultra-violet radiations. The effect is abolished by heat; in the case of yeast it is also destroyed by H_2O_2 , KMnO_4 , KCN, or CO, but not by CO_2 or N_2 . No radiation is given off by pure cholesterol, calciferol, ascorbic acid, alkaloids, or synthetic adrenaline. The radiation is associated with the chemical function of respiratory enzymes; metabolic products radiate only in presence of the enzymes. R. N. C.

Infant feeding and nutrition. S. FRIEDMAN (Amer. J. Dis. Children, 1935, 49, 152—190, 460—473).—A review. CH. ABS. (p)

Effect of low calorific diets and resultant loss in weight on plasma-cholesterol in the obese. C. A. POINDESTER and M. BRUGER (Arch. Int. Med., 1935, 56, 884—890).—Plasma-cholesterol (I) in complicated or uncomplicated obesity is not altered primarily by reduction in wt. on a low-calorific diet; but an increase is noted in some cases due to the "starvation effect." Some high vals. of (I) show a decrease due to secondary changes. H. G. R.

Growth, reproduction, lactation, longevity, and hæmoglobin formation in albino rats on meat diets contrasted with their response on the Steenbock stock diet and on the Sherman milk diet. P. M. NELSON and P. P. SWANSON (Iowa Agric. Exp. Sta. Rept. on Agric. Res., 1933, 116; 1934, 144—145).—As a N source dried beef muscle was superior to cereal or milk proteins. Neither pork nor beef muscle at a level of 15% protein was adequate for maintenance of body-wt., reproduction, and lactation. Pork at 15 and 30% protein levels and beef at the 15% level fed to female rats allowed no reproduction beyond the second generation. Beef was

superior to pork. With 30% beef protein rats reproduced freely. CH. ABS. (p)

Supplementary values of animal protein concentrates in chick rations. H. J. ALMQUIST, E. L. R. STOKSTAD, and E. R. HALBROOK (J. Nutrition, 1935, 10, 193—211).—Vals. of various meat products as protein (I) supplements are determined. The cystine, tryptophan, and H_2S contents of (I) feeds do not afford a basis for predicting their nutrient vals. Determinations of intact (I) (Cu ppt.), (I) decomp. products (phosphotungstic acid ppt.), undigestible (I) (pepsin-HCl), and hot H_2O -sol. (I), to which are assigned the relative nutrient vals. 100, 40, 0, and 40, respectively, permit the determination of nutrient vals. of (I) concentrates which agree closely with biological trials. A. G. P.

Is linoleic acid essential in the nutrition of rats? E. BECKER (Z. Vitaminforsch., 1935, 4, 241—249).—Without small amounts of linoleic acid (I) rats fail to maintain normal growth and develop a deficiency disease, which can be cured by daily doses of 5 mg. of walnut oil containing 2—3 mg. of (I). The growth curves of rats run parallel with the amount of (I) in the oil. It is not known which isomeride of (I) is responsible for the action. J. N. A.

"Bukuryo," sclerotia of *Pachyma Hoelen*, Rumph. V. Nutritive value of pachyman. K. TAKEDA (J. Agric. Chem. Soc. Japan, 1934, 10, 685—690).—Pachyman is not easily digested, and its nutritive val. resembles that of cellulose. Neither it nor "Bukuryo" can be used as a substitute for cereals. J. N. A.

Biochemistry of fermented soya-bean paste ("miso"). III. Effect of cystine on the nutritive value of miso-protein given as supplement to rice. I. IWAMURA (Bull. Agric. Chem. Soc. Japan, 1935, 11, 128—134).—The nutritive val. of the miso-protein, when used as a supplement to a rice diet for albino rats, is increased by addition of cystine (I). For young rats the optimum amount of (I) is about 0.1% (>0.5% is harmful), but for adult rats 0.5% is favourable. W. McC.

Substitution of dithioethylamine (cystine-amine) for cystine in the diet of the white rat. H. H. MITCHELL (J. Biol. Chem., 1935, 111, 699—705).—Addition of cystine-amine (I) to a cystine-deficient diet depresses the growth of the animal and impairs appetite. There is therefore no evidence that (I) can replace cystine in a diet. E. A. H. R.

Protein requirements of chicks. J. D. MCCONACHIE, W. R. GRAHAM, jun., and H. D. BRANION (Sci. Agric., 1935, 15, 754—764).—Optimum levels of protein feeding are determined for chicks of various ages. The efficiency of food utilisation declines with age. Mortality decreases as the proportion of protein fed approaches the optimum. High and low protein intakes tend to modify the contour and texture of feathers, although the optimum protein requirement for correct feather development is not necessarily the same as that for growth. Slipped tendons are not directly due to high-protein feeding. The occurrence of "crow heads" is a dietary rather than a genetic factor. A. G. P.

Effect of protein and amino-acid metabolism on the urea and xylose clearance. R. F. PITTS (J. Nutrition, 1935, 9, 657—666).—Post-absorptive clearances of urea and xylose on a basal diet are low and not greatly affected by feeding the diet. Introduction of meat into the diet produces a gradual and prolonged post-prandial rise in both clearances. When meat feeding is prolonged, post-absorptive clearances are raised without obliteration of the post-prandial effect. Similar effects are produced by feeding casein, by administration of thyroxine to dogs on a basal diet or of phloridzin to fasting dogs, or by replacement of part of the carbohydrate of the basal ration with glycine. The primary effect of protein on renal function results from the action of NH_2 -acids or OH-acids produced in the course of their metabolism on glomerular activity. A. G. P.

Effects of varying amounts of animal protein fed to white Leghorn pullets. I. Influence of low-, medium-, and high-protein diets on the weight and number of eggs. C. C. RHODES, L. H. BARTEL, and P. E. F. JOOSTE (Empire J. Exp. Agric., 1935, 215—228).—Comparison is made of the food consumption with different rations and varying levels of protein content. Differences in the ratio of carbohydrate to protein consumed were apparent, but there was a definite tendency for birds to balance the ration to a common nutritive ratio. The amount of protein consumed produced little significant effect on the body-wt. of the birds or on egg size, but was directly related to the average no. of eggs per bird. A. G. P.

Effect of feeding vegetable protein on copulation and fertilisation in the fowl. T. HATANO (Bull. Agric. Chem. Soc. Japan, 1935, 11, 125—128).—Vegetable (soya-bean) is more effective than animal (fish-meal) protein. W. McC.

Utilisation of meat by human subjects. II. Nitrogen and phosphorus of round and liver of beef. Z. LONG and M. S. PITTMAN. **III. Nitrogen and phosphorus of beef heart.** B. L. KUNERTH, I. M. CHITWOOD, and M. S. PITTMAN (J. Nutrition, 1935, 9, 677—683, 685—690).—II. The N of round of beef was as effectively utilised as that of liver. A higher proportional utilisation of liver-P is indicated.

III. Utilisation of the N and P of beef-heart was not appreciably different from that of round.

A. G. P.

"Continuing" metabolism of nitrogen in animals. H. BORSOOK and G. L. KEIGHLEY (Proc. Roy. Soc., 1935, B, 118, 488—521).—The continuing N metabolism (I) is defined as the N already present in the tissues metabolised on any one day, and is distinct from "wear-and-tear" metabolism. For man in N equilibrium at a level of 10—11 g. of urinary N per day, (I) constitutes > 50% of total urinary N. S excretion is lowered, but only by about 50%, when a normal diet is interrupted either by a day of N starvation or a day on which N is ingested in the form of compounds low in S; the lowering persists for a short period after restoration of the original diet. NH_3 may serve as precursor of urinary uric acid in man. NH_2 -acids do not stimulate either (I) or endogenous N metabolism. F. A. A.

Digestion of foods. V. Synthetic fats. S. SUZUKI (J. Agric. Chem. Soc. Japan, 1935, 11, 1—10; cf. A., 1934, 920, 1027).—Comparison is made of triacetin (I), tributyrin (II), trioctoin, and tridecain fed at the rates of 2 and 12% with a fat-free polished rice ration. At the lower level differences between the real and apparent digestion coeffs. were considerable, but there was little influence on the digestion of other food constituents. At the 12% level fats retarded protein digestion. Except for (I) and (II), the lower acid compounds were the more digestible and had the higher nutrient vals. CH. ABS. (p)

Fat metabolism. VII. β -Oxidation of normal saturated dicarboxylic acids administered *per os*. P. E. VERKADE, J. VAN DER LEE, A. J. S. VAN ALPHEN, and M. ELZAS (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 943—948).—After administration to dogs of the Na salts of sebacic (I) or undecanedicarboxylic (II) acids, the urine was found to contain (I), suberic, and adipic acids or (II), azelaic, and pimelic acids, respectively. The ratios in which these acids are found varies, but (I) or (II) always occurs in a greater amount. H. G. R.

Carbohydrate metabolism in the guinea-pig. F. GOTTDENKER (Biochem. Z., 1935, 281, 128—139).—In autumn the blood-sugar is greatly (up to 250%) increased by fasting, but in the same animal, in winter, fasting causes only slight increase or even decrease, the difference not being due to the change in temp. of the surroundings. Oral administration of overdoses of glucose causes hyperglycæmia, which reaches its max. within 0.5—1.0 hr., then decreases in intensity, and finally attains a val. < that first reached. Overdoses of adrenaline cause increases of 250—300% in blood-sugar. Hypoglycæmic convulsions are produced by overdoses of insulin, but the blood-sugar level is only slightly lowered or even raised, there being no accompanying increase in the content of reducing substances other than sugar. W. McC.

Nutritive value of lactose in man. A. E. KOEHLER, I. RAPP, and E. HILL (J. Nutrition, 1935, 9, 715—723).—In normal adults ingestion of 1.5 g. of lactose per kg. had no appreciable effect on blood-sugar (I) levels. A similar ingestion of starch (II) produced an increase in (I) which was nearly as great as that produced by glucose (III). The total hyperglycæmia after (II) was > that after (III). In these individuals lactose produced a slight and in diabetics a marked rise in (I). A. G. P.

Xylan. H. IWATA (Bull. Imp. Coll. Agric. Morioka, 1935, No. 21, 120 pp.).—Xylanase was not present in the saliva, pancreas, or bile of higher animals, and only in small amounts in the intestines. Decomp. of xylan (I) in the intestines into xylose (II) and small quantities of org. acids by micro-organisms was very active and several new species were isolated; these also hydrolyse starch, dextrin, inulin, and several carbohydrates, but do not affect xylose. The digestion velocity of (I) was < that of starch, but was increased by mild treatment with alkali. On feeding (I) there was little change in the blood constituents and no increase in the urinary excretion of (II), but a protein-sparing action was observed. Both glycogen

and fat accumulation were nearly equiv. to that due to starch. The total calorific val. of (I) was 4167—4184 and the assimilation 61.6%. H. G. R.

Influence of calcium on carbohydrate metabolism. T. HARADA (Bull. Chem. Soc. Japan, 1935, 10, 494—503).—Injection of Ca lactate into albino rabbits decreases the hyperglycaemia and glycosuria caused by simultaneous injection of glucose, but does not alter the effect of adrenaline on the blood-sugar. R. S. C.

Hydrolysis, oxidation, and energy exchanges in the dog. III. Absorption and assimilation of hexoses in the organs during intravenous administration of galactose, maltose, and glucose. M. WIERZUCHOWSKI and H. FISZEL (Biochem. Z., 1935, 282, 124—145; cf. A., 1935, 522).—The absorption from and delivery to the blood of the carbohydrates by various organs are studied. As regards rate and extent of absorption of glucose (I) and galactose (II), the organs form the series liver > portal vein organs > organs of the head > motor system. The liver plays little part in absorption of maltose (III), the other groups of organs exhibiting absorptions equal to those shown with (I). As regards extent of absorption of (I) from the liver, the order is organs of the head > portal vein organs > motor system, the amounts of lactic acid (IV) simultaneously produced by those absorbing organs corresponding respectively with 14—17, 96—164, and 40—60% of the amount of (I) injected. 5—15% of the injected and absorbed (I) or (II) is given up by these organs as (IV) to the blood. Absorption of injected (I) by these organs is at first slight, whilst urinary (I) excretion increases but later becomes more pronounced. The (I) consumption of the organs during injection of (II) is about the same as it is during fasts. During (II) injection the liver ceases to give out (I), about 40% of the (II) absorbed by the organs being subsequently utilised or excreted in the urine. Amytal narcosis has no effect on the assimilation of carbohydrates. Loss of blood and laparotomy have no effect on assimilation of (II), but they interfere slightly with that of fructose (V) and considerably with that of (I) and (III). Of the intravenously injected carbohydrates tested (V) is the best utilised during the narcosis. W. McC.

Effect of sulphur administration on carbohydrate metabolism. T. YOSHIKAWA (Sei-i-kwai Med. J., 1934, 53, No. 6, 74—84).—Administration of S by rubbing S-ointment on rabbit's ears, by mouth, or intravenously produced no appreciable change in blood-sugar. CH. ABS. (p)

Chief sulphur compounds in nutrition. H. B. LEWIS (J. Nutrition, 1935, 10, 99—116).—A review. A. G. P.

Calcium, phosphorus, and nitrogen retention of children. Effects of acid- and base-forming diets. N. J. DAVIS (Amer. J. Dis. Children, 1935, 49, 611—624).—The total Ca output was similar on acid- and base-forming diets. Acid diet led to decreased faecal P and slightly increased urinary P. Basic diets induced greater N retention and higher NH_3 excretion. CH. ABS. (p)

Minerals for dairy cattle. J. C. KNOTT (Proc. 7th Ann. State Coll. Washington Inst. Dairying, 1934, 120—124).—The occurrence and functions of Na, K, Mg, S, Cu, Fe, F, Zn, Mn, I, Ca, and P in dairy cows are discussed. CH. ABS. (p)

Mineral requirements of milk production. Annual cycle of mineral and nitrogen metabolism of the milch cow as affected by lucerne hay, timothy hay, bone flour, and ground limestone. E. B. FORBES [with A. BLACK, W. W. BRAMAN, D. E. H. FREAR, O. J. KAHLLENBURG, F. J. McCLURE, R. W. SWIFT, and LE R. VORIS] (Penn. Agric. Exp. Sta. Bull., 1935, No. 319, 152 pp.).—Monthly determinations of balances of N, Ca, Mg, P, Na, K, and Cl resulting from the different rations are recorded and discussed. A. G. P.

Chemical reactions in muscle. X. P. OSTERN and T. BARANOWSKI (Biochem. Z., 1935, 281, 157—167; cf. A., 1935, 1150).—In dialysed and non-dialysed extracts of autolysed skeletal muscle [free from adenosinetriphosphoric acid (I) and adenylic acid (II)] phosphoglyceric acid and (II) successively added are converted into (I) [yield 40% calc. on (I)]. In heart extracts (horse) the products are diadenosine-pentaphosphoric acid and a substance (possibly a nucleotidephosphoric acid) yielding a Ba salt insol. in dil HCl. Extracts of rabbit heart contain free (II), very little phosphocreatine, and half as much adenosinepolyphosphoric acid and total phosphate as does skeletal muscle. The direct transfer of phosphate [from phosphopyruvic acid to (II) and from (I) to creatine] is accelerated by Mg^{++} , which only slightly affects liberation of free phosphate. In heart the transfer of phosphate is the same as in skeletal muscle, but (II) is here more stable and more slowly deaminated by enzymes. W. McC.

Fission of adenylypyrophosphoric and arginine-phosphoric acid in crab muscle. K. LOHMANN (Biochem. Z., 1935, 282, 109—119; cf. A., 1934, 1033, 1034).—Only one of the readily eliminated H_3PO_4 residues is removed from adenylypyrophosphoric acid (I) by washed crab muscle and dialysed extract of the muscle. On addition of Mg^{++} the adenosine-diphosphoric acid (II) produced is converted into adenylic acid (III). Hence dephosphorylation of (I) is a two-stage process (as in vertebrate muscle), different enzymes being involved. In the dialysed extract argininephosphoric acid (IV) is hydrolysed only if (I) or (II) is present because the extract, in presence of (IV), cannot convert (III) into (II) or (I), whilst (II) is easily rephosphorylated. Crab muscle contains no adenylic acid deaminase. W. McC.

Production of kynurenic acid from tryptophan and indole derivatives. L. C. BAUGUENESS and C. P. BERG (Proc. Iowa Acad. Sci., 1934, 41, 174—175).—When administered to rabbits *l*-tryptophan-amides (free amide, mono- and di-ethyl-amides, anilide, and ethylanilide) were as readily converted into kynurenic acid (I) as was *l*-tryptophan (II). Substituted carboxylic acid derivatives were not converted. β -3-Indolylypyruvic and *dl*- β -3-indolylyl-lactic acids, but not β -3-indolylylacrylic or α -oximino- β -3-indolylylpropionic acids, were also converted into

(I), but in amounts < those from (II) derivatives. Indole derivatives are probably not intermediates in the conversion of (II) into (I). CH. ABS. (p)

Transformation of urobilinogen in the liver. K. FELIX and H. MOEBUS (Z. physiol. Chem., 1935, 236, 230—236).—Fresh liver pulp (pig) attacks urobilinogen (p_{11} optimum at 7.1) in presence of O_2 causing cessation of power to react to the aldehyde test. Boiled liver pulp has no such effect.

W. McC.

Absorption of salicylic acid after intramuscular injection. Absorption by the bladder. W. BLUME and F. W. FISCHER (Arch. exp. Path. Pharm., 1935, 179, 646—654).—Following intramuscular injection of 10 c.c. of 2.5% Na salicylate into rabbits, salicylic acid (I) appears in the blood after 1—2 min. and in the urine after approx. 30 min. The rate of excretion is fairly const., 70% of the administered (I) being excreted within 24 hr. The blood-(I) attains a max. within 1 hr. and returns to zero in 6—7 hr. Absorption into the blood after intramuscular injection is > that after rectal or subcutaneous administration. (I) is absorbed by inflamed (EtOH), but not by normal, bladder mucosa.

F. O. H.

Absorption of intrapleurally and intraperitoneally injected salicylic acid. W. BLUME and K. PLUM (Arch. exp. Path. Pharm., 1935, 179, 655—661).—Following intrapleural and intraperitoneal injection of Na salicylate into rabbits, salicylic acid (I) appears in the blood after 3—10 and 1—2.5 min. (max. being attained after 1 and 0.5 hr.) and in the urine after 40 and 26 min., the total excretion being 77 and 59%, respectively. With both routes, max. excretion occurs after $\frac{1}{2}$ hr. and falls to zero in approx. 7 hr. At max. excretion, the blood-(I) indicates a ratio of absorption by buccal mucosa, stomach-intestine, rectal mucosa, pleural cavity, muscle, and abdominal cavity of 3 : 6 : 8 : 10 : 12 : 14. F. O. H.

Relationship between dielectric polarisation and pharmacological action. K. W. ROSENMUND (Angew. Chem., 1935, 48, 701—705; cf. A., 1934, 652).—The anthelmintic properties of different phenolic lactones are not related to surface activity, action on membrane permeability, or action on the swelling of proteins, but to the polarity of the mols., as varied by the relative positions of substituents in the C_6H_6 ring.

F. A. A.

Relation of cell types in leucæmia to sensitivity to radium. R. ISAACS (Folia Hematol., 1934, 52, 414—425).—Within 24 hr. of application of X-rays or Ra, metabolic rates rise, showing increased O_2 utilisation, and chemical changes associated with cell growth are accentuated. CH. ABS. (p)

Action and hæmolytic dose of X-rays. A. ROGOZINSKI and B. S. LEVIN (Compt. rend., 1935, 201, 798—799).—The dose required for complete hæmolysis is increased if irradiation is carried out in several stages, probably as a result of the formation of antilytic substances.

