

# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

APRIL, 1934.

### General, Physical, and Inorganic Chemistry.

- Continuous spectra of the atom and molecule of hydrogen.** D. CHALONGE (*Ann. Physique*, 1934, [xi], 1, 123—214).—Secondary and continuous spectra are excited by an uncondensed discharge, and a spectrum by a condensed discharge in a tube at low pressure. The energy distribution curve as a function of the wave-length consists, in the latter case, of a level beyond the Balmer lines and a level to beyond 9000 Å., corresponding respectively with the Balmer and Paschen continuous series. The influence of the Stark effect is observed. The mol. spectrum energy distribution curve reaches a max. at 2350 Å., falling to the Schumann ultra-violet. Data are obtained for the effect of different discharge conditions. N. M. B.
- Accidental pre-dissociation in band spectra.** G. P. ITTMANN (*Naturwiss.*, 1934, 22, 118—119).—Theoretical. The perturbations of the band spectrum of  $N_2$  (3 $\pi$  state) noticed by Coster *et al.* (*A.*, 1933, 991) can be explained assuming accidental pre-dissociation. A. J. M.
- Active nitrogen and the auroral spectrum.** J. KAPLAN (*Nature*, 1934, 133, 331; cf. this vol., 125).—The spectrum of the afterglow of N now obtained is like that of the auroral spectrum except for the green auroral line. L. S. T.
- Mean lives of excited neon atoms.** J. H. E. GRIFFITHS (*Proc. Roy. Soc.*, 1934, A, 143, 588—604).—A method depending on the measurement of the lag which exists between the excitation and emission of light from atoms in a high-frequency discharge is used to find the average lives ( $T$ ) of six excited states of Ne. The vals. of  $T$  range from  $3.9 \times 10^{-8}$  sec. for the line 5853 to  $20 \times 10^{-8}$  sec. for 6402. Lines originating from the same upper level lead to the same val. of  $T$ . The method may be used for any substance of which the spectrum can be obtained from a high-frequency discharge. L. L. B.
- Isotope displacement and hyperfine structure in the arc spectra of chromium, molybdenum, and tungsten.** N. S. GRACE and K. R. MORE (*Physical Rev.*, 1934, [ii], 45, 166—169).—Structure is found for several stronger lines of Mo I and W I in the range 4000—6100 Å. The W I lines give three components with 0.1  $cm^{-1}$  overall displacement, attributed to isotope displacement of the even isotopes. Mo I lines give two components with 0.05  $cm^{-1}$  separation, attributed to spin splitting of the odd isotopes, and broad lines of 0.06  $cm^{-1}$  width attributed to a small isotope displacement.  $I=1/2$  is indicated for the odd isotopes of both Mo and W. N. M. B.
- Investigations in the Schumann region. III. Spectra of iron, cobalt, and nickel between 2000 and 1670 Å.** R. GRÄFIN ZU DOHNA (*Z. Physik*, 1934, 87, 616—632). A. B. D. C.
- New spectrum of zinc: Zn IV.** L. BLOCH and E. BLOCH (*Compt. rend.*, 1934, 198, 645—647).—Using the vac. spark spectrum, 133 lines (4039.34—2589.90) of Zn IV have been measured. This spectrum has no lines between 4900 and 4040, or beyond 2580 Å. (cf. *A.*, 1925, ii, 1100). C. A. S.
- Disruptive discharge produced by selenium.** V. BIANU (*Bul. Soc. Fiz. Român.*, 1933, No. 56, 1—6). R. T.
- Perturbation in the spectrum of Se II.** K. R. RAO and S. G. KRISHNAMURTI (*Nature*, 1934, 133, 328). L. S. T.
- Spectra of Br V, Br VI, and Br VII.** A. S. RAO and K. R. RAO (*Proc. Physical Soc.*, 1934, 46, 163—168).—Using a Siegbahn spectrograph, the lines of the vac. spark spectra of Br in the region  $\lambda\lambda$  1400—400, under different degrees of excitation, are classified and assigned to the different ionisation stages. Doublet combinations are established by the application of the regular and irregular doublet laws, and principal members involving the low-lying terms are identified. N. M. B.
- Reversibility of red line of cadmium.** A. PÉRARD (*Compt. rend.*, 1934, 198, 727—729).—An improved form of Cd-vapour lamp is described showing more readily the reversal of the Cd red line, and its resolution into two components. The possible error due to this makes the line of doubtful val. as an international standard of length. C. A. S.
- Fluorescence of vapour of iodine excited by circularly polarised light and viewed longitudinally.** R. DAURE and A. KASTLER (*Compt. rend.*, 1934, 198, 557—559; cf. *A.*, 1918, ii, 90). C. A. S.
- Nuclear moment of xenon.** H. KOPFERMANN and E. RINDAL (*Z. Physik*, 1934, 87, 460—469).— $X^{129}$  has a mechanical moment 1/2,  $X^{131}$  has 3/2, and the even isotopes showed no splitting. The ratio of the magnetic moments 129 : 131 is 1.1. A. B. D. C.
- Degree of polarisation of fluorescence of mercury vapour.** A. KASTLER (*Compt. rend.*, 1934, 198, 723—725; cf. *A.*, 1933, 992).—The degree of

polarisation produced in Hg vapour by light from a Hg arc in various states of polarisation and unpolarised (in the last case with a magnetic field in the direction of the incident beam) has been calc. The calc. result for the unpolarised beam agrees with the experimental, but varies greatly with temp.

C. A. S.

**Degree of polarisation of fluorescence of mercury vapour in presence of nitrogen.** A. KASTLER (Compt. rend., 1934, 198, 814—816; cf. preceding abstract).—Addition of N<sub>2</sub> (up to a pressure of 1—2 mm. Hg) increases the intensity of fluorescence 10—20 times, the result depending only on the fluorescence of  $\lambda$  4046 Å. Previous results and calculations are corr. (cf. A., 1931, 8; 1932, 208; 1933, 760).

C. A. S.

**Spark spectra of bismuth, Bi III and Bi II.** M. F. CRAWFORD and A. B. MCLAY (Proc. Roy. Soc., 1934, A, 143, 540—557; cf. A., 1932, 8).—An extended investigation of the term structures of Bi III and Bi II has been carried out. Term and classified wave-length tables are given, together with information on the hyperfine structures of the lines analysed.

L. L. B.

**Arc spectrum of radium.** E. RASMUSSEN (Z. Physik, 1934, 87, 607—615).—This spectrum was photographed from 10,000 to 3000 Å.; the ionisation potential is given as 5.176 volts.

A. B. D. C.

**Quenching of atomic thallium fluorescence by foreign gases.** N. A. PRILESHAeva (Compt. rend. Acad. Sci. U.R.S.S., 1933, 282—283).—Measurements of the decrease of the intensity of the fluorescence 5351 Å. line in the presence of foreign gases at 0—500 mm. pressure indicate the probability of reaction between the excited Tl atom and O<sub>2</sub> and CO<sub>2</sub>, and collisions of the second kind in presence of N<sub>2</sub>, CO, H<sub>2</sub>O, and A. No quenching is observed in presence of H<sub>2</sub>.

J. W. S.

**Absorption spectrum of thallium vapour in the short-wave ultra-violet.** G. S. KVATER, N. V. KREMENEVSKI, and A. N. FILIPPOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 111—112).—Measurements have been made using a 70-cm. column of Tl vapour, and lines and bands in the neighbourhood of 2000 Å. are discussed.

W. R. A.

**Nuclear spins and magnetic moments.** W. E. CURTIS (Nature, 1934, 133, 256).

L. S. T.

**Probe measurements in the positive column of inert gases.** K. SOMMERMEYER (Z. Physik, 1934, 87, 741—743).—Measurements of Seeliger and Hirschert (A., 1932, 105) have been repeated and extended, and the variation of the probe characteristic with probe length supports Pupp's theory (Physikal. Z., 1932, 33, 844) rather than that of disturbance of the Maxwell distribution.

A. B. D. C.

**Deviations from Paschen's law.** S. P. MCCALLUM and L. KLATZOW (Phil. Mag., 1934, [vii], 17, 291—297).—For most gases the sparking potential (I) between parallel plates depends on the product of the pressure  $p$  and the distance apart  $S$  of the electrodes. This applies to He, but with Ne, A, and Kr (I) increases with increase of  $S$  for const. vals. of  $pS$ . This is due to the diffusion of the electrons

perpendicular to the direction of the electric force, which in Ne and A is  $>$  in He.

H. S. P.

**Spectrum of the red stars of the  $M$  and  $N$  types.** G. PICCARDI (Atti R. Accad. Lincei, 1933, [vi], 17, 952—954).—Spectroscopic examination of the different regions of an O<sub>2</sub>-H<sub>2</sub> flame fed with TiCl<sub>3</sub> indicates that C<sub>2</sub> and TiO are never present together in any zone of the flame, and this may explain the similar behaviour in the spectra of the  $M$  and  $N$  red stars.

O. J. W.

**Influence of certain photographic errors on the profiles of absorption lines in stellar spectra.** C. T. ELVEY and (Miss) C. WESTGATE (J. Opt. Soc. Amer., 1934, 24, 43—50).—The influence of the Eberhard effect was investigated by the measurement, under various conditions of exposure, density, and development, of the depression of the background at the edge of an image, due to the inhibiting action of the products of development.

N. M. B.

**Spectroscopic observations of the variable star RS Ophiuchi (Nova Opchiuchi n. 3).** A. COLACEVICH (Atti R. Accad. Lincei, 1933, [vi], 18, 307—310).—The intensities of the spectral lines of this star have been measured, and many of the lines identified.

O. J. W.

**Electrical nature of iron sparks emitted from a grinding wheel.** U. NAKAYA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 23, 185—201).—The charge is positive at first, and changes to negative. Both positive and negative ions are emitted, at a rate of 10<sup>-2</sup> to 10<sup>-3</sup> e.s.u. per cm.

C. W. G.

**Limits of validity of the Klein-Nishina formula.** M. BRONSTEIN (Compt. rend. Acad. Sci. U.R.S.S., 1933, 273—275).—The formula is more limited in its applicability than is indicated by Bohr (Atti Conv. Fis. Nucl., 1932, 125).

J. W. S.

**X-Ray absorption spectra of the Au-Cu alloy.** T. HAYASI (Naturwiss., 1934, 22, 90).—The absorption max. of the Au L<sub>111</sub> spectrum of Au correspond with the Cu K absorption min. of the Au-Cu alloy. The absorption min. of the first also correspond with the absorption max. of the second. Similarly, relationships are found with the Cu K absorption spectrum of pure Cu and the Au L<sub>111</sub> spectrum of the alloy.

A. J. M.

**Structure of K-rays of light atoms. II.** A. HAUTOT (J. Phys. Radium, 1934, [vii], 5, 20—26; cf. A., 1933, 656, 760).—Previous results for O<sub>2</sub>, N<sub>2</sub>, C, B, and Be are amplified with improved apparatus.

N. M. B.

**Measurements of the K-absorption edges of carbon, nitrogen, and oxygen, and of the components of carbon K $\alpha$ .** F. C. CHALKLIN and L. P. CHALKLIN (Phil. Mag., 1934, [vii], 17, 544—553).

H. J. E.

**Fine structure of the K $\alpha$  line of beryllium.** F. C. CHALKLIN (Nature, 1934, 133, 293—294).

L. S. T.

**X-Ray spectra of the L series of silicon and silica.** M. SIEGBAHN and T. MAGNUSSON (Nature, 1934, 133, 257; cf. this vol., 125).—Si exhibits a broad band containing max. at 134.3±0.5 and

138.2±0.5 Å. with a sharp limit towards the shorter wave-lengths. SiO<sub>2</sub> gives a spectrogram of a different character with strong lines at 130.7 and 139.5 Å. and a broader, fainter line at 162 Å. L. S. T.

**Extension of X-ray spectrography. Curved crystal focussing spectrograph. X-Ray emission spectra of gases.** (MLLE.) Y. CAUCHOIS (Ann. Physique, 1934, [xi], 1, 215—266).—Using a curved-crystal spectrograph previously described (cf. A., 1932, 246) results are obtained for the K spectrum of Kr excited in a separate tube by an electron stream from a high-power Lennard-Coolidge tube. N. M. B.

**Ionisation of the K shell by electron collision.** D. G. SODEN (Ann. Physik, 1934, [v], 19, 409—433).—Theoretical. A. J. M.

**Inner conversion in X-ray spectra.** M. N. SAHA and J. B. MUKERJIE (Nature, 1934, 133, 377).—Inner conversion is responsible for many of the intensity anomalies observed in X-ray line spectra. L. S. T.

**Ionisation of caesium vapour by ultra-violet light.** J. KUNZ (Phil. Mag., 1934, [vii], 17, 483—491).—Measurements have been made at 25°, 75°, and 125° and with wave-lengths 3130, 2800, and 2537 Å. of the coulombs liberated per erg of the incident beam. The at. ionisation coeff. has a max. at the ionisation limit (3184 Å.), and a min. at 2800 Å. H. J. E.

**Ionisation by collision in helium.** J. S. TOWNSEND and S. P. MACCALLUM (Phil. Mag., 1934, [vii], 17, 678—698).—The coeffs. of ionisation have been measured and compared with vals. for Ne (cf. A., 1928, 567). Traces of impurities give similar effects for Ne and He. H. J. E.

**Theory of Dirac's magnetic electron.** L. DE BROGLIE (Arch. Sci. phys. nat., 1933, [v], 15, 465—483).

**Theory of the positive electron.** V. FOCK (Compt. rend. Acad. Sci. U.R.S.S., 1933, 267—271).—Mathematical. J. W. S.

**Scattering and absorption of positive electrons traversing matter.** J. THIBAUD and F. D. LA TOUR (Compt. rend., 1934, 198, 805—808; cf. this vol., 126).—Application of the method used in the case of Pt to screens of seventeen other elements shows that the range of positrons is generally equiv. to a passage through matter amounting to < 500 mg. per sq. cm., and  $\mu/\rho$  is approx. const. = 8.5. This val. is also obtained by the same method for negative electrons. Both behave alike until the positrons, after losing most of their kinetic energy, begin to dematerialise. C. A. S.

**Dematerialisation of positive electrons.** J. THIBAUD (Compt. rend., 1934, 198, 562—564; cf. this vol., 126).—The conclusion as to the dematerialisation of positrons is substantiated by the facts that: (1) photographs show that the well-defined tracks of the positrons end in secondary radiation (photons) spreading in every direction; (2) the yield in photons is < 1, and more probably is 2 per positron, and such yield from a particle that has lost most of its kinetic

energy must be due to dematerialisation; and (3) a modification of the author's magnetic method shows the absorption of positrons of range 1—5×10<sup>2</sup> cm. (in air at ordinary pressure) to be exponential with  $\mu/\rho=8.5$ . Joliot's results (cf. *loc. cit.*) are adversely criticised as due to cosmic radiation. C. A. S.

**Designation of the positive electron.** H. DINGLE (Nature, 1934, 133, 330). L. S. T.

**Positron.** C. D. ANDERSON (Nature, 1934, 133, 313—316).—An address. L. S. T.

**Radiation and ionisation produced by high-energy electrons.** A. BRAMLEY (Nature, 1934, 133, 259). L. S. T.

**External emission potential  $W_a$ .** F. ROTHER and H. BOMKE (Z. Physik, 1934, 87, 806—809).—Electron diffraction measurements do not lead to vals. of  $W_a$ . This const. is 3.68 volts for Zn, and metals of higher valency have on the average one free electron per atom (cf. this vol., 3). A. B. D. C.