J. L. D.

Ionisation in air and the biological effects of γ -rays. G. FAILLA (Physical Rev., 1934, [ii], 45, 564).—Contrary to the conclusions of Packard,

equal ionisations in air produced by X- and γ -rays are not equally effective in killing fruit-fly eggs. The therapeutic efficacy of high-voltage X- and γ -rays cannot be predicted by the usual biological and physical tests.

L. S. T.

Action of solar (ultra-violet) rays on the skin and the formation of cholesterol. A. H. ROFFO (Compt. rend., 1935, 201, 566—568).—The ratio of the cholesterol (I) content of the skin of the cheek to that of the abdomen is in adults 3.42, in infants 1.4, and in the foetus 1.1. Skin exposed to sunlight or ultra-violet light *in vivo* or *in vitro* increases in (I) content.

J. L. D.

Radio-hæmolysis and cholesterol. B. S. LEVIN and C. PIFFAULT (Compt. rend. Soc. Biol., 1935, 120, 712—714).—The resistance of guinea-pigs' corpuscles to X-rays is increased by injection or ingestion of cholesterol.

R. N. C.

Fats and a theory of pharmacodynamic actions of alkali and alkaline-earth ions. J. WAJZER and L. LAPICQUE (Compt. rend. Soc. Biol., 1935, 120, 707—710).— K^+ and Na^+ decrease, and Ca^{++} increases, σ between H_2O and oils, by the formation of a unimol. layer of soap at the interface. The effect is unaltered by aliphatic amines.

R. N. C.

Salt requirements and space orientation of the littoral isopod *Ligia* in Bermuda. T. C. BARNES (Biol. Bull., 1932, 63, 496—504).—Toxicity of cations in sea- H_2O to *L. baudiniana* decreases in the order K, Mg, Ca, Na . K exerts a sp. paralyzing action on gill movements.

CH. ABS. (p)

Difference in action of ter- and quinque-valent arsenic compounds on the explanted spleen from chick embryo. H. OKADA (Folia Pharmacol. Japon., 1935, 19, 271—282).—The growth of spleen-tissue is increased by low concns. of Na_3AsO_3 (I), Na_3AsO_4 (II), atoxyl (III), and nearsphenamine (IV). Tissue is killed by high concns. Potency decreases in the order (I), (IV), (II), (III).

CH. ABS. (p)

Influence of bromine on the growth and metamorphosis of the larvæ of *Bufo vulgaris*. V. FAMIANI (Atti R. Accad. Lincei, 1935, [vi], 21, 821—824).—Toad tadpoles fed on egg-yolk to which a trace of $Br-H_2O$ had been added grew more rapidly than controls fed on unbrominated yolk. Metamorphosis commenced earlier, but the tadpoles died during metamorphosis; the liver and intestines had developed to the adult state, the legs had appeared early, but were stunted, and the respiratory system had failed to develop.

D. R. D.

Differential biological reaction of cobaltous compounds and of some cobaltic complexes (cobaltiammines). J. M. LE GOFF (Compt. rend., 1935, 201, 531—532).—The human organism can differentiate between subcutaneously injected Co^{II} and Co^{III} , and between Co and N in complexes.

R. N. C.

New toxicant occurring naturally in certain samples of plant foodstuffs. IX. Toxic effects of orally ingested selenium. K. W. FRANKE and V. R. POTTER. **X. Effect of feeding toxic foodstuffs in varying amounts and for different time**

periods. K. W. FRANKE (J. Nutrition, 1935, 10, 213—221, 223—231).—IX. Symptoms of poisoning produced by Na_2SeO_3 are practically identical with those shown by the natural toxicant.

X. Effects of feeding toxic grain are examined.

A. G. P.

Mechanism of the action of sulphur and mud baths. L. SCHMIDT (Orvosi Hetilap, 1935, 79, 318—319).—Absorption of chemical components of mineral waters is probable. The S of therapeutic muds is in steady circulation, but in dynamic equilibrium, part being oxidised and part reduced.

CH. ABS. (p)

Dietary depigmentation of young black and pied rats, promoted by rapid growth, prevented and cured by ingestion of copper. F. J. GORTER (Z. Vitaminforsch., 1935, 4, 277—293; cf. A., 1935, 1148).—The curative effect of yeast on depigmentation is due to its Cu content and not to its anti-pellagra property. Depigmentation in young growing rats is prevented by adding CuSO_4 to the diet, the daily preventive dose of Cu being 0.02—0.12 mg., and the curative dose 0.07—0.24 mg. Other metals are ineffective. Cu in cereals appears to be more available than Cu in proteins.

J. N. A.

Feeding and thyroid function. I. Effect of cyanides on the function and histological picture of the rat thyroid. F. BRUMAN and L. BERMAN (Z. ges. exp. Med., 1935, 95, 724—728; Chem. Zentr., 1935, i, 2202—2203).—MeCN given daily does not alter basal metabolism in rats. The diminution of tissue oxidation due to MeCN is compensated by increased thyroxine secretion.

R. N. C.

Effect of iodoacetate on *post-mortem* glycogenolysis in liver. H. R. NOLTIE (Quart. J. Exp. Physiol., 1935, 24, 377—382).—Iodoacetate did not prevent glycogenolysis in rabbit liver incubated in N_2 at 38°, or the accumulation of sugar (although exerting some inhibitory action), but caused the lactic acid content to remain stationary.

CH. ABS. (p)

Effect of dinitrophenol on calcium and phosphorus metabolism. C. L. ROBBINS (J. Nutrition, 1935, 10, 187—191).—Increased basal metabolism caused by administration of dinitrophenol was not accompanied by any change in the excretion of Ca, P, or N.

A. G. P.

Effects of moderate doses of dinitrophenol on the energy exchange and nitrogen metabolism of patients under conditions of restricted dietary. M. L. TAINTER, W. C. CUTTING, and E. HINES (J. Pharm. Exp. Ther., 1935, 55, 326—353).—0.3—0.4 g. of 2 : 4-(NO_2) $_2\text{C}_6\text{H}_3\cdot\text{OH}$ (I) was given daily for 1—2 weeks to normal human subjects maintained on a low-calorific diet with only sufficient protein to maintain N balance. (I) produced an increased loss in body-wt. associated with increased fat metabolism with the production of no ketones or acidosis. There was no extra metabolism of carbohydrates or proteins; (I) was not conjugated in the body as an org. sulphate and no extra secretion of Cl' in the urine, faeces, or sweat occurred.

H. D.

Antagonism of cryogenin and 2 : 4-dinitrophenol. A. LEULIER and G. BÉRUARD (Compt.

rend. Soc. Biol., 1935, 120, 650—651).—The temp. rise in pigeons given cryogenin and (NO_2) $_2\text{C}_6\text{H}_3\cdot\text{OH}$ (I) is < in those given (I) only.

R. N. C.

[Pharmacology of] phenanthrene derivatives. V. Homologous acids and aldehydes and some of their derivatives. N. B. EDDY (J. Pharm. Exp. Ther., 1935, 55, 354—364; cf. A., 1933, 858).—The action on cats of phenanthrenecarboxylic and β -(3-phenanthryl)propionic acids, their Me esters, amides, ketone and alcohol derivatives, and some position-isomerides of these compounds are compared. Effectiveness is greater in the higher homologues; that of the alcohols is > that of ketones. The amides and Me esters are less active than the acids. 3-derivatives are more active than the 2- or 9-derivatives. Of the compounds studied, *Me phenanthrene-3-*, m.p. 95°, and *-9-carboxylate*, m.p. 116°; *phenanthrene-3-carboxydimethylamide*, m.p. 120.5—121°, *-2-carboxylamide*, m.p. 242—243°, *-3-*, m.p. 79—80°, and *-9-aldehyde*, m.p. 100.5—101°; β -3-phenanthrylpropionic acid, m.p. 154.5—155° (*Me ester*, m.p. 61—62°; *amide*, m.p. 161—162°); *3-*, m.p. 100—103.5, and *9-hydroxymethyl-*, m.p. 149—149.5°; *3-*, m.p. 72°, *2-*, m.p. 143°, and *9-acetyl-*, m.p. 74.5°, *3-propionyl-phenanthrene*, m.p. 53—54°; *phenanthryl-3-*, m.p. 83—83.5°, and *-2-methylcarbinol*, m.p. 134.5—135.5°, are new.

Pharmacology of some hydroxyphenoxyethylalkylamines. D. BOVET, A. SIMON, and J. DRUEY (Compt. rend. Soc. Biol., 1935, 120, 690—691).—*sec.*-Hydroxyphenoxyethylalkylamines exhibit adrenolytic action, whilst the *tert.*-amines exhibit nicotine-like action and resemble hordenine in having a powerful ganglionic nicotine-like action which is abolished by methylation of the OH. Certain of the *tert.*-amines exhibit both the above actions.

R. N. C.

Renal activity. VIII. Effect of xanthine and histidine fractions isolated from various organs of cows. IX. Effect of endocrine preparations on renal activity. Y. MIZUNO (Sci-i-Kwai Med. J., 1933, 52, No. 10, 50—70, 71—90; cf. A., 1935, 258).—VIII. Xanthine fractions (especially from adrenals) markedly accelerated renal activity in rabbits. The histidine fraction is less effective. Arginine and lysine fractions have no action.

IX. Injection of thyreoglandol caused marked acceleration. Pituitrin and adrenaline were non-effective.

CH. ABS. (p)

Effect of bile acids on sugar assimilation in depancreatized dogs. T. HASEGAWA (Arb. Med. Fak. Okayama, 1935, 4, 453—460).—Injection of Na cholate, with or without glucose, reduced hyperglycaemia and glucosuria in depancreatized dogs.

CH. ABS. (p)

Influence of bile acids on calcium metabolism. VIII. Influence of bile acids and spleen extract on urinary calcium excretion. IX. Blood composition of normal and splenectomized rabbits under the influence of bile acids and spleen extract. M. IWADÔ (Arb. Med. Fak. Okayama, 1935, 4, 346—355, 356—364).—VIII. In normal or splenectomized rabbits subcutaneous injection of Na cholate (I) augments and spleen extract (II) decreases urinary Ca.

IX. Splenectomy is followed by hypercalcaemia, which gradually disappears. Blood-Ca is lowered by (II) in normal rabbits > in splenectomised rabbits. Post-operative hypercalcaemia is increased by (I) and lowered by (II). Spleen and liver are concerned in the regulation of blood-Ca. CH. ABS. (p)

Influence of fractionated liver extract on blood composition of normal dogs. M. IWADÔ (Arb. Med. Fak. Okayama, 1935, 4, 438—444).—The factor in aq. liver extracts which causes hypercalcaemia is sol. in EtOH and slightly less sol. in Et₂O (cf. preceding abstract). CH. ABS. (p)

Blood composition of normal and splenectomised rabbits under the influence of liver extracts from normal and splenectomised rabbits, spleen extracts, and bile salts. M. IWADÔ (Arb. Med. Fak. Okayama, 1935, 4, 424—437).—Subcutaneous injection of Na cholate increases blood-Ca (I). Splenectomy removes a factor from the liver which is capable of increasing (I). CH. ABS. (p)

Barbiturates. XI. Methods of barbital research. C. R. LINEGAR, J. M. DILLE, and T. KOPpanyi (J. Amer. Pharm. Assoc., 1935, 24, 847—852).—Prior to determination of barbiturates (I), highly pigmented urines are cleared by Na₂MoO₄-H₂SO₄ or CuSO₄-Na₂WO₄-H₂SO₄. Extraction of urines or cleared filtrates by CHCl₃ indicates that excreted (I) are present as acids even in alkaline urines. Following pptn. of blood with Na₂WO₄-H₂SO₄ (Folin-Wu), the CHCl₃ extract of the filtrate is free from substances interfering with the colorimetric determination. (I) are determined in brain by extraction of the powdered (liquid air) tissue with CHCl₃, concn. of the extract, and removal of phospholipins by pptn. with COMe₂ (cf. A., 1935, 118). F. O. H.

Barbiturate-picrotoxin antagonism. C. R. LINEGAR, J. M. DILLE, and T. KOPpanyi (Science, 1935, 82, 376—377). L. S. T.

Use of coramine for combating poisoning from narcotics and hypnotics. H. KILLIAN (Anesthesia and Analgesia, 1935, 14, 23—27). CH. ABS. (p)

Effect of ultra-violet irradiation on the anaesthetising power of methyl and ethyl alcohols. W. P. ELHART and O. S. ORTH (Anesthesia and Analgesia, 1935, 14, 15—19).—The anaesthetic action of MeOH and EtOH on goldfish was accelerated by irradiation as a result of formation of the aldehydes and acids. CH. ABS. (p)

Rate of production of anaesthesia in mice by ether containing aldehyde and peroxide. P. K. KNOEFEL and F. C. MURRELL (J. Pharm. Exp. Ther., 1935, 55, 235—241).—Et₂O containing > 0.07% MeCHO and 0.02% H₂O₂ is less effective anaesthetically than pure Et₂O. EtOH acts merely as a diluent. H. D.

cycloPropane anaesthesia: post-operative morbidity in 2200 cases. E. R. SCHMIDT and R. M. WATERS (Anesthesia and Analgesia, 1935, 14, 1—3).—Respiratory, nausea, and emetic after-effects of cyclopropane and Et₂O were < those of C₂H₄ and N₂O (with CO₂ absorption), but circulatory complications were slightly greater. CH. ABS. (p)

Novocaine oxide.—See this vol., 70.

Influence of morphine on local anaesthesia of the cornea through various local anaesthetics in rabbits. K. ARIMA (Folia Pharmacol. Japon., 1935, 19, 283—286).—Small amounts of morphine which do not affect the sensitivity of the cornea increased and lengthened the action of cocaine, tutocaine, and pantocaine. CH. ABS. (p)

Morphine and ether hyperglycaemia in hypophysectomised dogs. E. DI B. DE SABELLI and E. J. DI BENEDETTO (Compt. rend. Soc. Biol., 1935, 120, 738—739).—Hyperglycaemia from morphine in hypophysectomised dogs is > in normal dogs, whilst that from Et₂O is less. R. N. C.

[Pharmacology of] morphine, codeine, and their derivatives. X. Deoxymorphine-C, deoxycodine-C, and their hydrogenated derivatives. N. B. EDDY and H. A. HOWES (J. Pharm. Exp. Ther., 1935, 55, 257—267; cf. A., 1935, 780).—Reduction of the alcoholic OH in members of the morphine and codeine series increases the analgesic and depressor effects and decreases the emetic effect. Of the compounds formed, tetrahydrodeoxymorphine, m.p. 260°, [α]_D²⁵ -45.5° in EtOH, is new. H. D.

Effects of morphine and its derivatives on intestinal movements. IV. Dihydro-ψ-codeine and dihydroallo-ψ-codeine. H. KRUEGER, H. HOWES, and H. GAY (J. Pharm. Exp. Ther., 1935, 55, 288—318).—The quantities of morphine, ψ- and allo-ψ-codeine, dihydro-ψ-codeine and -allo-ψ-codeine required to reduce the frequency of rhythmic contractions of the dog's intestine were as 1:22:108:35:27, respectively; for producing peristalsis 1:45:65:31:54, and for equivalently maintained effects on tone 1:75:22:30:60. H. D.

Emetic action of apomorphine in rabbit lymph. S. TAKAHASHI (Arb. dritt. Abt. Anal. Inst. Univ. Kyoto, D, 1934, No. 4, 138—139).—The emetic effect is lost by incubation with blood-serum or lymph. CH. ABS. (p)

Combined action of quinine and pituitrin, histamine, and barium on the excised uterus and isolated urine bladder of the rabbit. K. KUNISHO (Folia Pharmacol. Japon., 1935, 19, 333—345).—Stimulative effects were obtained by use of half the min. active dose of one of the drugs with half the dose of any other. A potentiation was observed in all cases except with histamine and quinine on the pregnant uterus. CH. ABS. (p)

Comparative toxicity of anabasine and nicotine sulphates to insects. J. M. GINSBURG, J. B. SCHMITT, and P. GRANETT (J. Agric. Res., 1935, 51, 349—354).—Anabasine sulphate was more toxic to a no. of insects than was nicotine, but when used as a stomach poison for grasshoppers and silk-worm larvae was much inferior. A. G. P.

Effect of nicotinism in the albino rat. C. S. SMITH, S. ROSENFELD, jun., and L. J. SACKS (J. Pharm. Exp. Ther., 1935, 55, 274—287).—Injection of 0.005—0.0075 mg. of nicotine per g. of body-wt. in rats decreased their voluntary muscular activity

and their fat contents; it had no influence on the growth curves or œstrus cycles. H. D.

Balance of nicotine in the smoking of tobacco in cigarettes. A. KOPERINA (Tabacn. Prom., 1934, No. 5, 37—40).—Of the nicotine (I) in tobacco, 60% is burned during smoking, 27% escapes on exhalation, and 12% is absorbed by the smoker. Absorption of (I) is through the lungs and not through the stomach or saliva. CH. ABS. (p)

Use of rabbits in the assay of digitalis, strophanthus, and squill. G. N. RAPSON and S. W. F. UNDERHILL (Quart. J. Pharm., 1935, 8, 409—423).—Application of the infusion method of assay (Gaddum, A., 1932, 964) indicates that rabbits are less sensitive than cats to ouabain (I), strophanthus (II), or squill, but more sensitive than dogs or guinea-pigs to (I) and (II); to digitalis, rabbits are the most resistant of the four species. With strict adherence to conditions characteristic for each drug, results from rabbits agree with those from cats. F. O. H.

[Pharmacology of] samandarine and its derivatives and fission products. O. GESSNER and W. ESSER (Arch. exp. Path. Pharm., 1935, 179, 639—645).—The pharmacological action and min. lethal dose of samandarine (I) and 9 derivatives (A., 1935, 97) were determined in mice. Samandarone approximates to (I) in its activity. No correlation between constitution and pharmacological (especially convulsive) action is apparent. F. O. H.

Pharmacological action of dendrobine, the alkaloid of Chin-shih-hu. K. K. CHEN and A. L. CHEN (J. Pharm. Exp. Ther., 1935, 55, 319—325).—Dendrobine produces moderate hyperglycæmia, diminishes cardiac activity in large doses, lowers blood pressure, suppresses respiration, inhibits isolated rabbit's intestine, and contracts the guinea-pig's uterus. H. D.

Yolk-sac vessels of the chick embryo. IV, V. T. NAKANO (Folia Pharmacol Japon., 1935, 19, 293—299, 300—305; cf. A., 1935, 893). CH. ABS. (p)

Comparative actions of sympathomimetic compounds: bronchodilator actions in experimental bronchial spasm of parasympathetic origin. J. R. PEDDEN, M. L. TAINTER, and W. M. CAMERON (J. Pharm. Exp. Ther., 1935, 55, 242—256; cf. A., 1934, 1134).—Of fourteen amines tried, the most effective in producing bronchial dilation in dogs treated with arecoline were adrenaline, arterenol, and epinine; activity appeared to be associated with the pyrocatechol nucleus. H. D.

Action on the gaseous metabolism of poisons for the vegetative nervous system. F. PÉTER (Biochem. Z., 1935, 281, 111—120).—Subcutaneous administration of ergotamine increases the basal metabolic rate of fasting male rats at 28° (max. 42%) and its effects last 5—6 hr.; atropine (II) slightly reduces the rate, and Na luminal (III) does not affect it. (I)+(III) cause increase, (II)+(III) slight increase, and (I)+(II) and (I)+(II)+(III) have no effect. W. McC.