**Contrasting properties of ions, zwitterions, and uncharged molecules.** E. J. COHN (Science, 1934, 79, 83—84). L. S. T.

**Field combinations in velocity- and mass-spectrography.** I. W. HENNEBERG (Ann. Physik, 1934, [v], 19, 335—344).—Mathematical. The work of Bartky and Dempster (A., 1929, 863, 972) on the conditions for focussing positive rays is extended. The paths of charged particles in a homogeneous magnetic field and in the electric field of a cylindrical condenser are considered as regards focus, dispersion, and mass-separation. A. J. M.

**Theoretical investigation of the mass-spectrometer without magnetic field.** R. HERZOG and J. MATTAUCH (Ann. Physik, 1934, [v], 19, 345—386).—The theory of the mass-spectrometer of Smythe and Mattauch (A., 1932, 668) which uses two high-frequency fields instead of the magnetic field of the ordinary spectrograph is discussed. A. J. M.

**Deposits of elements by high-frequency discharge.** D. BANERJI and D. BHATTACHARYA (Phil. Mag., 1934, [vii], 17, 313—316). H. S. P.

**At. wt. of lithium.** M. HŁASKO and J. KUSZPECIŃSKA (Rocz. Chem., 1934, 14, 1—9).—Na and K were separated from Li<sub>2</sub>CO<sub>3</sub> (I) by extracting the LiCl prepared from (I) with 1:1 EtOH-H<sub>2</sub>O saturated with HCl. The LiCl so obtained still contained Fe, from which it was freed by conversion into (I), of which solutions saturated at 0° were heated at 100° in Pt vessels. The at. wt. of Li in LiCl prepared from (I) so pptd. is 6.934±0.001. R. T.

**Constitution of dysprosium, holmium, erbium, thulium, ytterbium, and lutecium.** F. W. ASTON (Nature, 1934, 133, 327).—Dy (66) consists of 161, 162, 163, and 164 in approx. equal relative abundance; Ho (67) is simple 165; Er gives three strong lines 166, 167, 168, and a weak fourth 170; Tm (69) is simple 169; Yb (70) appears to contain 171, 172, 173, 174, and 176, of which 174 is the strongest; and Lu (71) is simple 175. None of these

elements shows isobares. International vals for the at. wts. of several of the rare earths need revision.

L. S. T.

**Designation of heavy hydrogen.** N. V. SIDGWICK (Nature, 1934, 133, 256).

L. S. T.

**Nomenclature for the isotopes of hydrogen (proto- and deuto-hydrogen) and their compounds.** W. D. HARKINS (Science, 1934, 79, 138—140).

L. S. T.

**Isotopic nomenclature.** J. B. FICKLEN (Science, 1934, 79, 140).

L. S. T.

**Artificial disintegration of magnesium by polonium  $\alpha$ -rays.** H. KLARMANN (Z. Physik, 1934, 87, 411—424).—Four proton groups were observed, at least one of which is a resonance group.

A. B. D. C.

**Relative velocities of the  $\alpha$ -particles from radon, radium -A, and radium -C'.** G. H. BRIGGS (Proc. Roy. Soc., 1934, A, 143, 604—617).—Using the direct deflexion method, the relative velocities of the  $\alpha$ -particles from Rn, Ra-A, and Ra-C' have been measured with a probable error of 1 in  $8 \times 10^4$ . The vals. found for Rn and Ra-A are  $>$  those found by other observers.

L. L. B.

**Emission of corpuscular rays ( $\beta$ -rays and positrons) and the symmetry between corpuscles and anti-corpuscles.** J. L. DESTOUCHES (Compt. rend., 1934, 198, 467—471).—Wave mechanics are applied to demonstrate a theorem whereby the probability of the emission or absorption of a particle by an at. nucleus can be calc. This is applied to Joliot's "new form of radioactivity," and the corpuscle and anti-corpuscle, and also implies that the neutrino and antineutrino are physically indistinguishable (cf. this vol., 127, 234, 236).

C. H. S.

**$\beta$ -Spectrum of Th-B+C+C'.** K. C. WANG (Z. Physik, 1934, 87, 633—646).— $\beta$ -Spectra of Th-B+C+C' and of Th-C+C' were observed to determine the relative intensity of the most intense groups and the end of the primary spectra of Th-B and Th-C'.

A. B. D. C.

**Calculation of internal conversion coefficients of  $\gamma$ -rays.** J. B. FISK (Proc. Roy. Soc., 1934, A, 143, 674—678).—The internal conversion coeff. of  $\gamma$ -rays has been calc. for the  $L_1$  shell of Ra-C, applying Taylor and Mott's theory (A., 1933, 1224). Previous results for the K shell have been corrected and extended, and limiting vals. for very soft  $\gamma$ -rays for the K and  $L_1$  shells, quadripole and dipole, have been obtained.

L. L. B.

**Anomalous absorption of high-energy  $\gamma$ -radiation.** II, III. L. H. GRAY and G. T. P. TARRANT (Proc. Roy. Soc., 1934, A, 143, 681—706, 706—724; cf. A., 1932, 791).—II. The results of experiments on the absorption of the secondary  $\gamma$ -radiation emitted by at. nuclei when irradiated with very high-energy  $\gamma$ -radiation are discussed. There is definite experimental ground for rejecting any hypothesis which implies that the major portion of the emission is a "characteristic radiation" of the absorbing system.

III. Experiments are described which show that the whole of the energy of the high-frequency  $\gamma$ -radiation absorbed by a nucleus is re-emitted by it as secondary

radiation. This holds for all elements investigated (C, K, Cu, Fe, Sn, and Pb) with Th-C' radiation. This secondary radiation consists mainly of a radiation of energy  $< 0.5 \times 10^6$  ev. The assumption of isotropic emission from which this result follows is justified between  $60^\circ$  and  $145^\circ$ .

L. L. B.

**Secondary radiation of hard  $\gamma$ -rays.** W. BOTHE and W. HORN (Naturwiss., 1934, 22, 106—107).—The intensity of secondary radiation emitted when hard  $\gamma$ -rays from Th-C' ( $4.7$  X) fell on thin layers of scattering substances has been measured. For the lightest elements pure Compton radiation only was present, but for the higher elements an additional strongly anisotropic radiation was produced. The intensity of this additional radiation at  $90^\circ$  is proportional to the at. no. of the target. At  $114^\circ$ , thin graphite and Pb gave pure Compton radiation, but with greater thicknesses hard secondary radiation was produced, due to multiple scattering of the primary rays in the material of the target. For a 3-cm. thickness of Pb, however, a secondary radiation, of which the hardness approached that of the primary radiation, was produced, which was not due to multiple scattering.

A. J. M.

**Equations of motion of a neutron.** W. M. ELSASSER (Compt. rend., 1934, 198, 441—443).—Mathematical.

C. A. S.

**Experiments with neutrons.** L. MEITNER and K. PHILIPP (Z. Physik, 1934, 87, 484—497).—The neutron-proton collision is spherically symmetrical, and the effective cross-section depends on the neutron velocity. Neutron- $N_2$  collisions were also investigated, and the mass of the neutron is deduced to be 1.0056.

A. B. D. C.

**Corpuscular radiation from atomic disintegration of lithium by rapid protons.** K. DIEBNER and G. HOFFMANN (Naturwiss., 1934, 22, 119).—A new determination confirms the result of Rutherford and Oliphant that for protons of 70 kv., the ranges of the groups of  $\alpha$ -particles emitted are 1.8 and 4.0 cm. Proton groups of ranges between 15 and 21 cm. were also found. The emission of  $\alpha$ -rays commences when Li is bombarded with protons of 34 kv.

A. J. M.

**Bombardment of the heavy isotope of hydrogen by  $\alpha$ -particles.** (LORD) RUTHERFORD and A. E. KEMPTON (Proc. Roy. Soc., 1934, A, 143, 724—730).—Experiments to test whether the dipton can be broken up into a neutron and proton by the bombardment of  $H_2^+$  by the  $\alpha$ -particles from Po gave inconclusive results. The no. of neutrons, if any, was  $< 1$  in  $10^7$  of the no. of  $\alpha$ -particles. The stopping power of the  $\alpha$ -particles from Po is the same in  $H_2^+$  as in  $H_2$ . It is deduced that the max. range of recoil in air of the dipton in a head-on collision with an  $\alpha$ -particle should be about 7%  $>$  that of the proton; this is in agreement with experiment. No difference could be detected between the scattering of  $\alpha$ -particles by  $H_2^+$  and by  $H_2$ , and it is concluded that the fields of force surrounding the dipton and the proton are the same.

L. L. B.

**Production of induced radioactivity by high-velocity protons.** J. D. COCKROFT, C. W. GILBERT, and E. T. S. WALTON (Nature, 1934, 133, 328).

—Bombardment of an Acheson graphite target by protons of 600 kv. energy and examination by a Geiger counter for radiations (I) after the bombardment had ceased showed that the no. of counts (II) was increased approx. 40 times the natural effect. (II) decayed exponentially with time and the half-life period (III) is  $10.5 \pm 0.5$  min. (I) consist, in part at least, of positive particles. The results suggest that the unstable isotope  $N^{13}$  is produced by the addition of a proton to  $C^{12}$ . The difference between the (III) observed and the val. obtained by Curie and Joliot (this vol., 234) may be due to the formation of  $N^{13}$  in a different excited state. No marked increase in (II) resulted when a mixed beam of heavy H ions and protons replaced the proton beam. L. S. T.

Disintegration of the separated isotopes of lithium by protons and by heavy hydrogen. M. L. OLIPHANT, E. S. SHIRE, and B. M. CROWTHER (Nature, 1934, 133, 377; cf. A., 1933, 1100).— $Li^6$  and  $Li^7$  have been separated by two methods depending on the passage of Li ions through electric and magnetic fields. After fixation of the separated isotopes on metal discs by HCl, bombardment by protons (I) and deuterons (II) revealed several hundred disintegration particles per min. from  $Li^7$  and about half this no. from  $Li^6$ . With (I),  $Li^6$  gives  $\alpha$ -particles of 11.5 cm. range, and  $Li^7$   $\alpha$ -particles of 8.4 cm. range; with (II),  $Li^6$  gives  $\alpha$ -particles of 13.2 cm. range and protons of 30 cm. range, whilst  $Li^7$  gives  $\alpha$ -particles up to 8 cm. range and neutrons. L. S. T.

Chemical separation of new positive electron-emitting radioelements. (MME.) I. CURIE and F. JOLIOT (Compt. rend., 1934, 198, 559—561; cf. this vol., 234).—The probable formation of radioactive, positron-emitting  $N^{13}$ ,  $Si^{27}$ , and  $P^{30}$  (for which the names *radio-nitrogen*, *-silicon*, and *-phosphorus* are proposed) by capture of  $\alpha$ -particles from Po by B, Mg, and Al, respectively, is supported by chemical examination of irradiated BN and Al. The radioelement from B behaved like N, that from Al as P. C. A. S.

Representation of nuclear transformations. G. PÉTIAT (Compt. rend., 1934, 198, 564—566).—Theoretical (cf. A., 1933, 1224; this vol., 236). C. A. S.

Half-value period of uranium. II. O. A. GRATIAS (Phil. Mag., 1934, [vii], 17, 491—496).— $U_{II}$ , produced by decay of  $U-X_1$ , is not completely separated by electrolysis (cf. Collie, A., 1931, 891).  $U_{II}$  recovered from the solution and separated from  $U-X_1$  and  $Io$  had a half-val. period of  $1.70 \times 10^5$  years. H. J. E.

Half-value period of radium-D. E. WALLING (Z. Physik, 1934, 87, 603—606).—This is given as 22.3 years with an error  $\pm 2\%$ . A. B. D. C.

Diffusion coefficient of radium emanation. N. MORTARA (Atti R. Accad. Lincei, 1933, [vi], 17, 949—951).—The diffusion coeff. is found to be 0.11. O. J. W.

Distribution of radium in crystals of radiferous barium bromide. B. E. MARQUES (Compt. rend., 1934, 198, 819—821; cf. this vol., 22).—There is a marked decrease in the relative amount of Ra from the centre to the periphery of such crystals (cf. A., 1929, 132). C. A. S.

Decomposition of lead atoms. A. SMITS, (FRL.) H. S. V. MEINESZ, (FRL.) J. A. A. KRUGER, and H. G. ROEBERSEN (Z. Elektrochem., 1934, 40, 71—73).—Irradiation of Pb plates by X-rays in air renders them active, but not so Al plates. An air current has no effect on the activity, which seems to exclude the possibility of its being due to radioactive dust. No activation could be obtained in a vac., and later experiments gave none in air. Irradiation with sunlight gave doubtful results. M. S. B.

Steady states produced by radiation with application to the distribution of atmospheric ozone. O. R. WULF (Phil. Mag., 1934, [vii], 17, 251—263).—Theoretical. The equilibrium distribution of  $O_3$  in the earth's atm. due to the absorption of radiation is calc., mechanical transport of the gases being neglected. The  $O_3$  will not occur in a layer, but be spread over a range of altitude. Calculations are also made regarding stellar atm. H. S. P.

Contemporary knowledge of cosmic rays. P. AUGER (J. Phys. Radium, 1934, [vii], 5, 1—5).—A concise summary of available data and explanatory hypotheses. N. M. B.

Three types of cosmic-ray fluctuations and their significance. R. A. MILLIKAN, C. D. ANDERSON, and H. V. NEHER (Physical Rev., 1934, [ii], 45, 141—143).—A theory of cosmic-ray bursts attributes the released energy to the battery which charges the electroscope. Assuming the remainder of the observed ionisation to be due to positrons and "negatrons," fluctuations due to random distribution of these electron shots, and hence the % of cosmic ray "showers," can be computed. N. M. B.

Nature of statistical fluctuations with applications to cosmic rays. R. D. EVANS (Physical Rev., 1934, [ii], 45, 144—151).—Mathematical. The effect of random processes in relation to ionisation chambers and counters is investigated. N. M. B.

Fluctuations of cosmic rays. III. W. MESSERSCHMIDT (Z. Physik, 1934, 87, 800—805).—Daily fluctuations are recorded. A. B. D. C.

Quantum mechanics of photons. Pauli's approximation. A. PROCA (Compt. rend., 1934, 198, 452—454; cf. this vol., 236).—Mathematical. As an interpretation of negative energy of a particle, photon, or electron, it is suggested that its sign must indicate merely the direction of rotation of some component of a field attached to the particle. C. A. S.

Particles which can be associated with propagation of a light wave. A. PROCA (Compt. rend., 1934, 198, 643—645; cf. this vol., 236).—It is shown mathematically that a free particle, of zero mass when in repose, and according to Dirac's equations, can be associated with every group of light waves subject to Maxwell's equations. Such a particle, in a state in which its energy is  $h\nu$ , corresponds with circularly polarised light of frequency  $\nu$ , which is dextro if the energy of the particle is positive, lævo if negative. The particle is not a photon, as its spin is  $0.5h/2\pi$ , but it resembles Pauli's neutrino, which, coupled with an antineutrino, gives a photon. C. A. S.

**Waves and photons. I. Schrödinger approximation.** A. PROCA (J. Phys. Radium, 1934, [vii], 5, 6—19).—Mathematical. An attempt to establish a theory of photons in configuration space, with a view of eliminating difficulties in radiation theory, leads to three types of approximation analogous to those of Dirac, Pauli, and Schrödinger, of which the last-named, examined here, shows that classical energy density expression is true only to a first approximation and is inapplicable to light.