Toxicity of optically active and inactive dihydrodeguelins. W. A. GERSDORFF (J. Agric. Res., 1935, 51, 355—361).—The order of toxicity to goldfish was rotenone > active dihydrodeguelin (I) > deguelin > inactive (I), although the relative proportional toxicity varied somewhat with the concns. examined. A. G.

Toxicity of methyl alcohol. A. BENEDICENTI (Mem. R. Accad. Italia, 1935, 6, 601—633).—Injection of MeOH into rabbits and dogs lowers the alkaline reserve of the blood. The toxic action is not influenced by administration of cholesterol (I) or oils containing (I). Most animals tolerate 0.2—0.4 vol.-% in the inspired air, but considerable variations occur with different species and also with animals of the same species. MeOH in air is determined by conversion into Me₃BO₃ and subsequent decomp. in 0.1N-NaOH. Severe poisoning is followed by accumulation of MeOH in blood, brain, etc. Normal combustion produces (non-toxic) traces of CO, CH₂O, and other reducing substances. Industrial hazards are discussed. F. O. H.

Mechanism of mercury diuresis. J. J. BERTERVIDE and C. RECHNIEWSKI (Prensa med. Argentina, 1934, 21, No. 50—51).—Novasural causes hydræmia only when H₂O is retained in the tissues. The globulin content of blood is reduced. CH. ABS. (p)

Influence of mercury on cultivated tissues. III. How will the action of mercury compounds on cultures of fibroblast *in vitro* be influenced by glucose? K. HIRASHIMA (Folia Pharmacol. Japon., 1935, 19, 323—332).—The toxic action of 1×10⁻⁶M-HgCl₂ is decreased by raising the glucose concn. in fibroblast culture media 0.01M > that in normal media. Cultures in such media show normal resistance to HgCl₂. CH. ABS. (p)

Repeated injections of a thio-derivative of gold: tolerance and localisation. A. LEULIER and G. BÉRUARD (Compt. rend. Soc. Biol., 1935, 120, 651—654).—Sr aurothiopropansulphonate (I) is less toxic than the corresponding Na and Ca salts to guinea-pigs, and diffuses less readily through the organs on account of its low solubility; it is excreted less rapidly in the urine. The Au storage in the kidneys, spleen, liver, and other organs produced by repeated injections of (I) is not much > that produced by the more sol. salts. R. N. C.

Has glucose any influence on the arsphenamine action on cultivated tissue? H. OKADA (Folia Pharmacol. Japon., 1935, 19, 287—292).—Combination of glucose and neo- or myo-arsphenamine causes better growth in spleen-tissue cultures than arsenicals alone. CH. ABS. (p)

Cyanide antidotes. P. J. HANZLIK and A. P. RICHARDSON (J. Amer. Med. Assoc., 1934, 102, 1740—1745).—Intravenous injection of methylene blue is recommended. A mixture of NaNO₃ and Na₂S₂O₃ is also effective. CH. ABS. (p)

Antidote for acute mercury poisoning. S. M. ROSENTHAL (J. Amer. Med. Assoc., 1934, 102, 1273—

1276).—Oral or intravenous administration of Na formaldehydesulphoxylate proved satisfactory.

CH. ABS.

Influence of chronic fluorine toxicosis in laying hens on the fluorine content of the egg and its relation to the lipin content of the egg-yolk. P. H. PHILLIPS, J. G. HALPIN, and E. B. HART (J. Nutrition, 1935, 10, 93—98).—Addition of F-containing rock phosphate to hen's rations increases the F content of egg-yolks. Within the yolk the additional F occurs mainly in the COMe_2 -insol. fraction of the fatty matter, possibly in combination with complex lipins. Ingestion of F by means of mineral phosphate did not reduce egg size.

A. G. P.

Oxidation-reduction catalysis in the living cell. P. JOYET-LAVERGNE (Protoplasma, 1935, 23, 50—69).—Published work is discussed in support of the concept that vitamin-A and glutathione act as complementary constituents of a catalytic system controlling intracellular oxidation-reduction processes located on the surface of the chondriome. A. G. P.

Catalase in lymphocytes. K. FUKUCHI (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 65—67).—The catalase activity of lymphocytes from the popliteal gland of rabbits is determined.

CH. ABS. (*p*)

Iron. IX. Catalase and "readily eliminated" iron of blood. G. BARKAN (Z. physiol. Chem., 1935, 236, 197—200).—Since the catalase (I) is not affected by CO under conditions in which elimination of Fe is greatly restricted, it follows that (I) is not identical with the "readily eliminated" blood-Fe.

W. McC.

Cytochrome-c. IV. K. ZEILE (Z. physiol. Chem., 1935, 236, 212—215; cf. A., 1934, 109; Theorell, A., 1935, 1277).—The mol. wt. (18,000) and hæmin content (3.5%) of the smallest unit of the cytochrome (I) are determined, taking advantage of the non-adsorption of reduced (I) on kaolin. The isoelectric point of (I) is at p_H 8.2.

W. McC.

Tyrosinase action on mono- and di-hydric substrates. M. GRAUBARD and J. M. NELSON (J. Biol. Chem., 1935, 111, 757—770).— p_H -activity curves for *p*-cresol (I) with various preps. of tyrosinase (II) are given. The system (I)-(II) proceeds differently from the system pyrocatechol (III)-(II), for in the former (II) is not inactivated, whilst in the latter it is inactivated very quickly and addition of NH_2Ph produces very little change. With (I) the rate of reaction \propto concn. of (II), whilst with (III) the total O uptake depends on the p_H and amount of (II). Neither NH_2Ph nor NaHSO_3 inhibits the reaction, but there may be prolonged induction periods. It is concluded that (II) consists of only one enzyme and that it acts like a peroxidase.

J. N. A.

Activation by glutathione of the enzymic dehydrogenation of alcohol. T. WAGNER-JAUREGG and E. F. MÖLLER (Z. physiol. Chem., 1935, 236, 222—227).—Reduced (but not oxidised) glutathione (I), and also KCN [action > that of (I)], Na_2S , α -amino- β -naphthol-4-sulphonic acid, and thioglycollic acid (but not pyrophosphate) in presence of dialysed extract of washed yeast activate the enzymic dehydro-

genation of EtOH. The activation is due to the binding of heavy metals, since, when these are as completely removed as possible, the effects of reduced (I) and KCN are < usual and the inhibition caused by added CuSO_4 is counteracted by addition of reduced (I) or KCN [\leq about 10 mols. of reduced (I) or KCN per mol. of CuSO_4]. Cysteine (II) does not accelerate the dehydrogenation and even counteracts the effect of reduced (I), probably because heavy-metal compounds of (II) catalyse oxidation of reduced (I).

W. McC.

Dehydrogenase of lactic acid. T. WAGNER-JAUREGG and E. F. MÖLLER (Z. physiol. Chem., 1935, 236, 216—221; cf. Adler *et al.*, A., 1935, 1276).—The yellow (flavin) enzyme of yeast plays no part in the aerobic enzymic conversion of lactic acid into AcCO_2H .

W. McC.

Enzymes of liver. III. Aldehydease. IV. Alcohol-dehydrase. L. REICHEL and H. KÖRLE (Z. physiol. Chem., 1935, 236, 145—157, 158—167; cf. A., 1934, 807; Battelli *et al.*, A., 1910, ii, 980).—III. Dry preps. of the aldehydease (I) (from pig liver), which retain their activity almost unchanged for > 1 year, have optimal effect at p_H 7.5—7.8, are destroyed at 69°, and cease to act after 2 hr. The action is greatly (> 50%) diminished by KCN, probably because of cyanohydrin production, and decreases as the concn. of substrate increases. Benzoquinone (II) in high concn. inhibits anaerobic dismutation by (I), methylene-blue (III) in high concn. increases it, and the oxidation product (IV) of adrenaline has no effect. Cytochrome and indophenol-oxidase accompany (I), which acts only if they are present. In fresh liver, in presence or absence of O_2 the action of (I) is slight, most of the EtCHO being consumed in other ways.

IV. Alcohol-dehydrase (from frog-liver) does not act in absence of O_2 , converts Pr°OH (optimum at p_H 6.7—7.3) into EtCHO, no EtCO_2H being produced, retains its activity for 6—8 weeks in a vac., but loses it in a few days in air, is destroyed at 47.5° (p_H 7.8), is not affected by KCN, and ceases to act after 80 min. The extent of action decreases as the concn. of substrate increases. (II), (III), and (IV) act as intermediate H acceptors in the process and increase the extent of dehydrogenation, but ascorbic acid diminishes it. The extent of dehydrogenation is also increased by preps. from spleen (calf).

W. McC.

Cabbage-amylase. B. A. RUBIN and V. E. TRUPP (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 229—232).—In addition to amylase (I) an enzyme cytase (II) exists, capable of hydrolysing cellulose to reducing sugar. In "Amager," a late variety, the leaves are richest in (II), whilst in "No. 1" the stalks have a higher (II) content. The (I) content is const. during storage for 6 months, whilst (II) gradually decreases.

P. G. M.

Reversible inhibition of β -malt-amylase by ascorbic acid and related compounds. C. S. HANES (Biochem. J., 1935, 29, 2588—2603).—The degree of inactivation of β -malt-amylase (I) by ascorbic acid (II), dihydroxymaleic acid (III), and reductone (IV) increases with the time of treatment. With low

conens. of (II) regeneration of activity occurs after 10 min. treatment; the regeneration is more rapid with (III) and (IV), and is correlated in all cases with decreases in the I vals. of the inhibitor-enzyme mixtures. (I) stabilises (II) against oxidation, whilst it accelerates the oxidation of (III) and (IV), thus explaining the difference in inhibiting powers of these three. Preliminary oxidation of the inhibitors, or the addition of a no. of reducing substances such as HCN, reverses the inhibition. CuSO_4 causes increased inhibition. It is concluded that the sp. effect of (I) lies in its dienol group as opposed to its reducing powers.

H. D.

α - and β -Amylase in ripening wheat grain. P. S. UGRUMOV (Biochem. Z., 1935, 282, 74—78; cf. Purr, A., 1934, 934; Stenstam *et al.*, *ibid.*, 1258).—During the early stages of the ripening, β -amylase, which is predominantly a saccharifying agent, and α -amylase (I), which produces dextrin, are present. (I) becomes inactive at the "milky" stage and cannot be detected during subsequent ripening or in resting wheat, but it reappears during germination.

W. McC.

Effect of potassium cyanide on amylase activity. J. O. PAGE and D. T. ENGLIS (Trans. Illinois State Acad. Sci., 1934, 27, 74).—The rate of saccharification by barley amylase is unaffected by KCN at p_{H} 4.56. At p_{H} 7.0 KCN increases the rate until it approximates to that at p_{H} 4.56.

CH. ABS. (p)

Conversion of rutin into a brown pigment by tobacco enzymes. C. NEUBERG and M. KOBEL (Naturwiss., 1935, 23, 800—801).—The enzymes of the tobacco leaf convert rutin (quercetinramnogluco-side) into a dark brown H_2O -sol. product which on hydrolysis yields a H_2O -insol. aglucone. The reaction, which apparently consists in the oxidation of the rutin, is accelerated by the presence of 0.03% H_2O_2 .

W. O. K.

Enzymes of pectin. III. Complete direct hydrolysis of pectolic acid to *d*-galacturonic acid by pectolase. F. EHRLICH, R. GUTTMANN, and R. HAENSEL (Biochem. Z., 1935, 281, 93—102; cf. A., 1933, 491).—Crude material obtained from pectin by heating with HCl and washing with H_2O and EtOH is rapidly (3—4 days) converted by pectolase into pure cryst. *d*- α -galacturonic acid in 87% yield. The conversion of purified material is much slower (2 months) and is incomplete except at p_{H} 6—4.

W. McC.

Cellobiase activity of the bovine rumen. C. ANTONIANI (Biochim. Terap. sper., 1935, 22, 48).—Neither the mucosa of the rumen nor aq. extracts made by prolonged maceration in presence of PhMe at 37° hydrolyse cellobiose, although the presence of cellobiase (I) is readily demonstrated in expressed fluid. Possibly (I) is of alimentary origin.

NUTR. ABS. (m)

Retarding action of formaldehyde, acetaldehyde, and acetone on the enzymic hydrolysis of sucrose. A. CHAUDIN (Bull. Soc. Chim. biol., 1935, 17, 1346—1350).—The effect of CH_2O , MeCHO, and COMe₂ on the hydrolysis of sucrose by invertase, like that of alkalis, MeOH, and EtOH, is to retard the

reaction, and displace the curve of reaction rate against time so that the amount of enzyme present appears to be increased.

A. L.

Purification of choline-esterase. E. STEDMAN and (Mrs.) E. STEDMAN (Biochem. J., 1935, 29, 2563—2567; cf. A., 1933, 1081).—Preps. of choline-esterase, 50 to 100 times as active as serum, may be prepared from the latter by fractional pptn. with $(\text{NH}_4)_2\text{SO}_4$ and AcOH and adsorption on Al_2O_3 or $\text{Fe}(\text{OH})_3$ from acid solution using aq. NH_3 and *M*/3-phosphate buffer at p_{H} 8 as eluents. These preps. do not attack PrCO_2Me .

H. D.

Action of magnesium on the aspartase system. K. P. JACOBSON and F. B. PEREIRA (Compt. rend. Soc. Biol., 1935, 120, 551—554).—Addition of Mg^{++} to the aspartase system displaces the equilibrium in favour of fumaric acid formation, K_c^{37} showing a considerable decrease.

R. N. C.

Enzymes of snake venom. I. Activation of dipeptidase by the venom of the snake *Trimeresurus mucrosquamatus*. Y. TSUCHIYA (J. Agric. Chem. Soc. Japan, 1935, 11, 720—730).—The dipeptidases of extract of dried tortoise liver and of fresh or dried intestinal mucous membrane of the pig are activated by the venom, the effect being pronounced with respect to hydrolysis of leucylglycine, slight with respect to that of valylglycine, and absent with respect to that of glycyl- and alanyl-glycine when the tortoise liver extract is used. The p_{H} -activity curve exhibits max. within a certain $[\text{H}^+]$ zone. The activating power decreases with time and the amount of venom required for max. activation \propto the amount of enzyme used.

W. McC.

Enzymic proteolysis. VI. Structure of protamines. II. Clupein. E. WALDSCHMIDT-LEITZ and E. KOFRANYI (Z. physiol. Chem., 1935, 236, 181—191; cf. A., 1931, 984).—Clupein is hydrolysed by activated trypsin, 4 peptide linkings being broken [no arginine (I) produced] and the product yields two fractions separated by pptn. with aq. EtOH. The less sol. (N : NH_2 ratio 9) forms 73% of the product and is a mixture of tripeptides containing 2 (I) residues and 1 $(\text{NH}_2)_1$ -acid residue. The more sol. (N : NH_2 5) forms 27% and is a mixture of dipeptides containing 1 (I) and 1 $(\text{NH}_2)_1$ -acid residue. The results of acid and enzymic (aminopolypeptidase, arginase, carboxypolypeptidase, dipeptidase) hydrolysis of these fractions indicate the structure of clupein (mol. wt. 2021), which is a chain of 10 (I), 4 $(\text{NH}_2)_1$ -acid, and 1 proline residues, the position of the latter alone being uncertain, although only 3 positions are possible.

W. McC.

Proteolytic enzymes. VIII. Proteolytic systems of papain. M. BERGMANN and W. F. ROSS (J. Biol. Chem., 1935, 111, 659—666).—The enzymic homogeneity and the activation processes of papain (I) are investigated. Substrates such as hippuryl-amide (II) and carbobenzyloxydiglycylglycine are acted on by (I) only after activation by HCN, H_2S , and thioglucose. (I) inactivated by oxidising agents (H_2O_2 , I) has its proteinase but not its polypeptidase (III) action reactivated by the above activators,

so that (I) must contain two different proteolytic enzymes. NHPh-NH_2 completely inhibits the splitting of (II) by HCN-activated (I), but the hydrolysis of gelatin is only slightly affected. Excess of I added to HCN-activated (I) destroys both enzymes, but small amounts inhibit (III) only. The results are in accord with the presence of a CHO group in (III).
E. A. H. R.

Enzymic amylolysis. V. Amylophosphatase of barley. E. WALDSCHMIDT-LEITZ and K. MAYER (Z. physiol. Chem., 1935, 236, 168—180; cf. A., 1934, 449).—Barley and malt extracts contain an enzyme, amylophosphatase (I), which eliminates all bound H_3PO_4 from starch paste, and the accompanying decrease in viscosity \propto the amount of H_3PO_4 eliminated. The degradation (optimal at p_{H} 5.6) results in the production of reducing substances apparently consisting of chains of about 36 glucose residues. (I), which is not activated by amylokinase from malt, is purified and freed from accompanying enzymes by selective adsorption on Al_2O_3 and kaolin. Kidney-phosphatase behaves very similarly towards starch paste, but at p_{H} 5.6 its action is very much slower.
W. McC.

Phosphatase of the prostate gland. W. KUTSCHER and H. WOLBERGS (Z. physiol. Chem., 1935, 236, 237—240; cf. A., 1935, 1268).—The human prostate gland and seminal fluid contain large amounts of a phosphatase (I) not identical with urinary phosphatase. (I), which is destroyed in 5 min. at 60° , exhibits specificity as regards its action on phosphates, α - and β -glycerophosphates being readily attacked, hexose diphosphate and pyrophosphate only slightly affected.
W. McC.

Glycerophosphatase activity of the tissue of animals in avitaminosis-A. L. EMERIQUE (Bull. Soc. Chim. biol., 1935, 17, 1372—1377).—The phosphatase (I) content of the kidneys and liver of rats suffering from vitamin-A deficiency is the same as that in normal animals. In the lung, however, (I) is $>$
A. L.

Combining power of taka-diastrase towards glycerophosphates. J. COURTOIS (Bull. Soc. Chim. biol., 1935, 17, 1340—1345).—The reaction coeffs. for the rates of hydrolysis of α - and β -glycerophosphates by taka-diastrase increase regularly with increasing amounts of enzyme up to a certain point and thereafter both remain const., the amount of diastrase at this point being the same in both cases. This behaviour is explained by the affinities of the enzyme for both substrates being the same, but the rates of hydrolysis different.
A. L.

Comparative hydrolysis of α - and β -glycerophosphoric acids by vegetable phosphatases. II. Taka-diastrase. J. COURTOIS (Bull. Soc. Chim. biol., 1935, 17, 1318—1339; cf. A., 1935, 122).—The vals. of the optimum p_{H} for the hydrolysis of α - and β -glycerophosphoric acids increase with the substrate concn., the displacement being greater for the β - than the α -compound. This behaviour is the result of two simultaneous reactions, one involving the affinity of the enzyme for the substrate which increases with acidity and on which depends the

optimum p_{H} val. for the reaction at low substrate concn., and the other the actual hydrolytic activity, which at high concn., when the enzyme surface is saturated, controls the p_{H} optimum. This interpretation is applied to corresponding observations made with laccase and urease.
A. L.

Inhibitory effect of phloridzin on an enzymic dismutation. H. KALCKAR (Nature, 1935, 136, 872—873).—The dismutative conversion of triose-phosphoric acid into phosphoglyceric acid and glycerophosphoric acid is prevented or markedly inhibited by approx. 0.01*N*-phloridzin (I). The velocity of conversion of hexose diphosphate into dihydroxy-acetone phosphate (II), and of (II) into glyceraldehyde phosphate, is not affected by this concn. of (I).
L. S. T.