N. M. B.

**Hydrogen molecule ion.** G. JAFFÉ (Z. Physik, 1934, 87, 535—544).—The  $\xi$  equation is solved in the form of a convergent power series.

A. B. D. C.

**Calculations of atomic wave functions. II.  $K^+$  and  $Cs^+$ .** D. R. HARTREE (Proc. Roy. Soc., 1934, A, 143, 506—517).—The results of calculations of at. wave functions by the method of the "self-consistent field" (cf. A., 1933, 1101) are given for  $K^+$  and  $Cs^+$ , together with some additional results for  $Cu^+$ .

L. L. B.

**Relation of the  $H$  function and entropy according to Fermi statistics.** M. SATÔ (Z. Physik, 1934, 87, 498—499).—The ordinary relation holds.

A. B. D. C.

**Elementary indeterminacy, limit of the periodic system, and the mass ratio of the electron and proton.** W. GLASER and K. SITTE (Z. Physik, 1934, 87, 674—685).—The limit of ninety-two chemical elements is shown to follow from an elementary indeterminacy in time. Assuming the neutron to be a quantum-mechanical system of proton and electron, the elementary indeterminacy gives the electron-proton mass ratio.

A. B. D. C.

**Constitution of heavy nuclei.** A. SCHIDLÖF (Arch. Sci. phys. nat., 1933, [v], 15, Suppl., 223—227).—Theoretical.

R. S.

**Molecular and micellar dissymmetry.** C. E. GUYE (Arch. Sci. phys. nat., [v], 15, Suppl., 219—223).

R. S.

**Self forces of elementary particles. III.** G. WENTZEL (Z. Physik, 1934, 87, 726—733).—Theoretical.

A. B. D. C.

**Value of  $e/m$ .** W. N. BOND (Nature, 1934, 133, 327).

L. S. T.

**Gratings as an aid to photographic spectrophotometry.** R. LANDWEHR (Z. Physik, 1934, 87, 447—459).—The method of Hertzprung and Merton of using a coarse grating crossed with the normal dispersion apparatus to give a series of lines of varying intensity for each original line has been developed.

A. B. D. C.

**Resonance excitation of the thallium spectrum in thallium halide vapour.** G. G. NEUJMIN (Compt. rend. Acad. Sci., U.R.S.S., 1933, 213—214).—On illuminating TlX vapours with ultra-violet light, emission lines of the metal were observed which could not be ascribed to photo-dissociation of the TlX. The intensities of these lines were dependent on the intensity of the exciting light; the exciting wavelengths differ for each energy level, and lie near to

an absorption line of Tl. A probable explanation is suggested.

W. R. A.

**Spectrum of  $F_2O$ .** A. GLISSMANN and H. J. SCHUMACHER (Z. physikal. Chem., 1934, B, 24, 328—334).—Absorption starts at about 5400 Å., and is still very strong at 2100 Å. It is continuous, and exhibits several max. It is concluded that the whole absorption region corresponds with primary dissociation into  $F_2+O$  or  $F+FO$ ; a max. below 2100 Å. may indicate dissociation into three atoms. Light absorption is accompanied by decomp. with formation of O, much of the F formed yielding, in quartz,  $SiF_4$  and O.

R. C.

**Measurements of the intensity and width of predissociation lines of the AlH molecule.** H. C. BURGER and P. H. VAN CITTERT (Z. Physik, 1934, 87, 545—546).—Farkas and Levy (A., 1933, 879) have omitted the "apparatus width" in their observations on these lines.

A. B. D. C.

**Band spectrum of phosphorus nitride.** P. N. GHOSH and A. C. DATTA (Z. Physik, 1934, 87, 500—504).—Observations are given in agreement with Curry, L. Herzberg, and G. Herzberg (cf. this vol., 7).

A. B. D. C.

**Spectrum of gadolinium oxide.** G. PICCARDI (Gazzetta, 1933, 63, 887—898).—The flame spectrum of GdO between 4462 and 6272 Å. is recorded and the lines are classified. The emission is due to the GdO mol. A new spectrum in the blue (4614—4854 Å.) and several new bands in the red are described. The blue system is relatively sensitive to temp. changes.

H. F. G.

**Rotational analysis of the absorption bands of  $ICl$ .** W. E. CURTIS and J. PATKOWSKI (Phil. Trans., 1934, A, 232, 395—430).—Analyses of twelve bands of the progressions ( $v''=0, 1, 2$ ) and each consisting of  $P, Q,$  and  $R$  branches are tabulated. The rotation const.  $B$  is determined for each state. Band origins are established. A very small  $\Lambda$  type doubling is found, and its variation with  $J$  is examined. Relationships between rotational and vibrational consts. are tested, and vals. of the chief consts. are found.

N. M. B.

**Thermo-optical dissociation of sulphur dioxide.** K. WIELAND (Trans. Faraday Soc., 1934, 30, 260—265).—The absorption spectrum of  $SO_2$  vapour at  $<450^\circ$  has been extended to 1600 Å. Light from the  $H_2$  lamp does not cause decomp. at room temp., but above  $300^\circ$ , parallel with the fading of the  $SO_2$  bands, two systems of bands due to  $S_2$  develop in the ranges 2850—2570 Å. and 1800—1650 Å. (strong). The changes are reversed by fall of temp. Since the reaction  $SO_2 \rightarrow 1/2S_2 + O_2$  requires 83 kg.-cal., the net thermo-optical dissociation  $SO_2 \rightarrow 1/6S_2 + 4/6SO_3$  (requires 12.6 kg.-cal.) is more probable (cf. A., 1933, 6).

J. G. A. G.

**Absolute values of the optical absorption constants of crystals of the alkali halides in the region of their ultra-violet characteristic frequency.** G. BAUER (Ann. Physik, 1934, [v], 19, 434—464).—The absorption consts. of vaporised layers of NaBr, KBr, and KI were determined in the neighbourhood of the first ultra-violet absorption

band. The mechanism of the absorption is discussed on the basis of electro-magnetic theory. A. J. M.

**Titanium oxide and zirconium oxide bands in stellar spectra.** R. S. RICHARDSON (Astrophys. J., 1933, 78, 354—358).—The % of ZrO and TiO mols. dissociated at different temp. and pressures has been calc. L. S. T.

**Red titanium oxide system in  $\alpha_1$  Herculis.** N. T. BOBROVNIKOFF (Astrophys. J., 1933, 78, 211—218).—66 bands, 11 of which have not been observed in the laboratory, have been measured between 6292 and 8506 Å. in the spectrum of the red system of TiO. L. S. T.

**Photographic measurement of the transmission of fluorite in the extreme ultra-violet.** E. G. SCHNEIDER (Physical Rev., 1934, [ii], 45, 152—153).—Transmission measurements by photographic methods and by a photo-electric cell are compared for the range 1600—1240 Å. (cf. following abstract). N. M. B.

**Photo-electric measurements of the transmission of fluorite in the Schumann region.** W. M. POWELL, jun. (Physical Rev., 1934, [ii], 45, 154—157).—Transmission coeffs. and the ratio intensity of light entering cell/current from cell were measured at ten wave-lengths in the range 1600—1235 Å. N. M. B.

**Thermo-luminescence spectra of fluorites. IV. Spectra restored by X-rays.** E. IWASE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 23, 212—223; cf. this vol., 130).—Fluorites can be classified as those which, after heating, (a) are restored by X-rays to their original condition, (b) give the same bands, but of different relative intensities, (c) give new bands. C. W. G.

**Cathodo-luminescence spectra of fluorites, calcites, and certain synthesised phosphors containing samarium.** J. YOSHIMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 23, 224—247).—Green fluorites generally contain more rare earths than those of other colours. C. W. G.