Yeast zymin. I. Effect of some electrolytes on carbon dioxide production. II. Effect of ethanol on the production of carbon dioxide. III. Effect of some electrolytes, and of ethanol, on the phosphate content during fermentation. H. E. STAVELEY, L. M. CHRISTENSEN, and E. I. FULMER (J. Biol. Chem., 1935, 111, 771—783, 785—790, 791—802).—I. The optimum p_{H} for the production of CO_2 by zymin (I) is 5.8—6.2, and (I) is most active when prepared from yeast which has been kept for several days at refrigerator temp. NH_4Cl , MgSO_4 , NaCl, and KCl increase the initial max. rate of CO_2 formation by (I), whilst NH_4Cl (most active), MgSO_4 , NaCl, and CaCl_2 increase the steady const. rate of CO_2 . NH_4Cl and MgSO_4 increase the rate of CO_2 formation in presence of added inorg. PO_4''' , but the effect of the two salts is not additive.

II. Production of CO_2 by dried yeast, yeast juice, living yeast, and (I) is increasingly lowered by EtOH in the order named. 1.86% of EtOH reduces the activity of (I) 50%, whereas 14% is necessary to reduce the activity of dried yeast 50%. Inorg. PO_4''' does not decrease the sensitivity of (I) towards EtOH. NH_4Cl in presence of EtOH increases the rate of CO_2 production to $>$ that observed in absence of EtOH.

III. The optimum p_{H} for disappearance of inorg. PO_4''' from a (I) fermentation mixture is 6.2—6.4. Electrolytes markedly decrease the time which elapses before PO_4''' attains a min. val., and the effects of the cations are in the order $\text{NH}_4 > \text{Mg} > \text{Na} > \text{K} > \text{Ca}$. EtOH in low concn. increases the time required for esterification and the min. steady state val. of PO_4''' , but the latter is decreased if NH_4Cl , KCl, or NaCl be present also. For compounds of the type $\text{R}\cdot\text{NH}_3\text{Cl}$, the influence of R in decreasing the time necessary for inorg. PO_4''' to reach a min. val. is $\text{C}_6\text{H}_{11}\text{O}_5 > \text{H} > \text{Me}$.
J. N. A.

Fermentation of carbohydrates. G. MALYOTH and E. SOMMERFELD (Biochem. Z., 1935, 281, 49—79).—The effect of changes in amount of enzyme, vol. of H_2O , and amount of sugar and of addition of KH_2PO_4 with and without nutrient media on the rate and results of fermentation of glucose by yeast has been measured (error usually $\pm 4\%$) in a modification of the micro-apparatus of Krogh. When cell-free press juice is used, 100% fermentation is recorded, the deficit with living yeast being due to sugar con-

sumption for building up the cells, to undetected gaseous exchanges, and to related causes. With living yeast, alone or in nutrient media, the fermentation is accelerated by KH_2PO_4 , especially when the proportion of yeast is small. When the juice is used, KH_2PO_4 with nutrient medium causes acceleration $>$ that found with living yeast. The apparatus may also be used to measure the fermentation of polysaccharides (*e.g.*, hydrolysis of maltose by leucocytes from horse blood). W. McC.

Chemical reactions during alcoholic fermentation. I. Production and hydrolysis of adenosinetriphosphoric acid and their connexion with hydrolysis of sugar. C. LUTWAK-MANN and T. MANN. **II. Theoretical considerations.** J. K. PARNAS, C. LUTWAK-MANN, and T. MANN (Biochem. Z., 1935, 281, 140—156, 168—174).—I. Fresh bottom yeast contains appreciable amounts and Lebedev extract only small amounts of adenylic acid (I) and adenosinetriphosphoric acid (II). The extract contains an enzyme which converts (II) into (I), but no enzyme which produces NH_3 and inorg. phosphate from (I). During alcoholic fermentation with yeast or extract (I) is converted into (II), phosphate being transferred to (I) from hexosediphosphoric acid (III) when the extract is used and otherwise from phosphoglyceric (IV) and phosphopyruvic acid (V) with accompanying production of AcCO_2H . In the first case the process is not affected by NaF , in the second it is completely inhibited. (II) added to the extract in presence of glucose yields (III) and (I), but no dephosphorylation of (II) occurs if (III) is present. It is concluded that when fermentable substances are added to (II) fructosediphosphoric acid is produced, and that the transformation of (IV) and (V) into AcCO_2H provides the occasion for a transformation of (II) additional to that which occurs during the first phase of fermentation by yeast.

II. The above (and other) results indicate that (I) and (II) act as phosphate carriers during alcoholic fermentation much in the same way as they do in muscle. W. McC.

Effect of cholesterol and insulin on fermentation by yeast. S. HERMANN [with R. NEIGER] (Biochem. Z., 1935, 281, 121—127).—The fermenting power of living yeast is specifically restricted by cholesterol (I) sols which, however, accelerate fermentation by autolysed yeast. Some samples of insulin (II) accelerate fermentation by living yeast, but this acceleration is checked by (I) sols. Fermentation by autolysed yeast is not accelerated by (II). The sensitivity of yeast to poisoning with H_2SO_4 and salicylic acid is increased by washing with light petroleum. The acceleration of fermentation caused by cozymase (III) is checked by (I) sols. Apparently the samples of (II) contain a thermostable (not destroyed in 30 min. at 100°) substance which is not (III). W. McC.

Effect of vitamin-C on fermentation by yeast and on lactic acid production in *B. aërogenes* cultures and muscle pulp. K. ZIPF and M. THURAU (Biochem. Z., 1935, 282, 51—55).—Alcoholic fermentation by yeast is not inhibited by ascorbic acid in concns. of 1 : 10^6 —1 : 125. Concns. $<$ 0.004M

inhibit production of lactic acid (I) by *B. aërogenes* and those $<$ 0.02M inhibit production of (I) in rabbit muscle pulp, but addition of glycogen to the pulp prevents the inhibition. W. McC.

Determination of oxygen consumption of yeast. G. NEUMANN (Biochem. Z., 1935, 281, 181—185).—Spectroscopic examination of a standard oxyhæmoglobin (I) solution (saturated with O_2) to which a known amount of yeast has been added (with exclusion of O_2) permits determination of the time required for the yeast to reduce (I) and hence of the O_2 consumption of the yeast. If the time of reaction is suitably chosen, the vol. of O_2 consumed by 1 mg. of yeast is about 17 c.c. with dil. and 22 c.c. with conc. (I) solutions. W. McC.

Determination of phosphorus in yeast by the bomb calorimeter. R. ATROLDI (Annali Chim. Appl., 1935, 25, 523—525).—Application of the method of Garelli and Carli (A., 1933, 621, 1179) to yeast is described. F. O. H.

Influence of buffer on sugar consumption and acid production by *Aspergillus*. V. BOLCATO (Annali Chim. Appl., 1935, 25, 515—523).—Production of acid by *Aspergillus* grown in aq. sucrose is increased by the presence of citrate buffer, due to both buffering action and diminished rate of carbohydrate consumption. Utilisation of the citric acid produced is unaffected. F. O. H.

Chemistry of mould tissue. VIII. Innate factors influencing growth and sterol production of *Aspergillus fischeri*. P. R. WENCK, W. H. PETERSON, and H. C. GREENE. **IX. Cultural factors influencing growth and sterol production of *A. fischeri*.** P. R. WENCK, W. H. PETERSON, and E. B. FRED (Zentr. Bakt. Par., 1935, II, 92, 324—330, 330—338; cf. A., 1935, 535).—VIII. Growth and sterol (I) production varied with the strain used.

IX. With a no. of C sources the amount of mycelium produced and its (I) content were inversely related. Urea was the best N source in CaCO_3 -free media, whereas NH_4NO_3 was superior in the presence of CaCO_3 . The % of (I) in mycelium increased with the glucose concn. in the medium, with the glucose : urea ratio (optimum 40 : 1), and with temp. (optimum 37°). With prolonged incubation, production of (I) increased even after autolysis of mycelium set in. Aëration influenced the rate of fermentation, but not of (I) formation. The max. % of (I) was obtained in low-urea media at p_{H} 2.0. A. G. P.

Production of dimethylpyruvic and pyruvic acids by *Aspergillus niger*. T. HIDA (J. Shanghai Sci. Inst., 1935, IV, 1, 201—214).—The mycelium of *A. niger*, when transferred to a medium of p_{H} 7, containing glucose or sucrose 5%, Na_2SO_3 5%, NH_4Cl 1%, KH_2PO_4 2%, produces $\text{Pr}^{\beta}\text{CO}\cdot\text{CO}_2\text{H}$ (I) and AcCO_2H (II). (I) was synthesised by the interaction of $\text{Et}_2\text{C}_2\text{O}_4$, $\text{Pr}^{\beta}\text{Br}$, and Mg in Et_2O . The Mg compound on decomp. with H_2O affords the Et ester of (I). NH_4^+ favours the production of (I) and inhibits that of (II). J. H. B.

Effect of thymol on progress of rabbit moniliasis. W. D. STOVALL, S. B. PESSIN, and L. ALMON (J. Lab. Clin. Med., 1935, 20, 572—582).—Thymol

(I) inhibits growth of *Monilia* in cultures, but has no effect on the progress of infection in rabbits. (I) is completely absorbed and can be recovered from urine, blood, or liver, but not in appreciable amounts from faeces.

CH. ABS. (p)

Effect of certain nitrogen compounds on growth of *Chlorogonium* and *Chilomonas*. J. B. LOEFER (Arch. Protistenk., 1935, 85, 74—86).—*Chilomonas* cannot utilise NH_2 -acids, whereas *Chlorogonium* produces markedly increased growth, notably with aspartic acid. Neither species can use amide-N.

A. G. P.

Alcohol- and carbohydrate-oxidising bacteria isolated from fruits, and a new classification of oxidising bacteria. II. T. ASAI (J. Agric. Chem. Soc. Japan, 1934, 10, 1124—1136; 1935, 10, 50—60; cf. A., 1934, 1036).—Organisms are grouped according to the optimum temp. for multiplication. The optimum p_{H} for production of gluconic acid is < that for multiplication. Peptone and glucose are the best sources of N and C, respectively.

CH. ABS. (p)

Deamination of alanine by bacteria. E. AUBEL and F. EGAMI (Compt. rend. Soc. Biol., 1935, 120, 684—685).—"Resting" bacteria in aerobiosis convert alanine into AcCO_2H more readily in presence of NO_3^- , which is reduced, or of NH_2OH . The process is therefore probably a dehydrogenation; the action of catalase on the H_2O formed, which would otherwise destroy the AcCO_2H , is partly inhibited.

R. N. C.

Mechanism of non-symbiotic fixation of atmospheric nitrogen. T. R. BHASKARAN and V. SUBRAHEMANYAN (Current Sci., 1935, 4, 234—235).—In cultures of soil organisms glucose decomp. was rapid during the first 4 days. During this period CO_2 and org. acids were produced and approx. $\frac{1}{3}$ of the expected amount of N was fixed. Of this much was in a H_2O -sol. form. Subsequently (4—8 days) org. acids were destroyed, mucilage was formed, and N was fixed. Formation of mucilage and N fixation are related, but not proportional.

A. G. P.

Occurrence of *Azotobacter* at high temperatures. J. SINGH and A. HUSSAIN (Current Sci., 1935, 4, 235—236).—*Azotobacter* survive in a vegetative condition at 45° .

A. G. P.

Can *Azotobacter chroococcum* synthesise vitamin-D? J. E. GREAVES (J. Bact., 1935, 30, 143—148).—When grown on synthetic media *A. chroococcum* can synthesise ergosterol, which is transformed into vitamin-D by irradiation.

A. G. P.

Occurrence of a strain of *Azotobacter chroococcum* which does not ferment mannitol. N. R. SMITH (J. Bact., 1935, 30, 323—328).—The organism is widely distributed in soils.

A. G. P.

Bacterium acidi lactici, Hueppe, and its systematic classification on the basis of its properties. G. PRANGE (Zentr. Bakt. Par., 1935, II, 92, 305—324).—Comparison is made of the biochemical activities of various organisms of the *coli-aerogenes* group and of *B. acidi lactici*. The latter does not ferment sucrose, raffinose, dextrin, starch, inulin, dulcitol, or inositol, fails to grow in citrate-

NH_4Cl media, and produces indole from trypsin-peptone- H_2O .

A. G.

Toxin formation by bacteria. I. Stimulatory and inhibitory substances in peptones. P. STADLER and I. MEISSNER (Zentr. Bakt. Par., 1935, I, 134, 102—109).—The influence of peptones on toxin production by *B. botulinus* varied with their source and method of prep., and was dependent on the presence of certain chemical substances. Decomp. products of animal proteins have an inhibitory action.

A. G. P.

Metabolism of *Bact. coli*. Production of biogenic amines. P. STADLER and E. NEUS (Zentr. Bakt. Par., 1935, I, 134, 110—114).—Some strains of *B. coli* converted tyrosine into tyramine, others produced OH-acids by deamination.

A. G. P.

Influence of lithium chloride on *Bact. coli*. II. K. RICHTER (Zentr. Bakt. Par., 1935, II, 92, 249—256).—Addition of LiCl_2 to agar media lowered the dry-matter production, sugar fermentation, and respiration rates of cultures.

A. G. P.

Acid and gas formation by members of the *coli-aerogenes* intermediate groups in the presence of certain sugar alcohols and their anhydrides. K. P. DOZOIS, F. HACHTEL, C. J. CARR, and J. C. KRANTZ, jun. (J. Bact., 1935, 30, 189—192).—Dulcitol and mannitol are fermented by many organisms of the group, but the anhydrides are not utilised.

A. G. P.

Amino-acids necessary for growth of *Cl. sporogenes*. P. FILDES and G. M. RICHARDSON (Brit. J. Exp. Path., 1935, 16, 326—335).—Growth occurs in a medium containing NH_2 -acids as N source, the indispensable NH_2 -acids being tryptophan, tyrosine, phenylalanine, arginine, and leucine; histidine, cystine, methionine, and valine are also probably indispensable.

R. N. C.

Gonococcal polysaccharides. S. MUTERMILCH and A. GRIMBERG (Compt. rend. Soc. Biol., 1935, 120, 587—589).—A polysaccharide with the properties of a hapten is isolated from *Gonococci* by dissolving in Na taurocholate, acidification with AcOH , filtration, neutralisation with NaOH , and evaporation in vac.; proteins are coagulated by heating to 100° and removed by filtration, and the polysaccharide is repeatedly pptd. with EtOH in alternately acid and alkaline solutions. The final product is protein-free, and yields a reducing sugar on hydrolysis. It fixes the antigonococcal antibody.

R. N. C.

Interrelationship between the amount of V-factor and the amount of air necessary for growth of *Haemophilus influenzae*, type b, in certain media. M. PITTMAN (J. Bact., 1935, 30, 148—161).—Growth of the organism in certain media containing small amounts of V-factor is initiated only if the culture is well aerated. With more V-factor less air is necessary.

A. G. P.

Biochemistry of *Bacillus mesentericus hydrolyticus*. S. HERMANN and P. NEUSCHUL (Biochem. Z., 1935, 281, 219—230).—The bacillus, obtained from carrots, grows very poorly or not at all anaerobically, liquefies gelatin, and coagulates milk (clots

later liquefied). It grows best in media (*e.g.*, vegetables or suspensions containing them) containing org. N (no growth if no org. N) and cellulose or hemi-cellulose. Growth on bouillon or peptone solutions is not accompanied by production of H_2S or indole. Acid production is very small; no gas is evolved and no reducing substances (Fehling) are produced except from starch, which, like sugars (glucose, fructose, sucrose, galactose, maltose, lactose), is hydrolysed. The bacillus and enzymes obtained from it have powerful softening action on vegetables, the connective tissue being destroyed. W. McC.

Relation of micro-organisms to carotenoids and vitamin-A. II. Production of carotenoids by *Mycobacterium phlei*. M. A. INGRAHAM and H. STEENBOCK (Biochem. J., 1935, 29, 2553—2562).—On a medium containing asparagine (I), glucose (II), K_2HPO_4 , $MgSO_4$, and Na and Fe^{III} citrates *M. phlei* produced less pigment than when $[K^+]$ and $[HPO_4^{''}]$ were lowered, or when glycols and alcohols replaced (II); at normal p_H replacing (I) with NH_4^+ , $CO(NH_2)_2$, and peptones was without influence on pigmentation. Increasing the $[Fe^{''}]$ prevents pigmentation; excess of (I) causes autolysis, and on media containing glycerol or low concn. of (II), (I) is attacked by the bacteria. C_2H_4 , Na^+ , Li^+ , Ca^{++} , Mg^{++} , and Se, the redox potential, the light intensity, and temp. were without effect on pigmentation. By separating the pigments from light petroleum on an adsorption column the presence of α - and β -carotene, kryptoxanthin, and esters of lutein, zeaxanthin, and azafrin was established. H. D.

Solubility of *Pneumococcus* in saponin. III. Saponinlysis reaction as a means of differentiating *Pneumococcus* and *Streptococcus*. S. J. KLEIN (J. Bact., 1935, 30, 43—48; cf. A., 1933, 1207). A. G. P.

Kinetics of the attack on glucose and lactic acid by small concentrations of bacteria; concept of minimum active concentrations. P. CHAIX (Compt. rend., 1935, 201, 626—628).—Of three species of propionic bacteria, one exhibited a threshold concn. below which it decomposed neither glucose nor lactic acid, the second a threshold for short but not for long periods of incubation, and the third a threshold for glucose, but for lactic acid only some retardation of decomp. W. O. K.

Physiology of *Rhizobium*. III. Respiration and growth as influenced by the reaction of the medium. D. W. THORNE and R. H. WALKER. **IV. Utilisation of carbonaceous materials.** O. R. NEAL and R. H. WALKER (J. Bact., 1935, 30, 33—42, 173—187; cf. A., 1933, 638, 752).—III. Growth of *R. meliloti* and *R. japonicum* reached max. at p_H 7.0, 6.7—6.9, decreasing to zero at 4.6—4.9, 4.2 and 9.6, 9.5, respectively. The optimum p_H for respiration was $>$ that for growth in both cases.

IV. No significant differences in the rate and extent of O_2 consumption by *R. meliloti* were apparent in media containing glucose (I), mannitol (II), or sucrose (III). Galactose (IV) and arabinose (V) were more effectively utilised than (I) on NO_3^- and on NH_4^+ media. Maltose (VI), lactose (VII), inositol, dulcitol,

and sorbitol with both forms of N and raffinose and erythritol (VIII) on NH_4^+ media were inferior to (I). As measured by total O_2 consumption NH_4^+ was more readily utilised than NO_3^- . For *R. japonicum*, (V) was the best energy source, (I), (IV), and xylose were equally effective, whereas (II), (VI), (VII), (III), and (VIII) were utilised little or not at all. NO_3^- was more effective than NH_4^+ . A. G. P.