**Polyatomic molecules. Structure and activation of benzaldehyde. III. Optical properties of the benzaldehyde molecule.** F. ALMASY (J. Chim. phys., 1933, 30, 713—725; cf. A., 1929, 409).—The absorption spectra of the vapour and solutions in  $n$ -C<sub>6</sub>H<sub>14</sub> are very similar, and consist of three regions. The frequencies of the vibrational terms correspond with those of the Raman and infra-red spectra. As the temp. is raised to 270° the narrow bands change over to a continuous spectrum and photo-dissociation occurs. At 270°, radiation below  $\lambda$  3200 produces dissociation, but that  $< \lambda$  2438 gives photochemical decomp. into CO and C<sub>6</sub>H<sub>6</sub> at room temp. J. G. A. G.

**Ultra-violet absorption spectra of some aromatic substances. I.** A. HILLMER and P. SCHORNING (Z. physikal. Chem., 1934, 167, 407—420).—The effect on the absorption spectrum of the introduction into C<sub>6</sub>H<sub>6</sub>, PhPr<sup>3</sup>, allyl- and propenyl-benzene of one or two phenolic OH or alkoxy groups into the *o*-positions has been studied. R. C.

**Determination of the light transmission of anisotropic melts of *p*-azoxyanisole in magnetic**

**fields. Swarm theory of liquid crystals.** W. KAST and L. S. ORNSTEIN (Z. Physik, 1934, 87, 763—767).—Determination of this light transmission immediately a magnetic field is removed shows that orientation imposed by the field is destroyed in accordance with the swarm theory. A. B. D. C.

**Infra-red absorption spectra of nitrogen dioxide and tetroxide.** L. HARRIS and G. W. KING (J. Chem. Physics, 1934, 2, 51—57).—Data are given for new bands in the region 1.9—4  $\mu$  for NO<sub>2</sub>, analysed as combinations of two fundamentals, and for N<sub>2</sub>O<sub>4</sub>, interpreted as combinations and harmonics of reported fundamentals. The spectrum demands models in which the NO<sub>2</sub> groups are joined by the N atoms, and there is evidence for non-planar arrangement of the NO<sub>2</sub> groups in the mol. N. M. B.

**Infra-red absorption spectra, and the structure of polyatomic molecules.** R. TITEICA (Bul. Soc. Fiz. Român., 1933, No. 57, 31—38).—Data are given for the infra-red absorption spectra of MeOH, EtOH (cf. A., 1933, 337), and COMe<sub>3</sub>, in the low-pressure gaseous condition, and the results have been compared with the Raman spectra, and with those calc. from Mecke's formula (Leipzig Vorträge, 1931). The distances C—C=1.50 Å., and the angle of C—C—C=127°. R. T.

**Infra-red absorption of stereoisomeric 1:2-dimethylcyclohexanes.** O. MILLER and J. LECOMTE (Compt. rend., 1934, 198, 812—813; cf. A., 1933, 815, 990).—The infra-red absorption spectra (333—1455 Å.) of the *cis*- and *trans*-isomerides differ markedly *inter se*, and from their Raman spectra. C. A. S.

**Reflexion spectrum of quartz in the region of 9  $\mu$ .** S. SILVERMAN (Physical Rev., 1934, [ii], 45, 158—160; cf. A., 1931, 408).—Previous work is extended, using polarised light and a crystal cut parallel to the optic axis. Complex fine structure was found. N. M. B.

**Rotational Raman effect in liquids.** S. BHAGAVANTAM (Indian J. Physics, 1933, 8, 197—207).—The intensity distribution in the rotational Raman spectra of C<sub>6</sub>H<sub>6</sub>, HCO<sub>2</sub>H, and molten salol are not in accord with any existing theory. Regarding the liquid state as consisting partly of gas mols. and partly of solid mols., and applying Pauling's theory (A., 1930, 1357) for determining the state of motion of mols. in a solid, it is concluded that liquids are of two types. In the first type (H<sub>2</sub>, HCl, O<sub>2</sub>, N<sub>2</sub>, etc.) the intensity distribution should accord with the gas laws; in the second type neither the intensity nor its distribution can be predicted from the gas laws, the patterns being due to internal oscillations in the liquid similar to those existing in a solid. J. W. S.

**Molecular scattering of light in liquids.** E. CANALS, (MLLE.) G. CAUQUIL, and P. PEYROT (Compt. rend., 1934, 198, 471—473; cf. A., 1926, 559).—The depolarisation factor,  $\rho$ , for Hg light filtered through quinine sulphate and scattered at 90° to the incident beam, has been determined for twelve cyclanes, twelve cyclenes, ten alkyl halides or esters, and three other compounds. Few generalisations are possible:

$\rho$  for the cyclanes (0.077—0.222) is definitely  $<$  for the cyclenes (0.222—0.375), and the variations point to a non-planar configuration for both. Introduction of an alkyl group generally increases  $\rho$ . C. A. S.

**Raman effect. XXXI. Raman spectrum of organic substances. (Multi-substituted benzenes. III.)** K. W. F. KOHLRAUSCH (Monatsh., 1933, 63, 427—444).—Data are given for *o*-, *m*-, *p*-compounds of the type  $C_6H_4MeX$ , where X is Me,  $NH_2$ , OH, CN, F, Cl, Br, I,  $CO_2Me$ , or  $CO_2Et$ .

E. S. H.

**Raman effect in nitrobenzene.** H. F. HERTLEIN (Z. Physik, 1934, 87, 744—748).—The sharp change in dielectric const. observed by Wolfke and Mazur (A., 1932, 329) just above the m.p. of  $PhNO_2$  is not reflected in the Raman spectrum, and the two phases cannot therefore differ in at. structure.

A. B. D. C.

**Raman effect. XXIX. Raman spectra of halogen acetic esters.** H. C. CHENG (Z. physikal. Chem., 1934, B, 24, 293—312; cf. A., 1933, 1228).—From a study of the esters of chloro- and bromo-acetic acids frequencies have been assigned to various groups. If in  $X\cdot CO_2R$  ( $X=H$  or Me) X is replaced by Cl, the frequency of the CO group is increased considerably, but if the Cl is separated from the CO by  $CH_2$ , the increase is slight, and the introduction of two or three Cl atoms is required to produce a notable increase. With progressive substitution of  $CO_2Et$  for H in  $EtOAc$  the frequency of the CO group rises steadily, whereas substitution by Me causes a continual fall. The CO frequencies of all the  $Pr^s$  esters lie below the average val. for normal ester chains. The results in general justify the assumption that the spectrum of  $X\cdot CO_2R$  consists of the superimposed partial spectra of  $\bar{X}$ , CO, and OR. R. C.

**Molecular scattering of light in fluorescent liquids. [Determination of quinine.]** E. CANALS and P. PEYROT (Compt. rend., 1934, 198, 746—749).—With dil.  $H_2SO_4$  solutions of quinine sulphate of const.  $\rho_H$  (2), but varying concn. in quinine, at  $18^\circ$ , and a quartz-Hg lamp (cf. A., 1927, 932) the depolarisation factor,  $\rho$ , is const., whilst the intensity of fluorescence is proportional to  $c$  and obeys Vavilov's law (cf. A., 1925, ii, 474). The proportionality is such that the method may be used for the determination of small amounts of quinine. C. A. S.

**Circular polarisation of Raman lines of pinene illuminated by circularly polarised light and observed longitudinally.** P. DAURE (Compt. rend., 1934, 198, 725—727; cf. A., 1930, 1498; 1932, 212).—The ratio of the intensities of the light polarised in the reverse and same directions as that of the incident beam has been determined visually for forty-four lines ( $\Delta\nu=139$ —1659  $cm^{-1}$ ). It varies for the different lines, but is independent of the direction of rotation of the incident beam. C. A. S.