Factors influencing the respiration of *Rhizobium*. D. W. THORNE and R. H. WALKER (Proc. Iowa Acad. Sci., 1934, 41, 63—70).—Stimulation of *R. meliloti* by certain substances (yeast and legume extracts) is attributable to their nutrient content. The assumption that there is a co-enzyme of respiration is not substantiated. CH. ABS. (p)

Oxidation of glucose by *Rhizobium meliloti*. O. R. NEAL and R. H. WALKER (Proc. Iowa Acad. Sci., 1934, 41, 167—168).—In media containing $M/540—M/180$ concns. of glucose the O_2 consumption of *R. meliloti* increased rapidly for 4—8 hr. and subsequently declined to a low and fairly const. level, the total consumption being approx. $\frac{1}{3}$ of that required for complete oxidation. The proportion of glucose-C converted into CO_2 in the presence of NH_4^+-N was $<$ that in the presence of NO_3^-N . CH. ABS. (p)

Inhibition of growth of *Bacillus subtilis* on a modified extract agar by X-irradiation of the medium. I. H. BLANK and H. KERSTEN (J. Bact., 1935, 30, 21—32).—The action of soft X-rays on agar produces a diffusible, non-volatile substance which is toxic to *B. subtilis*. A. G. P.

Metabolism of spirochætes *in vitro*. G. SCHEFF (Zentr. Bakt. Par., 1935, I, 134, 35—43).—In 4 species examined no O_2 consumption was apparent. Production of CO_2 occurs only in carbonate media and results from the action of lactic acid formed from sugars. A. G. P.

Evolution of dehydrogenases of *Staphylococcus aureus* during growth. D. BACH (Compt. rend. Soc. Biol., 1935, 120, 673—674).—The dehydrogenase content of the cultures falls as their age increases; the nature of the H donator does not affect the rate of decrease. R. N. C.

Hydrogen donators for *Staphylococcus aureus*. D. BACH (Compt. rend. Soc. Biol., 1935, 120, 608—610).—The active H donators include most carbohydrates and related substances and eight org. acids. EtOH and BuOH are the only active alcohols, and cysteine and glutamic acid the only active NH_2 -acids; the activities of these are very feeble. Simple aldehydes, ketones, and natural bases are inactive. R. N. C.

***Staphylococcus* toxins and anti-toxins.** A. T. GLENNY and M. F. STEVENS (J. Path. Bact., 1935, 40, 201—210).—Certain strains produce two toxins for which there are corresponding antibodies. CH. ABS. (p)

Differentiation of *Streptococcus pyogenes* from man and animals by the sorbitol-trehalose test. F. C. MINETT (J. Path. Bact., 1935, 40, 357—364).—Trehalose is usually fermented by human, and sorbitol by bovine, strains. CH. ABS. (p)

Toxic fraction of scarlatinal streptococci. C. A. GREEN (Quart. J. Med., 1935, 4, 93—115).—All strains produced a heat-labile exotoxin. Broth filtrates also contained an acid-insol. toxic fraction similar to that from an alkaline extract of washed bacterial bodies. It was species-sp. CH. ABS. (*p*)

Differences in effect of mercuric phenyl chloride on different races of bacteriophage and similarity in effect on a phage and its homologous organism. N. R. GOLDSMITH (J. Bact., 1935, 30, 237—242).—Lysis by bacteriophages of *Staphylococcus* or of *Escherichia coli* was not affected by HgPhCl (1 : 20,000—80,000) in a contact period of 30 min. After 6 weeks' contact the *Staphylococcus* phage was destroyed, but that of *E. coli* remained unaffected. Toxicity of the antiseptic to the sp. phage is paralleled by that to the homologous organism.

A. G. P.

Stimulation of bacterial growth rate by germanic methyl oxide. P. L. CARPENTER, MCD. FULTON, and C. A. STUART (J. Bact., 1935, 30, 137—142).—As compared with nutrient broth cultures those in germanic Me oxide broth are inhibited during the lag phase, stimulated during the early logarithmic phase, and show a premature period of decline.

A. G. P.

Action of sulphurous acid on bactericidal power of blood. H. CREMER (Z. Unters. Lebensm., 1935, 20, 315—317).—Prolonged administration of small amounts of H₂SO₃ to rabbits markedly decreases the power of the blood to destroy staphylococci.

E. C. S.

Bactericidal principle in excretions of surgical maggots, which destroys important etiological agents of pyogenic infections. S. W. SIMMONS (J. Bact., 1935, 30, 253—267).—The active bactericidal principle (not a bacteriophage) isolated from excreta of surgical maggots is heat-stable and retains its activity longer in a desiccated condition than in solution.

A. G. P.

Therapeutic application of phenylmercuric salts. Use of basic phenylmercuric nitrate in gynæcology. L. H. BISKIND (Lancet, 1935, 229, 1049—1052).

L. S. T.

Antiseptic action of certain metals. V. JENSEN and A. JENSEN (Zentr. Bakt. Par., 1935, I, 134, 86—96).—The efficiency of Ag—Hg, Ag, Ag₂O, and AgCl as urinary disinfectants is examined.

A. G. P.

Microbiological basis of chemotherapeutic action. II. Microscopical detection of therapeutically applied gold in spirochætes, trypanosomes, and bacteria by ultracrystallisation. N. VON JANCSÓ and E. NOVÁK (Zentr. Bakt. Par., 1935, I, 134, 76—86).—The method is based on the absorption of injected Au by spirochætes in rats or mice. Spirochætes are removed centrifugally from a blood sample. From a smear on a slide org. matter is removed by gentle ignition and the remaining minute Au crystals serve as nuclei for crystal formation from a "developing" solution of AuCl₃—K₃Fe(CN)₆. The Au "picture" is examined microscopically.

A. G. P.

Influence of various metallic compounds on the growth of bacteria. W. HAASE (Med. Klin., 1934, 30, 1585—1587; Chem. Zentr., 1935, i, 2199).—The germicidal action of Cu, brass, Sn, Al, and Ag foil was relatively small compared with that of Simanit (Ag₂O₂, MnO₂) or Euthagen (Ag salt of thiocellobiose).

A. G. P.

Effect of hormones on alcohol metabolism. E. M. P. WIDMARK (Biochem. Z., 1935, 282, 79—84; cf. A., 1934, 213; 1935, 655).—In dogs, administration of pituitrin, adrenaline, and thyroxine has no effect on the metabolism of EtOH, but that of insulin (I) greatly increases slow rates of EtOH metabolism until the max. attainable under normal conditions is reached; high rates are not affected. The naturally occurring differences in the rates are partly dependent on the (I) content of the organism. The effect of (I) is not counteracted by giving sucrose.

W. McC.

Adrenaline content of adrenals of splenectomised dogs. S. TSUJIOKA (Arb. Med. Fak. Okayama, 1935, 4, 445—452).—The abs. content of adrenaline and the amount per g. of gland increase until the 15th day after splenectomy and subsequently decline to normal (30th day).

CH. ABS. (*p*)

Adrenal cortex. I. Fractionation of hormone concentrates. J. J. PFIFFNER, O. WINTERSTEINER, and H. M. VARS. **II. Isolation of several physiologically inactive crystalline compounds from active extracts.** O. WINTERSTEINER and J. J. PFIFFNER (J. Biol. Chem., 1935, 111, 585—597, 599—612).—I. The cortical hormone preps. were assayed by an earlier method (A., 1934, 566). Preps. from ox glands (*ibid.*, 1267) were purified by alternate dissolution in H₂O and Et₂O and contained 100—200 dog units per mg.; these preps. gave phenylhydrazones in cold aq. AcOH. More active preps. which did not reduce alkaline AgNO₃ were obtained by using C₆H₆ in place of Et₂O in the alternate dissolution procedure. By fractionation of these preps. one containing 400 dog units per mg. was obtained; this absorbed at 236 mμ, was pptd. by NHPh·NH₂, but no insol. NaHSO₃, semicarbazide, oxime, or dimedon derivatives were obtained.

II. Four physiologically inactive compounds were separated from the most active preps.: C₂₀H₃₄O₅ or C₂₁H₃₆O₅, m.p. 214°, C₂₁H₃₂O₅ (I), m.p. 210—214°, C₂₄H₄₀O₇, m.p. 126—128°, and one with undetermined empirical formula, m.p. 236—239°. (I) reduces Benedict's solution and alkaline AgNO₃ and is possibly identical with the life maintenance hormone of Kendall, but the absence of physiological activity is stressed. Leucylproline anhydride was also separated.

H. D.

Physico-chemical state of the adrenal hormone in the blood. D. BROUN and H. SCHEINER (Compt. rend., 1935, 201, 794—795).—Minced adrenal capsules give up their adrenaline (I) to serum (II), distilled H₂O (III), or H₂O at *p_H* 3.5—4.0 (IV). (III) and (IV) when injected into atropinised dogs under chloralose anæsthesia affect the blood pressure as does (I); (II) produces a much more prolonged, but less abrupt, rise in arterial pressure and there is no apnœa. The (I) in (III) and (IV) is completely

ultrafilterable, but in (II), practically not at all. Extraction of (II) with Et_2O or C_6H_6 , or acidification to p_{H} 3.5—4.0, or dilution with H_2O , or treatment with Ca^{++} , renders the (I) completely ultrafilterable. The hormone is probably bound to the protein-lipin complexes of the blood.
J. L. D.

Action of adrenaline on liver suspensions. E. GEIGER (Biochem. Z., 1935, 281, 86—92; cf. A., 1932, 188).—The sedimentation of the material pptd. from colloidal liver preps. (frog) by $\text{CCl}_3\cdot\text{CO}_2\text{H}$ is specifically accelerated (thyroxine, insulin, histamine, ergotamine, ephedrine, morphine, and atropine in equiv. concns. have no effect) by added adrenaline (I) (concn. 10^{-6} — 10^{-16}), although degradation of glycogen (II) and sugar production are unaffected. The effect appears after \approx 5 min., reaches its max. after about 20 min., and then becomes less pronounced. In the absence of (II) or at p_{H} outside the range 5.5—7.5, or if the diastatic activity of the preps. is destroyed by heating for 1 hr. at 48—50°, there is no effect, but sedimentation is more rapid when (II) is absent. Added (I) has no effect on the extent of degradation or on production of simplexes. Possibly (I) alters the physical state of (II), reducing its power as a protective colloid.
W. McC.

Influence of peripheral lymph on the blood-sugar fluctuation due to adrenaline. H. ARAKI (Arb. dritt. Anat. Inst. Univ. Tokyo, D, 1934, No. 4, 145—151).—Blood-sugar fluctuations were greatly suppressed when adrenaline-lymph mixtures were stored (notably at 37° for 24 hr.) prior to injection. Lymph alone caused very little fluctuation.

CH. ABS. (p)

[Slow] continuous injection of adrenaline: [absence of] effect on blood-urea, -cholesterol, and -calcium. A. BAUDOUIN, H. BÉNARD, J. LEWIN, and J. SALLET (Compt. rend. Soc. Biol., 1935, 120, 629—631).
R. N. C.

Influence of oxidation-reduction system on adrenaline action. III. K. TERAI and H. ICHITSUBO (Folia Pharmacol. Japon., 1935, 19, 306—322; cf. A., 1935, 1172).—Injection of NaHSO_4 instead of quinol into rabbits produced the quinol-effect on adrenaline action.
CH. ABS. (p)

Inactivation of adrenaline by acetaldehyde verified on several plain-muscle organs. A. M. BAPTISTA (Compt. rend. Soc. Biol., 1935, 120, 547—550).—The inactivation of adrenaline by MeCHO is confirmed on the Löwen-Trendelenburg vascular prep., the isolated rabbit intestine, the enucleated frog's eye, and the bronchial muscle of the cat or dog.
R. N. C.

Inactivation of adrenaline by methylglyoxal, glyceraldehyde, and acetaldehyde. J. T. RICO and A. M. BAPTISTA (Compt. rend. Soc. Biol., 1935, 120, 545—546).—Adrenaline is inactivated as regards its pressor effect in decerebrate dogs by AcCHO , glyceraldehyde, and MeCHO , but not by AcCO_2H or phosphoglyceric acid. The inactivation is not opposed by ascorbic acid.
R. N. C.

Hypocalcaemia of depancreatized dogs. R. GERSCHMAN and A. D. MARENZI (Compt. rend. Soc. Biol., 1935, 120, 737—738).—Total pancreatectomy

in normal and hypophysectomised dogs induces a fall of blood-Ca and an increase of plasma- PO_4 . Ca is restored to normal by parathormone, but depressed still further by anterior pituitary extract. The Ca depression is due to parathyroid lesions following pancreatectomy.
R. N. C.

Use of mice in the standardisation of parathyroid hormone. Effect of parathyroid on rachitic rats examined by the "line" test. F. J. DYER (Quart. J. Pharm., 1935, 8, 513—524).—The Mg-Ca antagonism method of Simon (A., 1935, 539) is applied by using at least 20 mice in each group, administering 1.7—1.8 mg. of $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ per g. body-wt., and recording the max. no. of mice affected 20—60 min. after injection of Mg. The % obtained for parathyroid prep. and control are then referred to a standard curve. Parathyroid preps. supplement the calcification produced by vitamin-D as indicated by the "line" test (A., 1928, 1288), but the test when used for parathyroid alone is insensitive and non-sp.
F. O. H.

Influence of temperature on the secretion of thyrotropic hormone. G. KUSCHINSKY (Arch. exp. Path. Pharm., 1935, 179, 726—737).—Exposure of rats to cold (4°) is accompanied by normal activity of the thyroid gland (indicated histologically) for 10 days, after which the activity markedly increases. At 38—40°, the gland is normal for the first few days, inactive at the 14th, and, in some cases, again active after 26—33 days. These changes are correlated with those in thyrotropic activity of the pituitary gland and the presence of an inhibitory factor.

F. O. H.

Thyroid standardisation and dosage. R. F. CORRAN, J. PRITCHARD, and F. E. RYMILL (Quart. J. Pharm., 1935, 8, 331—336).—Variations in total and thyroxine (I)-I contents of fresh and of dried defatted glands invalidate any correlation between "thyroid B.P. 1932" and preps. expressed as fresh or dried gland. The relative activities of U.S.P. X and B.P. 1932 thyroid preps. are approx. $74 \pm 12 : 100$. Following hydrolysis, direct determination of I on the acid-insol. [(I)-containing] ppt. affords a check for the B.P. 1932 method for (I) in thyroid preps.
F. O. H.

Rôle of the thyroid in the process of plumage development in chicks. I. N. LEKTORSKY and N. A. KUSMINA (Biol. Zentr., 1935, 55, 16—29).—The thyroid hormone shows no preferential effect on plumage development.
R. N. C.

Influence of thyroxine on the hypoglycaemic action of cholic acid. H. KOSAKA (Arb. Med. Fak. Okayama, 1935, 4, 370—378).—Thyroxine does not alter the blood-sugar level of normal rabbits, but lowers the capacity of Na cholate to produce a hypoglycaemia when injected simultaneously.

CH. ABS. (p)

Preparation of prolactin. R. W. BATES and O. RIDDLE (J. Pharm. Exp. Ther., 1935, 55, 365—371).—Prolactin (I) free from follicle-stimulating (II) and thyrotropic hormone (III) is prepared by extraction of the anterior lobe with 60—70% aq. EtOH at p_{H} 9—10 and pptn. of (I) at higher EtOH concns. (I) is separated from (II) and (III) by pptn. from aq.

solution with H_2SO_4 and is further purified by dissolution in aq. EtOH and repeated pptn. with NaCl at p_H 6. Preps. so obtained have a potency of 5—10 units per mg. and may be boiled at p_H 8 for 1 hr. without loss of potency. H. D.

Diabetogenic anterior pituitary action independent of the adrenals. B. A. HOUSSAY and L. F. LELOIR (Compt. rend. Soc. Biol., 1935, 120, 670—672).—Adrenaline produces a transitory hyperglycæmia, but neither it nor cortin is diabetogenic. Anterior pituitary extract (I) produces diabetic hyperglycæmia in hypophysectomised, pancreatectomised, and adrenalectomised toads, and in adrenalectomised dogs, together with glycosuria; splanchnic section or sympathectomy does not inhibit the action. The hyperglycæmia produced in partly adrenalectomised dogs persists after complete adrenalectomy only if (I) administration is continued; the diabetogenic action of (I) is therefore independent of the adrenals. R. N. C.

Effect of hypophysectomy on pregnancy and lacteal secretion in the bitch. B. A. HOUSSAY (Compt. rend. Soc. Biol., 1935, 120, 496—497).—Hypophysectomy results in abortion in pregnant, and cessation of secretion in lactating, bitches. The anterior pituitary is the necessary part of the gland; the effects are not induced by removal of the posterior lobe only, and are abolished by anterior pituitary extract. R. N. C.

Lacteal secretion provoked by anterior pituitary extract in the dog. B. A. HOUSSAY (Compt. rend. Soc. Biol., 1935, 120, 502—503). R. N. C.

Lacteal secretion through the action of anterior pituitary extract in male guinea-pigs. J. L. SARDI (Compt. rend. Soc. Biol., 1935, 120, 503—504). R. N. C.

Glutathione in the tissues of the hypophysectomised dog: evidence for a pituitary-thyroid and pituitary-testicular association. L. BINET, L. KÉPINOV, and G. WELLER (Compt. rend. Soc. Biol., 1935, 120, 589—590).—Hypophysectomy produces a fall of total glutathione (I) of blood < that of reduced (I). The red cell count is only slightly reduced. (I) is normal in the adrenals, spleen, pancreas, and cardiac muscle, and only reduced (I) falls in skeletal muscle. Both total and reduced (I) fall considerably in the liver, thyroid, and testicle, the falls being similar to those noted by Marenzi in the toad. The results favour a biochemical association between the pituitary and the thyroid and testicle. R. N. C.

Influence of extract of posterior lobe of pituitary gland on urine- and blood-inorganic phosphate. G. DODERO (Arch. Farm. sperim., 1935, 60, 422—429).—Subcutaneous or intravenous injection of posterior pituitary extracts into rabbits increases the serum-inorg. PO_4''' ; the urinary level tends to decrease. The phenomena are apparently independent of changes in renal function. F. O. H.

Influence of luteinising substance on (a) function of the lipin-containing cells of ovaries, (b) testes. G. KUSCHINSKY and TANG-SŪ (Arch.

exp. Path. Pharm., 1935, 179, 717—721, 722—725).—(a) Administration to rats of anterior pituitary-like prep. from pregnancy urine (prolan) (I) inhibits formation and ripening of follicles and promotes luteinisation in the ovaries. (b) (I) enlarges the lipin-containing cells of rats' testes. F. O. H.

Estrogenic activity of cow's urine during pregnancy. M. M. O. BARRIE, J. B. E. PATTERSON, and S. W. F. UNDERHILL (Quart. J. Pharm., 1935, 8, 424—428).—Only small amounts of œstrin (< 50 international units per litre) are excreted by cows during the first 23 weeks of pregnancy; after this period the level increases to 700 units per litre at the 30th week, 4000 at the 34th, and 17,000 at the 37th. During the final weeks, the content varies probably due to variations in the concn. of urine. F. O. H.

Action of œstrin on mammary secretion. J. W. ROBSON (Quart. J. Exp. Physiol., 1935, 24, 337—344).—In lactating mice cryst. ketohydroxy-œstrin temporarily inhibits mammary secretion according to the dosage and method of administration. CH. ABS. (*p*)

Hormone of the corpus luteum. E. FELS (Compt. rend. Soc. Biol., 1935, 120, 730—731).—A mixture of luteosterone-*C* and -*D*, or of either with pregnandione, is more potent than either separately. R. N. C.

Dehydroandrosterone.—See this vol., 77.

Androstendione.—See this vol., 77.

Testosterone.—See this vol., 77.

Sexual hormones, and related substances. V.—See this vol., 77.

Sex hormones. VIII—X. See this vol., 76.

Recent progress in the study of vitamins. P. KARRER (Chim. et Ind., 1935, 34, 1027—1035).—A review.

International vitamin standards. E. M. NELSON (J. Assoc. Off. Agric. Chem., 1935, 18, 610—611).—The standards adopted by the International Conference on Vitamin Standards (1935) are discussed. E. C. S.

Aseptic culture of insects in vitamin research. E. G. VAN'T HOOG (Z. Vitaminforsch., 1935, 4, 300—324).—Symbiont-free, aseptic cultures of *Drosophila melanogaster* can be obtained from ova sterilised by EtOH and chloramine-*T*, provided that the synthetic food complies with certain requirements. *D. melanogaster* requires traces of vitamin- B_1 and - B_2 and other H_2O -sol. yeast factors together with a very small amount of fat or unsaponifiable fraction, and the absence of - B_1 or - B_2 can be determined easily with these cultures. The insect does not require vitamin-*A*, -*D*, or -*E*. J. N. A.

Vitamin-*A*, -*C*, and B_2 . Constitution and constitution specificity of action. P. KARRER (Monatsh., 1935, 66, 367—392).—The development of the chemistry of these compounds and the connexion between constitution and physiological action are discussed. H. W.

Sterol content and vitamin value of avocado oil. R. C. ROBBINS and L. N. BELGER (Hawaii Agric. Exp. Sta. Rept. [1933], 1934, 23—24).—

Sterols are isolated from the expressed oil. The oil also contains vitamin-A and possesses strongly antirachitic properties. CH. ABS. (p)

Influence of experimental technique during the preliminary period in vitamin-A determinations on the response of the test animal to supplementary feeding of the vitamin. P. M. NELSON and P. P. SWANSON (Iowa Agric. Exp. Sta. Rept. on Agric. Res., 1933, 116—117; 1934, 145).—Vitamin-A supplements must be fed to the rats separately. The influence of the body-wt. at the end of the depletion period is shown. Females are more responsive to -A than are males. CH. ABS. (p)

State of combination of vitamin-A in liver oils. L. RETI (Compt. rend. Soc. Biol., 1935, 120, 577—580).—Extraction with MeOH of unsaponified liver oils dissolved in light petroleum removes none of the vitamin-A; if the unsaponifiable matter is extracted in the same way, the whole of the -A is removed. -A is therefore present in the oil as an ester of a higher fatty acid, and its formation in the liver from carotene is followed by esterification. R. N. C.

Detection of vitamin-A by the Rosenthal-Erdélyi test. H. WILLSTAEDT (Z. Vitaminforsch., 1935, 4, 272—276).—The test has no advantages over that of Carr and Price. Carotenoids do not give the rose-red to reddish-violet coloration, but interference can be caused by sterols. J. N. A.

Vitamin-A and carotene content of human milk. W. NEUWEILER (Z. Vitaminforsch., 1935, 4, 259—271).—The vitamin-A content of human milk varies from 25 to 300 rat units per 100 c.c. It is independent of the age of the mother, the no. of children, and daily vol. of milk, and is higher after suckling. Colostrum contains more -A than milk. Large doses of -A or of carotene (I) increase the -A content of milk. (I) is present to the extent of 0.005—0.400 mg. per 100 c.c. J. N. A.

Vitamin-A and carotenoids in the frog. C. RAND (Biochem. Z., 1935, 281, 200—205).—The liver and fat glands and to a smaller extent the other parts (skin, ovary, eggs, testicles, kidney, lung, fallopian tubes) of the frog (summer and winter) contain carotene accompanied by varying amounts of xanthophyll. The liver also contains vitamin-A. W. McC.

Increase in length in rats receiving vitamin-A. M. MALMBERG (Biochem. Z., 1935, 281, 215—218; cf. Orr *et al.*, A., 1934, 1040).—In young rats receiving a diet free from vitamin-A the length of the tail is increased by administration of 0.02 mg. of -A daily. Administration of thyroxine checks the increase. W. McC.

Physiological action of substances used in treatment of flour. II. Action on vitamin of flour and on the animal organism fed exclusively on bread. III. Effect of oxidising substances used in treatment of flour on vitamin of flour. S. VON VIRÉZ (Z. Unters. Lebensm., 1935, 70, 258—265, 265—269; cf. A., 1935, 529).—I. The harmful effect of the oxidising substance is due to destruction of carotene and vitamin-A. NaBO₃ is more harmful than (NH₄)₂S₂O₈.

III. The harmful effect of NaBO₃ and Bz₂O₂ is counteracted by simultaneous administration of -A, but not by -B. E. C. S.

Vitamin-A and -B of maize. E. TAKAHASHI and G. MASUDA (J. Agric. Chem. Soc. Japan, 1935, 11, 741—749).—There is a close relationship between vitamin-A content and the yellow pigment of the endosperms, but the colour of the pericarp has no significance. As regards vitamin-B content, neither colour has any significance. One out of 5 kinds of Japanese maize had a high -A content, but the -B content was much the same in all the kinds. Pigeons required $\leq 60\%$ of whole corn in the diet for normal growth. W. McC.

Occurrence of vitamin-B in organs. J. B. BRODIE and F. L. MACLEOD (J. Nutrition, 1935, 10, 179—186).—The -B content of organs decreased in the order liver, heart, brain, muscle. Only traces occur in blood, spleen, and lungs. The feeding of normal tissues to -B-deficient rats did not increase the survival period except in those receiving brain. The amount of -B in the body of the rat may be changed, within limits, by varying the dietary level of the vitamin. A. G. P.

B-Avitaminosis in rats. E. KODICEK and J. JOACHIM (Z. Vitaminforsch., 1935, 4, 250—255).—No hyperglycæmia could be observed in rats showing the typical nervous symptoms of B-avitaminosis, and the blood-cholesterol was normal. The hyperglycæmia in vitamin-B₁ deficiency in pigeons may be due to an increase in non-sugar reducing substances. J. N. A.

Vitamin-B in relation to carbohydrates, proteins, and fats in food. R. LECOQ (Bull. Soc. sci. Hyg. Aliment., 1934, 278—331; Chem. Zentr., 1935, i, 2205—2206).—The rate of assimilation of carbohydrate, protein, and fat is influenced by the supply of vitamin-B. The -B requirement is greatest with high-carbohydrate rations. Fats and proteins tend to lower the proportion of -B necessary. A. G. P.

Crystalline vitamin-B₁. IV. Injection method of assay. M. AMMERMAN and R. E. WATERMAN. V, VI. **Effect of graduated doses on growing rats and on pigeons.** R. E. WATERMAN and M. AMMERMAN (J. Nutrition, 1935, 10, 25—33, 35—44, 161—166).—IV. Appropriate technique is described.

V. The stimulative effect of the vitamin increases up to and probably beyond dosages of 160×10^{-6} g., an amount which is 80—160 times that necessary for maintenance of life.

VI. The min. dose of vitamin-B₁ hydrochloride to cure polyneuritis was 4×10^{-6} g. Larger amounts up to 160×10^{-6} g. increased the wt. of depleted pigeons, but failed to bring birds to normal wt. Results are discussed in relation to -B₃. A. G. P.

Physiological action of vitamin-B₁. H. G. K. WESTENBRINK (Arch. Néerland. Physiol., 1935, 20, 481—484; cf. A., 1934, 568).—In pigeons on a diet free from carbohydrate and vitamin-B₁ onset of polyneuritis is not delayed by increasing the fat content of the diet. Probably the disease is caused by chronic poisoning with carbohydrate or with

a degradation product or products of carbohydrate resulting from the absence of $-B_1$. W. McC.

Vitamin- B_1 in grapes and grape products. C. VACCA (Quad. Nutrizione, 1934—1935, 1, 424—432). Tests on pigeons show that the berry of the grape, as opposed to the seed, is wholly or almost devoid of vitamin- B_1 . NUTR. ABS. (m)

Vitamin content of beer. A. SCHEUNERT and M. SCHIEBLICH (Z. Vitaminforsch, 1935, 4, 294—299).—Beer contains very small amounts of vitamins of the B group only. Dark beer contains 3 international units of $-B_1$ and 7.4 biological units of $-B_2$ per 100 c.c. If extracts of $-B_1$ and $-B_2$ are added to the beer after manufacture, no loss of vitamins occurs during storage. Possibly yeast withdraws the vitamins from beer during manufacture. J. N. A.

Nutritive value of fungi. II. Vitamin- B_1 , $-B_2$, and $-B_4$ content of mycelium of *Aspergillus sydowi*. III. Growth of rats on supplemented and unsupplemented mould proteins. H. J. GORCICA, W. H. PETERSON, and H. STEENBOCK (J. Nutrition, 1935, 9, 691—700, 701—714; cf. A., 1934, 220).—II. When fed at a 10% level in a vitamin- B_1 -deficient diet the mycelium protected chicks from polyneuritis and produced good growth. Pellagra was prevented by additions of 1% of mycelium to a $-B_2$ -deficient ration, although 3% was necessary for good growth. At a 30% level in an otherwise $-B_4$ -deficient ration the mould prevented the onset of paralysis.

III. Proteins of *A. sydowi* produced little growth in rats and failed to sustain life for > 7—9 weeks. Growth was resumed by supplementing mould-protein with casein, egg-white, or yeast-protein. Still better results were obtained with proteins of whole wheat or of maize-gluten feed. No improvement was obtained by use of gelatin, cystine (I), histidine, tyrosine (II), or a (I)-(II) mixture. A. G. P.

Flavin syntheses. VIII.—See this vol., 85.

Preparation and nutritional value of hepatoflavin. F. J. STARE (J. Biol. Chem., 1935, 111, 567—575).—Hepatoflavin (I) does not prevent dermatitis in vitamin- B_2 -deficient rats and chicks, whilst a fraction of the liver extract not adsorbed by fuller's earth does. Proper growth appears to depend on the presence of both these factors in the diet. The prep. of (I) is modified by pptn. from EtOH with hot $Ba(OH)_2$, p_H fractionation of the Ag ppt., and extraction of the Ag ppt. with hot $AcOH + H_2S$. H. D.

Modification of the Sherman method of studying the multiple nature of vitamins, with an application to vitamin- B_2 . T. S. HAMILTON and H. H. MITCHELL (J. Nutrition, 1935, 10, 117—128).—The precision of assay methods is much increased by careful control of the intake of the basal diet as well as of the vitamin supplement. The technique described disclosed no evidence of the multiple nature of vitamin- B_2 . A. G. P.

Realisation of the normal ascorbic acid content in the organism responsive to deficiency. A. GIROUD, C. P. LEBLOND, R. RATSIMAMANGA, and M. RABINOWICZ (Compt. rend. Soc. Biol., 1935,

120, 633—635).—A guinea-pig requires 30 mg. of ascorbic acid (I) daily to maintain an adrenal (I) content > 1 mg. per g.-wt., and considerable quantities to maintain the normal (I) content. R. N. C.

Ascorbic acid in lens and aqueous humour. V. DEMOLE and H. K. MÜLLER (Biochem. Z., 1935, 281, 80—85).—Fresh aq. humour (from the eyes of cattle) exhibits pronounced antiscorbutic action (3 c.c. of humour equiv. to 5 mg. of ascorbic acid) when injected subcutaneously into guinea-pigs receiving a diet free from vitamin-C. A prep. from the lenses behaves similarly. In the humour the activity corresponds with 100%, in the lens with 50%, of the reducing power (dichlorophenol-indophenol). W. McC.

Ascorbic acid content of blood and cerebrospinal fluid. F. PLAUT and M. BÜLOW (Z. physiol. Chem., 1935, 236, 241—256; cf. A., 1935, 1036).—In human and rabbit cerebrospinal fluid the vitamin-C exists entirely in the reduced form, but in the blood most of the $-C$ occurs in the oxidised form. The variations which occur in the amount of $-C$ in blood (caused, e.g., by diet changes) concern the reduced part only and are not parallel to accompanying variations in the $-C$ content of the fluid. Oral administration of moderate amounts of $-C$ increases the $-C$ content of the fluid and slightly increases that of blood. With large doses there are large increases in both. $-C$ introduced into the blood is transported in reduced form, is not oxidised by blood *in vitro* or *in vivo*, and disappears rapidly. Oxidised $-C$ is not reduced by the fluid *in vitro* or *in vivo* but is more rapidly absorbed than is reduced $-C$. In rabbits, injected $-C$ can pass from blood into fluid and conversely but under physiological conditions the passage from fluid to blood is in some way controlled. In the fluid $-C$ persists much longer than it does in blood. There is no evidence that the $-C$ of the fluid is reduced in the nervous system or that this system produces reduced $-C$. W. McC.

Comparison of the vitamin-C (ascorbic acid) content of the cerebrospinal fluid and of the urine in hypervitaminosis-C. F. PLAUT and M. BÜLOW (Naturwiss., 1935, 23, 771).—The vitamin-C content of the cerebrospinal fluid can be used for diagnosis of vitamin-C-subnutrition in the same way as the urinary content (cf. A., 1935, 417), the results by the two methods giving close agreement. P. W. C.

Ascorbic acid in glands. Isolation from the pituitary. J. R. MENDIVE and V. DEULOFEU (Z. physiol. Chem., 1935, 236, 208—211).—As regards their content of the acid (I) organs of Argentinian cattle form the series: pituitary, corpus luteum, adrenals > thymus, spleen, > testicles, pancreas, thyroid gland > follicular fluid, the val. varying from 1.9 to < 0.2 g. per kg. (I) was isolated from the pituitary, but from the corpus luteum only 4-benzeneazo-3-*l*-threoglycerol-1-phenylpyrazolone could be isolated. W. McC.

Distribution of vitamin-C in lower organisms. G. BOURNE and R. ALLEN (Austral. J. Exp. Biol., 1935, 13, 165—174).—Unicellular animals and plants, algae, and fungi contain granules which stain with

the AcOH-AgNO_3 reagent and therefore presumably contain reduced vitamin-C. W. O. K.

Vitamin-C in fresh apples and in apple powder. M. POCHINO (*La Pediat. med. prat.*, 1935, 10, 16).—Administration of fresh apples to guinea-pigs receiving Bezssonoff's scorbutic diet prevented appearance of symptoms of scurvy, but did not permit normal development, whilst administration of apple powder only delayed onset of the symptoms.

NUTR. ABS. (m)

(A) Effect of sulphitising on the preservation of vitamin-C. B. I. JANOVSKAJA. (B) Antiscorbutic activity of "marmelad" jelly, enriched, after four months' storage, with vitamin-C by addition of a concentrate of infusion of pine needles. N. JARUSOVA. (C) Antiscorbutic properties of pine needles. V. Effect produced on the vitamin-C content of pine needles when cut pine branches are kept for a short time. N. E. SHEPILEVSKAJA. (D) Antiscorbutic properties of sulphitised dried cabbage. Antiscorbutic turnip preparation. S. N. MATZKO (*Problems of Nutrition, Moscow, 1935, 4, No. 2, 51—54, 54—55, 56—58, 59—60, 61—64*).—(A) The process of sulphitising black-currant juice for storage seemed to preserve the vitamin-C (I) activity, which was lost in untreated, stored juice.

(B) Four months' storage at room temp. of a jam enriched with (I) concentrate from pine needles caused very little destruction of (I).

(C) Infusions in very dil. HCl of fresh pine needles and of needles from a bough that had been kept indoors for 10 days were almost equal in their antiscorbutic activity.

(D) The expressed juice from cooked, dried white cabbage, which had been sulphitised for storage, protected guinea-pigs from scurvy in a min. dose equiv. to 6 g. of original dry cabbage, so that in 1 kg. of dried cabbage there were about 160 "units" of (I). Juice of a damaged white "semi-table" turnip gave fairly good protection from scurvy in guinea-pigs.

NUTR. ABS. (m)

Ascorbic acid in sprouted oats. R. BOGART and J. S. HUGHES (*J. Nutrition, 1935, 10, 157—160*).—The vitamin-C content of sprouting oats increased to a max. at the tenth day. Vals. were similar whether sprouting was in light or in darkness.

A. G. P.

Vitamin-C (ascorbic acid) content of the paprika product "Vitapric." E. BECKER (*Z. Vitaminforsch.*, 1935, 4, 255—259).—Vitapric contains about 0.45% of ascorbic acid (cf. B., 1935, 1116), and increases the resistance of animals not only to scurvy, but also to other diseases. J. N. A.

Reducing power of vitamin-C in urine in health and disease. (A) T. BAUMANN. (B) W. VON DRIGALSKI (*Z. Vitaminforsch.*, 1935, 4, 354—356, 356—357).—(A) Von Drigalski's method of iodometric titration (A., 1935, 793) for the determination of ascorbic acid (I) in urine is untrustworthy.

(B) The method is upheld.

J. N. A.

Chemical method for determining vitamin-C. V. A. DEVIATNIN and V. M. DOROSCHENKO (*Compt. rend. Acad. Sci. U.R.S.S.*, 1935, 3, 177—180).—The

following modification of the method of Tillmans *et al.* (A., 1932, 310, 658) removes the reducing activity of most foreign substances in extracts of vitamin-C. The material is boiled with 5% AcOH (CO_2 stream), cooled, neutralised (p_H 5.0) with CaCO_3 , and pptd. with Pb(OAc)_2 . After filtration the extract is acidified with AcOH to p_H 3.0 and titrated with 2 : 6-dichlorophenol-indophenol to a slight pink (CO_2 stream). Good agreement with biological assays is obtained. J. W. B.

Determination of ascorbic acid by titration. B. AHMAD (*Nature, 1935, 136, 797*).—Boiling before extraction with $\text{CCl}_3\text{-CO}_2\text{H}$ increases the ascorbic acid val. for Darjeeling cabbage. The results support the views of McHenry *et al.* (A., 1935, 903) as opposed to those of van Eekelen (*ibid.*, 1176). L. S. T.

Value of the chemical titration method in determining the vitamin-C potency of certain foodstuffs. N. B. GUERRANT, R. A. RASMUSSEN, and R. A. DUTCHER (*J. Nutrition, 1935, 9, 667—675*).—Titration of ascorbic acid with 2 : 6-dichlorophenol-indophenol gives approx. results suitable as preliminary data for biological assays of vitamin-C potency. The accuracy of the method varies with the nature of the test material. A. G. P.

Influence of vitamin-C level on resistance to diphtheria toxin. I. Changes in body-weight and duration of life. C. G. KING and M. L. MENTEN II. Production of diffuse hyperplastic arteriosclerosis and degeneration in various organs. M. L. MENTEN and C. G. KING (*J. Nutrition, 1935, 10, 129—140, 141—153*).—I. A wide zone of vitamin-C deficiency exists without the appearance of scurvy, but in which physiological processes are subnormal and sensitivity to bacterial toxins is increased. A. G. P.

Reactions of animals susceptible to deficiency to increasing doses of ascorbic acid. A. GIROUD, R. RATSIMANANGA, A. BARATTE, and F. SYLVA (*Compt. rend. Soc. Biol.*, 1935, 120, 701—703).—Vascular lesions and dental mobility decrease and hæmoglobin increases steadily as the quantity of ascorbic acid administered increases. R. N. C.

Fractionation studies on pro-vitamin-D. E. M. KOCH and F. C. KOCH (*Science, 1935, 82, 394—395*).—"Cholesterol W" and heated purified cholesterol (I) are superior to viosterol or purified, unheated (I) in preventing leg weakness in rats and chicks. The pro-vitamin-D of heated (I) separates readily in crystallisation from EtOH. L. S. T.

Antirachitic efficiency of irradiated milk, yeast milk, cod-liver oil, and irradiated cholesterol. R. W. HAMAN and H. STEENBOCK (*Proc. Amer. Inst. Nutrition, J. Nutrition, 1935, 9, No. 6, Suppl. 7*).—When fed to chicks on a rat unit basis, cod-liver oil, irradiated milk, and irradiated cholesterol showed 10—15 times the antirachitic potency of milk from cows fed on irradiated yeast.