**Scattering of light and molecular polymorphism.** R. LUCAS (Compt. rend., 1934, 198, 721—722).—It is suggested that, as in the case of rotatory power etc., polymorphism will affect scattering by a liquid, and in the case of Raman spectra will increase the no. and modify the relative intensities

of the lines, and that this explains the anomalies observed in the case of  $C_6H_6$  (cf. A., 1927, 295; 1933, 889; this vol., 132). C. A. S.

**Fine structure of the Rayleigh radiation.** W. RAMM (Physikal. Z., 1934, 35, 111—113; cf. A., 1932, 445).—The fine structure of the radiation emitted when monochromatic light is scattered by  $PhMo$  and  $CS_2$  has been studied. Lines displaced towards the red and blue, respectively, have been found, as required by theory. Their distance from the principal line is given by Brillouin's equation (Ann. Physique, 1922, [ix], 17, 88). Further lines of higher orders were not obtained even with the above strongly anisotropic substances (cf. A., 1930, 1237, 1345, 1498; 1932, 676); anisotropic substances show a continuous ground. A. J. M.

**Polarisation of Rayleigh radiation in crystals.** F. MATOSI (Physikal. Z., 1934, 35, 148—149).—The polarisation of the Rayleigh scattered radiation in quartz and calcite has been investigated, and the presence of an anisotropic effect, different from that of Lorentz, demonstrated. A. J. M.

**Continuous spectrum in the light scattered by glycerol and other liquids.** O. H. HOWDEN and W. H. MARTIN (Trans. Roy. Soc. Canada, 1933, [iii], 27, III, 91—96).—Repeated recrystallisation of glycerol (I) diminishes the continuous spectrum (II) in the Raman effect. (II) reappears if purified (I) is irradiated with the whole Hg spectrum, owing to light scattered by a fluorescent impurity produced by the photochemical decomp. of (I) by light of short wave-lengths. Hg line 4358 Å. is best for the investigation of Raman spectra to avoid decomp. of liquids by light  $<$  4100 Å. H. S. P.

**Influence of solvent on variation of fluorescent power of dyes as function of concentration of solution.** J. BOUCHARD (Compt. rend., 1934, 198, 649—651).—The linear relation between  $\log \Phi$  and  $c$  required by  $\Phi = \Phi_0 e^{-kc}$  (cf. A., 1924, ii, 713) was verified for many fluorescent dyes in various solvents, with const.  $\rho_H$ . If the viscosity,  $\eta$ , of the solvent is approx. that of  $H_2O$ ,  $k$  varies with the dielectric const., but if  $\eta$  is markedly  $>$  than that of  $H_2O$ ,  $k$  decreases more rapidly. The equation giving  $\Phi$  in presence of an inhibitor (cf. A., 1933, 337) is valid only when neither  $\eta$  or  $\epsilon$  is affected thereby. C. A. S.

**Polarisation of fluorescence. I. Solutions of some dyes.** S. M. MITRA (Indian J. Physics, 1933, 8, 171—188).—The degree of polarisation of the fluorescence of solutions of fluorescein, eosin, Magdalarred, æsculin, rhodamine B, and erythrosin in  $H_2O$ -glycerol mixtures varies with the wave-length of the exciting radiation, temp., concn., and the  $H_2O$ : glycerol ratio. J. W. S.

**[Fluorescence of substances in] filtered ultra-violet light.** N. D. COSTEANU and A. S. COCOSINSCHI (Bul. Fac. Ştiinţe Cernăuţi, 1931, 5, 169—175; Chem. Zentr., 1933, ii, 1150).—All uranyl compounds show a group of lines between 4850 and 5700 Å., and a red line, in the fluorescence spectrograms. Na H sulphosalicylate gives a faded field in the red, Na salicylate between 4100 and 4950 Å.,  $Hg_2Cl_2$  a weak faded field in the red,  $N_2H_4\cdot H_2O$  between 4250 and



4900 Å. Ignited  $ZnCO_3$  gives brown to dirty yellow fluorescence. L. S. T.

**Excitation of alkali halide crystals.** M. V. SAVOSTJANOVA (Compt. rend. Acad. Sci., U.R.S.S., 1934, 115—118).—KCl, KBr, and KI were illuminated and the phosphorescence was examined. W. R. A.

**Fluorescence of a marine diatom and the fluorescence spectrum of its chlorophyll-like colouring matter.** E. BACHRACH and C. DHÉRE (Compt. rend. Soc. Biol., 1933, 108, 385—387; Chem. Zentr., 1933, ii, 1195). L. S. T.

**Influence of intensity of light on photovoltaic phenomena.** R. AUDUBERT and (Mlle.) G. LEBRUN (Compt. rend., 1934, 198, 729—731; cf. A., 1933, 662).—The relation  $E = (RT/nF) \log(1+aI)$ , where  $a$  is a const. depending on the nature of the photo-sensitive substance, the liquid in contact therewith, and the temp.,  $I$  the intensity of the light, and  $R$ ,  $T$ ,  $n$ , and  $F$  have their usual meanings, is valid for Cu/CuO, Cu/Cu<sub>2</sub>O and several other electrodes, if  $n=1$ . It is concluded that the photolysis of  $H_2O$  is  $H_2O = H^+ + OH^-$ . C. A. S.

**Autoxidation and ionisation potentials of molecules.** N. A. MILAS (J. Amer. Chem. Soc., 1934, 56, 486—487).—The ionisation potentials (I) of the hydrides of elements in each of the fifth, sixth, and seventh groups of the periodic table decrease with rise in the at. wt. The regular diminution of (I) denotes an increased looseness of the reactive unshared electrons, and, hence, a relative increase in the tendency towards autoxidation. H. B.

**Rectifying layer of lead sulphide.** F. HEINECK (Physikal. Z., 1934, 35, 113—118).—The effect of various gases ( $H_2$ ,  $O_2$ ,  $N_2$ ,  $CO_2$ ,  $H_2S$ ) and vapours ( $H_2O$ ,  $C_6H_6$ ,  $COMe_2$ ,  $MeOH$ ) on the rectifying action of sublimed PbS was investigated.  $H_2$ ,  $O_2$ ,  $N_2$ , and  $CO_2$  caused inactive PbS to become a weak rectifier, but the effect disappeared on removing the gas in vac.  $H_2S$  has no effect. The vapours caused a considerable increase in rectifying power, which was removed in vac. in the case of  $H_2O$ , but remained with the others. Pure PbS does not rectify, the presence of foreign substances on the surface of the semi-conductor being necessary. There is no relationship between rectifying power and contact potential. A. J. M.

**Ionisation potential and heat of formation of non-polar molecules.** J. SAVARD (Compt. rend., 1934, 198, 751—753; cf. this vol., 11).— $D$  calc. from the relation previously deduced agrees with the val. determined thermochemically or spectrographically for  $H_2$ ,  $N_2$ ,  $C_2$ ,  $CO$ ,  $CO_2$ ,  $CH_4$ ,  $HCl$ ,  $Cl_2$ ,  $SO_2$ ,  $HCN$ ,  $C_2N_2$ , and  $O_2$ ; the results for the four last point, respectively, to mols.  $S_6$  and  $S_8$  in  $S$  vapour;  $HCN$  as  $H:C:N$ ;  $C_2N_2$  as  $N:C:C:N$ ; and  $O_2$  as  $O:O$ . C. A. S.

**Inner potential of semi-conductors.** K. R. DIXIT (Phil. Mag., 1934, [vii], 17, 732—733).—The val. for ZnS is  $+2.6 \pm 1$  volts (not  $-4.8$ ; cf. A., 1933, 1230).