NUTR. ABS. (m)

Sensitivity of rachitic rats for vitamin-D. J. VAN NIEKERK (*Arch. Néerland. Physiol.*, 1935, 20, 477—480).—The sensitivity of the rat stock

fell to about 50% of the initial val. from 1929 to 1932, but no seasonal variations were noted. H. G. R.

Relationship of the vitamin-D intake of the hen to the antirachitic potency of eggs produced. N. B. GUERRANT, E. KOHLER, J. E. HUNTER, and R. R. MURPHY (J. Nutrition, 1935, 10, 167—178).—The antirachitic potency of eggs depends on the vitamin-D intake of the hen. The transfer of -D from diet to egg is of low efficiency, and is more complete from cod-liver oil than from viosterol.

A. G. P.

Constitution of vitamin-D₂.—See this vol., 69.

Sitostanol and stigmastanol.—See this vol., 69.

Differences in age of cells of some water plants in relation to their reducing powers. M. LLIENSTERN (Protoplasma, 1935, 33, 86—92).—Differences in reducing power of laminae and midribs of leaves of varying age and under varying conditions of assimilation are examined by means of methylene-blue and thionine.

A. G. P.

Permeability studies of *Valonia* osmometers. Behaviour with neutral salt solutions. P. KORN-MANN (Protoplasma, 1935, 23, 34—49).—With a *Valonia* cell-membrane osmometer, K citrate, tartrate, phosphate, sulphate, and acetate solutions caused a withdrawal of fluid at rates which declined in the order of substances named. KNO₃ and KCl caused an intake of fluid. In isotonic solutions the order of intake of fluid was LiCl > NaCl > KCl. The phenomena are explained by differences in the degree of swelling of the internal and external sides of the membrane induced by the various salts.

A. G. P.

Dry matter production [by plants] in nitrogen and potassium deficiency. D. MÜLLER and P. LARSEN (Planta, 1935, 23, 501—517).—In H₂O-cultures of *Sinapis alba* respiration losses were substantially the same for plants in normal and deficient media. Assimilation intensity was lower in deficient plants, the difference between these and normal plants declining with light intensity. The compensation point was the same in normal and deficient plants. Lowered assimilation is not due to reduced opening of stomata or smaller chlorophyll contents, but to "protoplasmic factors." The wt. of dry matter produced in stems and roots per unit leaf area was the same for completely manured and K-deficient plants, but was approx. doubled in N-deficient plants.

A. G. P.

Heat-resistance of plants. I. SAPPER (Planta, 1935, 23, 518—556).—Starved plants have a decreased heat-resistance, although small differences in C nutrition have only a slight effect. Deficiency of nutrient salts causing increased osmotic pressure may increase the resistance. Heavy excess of nutrients lowers resistance. The latter is controlled by sp. structural characteristics of the protoplasm and merely modified by the H₂O content.

A. G. P.

Absorbing power of roots. P. MAZÉ, P. J. MAZÉ, jun., and R. ANXIONNAZ (Compt. rend. Soc. Biol., 1935, 120, 693—695).—The absorbing power varies with the N compounds in the nutritive solution,

the concn. of the solution, and the nature of the inorg. N salts in solutions of which the roots are placed.

R. N. C.

Root exudation and root types in sugar cane. H. EVANS (Mauritius Dept. Agric. Sugar Cane Res. Sta. Bull., 1934, 5, 13).—Mineral analyses of exudates from cut roots of various parts of the rooting system are recorded.

CH. ABS. (p)

Catadyn process for sterile cultures of higher plants. F. C. GERRETSEN (Planta, 1935, 23, 593—603).—The root system of the plant is protected from infection by means of a cork layer containing a catadyn (Ag)-infusorial earth prep.

A. G. P.

Regulation of protein exchange and the condition of proteolytic enzymes in plants. K. PAECH (Planta, 1935, 24, 78—129).—Anaerobic decomp. of protein in plant cells does not depend on deprivation of O₂, but is influenced by injury to the cell by prolonged anaerobiosis. In acid leaves death of cells in O₂ deficiency is not caused by increasing proteolysis. In wilting petals the "explosive" decomp. of protein is a post-mortal process resulting from destruction of protoplasts. Synthesis or hydrolysis of protein in intact cells is controlled by the relative amounts of active carbohydrate (monose) and sol. N (NH₃) present.

A. G. P.

Nitrogen fixation by germinating legume seeds without co-operation of nodule bacteria. K. GIRTSCHANOV (Zentr. Bakt. Par., 1935, II, 92, 349—363).—In the absence of nodule organisms germinating seeds of yellow lupin were unable to utilise atm. N₂ even under the influence of certain stimulants.

A. G. P.

Apparent assimilation of nitrogen by germinating peas. E. M. SMYTH and P. W. WILSON (Biochem. Z., 1935, 282, 1—25; cf. Vita, A., 1932, 436, 1180; Orcutt *et al.* A., 1934, 1273).—Apparent increases in the N content of peas germinating in presence of stimulants (salts, alkaloids) or H₂O are due to inaccuracies in analytical methods. The Kjeldahl method and its modifications yield untrustworthy results, and the Dumas method is recommended. There is no evidence that direct assimilation of elementary N₂ occurs.

W. McC.

Rôle of asparagine and glutamine in the higher plants. G. SCHWAB (Planta, 1935, 24, 160—162).—Asparagine (I) and glutamine (II) are present simultaneously in plants. Increased "amide" in germinating seedlings or that induced by shading plants or supplying NH₄ salts involves increases in (I) and (II) in normal proportions. The (II) content of roots of *Aspidium filix* declines with the total sol. N during the summer months. Protein exchange in plants is discussed in relation to org. acid and carbohydrate contents. Plant extracts contain enzymes sp. for (I) and (II). Yeast extracts contain only (I) and can only effect the fission of (I).

A. G. P.

Variation of saponins during germination and development in some species of grasses. T. SOLACOLU and E. WELLES (Compt. rend. Soc. Biol., 1935, 120, 662—664).—Saponin accumulates in the seeds when they reach maturity; it is then used up partly in germination and partly in growth until the

appearance of the fifth leaf, after which it has disappeared entirely.
R. N. C.

Influence of partial pressure of carbon dioxide on photosynthetic efficiency. B. N. SINGH and K. KUMAR (Proc. Indian Acad. Sci., 1935, 1, B, 909—927).—The rate of photosynthesis in radish leaves increases with rising $[\text{CO}_2]$ to a stationary stage followed by a decline as the proportion of CO_2 is further increased. With increasing light intensity the CO_2 -photosynthesis curves show a steeper rising phase and earlier evidence of toxic effects. The curves are discussed in relation to those obtained by earlier observers.
A. G. P.

Oxygen intake of oily and starchy seeds. E. REUHL (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 879—886).—In the early stages of germination *Brassica* seeds absorb O_2 at a normal rate with decreasing O_2 tension until it reaches 3%, whereas linseed shows a retarded rate almost immediately and buckwheat shows intermediate vals. During the later stages this behaviour is reversed.
H. G. R.

Energy of growth. XIV. Effect of zinc and manganese salts at toxic concentrations on the energy output during germination. G. BOY (Bull. Soc. Chim. biol., 1935, 17, 1414—1426).—The energy output of rice seeds (heat of combustion of the cotyledon/difference between the heats of combustion of the original and the germinated seeds) grown in the dark in aq. solutions of Mn and Zn salts is < that of seeds grown in H_2O . With Mn the decrease \propto the concn.; with Zn the toxic action is not so marked, and is the same at a concn. of 2 as at 4 g. of Zn per litre.
A. L.

Possible association of vitamin-A with nutritional conditions in plants. E. S. HABER, P. M. NELSON, and P. P. SWANSON (Iowa Agric. Exp. Sta. Rept. Agric. Res., 1933, 134—135; 1934, 163).—Poorly nourished plants were deficient in chlorophyll and in vitamin-A. The ability of plants to translocate -A is indicated.
CH. ABS. (p)

Effect of concentration of neutral salts on seedling growth. J. PORT (Acta Comment. Univ. Tartu., 1932, A, 23, No. 1, 166 pp.).—Growth was influenced by salt solutions absorbed by paper on which seeds were sprouted. Concns. of $< 0.1N$ inhibited the swelling of seed colloids and produced seedlings showing < normal growth and H_2O content. In wheat, diastatic activity was less in solutions of higher concn. The effect of salts on growth decreased in the order SCN' , NO_3' , Cl' , Br' , PO_4''' , SO_4'' and Li' , NH_4' , Ba'' , Ca'' , K' , Na' , Mg'' , in $0.1N$ concn. With concns. of 0.01 — $0.001N$ salt effects were sp. for different species. The favourable action of anions on root growth was in the reverse order of the lyotropic series. $0.0001N$ solutions of Li' , NH_4' , and Ba'' were particularly beneficial to growth, probably because of increased imbibition of H_2O .
CH. ABS. (p)

Elements indispensable for plant nutrition. A. FREY-WYSSLING (Naturwiss., 1935, 23, 767—769).—For the higher plants C, N, P, S, O, H, K, Mg, Ca, and Fe appear to be essential. In addition, the absence of Mn, B, Cu, and Zn often leads to deficient and

diseased growth. Many elements, e.g., Al, Si, Na, Cl, are utilised by particular groups of plants in considerable amounts, but it is difficult to say that they are essential to the life of the plant. Other elements, although not essential to life, stimulate the growth of the plant. The functions of the various elements are discussed and it is pointed out that all the indispensable elements lie on a line drawn in the periodic table from A through C to A.
P. W. C.

Effect of humic acid on assimilation in plants. A. V. BLAGOVESTSCHENSKI and A. A. PROSOROVSKAJA (Biochem. Z., 1935, 282, 99—103; cf. A., 1935, 265).—Humic acid (I) stimulates plant growth by increasing the permeability of the tissues and so facilitating osmosis. NH_4NO_3 enabled to penetrate the cells by (I) has no effect on the synthesis of proteins there.
W. McC.

Vegetable growth-substances. F. KÖGL (Naturwiss., 1935, 23, 839—843).—A lecture.

Physiological analysis of the growth substance. A. J. HAAGEN SMIT and F. W. WENT (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 852—857).—The cell-elongation and polar transport properties of a series of org. substances have been examined. Some, which have only growth-stimulating properties, do not exhibit polar transport and do not give the *Avena* bending test nor the bud-inhibition of the auxins. *allo*Cinnamic acid has the greatest cell-elongation power, comparable with that of 3-indolyl-acetic acid, whereas cinnamic acid has none.
H. G. R.

Analysis of the activity of two growth-promoting substances in plant tissues. K. V. THIMANN (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 896—912).—Both indene-3-acetic acid and coumaryl-1-acetic acid show biological activity, although the latter does not produce any *Avena* curvature, but they lack the property of being readily transported in the plant. It appears that cell-elongation, root-formation, root-growth inhibition, and bud-inhibition arise from one primary reaction in the cell.
H. G. R.

***Lambertella corni-maridis*, von Höhnel, a brown spotted parasitic discomycete.** T. H. HARRISON and A. F. EL-HELALY (Trans. Brit. Mycol. Soc., 1935, 19, 199—213).—Growth characteristics of the fungus are examined in relation to p_{H} of the medium.
CH. ABS. (p)

Xyloporosis—the new citrus disease. I. REICHERT and J. PERLBERGER (Hadar, 1934, 163—167, 172, 193—202).—Fruit from diseased trees contained less total solids, higher total and reducing sugars and total acids than healthy fruit.
CH. ABS. (p)

Biochemical modifications and phytopathology. Official oil of lavender from plants parasitised with *Septoria lavandulae*, Desm. R. SALGUES (Compt. rend. Soc. Biol., 1935, 120, 703—704).—The infection reduces the quantity of oil and its terpene alcohol content, and increases *d* and the cineole content of the essence.
R. N. C.

Toxicity of magnesium towards higher plants. D. RABINOVITZ-SERENI (Bull. Staz. Pat. veget.,

1933, 13, 346—366; Bied. Zentr., 1935, A, 5, 517).—Plants in solutions containing 1% of $MgSO_4$ showed loss of chlorophyll, restricted growth, and browning. Enzyme processes are concerned. Low $[Mg^{++}]$ stimulated and higher concns. retarded catalase activity. Oxidase activity was favoured at all concns. examined. Respiration was increased by 0.1% and retarded by 1% solution of Mg^{++} . A. G. P.

Toxins of wilting [in plants]. O. K. ELPIDINA (Compt. rend. Acad. Sci. U.S.S.R., 1935, 3, 360—364).—The toxin produced by the *Fusarium* which causes wilting of potatoes is NH_3 . A. G. P.

Action of potassium oxalate on the living protoplasts of *Allium cepa*. R. EICHBERGER (Planta, 1935, 23, 479—485).—Sections of *A. cepa*, after 10—15 min. treatment with aq. $K_2C_2O_4$ (I), show normal urea-plasmolysis only in the central area. Injury to plasma by (I) is counteracted by treatment with $CaCl_2$, K citrate, KNO_3 , NaCl, or $(NH_4)_2SO_4$, or by prolonged washing with H_2O . No sp. action of Ca^{++} in this respect was apparent. A. G. P.

Occurrence of lime in edible *Mormordica*. H. L. CHAKRAVARTY (Current Sci., 1935, 4, 239—240).—Cystoliths in various Indian species are described. A. G. P.

Iodine of seaweeds. III. E. MASUDA and K. NISHIDA (J. Pharm. Soc. Japan, 1934, 54, 243—245; cf. A., 1934, 336).—Of the total I in *Laminaria japonica*, Aresch, an average of 48% occurs in org. forms. *L. ochotensis* contains 65% of sol. I as org. compounds. Warming causes a gradual transition to inorg. forms. In *Ecklonia cava* I is present as iodoammonium salts or I salts of amines and not as KI or NaI. CH. ABS. (p)

Chemical composition of saltbushes from the Salmon Gums area. L. J. H. TEAKLE (J. Dept. Agric. W. Austral., 1935, 12, 188—189).—Complete analyses of *Atriplex prostratum* and *A. halimoides* are given. Both specimens are high in Na_2O and Cl, but low in P_2O_5 . NUTR. ABS. (m)

Saltbush. Its mineral composition. M. S. BENJAMIN (Agric. Gaz. N.S.W., 1935, 46, 309—310).—*Chenopodium triangulare* and *Atriplex semibaccatum* were analysed. < 54.06% of the sol. ash in the latter was NaCl. NUTR. ABS. (m)

Phytin of seeds of *Eleusine coracana* (besna), *Sorghum atropicum* (dura), *Eragrostis Teff* (teff), and *Pennisetum spicatum* (bultuc). R. MONTUORI (Ateneo parmense, 1934, 6, 89).—The ash, P, and phytin contents of the seeds are recorded. NUTR. ABS. (m)

Formation of acetic acid from ginkgo wood (*Ginkgo biloba*). Y. C. TANG, Y. W. WANG, and H. L. WANG (Cellulosechem., 1935, 16, 90—92).—The Ac content of 4 samples of the wood (I) of different age and habitat is const. (mean 1.18%). The lignin-freed portion (II) (68.74%) (ash content 0.58, 0.64, 0.41, and 0.38%) contains 1.70% Ac, in close agreement with the val. (1.72%) calc. from that of (I) and the loss resulting from isolation of (II). Thus no elimination of AcOH occurs during the process of

isolating (II), which must contain an Ac group and not a formyl group (semi-acetal). J. W. B.

South American drugs. I. Bixol, a new alcohol from the oil of *Bixa Orellana*. II. Chemical composition of *Canavalia obtusifolia*. M. BACHSTÉZ and G. CAVALLINI (Chimica e l'Ind., 1935, 17, 650—651, 652).—I. The unsaponifiable matter (2.5%) of annatto-seed oil was submitted to chromatographic analysis, using Al_2O_3 , which adsorbed ergosterol and vitamin-D (positive reactions in the Rosenheim and Brückner tests). The non-adsorbed portion was distilled in vac., yielding 0.58% (calc. on the seed) of *bixol*, $C_{18}H_{30}O$, b.p. $176^\circ/2$ mm., a pale green oil, probably $CMe_2[CH\cdot CH_2\cdot CMe]_3CH\cdot CH_2\cdot CH_2\cdot OH$, oxidised to the corresponding aldehyde, b.p. 175 — $180^\circ/6$ mm. (semicarbazone, m.p. 96 — 97°).

II. Ouari seeds contain 10.42% H_2O , 2.50% ash, 0.65% fatty matter, 4.25% N, 26.5% proteins (93.5% sol. in HCl+pepsin), 53.77% starch, 0.106% lecithin-phosphoric acid (calc. as P_2O_5). They contain no HCN or alkaloids and are not toxic to rabbits.

D. R. D.

"Bukuryo," sclerotia of *Pachyma Hoelen*, Rumph. III. Chemical constituents. K. TAKEDA (Trans. Tottori Soc. Agric. Sci., 1934, 5, 62—73).—"Bukuryo" contains approx. 93% of a carbohydrate, pachyman (I), and also gum, chitin, protein, adenine, histidine, *d*-glucose, sterol, lecithin, and fat, Cl, S, P, Ca, Fe, Mg, Mn, K, Si, Na, enzymes which decompose fat and (I), and traces of pepsin and trypsin. J. N. A.

Arabogalactan of Siberian larch. N. I. NIKITIN and I. A. SOLOVIEV (J. Appl. Chem. Russ., 1935, 8, 1016—1022).—The arabogalactan (I) (1 mol.) with 12 mols. of NaOH and 13 of Me_2SO_4 yields a product in which all the available OH-groups (20) are methylated. (I), CH_3PhCl , and NaOH (80° ; 16 hr.) afford the *dibenzyl ether*, and (I), $BzCl$, and NaOH (with cooling) give the *Bz*₂ ester. The mol. wt. of (I) cannot be determined cryoscopically, as the depression of f.p. is not \propto concn.; the I val. method gives a mol. wt. corresponding with $[C_5H_8O_4(C_6H_{10}O_5)_6]_2$.

R. T.

Lignin in straw and deciduous trees. R. S. HILPERT [with E. LITTMANN, O. PETERS, H. HELLWAGE, and O. LISSNER] (Cellulosechem., 1935, 16, 92—96).—The action of 72% H_2SO_4 at room temp. on various sugars produces insol. residues (I) which closely resemble lignin (II). Pentoses and fructose are especially sensitive, but aldohexoses (particularly glucose and galactose) are very stable. The amount of (I) formed decreases rapidly with fall in reaction temp. The amount of (II) similarly formed from straw also decreases from 41.66% at 60° to 2—3% at -10° , and dilution of the filtrate affords a carbohydrate material of composition $2C_6H_{10}O_5 - H_2O$. Thus the acid-sol. products are not (II) but carbohydrate. Treatment of straw with alkali effects dissolution of 20—30% (mainly hexoses) and dilution then ppt. a substance with the composition of a partly methylated cellulose anhydride (pentosan content increased from 24 to 29%; OMe reduced from 4 to 3.1%), which is acetylated in presence of 8%

H₂SO₄ to a substance (83% yield) of composition [C, 49.5, H 6.0, OAc 61.6, OMe 1.3 (? 3.1), pentosans 13%] closely resembling that of cellulose triacetate. Since the OMe content is the same as that of the original straw, this group is present not in lignin but in the carbohydrate of which straw is composed. Treatment of the wood (III) of deciduous trees with HCl at -10° affords a residue (12%) of composition intermediate between that of (III) and (II). The H₂O-pptd. material is also a cellulose anhydride. With HCl (*d* 1.19) at room temp. the C and H content of the residue is the same as that of (III), but the OMe content, and lignin formed, are higher. Hence the higher methylated portions are less readily attacked. The ground-substance is a cellulose anhydride which readily loses H₂O intramolecularly to give (II).

J. W. B.

New constituent of beechwood. E. WEDEKIND and O. MÜLLER (Naturwiss., 1935, 23, 833—834).—MeOH extraction of beech, eucalyptus, alder, cherry, and, to a smaller extent, oak and hornbeam, but not of pine and ash, yields a substance (I) (C 57.1, H 4.3, OMe 4.8%) giving an intense red-violet colour with conc. acids. (I), which is separated admixed with a less sol. substance converted into (I) by hot aq. alkali, readily forms a Ac₁ derivative which does not give the colour reaction. F. O. H.

Leaf starch: isolation and properties. H. A. SPOEHR and H. W. MILNER (J. Biol. Chem., 1935, 111, 679—687).—Depletion of starch (I) in leaves does not occur on drying if the leaves have been frozen or treated with CHCl₃. To prepare (I) the leaves are dried, ground, the pigments extracted with EtOH and light petroleum, polyuronides etc. are extracted with cold H₂O, and (I) with hot H₂O, from which, after cooling, it is separated by centrifuging. If a (I) solution is frozen for some time and then allowed to thaw, (I) is pptd. in a fibrous mass (retrogradation). Cooling for 3 days at -80° ppts. (I) completely, but 90—95% pptn. can be obtained if the solution is cooled only to -8°. Retrograded (I) dissolves in H₂O, but if thoroughly dried, it is more sparingly sol. Determinations of the amounts of (I) were made on the basis of the reducing power of the solution after acid hydrolysis with an accuracy of ±1%. *d*-Glucose is the chief product of hydrolysis. The apparent lower reducing power of retrograded (I) is due to its slower rate of hydrolysis. The leaves of *Nicotiana tabacum* give the highest yield. E. A. H. R.

Detection of hydroxylamine in autolysed green leaves. M. LEMOIGNE, P. MONGUILLON, and R. DESVEAUX (Compt. rend., 1935, 201, 1067—1069).—By modification of Blom's reaction NH₂OH has been detected in the juice of leaves allowed to autolyse for several days (1—3 mg. per kg. of original leaves), but is absent from the juice of fresh leaves. W. O. K.

Determination of starch in plants with special reference to woody plants. J. T. SULLIVAN (J. Assoc. Off. Agric. Chem., 1935, 18, 621—636).—The starch is extracted with slightly alkaline aq. CaCl₂, pptd. with EtOH, redissolved in H₂O, and pptd. with I in aq. KI in presence of (NH₄)₂SO₄. The starch is then hydrolysed and glucose determined by Cu reduction. A single extraction is sufficient if

the conditions specified with regard to [CaCl₂], duration of boiling, and fineness of grinding are adhered to. The method is more trustworthy than that of enzymic hydrolysis. The applications of the method are discussed. E. C. S.

Aromatic substances in maple sugar. J. RISI and A. LABRIE (Canad. J. Res., 1935, B, 13, 175—184).—The aromatic substances in the syrup and sugar of the maple contain vanillin (I), vanillic acid (II), and a resinous part, which is hydrolysed to guaiacol (III) by emulsin. The bark contains an enzyme (acerase) which hydrolyses coniferin and amygdalin; the sap also contains an enzyme. The wood contains a little coniferin, which may be the parent substance of (I). The odour is due to presence of hadromal, which, during heating of the sap, is decomposed into (I), (II), and (III). Hadromal may be synthesised from (I), (III), and sucrose. F. R. S.

Constituents of the sap of sugar maple (*Acer saccharum*, Marsh). G. H. FINDLAY and J. F. SNELL (Canad. J. Res., 1935, 13, B, 269—275).—The development of the maple flavour from its precursor in sap, during boiling, is not due to oxidative changes. No individual constituent of various maple extracts examined was capable of imparting the flavour to sugar syrups. A. G. P.

Biochemistry of amygdalin. A. VIEHOEVER and H. MACK (Amer. J. Pharm., 1935, 107, 397—450).—The physiological properties of amygdalin (the commercial product contains 2H₂O) and of its hydrolytic products are discussed. J. L. D.

Manchurian kaoliang (*Andropogon sorghum*, Brot.). S. HIRAO (J. Agric. Chem. Soc. Japan, 1935, 11, 921—924).—Three cryst. substances have been isolated from the hot aq. extract of kaoliang: (1) yellow, m.p. 249—250°, a quercetin monoglucoside, probably quercimeritrin; (2) long white needles, m.p. 240—242°, probably a new flavanonol; (3) short white crystals, m.p. 98—100°, similar to pyrocatechol. H. G. R.

Action of *Nuphar luteum* on the heart. M. BULAJEWSKI (Wiad. Farm., 1935, 62, 15—18, 29—32, 43—47, 57—62).—EtOH extracts of blossoms of *N. luteum* contain a cryst. glucoside, *nymphalin* (I), which exerts a toxic action on the animal heart. (I) has m.p. 40° (approx.) and gives a purple colour with α-C₁₀H₇-OH and H₂SO₄. Hydrolysis yields Cu-reducing substances. (I) is present in flowers and seeds but not in roots. CH. ABS. (p)

Ascorbic acid (vitamin-C) content of some Indian plant materials. M. DAMODARAN and M. SRINIVASAN (Proc. Indian Acad. Sci., 1935, 11, B, 377—386).—Data obtained by the Tillmans-Harris method are recorded. A. G. P.

Constituents of red sandal wood. Homoptero-carpin.—See this vol., 81.

Pigments of cotton flowers. I. Cambodia (*Gossypium hirsutum*). K. NEELAKANTAM, R. H. R. RAO, and T. R. SESHADRI (Proc. Indian Acad. Sci., 1935, 1, 887—890).—The presence is established of quercetin and quercimeritrin in proportions which varied with variety, locality, and season. A. G. P.

Fluorescence spectra of chlorophyll pigments. C. DHÉRE and A. RAFFY (Bull. Soc. Chim. biol., 1935, 17, 1385—1413).—The bands in the fluorescence spectra of α -chlorophyll in hexane, Et₂O, COMe₂, EtOH, MeOH, C₆H₆, cyclohexanol, CHCl₃, and CS₂ have axes at 663, 663.5, 666, 666.5, 667, 666.5, 668, 670, and 676.5 m μ , respectively, the corresponding val. for β -chlorophyll in Et₂O being 646.2 m μ . The bands in the fluorescence spectrum of the leaves of *Pelargonium zonale* (in vivo) occur at 738 and 686, whilst with an Et₂O extract of the leaves the vals. are 732.5 and 672 m μ , respectively. The fluorescence bands of α - and β -phytylphosphoribide in CS₂ have axes at 679 and 663.5 m μ , respectively. A. L.

Phlobaphen and durasantalin in the colouring matter of Manchurian kaoliang (*Andropogon sorghum*). K. OKANO and I. OHARA (J. Agric. Chem. Soc. Japan, 1935, 11, 767—772).—The Et₂O-insol. fraction of the colouring matter of the hulls contains phlobaphen (I) (43% of the whole colouring matter) and the COMe₂-insol. fraction contains durasantalin (II) (red dura) (35%). The colouring matter (2%) of the seed coats also contains (I) (82%) and (II) (15%). The coats contain 3% of H₂O-sol. tannin but no apigenin (cf. Perkin, J.C.S., 1910, 97, 220). W. McC.

Carotenoids and some lipins of *Ipomaea reptans* (L.). Pair. M. ISHII (J. Soc. Trop. Agric. [Nettai Nōgoku Kwaiishi], 1933, 5, No. 2, 192—197).—Analyses of the vegetable are given. β -Carotene, xanthophyll, and a trace of taraxanthin were separated. Lipins detected included *n*-hentriacontane, sitosterol and its glucoside, and a higher alcohol, m.p. 267°. CH. ABS. (p)

Daturic acid. R. W. CLARK (J. Amer. Pharm. Assoc., 1935, 24, 843—847).—Solid fatty acids were prepared from the oil of *Datura stramonium* seeds. Attempts to separate them by fractional crystallisation from EtOH, pptn. of Mg salts, and vac. distillation of the Me esters failed. The occurrence and identity of heptadecic acid are discussed. F. O. H.

Apple- and pear-seed oils. J. PRITZKER and R. JUNGKUNZ (Z. Unters. Lebensm., 1935, 70, 255—257).—Air-dried apple- and pear-seeds contained 19.23 and 21.44%, respectively, of their dry wt. of oil, which had refractometer val. (40°) 62.9 and 62.0, acidity 4.1° and 9.7°, acid val. 2.3 and 5.4, ester val. 185.4 and 184.1, sap. val. 187.7 and 189.5, I val. (Hanus) 122.4 and 124.1, Reichert-Meissl val. 0.22 and 0.33, Polenske val. 0.4 and 0.33, unsaponifiable matter 1.10 and 1.03%, phytosterol (min.) 0.36 and 0.28%, m.p. of phytosteryl acetate 122° and 119°, respectively. The fatty acids (95.8 and 95.7%) had refractometer val. 48.4 and 47.7, neutralisation val. 196.5 and 196.8, mean mol. wt. 285.5 and 285.1, solid fatty acids (Bertram) 7.2 and 10.3%, (Grossfeld) 4.9 and 6.0%, and isooleic acid 0.62 and 0.45%, respectively. Each oil gave positive Bellier, Bellier-Kreis, and HNO₃ tests, and the apple-seed oil a positive Kreis test. The latter oil was clear yellow, and had a bitter almond flavour, the pear-seed oil egg-yellow, and had a slightly acid taste. E. C. S.

Odoriferous substances of green tea. VI. Constituents of tea oil. S. TAKEI, Y. SAKATO, and M. ONO (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 1262—1274).—From tea-leaf oil were isolated CHMeEt·CHO, *n*-hexyl, benzyl, and benzyl- and phenyl-ethyl alcohols, PhOH, cresol, AcOH, and hexoic acid. No ester with an odour characteristic of that of the oil was isolated (cf. A., 1934, 571). F. O. H.

Agar-agar of Black Sea phyllophora. V. F. OPOTZKI and L. A. BORTNIK (Ukrain. Chem. J., 1935, 10, 331—335).—The washed dried agar-agar contains H₂O 19, protein 5.5, Ac 9.8, org. and total S (as SO₃) 10.7 and 14.6, galactosans 42.5, pentosans 0.64, methylpentosans 0.16, ash 11.73% (SO₃ 3.93, SiO₂ 1.81, Fe₂O₃+Al₂O₃ 2.01, CaO 2.52, MgO+Na₂O+K₂O 1.46%). Japanese agar differs chiefly in its lower protein (1.32%), org. S (4.35%), and ash content (3.98%). The hardness of the gels of Black Sea agar is considerably < that of Japanese agar, and the m.p. and setting points are lower. R. T.

Bitter principles of the Colombo root. III.—See this vol., 89.

Alkaloid of Chin-shih-hu.—See this vol., 88.

Chemistry and pharmacology of the alkaloids of *Duboisia Hopwoodii*. C. S. HICKS and H. LE MESSURIER (Austral. J. Exp. Biol., 1935, 13, 175—188).—The leaves contain an alkaloid, C₉H₁₂N₂, b.p. 266—268°, [α]_D²⁰ +38.6° (picrate, m.p. 186—188°; picronate, m.p. 252—253°), which yields nicotinic acid on oxidation with KMnO₄ and is probably *d*-nornicotine (cf. A., 1932, 177). W. O. K.

Alkaloids of European *Lycopodium* species. J. MUSZYŃSKI (Arch. Pharm., 1935, 273, 452—457).—*L. Selago*, *annotinum*, *inundatum*, *complanatum*, and *clavatum*, L., contain solid, non-volatile (amorphous salts) and volatile, H₂O-sol. alkaloids (cryst., hygroscopic salts). The latter, named *selagine*, *annotine*, *inundatine*, *complanatine*, and *clavatine*, respectively, confer poisonous properties on the plants. R. S. C.

Distribution of alkaloids in *Ephedra sinica* (Ma-Huang). M. TARLÉ (J. Chinese Chem. Soc., 1935, 3, 377—380).—In the young herb the total amount of ephedrine alkaloids (I) is almost evenly distributed between the pith and the rest of the stem, but in the ripe plant the former contains much > the latter. The percentage of *l*-ephedrine in (I) is nearly the same in early summer (56.45%) as in the autumn (57.7%). H. G. M.

Histochemical detection of sodium in plants. M. STEINER (Ber. deut. Bot. Ges., 1935, 53, 720—732).—An adaptation of the uranyl Zn acetate method is described. Other plant substances do not interfere. A. G. P.

Spectrographic micro-determination of zinc [in plant material].—See this vol., 43.

Method of making latent finger-prints visible. M. WAGENAAR (Pharm. Weekblad, 1935, 72, 1265—1271).—The latent finger-print is developed by treatment with I vapour and permanent impressions are taken from the developed stain on paper coated with a prep. consisting of 1 g. of rice starch, 2 g. of KI, and 0.3 g. of thymol in 20 c.c. of H₂O. S. C.

Impregnation of the nervous system with silver. J. SZEPSENWOL (Compt. rend. Soc. Biol., 1935, 120, 689—690).—Larvæ of batrachians are impregnated with Ag by means of a 10% solution of CH_2O in 4% HCl or HCO_2H as fixer, followed by AgNO_3 solutions of gradually increasing concn.

R. N. C.

Deproteinisation of blood and urine by copper ferrocyanide. R. VLADESCO (Compt. rend. Soc. Biol., 1935, 120, 664—665; cf. A., 1935, 1044).—Deproteinisation of blood and urine by $\text{Cu}_2\text{Fe}(\text{CN})_6$ removes uric acid and NH_2 -acids in the ppt. Urea, creatine, and creatinine may be determined in the filtrate if excess of Cu is first removed with H_2S , as it interferes with the determination of the latter two substances with Na picrate. Deproteinisation by this method is preferable to the older methods in diabetic urines.

R. N. C.

Determination of benzene by the Pulfrich step-photometer. L. VON SZÉCSÉNYI-NAGY (Biochem. Z., 1935, 281, 178—180; cf. Janovsky, A., 1891, 685).—The C_6H_6 is separated from the acidified material (biological) by distillation into a cooled nitration mixture. The $\text{C}_6\text{H}_4(\text{NO}_2)_2$ obtained is dissolved in COMe_2 , made alkaline with 33% aq. NaOH , and shaken. The intensity of the violet colour in the COMe_2 is measured. About 70% of the C_6H_6 is thus determined.

W. McC.

Spectrographic determination of phenol in different media. G. BARAC (Compt. rend. Soc. Biol., 1935, 120, 520—522).— PhOH is determined in aq. solution, and in plasma and whole blood after deproteinisation with H_2WO_4 , by extracting with Et_2O and spectroscopic examination of the extract in the Jobin-Yvon quartz spectrograph; PhOH shows three narrow bands at 267, 274, and 280.7 $\text{m}\mu$, the mol. extinction coeff. in Et_2O for the third of these being 2400.

R. N. C.

Sugar determination by the ferricyanide electrode. P. A. SCHAEFFER and R. D. WILLIAMS (J. Biol. Chem., 1935, 111, 707—723).—Reducing sugars may be determined by the ferri-ferro-cyanide electrode. Vals. are unaffected by p_{H} change, by the products of the sugar oxidation, or by changes in the vol. of the solution about the electrode. The method can be adapted for determinations with 20 cu. mm. of blood. As no supplementary reagents are used, side reactions are avoided.

E. A. H. R.

Rapid method for the determination of reducing sugars. G. I. SOLOMOS (Bull. Soc. Chim. biol., 1935, 17, 1465—1469).—The solution containing the reducing sugar is added from a burette to a known amount of 0.4% $\text{K}_3\text{Fe}(\text{CN})_6$ in N - NaOH until the red colour disappears. The method is applied to blood, urine, and milk.

A. L.

Determination of glutamine in presence of asparagine.—See this vol., 60.

Determination of carotenoids in blood, tissue, and fluids in clinical practice. P. RATCHEVSKY (Bull. Soc. Chim. biol., 1935, 17, 1187—1193).—The method is based on the observation that 0.03×10^{-6}

g. of carotene is the smallest amount detectable by the yellow residue obtained on evaporation of light petroleum solutions.

A. L.

Infra-red absorption spectra of plant and animal tissue etc.—See this vol., 9.

Iodine value as a biological constant. Rapid micro-determination by means of bromine vapour. H. WOLLSCHITT (Arch. exp. Path. Pharm., 1935, 179, 260—265).—The material (0.1—5.0 mg.) is exposed to Br vapour for 15—180 min. and then heated at 100° to const. wt. The increase in wt. $\times 160/\text{wt. taken}$ is the I val. Vals. for common fats and fatty acids agree with theoretical vals., but the indicated nos. of double linkings of some carotenoids (crocein, methylbixin) and unsaturated esters are < the known vals. The method differentiates various body fats.

F. O. H.

Determination of carbon in biological fluids. F. LAUERSON and K. VOIT (Biochem. Z., 1935, 280, 276—285).—The fluid is burned in air or O_2 in an electrically heated combustion furnace and the CO_2 produced is passed into aq. $\text{Ba}(\text{OH})_2$. Excess of 0.01 N - HCl is added and the solution is titrated with 0.01 N - NaOH using Tashiro's mixed indicator (Amer. J. Physiol., 1920, 60, 519). 0.002 mg. of C can be determined.

W. McC.

Calcium determination in biological material. C. C. WANG (J. Biol. Chem., 1935, 111, 443—453).—Use of a washing solution, for CaC_2O_4 ppts., consisting of 2% aq. NH_3 in equal parts of H_2O , EtOH , and Et_2O prevents loss by flotation and dissolution. Treatment with $\text{CCl}_3\text{CO}_2\text{H}$ and C allows direct Ca determinations to be made on urines.

F. A. A.

Determination of mercury in viscera. C. NEWCOMB, S. R. NAIDU, and K. S. VARADACHAR (Analyst, 1935, 60, 732—735).—The org. matter is destroyed by heating with $\text{HNO}_3 + \text{H}_2\text{SO}_4$, and the solution is distilled in a current of air until H_2SO_4 fumes appear. Distillation is continued in a stream of air charged with HCl , HgCl_2 distilling over. Hg in both distillates is pptd. as HgS , which is dissolved in $\text{Br-H}_2\text{O}$ and repptd. Separation is quant. from other heavy metals, including As^{III} , which is oxidised to As^{V} .

J. S. A.

Micro-determination of phosphoric acid in tissue. L. THIVOLLE (Bull. Soc. Chim. biol., 1935, 17, 1427—1450).—Conc. HNO_3 containing $\text{Cu}(\text{NO}_3)_2$ is used for the mineralisation of the material. The aq. solution of the phosphomolybdate ppt. is reduced with Zn, added to aq. Na phosphomolybdate, and titrated with KMnO_4 using benzidine as indicator.

A. L.

Micro-determination of sulphur in biological material. L. REVOL and M. FERRAND (Bull. Soc. Chim. biol., 1935, 17, 1451—1454).—Losses in the determination of S in org. compounds due to the escape of traces of SO_2 are avoided by passing the vapour from the $\text{HNO}_3\text{-H}_2\text{O}_2$ treatment of the material through aq. Br which is finally added to the main solution. The SO_4^{2-} is pptd. with benzidine.

A. L.