**Electronic conduction in crystals.** R. W. POHL (Physikal. Z., 1934, 35, 107—111).—The presence of electrons capable of wandering under an applied e.m.f. in transparent crystals is shown by the color-

ation produced in KBr in the neighbourhood of a point electrode. The absorption spectrum of this coloration is very simple, and alteration of temp. affects both the position of the absorption max. and the width of the band. Wandering of the electrons is accompanied by an electrolytic compensating charge effect. The photochemical production of colour centres is also due to freedom of motion of electrons. A. J. M.

**Electrical conductivity in thin metal layers.** A. JAGERSBERGER (Z. Physik, 1934, 87, 513—517).—Theoretical. Variation of the density of free electrons with thickness cannot be obtained from variation of the sp. resistance. A. B. D. C.

**Bloch's theory of electrical conductivity.** E. KRETSCHMANN (Z. Physik, 1934, 87, 518—534).—This theory is criticised. A. B. D. C.

**Electrical conductivity of thin layers of hydrocarbons.** A. E. VAN ARKEL and W. KOOPMAN (Physica, 1933, 13, 189—192; Chem. Zentr., 1933, ii, 1152—1153).—Thin layers of  $C_6H_6$ ,  $C_8H_{14}$ ,  $PhNO_2$ ,  $C_6H_4Cl_2$ , and hexachloropropylene like those of paraffin oil conduct an electric current. Conduction (I) is due to conducting C particles formed by decomp. (I) does not occur in liquid  $N_2$ . The distance between the electrodes varies with the nature of the electrode material. With Fe electrodes microscopic glowing points presumably of  $Fe_2O_3$  are visible. L. S. T.

**High-frequency loss, and molecular structure.** P. DEBYE (Physikal. Z., 1934, 35, 101—106).—Pure solvents with non-polar mols. show no loss. Loss occurs only with polar mols. and increases with increase of dipole moment. With substances with the same dipole moment, it increases with the size of the mol. The connexion between the relaxation time and the viscosity of the solvent is discussed. The calculation of the loss in a mixture is given. A. J. M.

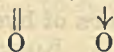
**Anisotropic liquids (liquid crystals) in electric fields. III. Measurements of dielectric loss of liquid-crystalline *p*-azoxyanisole.** W. KAST and P. J. BOUMA (Z. Physik, 1934, 87, 753—762).—Observations of the variation of energy loss with frequency and temp. for the liquid and solid cryst. states, distinguish loss max. peculiar to the liquid state from those due to dipole mols. A. B. D. C.

**Dispersion in short waves.** R. LUTHI (Helv. phys. Acta, 1933, 6, 139—159; Chem. Zentr., 1933, ii, 1151).—The anomalous dispersion of the dielectric const. of dil. solutions of  $PhNO_2$ ,  $BuOH$ , and  $C_5H_{11}OH$  in a mineral oil of high  $\eta$  has been investigated for temp. from  $0^\circ$  to  $35^\circ$ . L. S. T.

**Dielectric coefficients of gases. II. Lower hydrides of carbon and silicon, oxygen, nitrogen, oxides of nitrogen and carbon, and fluorides of silicon and sulphur.** H. E. WATSON, G. G. RAO, and K. L. RAMASWAMY (Proc. Roy. Soc., 1934, A, 143, 558—588).—The dielectric coeffs. of  $CH_4$ ,  $C_2H_6$ ,  $C_3H_8$ ,  $C_2H_4$ ,  $C_3H_6$ ,  $C_2H_2$ ,  $SiH_4$ ,  $Si_2H_6$ ,  $CO$ ,  $CO_2$ ,  $O_2$ ,  $N_2$ , air,  $N_2O$ ,  $NO$ ,  $SiF_4$ , and  $SF_6$  have been measured by the "series" method previously employed (A., 1931, 1113) and also by the "parallel" method, using a condenser specially constructed for measuring very small capacity changes. The results given by the two methods are in satisfactory agreement, and also agree

in most cases with the vals. given by previous observers. Compressibilities have been determined by making measurements at different pressures. Of the gases studied, only  $C_3H_6$ , CO,  $N_2O$ , and NO have a measurable electric moment. The existence of such a moment for  $N_2O$  is considered in connexion with the structure of the mol., and the possibility of a slightly bent N—O—N mol. is discussed. L. L. B.

Electric dipole moments of nitrosomesitylene and of the bimolecular forms of nitrosomesitylene and  $\beta$ -nitroso- $\beta$ -dimethylhexane. D. L. HAMMICK, R. G. A. NEW, and R. B. WILLIAMS (J.C.S., 1934, 29—32).—The moment of bimol. nitrosomesitylene is 1.37 at  $8^\circ$  and 1.63 at  $25^\circ$ , and that of  $\beta$ -nitroso- $\beta$ -dimethylhexane is 0.99. This supports the formula  $R-N \rightarrow N-R$ . W. R. A.



Dipole induction effect for molecular compounds. G. BRIEGLEB and J. KAMBEITZ (Naturwiss., 1934, 22, 105—106; cf. A., 1933, 25).—Direct experimental proof of the existence of moments induced in non-polar mols. by polar mols. in mol. compounds is difficult. The induced moments in the case of  $m-C_6H_4(NO_2)_2$ ,  $C_{10}H_8$  and  $PhNO_2$ ,  $C_{10}H_8$  should be small, but demonstrable.  $\mu_{ind. PhNO_2}$  should be  $> \mu_{ind. m-C_6H_4(NO_2)_2}$ . The dipole moments of  $s-C_6H_3(NO_2)_3$ ,  $m-C_6H_4(NO_2)_2$ ,  $PhNO_2$ , and  $PhCl$  in  $C_{10}H_8$  and in  $C_6H_6$  are given. All but  $PhCl$  form mol. compounds with  $C_{10}H_8$ . The moments in  $C_{10}H_8$  are  $<$  in  $C_6H_6$ , but the difference is small in the case of  $PhCl$ . The greatest effect is with  $PhNO_2$ . This decrease in the moment in  $C_{10}H_8$  is ascribed to the induced moment. A. J. M.

Relation between dipole moment and cohesive forces. VI. A. E. VAN ARKEL (Rec. trav. chim., 1934, 53, 246—256; cf. A., 1933, 8).—The distribution of substituted groups in various saturated, unsaturated, and halogenated hydrocarbon series is correlated with variations of b.p. H. J. E.

Dispersion in nitrogen. C. E. BENNETT (Physical Rev., 1934, [ii], 45, 200—207).—High-precision measurements with improved apparatus were made at four wave-lengths corresponding with pressure runs up to 14 atm. Results at n.t.p. are, for the Cauchy dispersion consts.  $A$  and  $B$ ,  $A_0 - 1 = 0.0002932$ ,  $B_0 = 1.637 \times 10^{-14}$ , and calc. dielectric const. 1.0005864. N. M. B.

Refractive index of  $H^2H^2O$ ; refractive index and density of solutions of  $H^2H^2O$  in  $H^1H^1O$ . D. B. LUTEN, jun. (Physical Rev., 1934, [iii], 45, 161—165).—Data are tabulated for a range of concns., temp., and wave-lengths. The dispersion of  $H^2O$  is  $<$  that of  $H^1O$ . Typical vals. for mol. refraction at  $20^\circ$  for  $D$  line are 3.7121 for  $H^2O$  and 3.687 for  $H^1O$ . N. M. B.

Refraction and dispersion of gases and vapours. I. General introduction. K. FAJANS. II. Refraction and dispersion of air, hydrogen sulphide, and water vapour in the visible region. J. WÜST and H. REINDEL. III. Refraction and dispersion of mercury halide vapours in the visible region. M. A. BREDIG, T. VON HIRSCH,

and J. WÜST. IV. Refraction and dispersion of aluminium chloride and bromide vapours in the visible region. M. A. BREDIG and F. K. V. KOCH. V. Refraction, and dispersion of aluminium iodide vapour in the visible region. F. K. V. KOCH and H. KOHNER. VI. Refraction and dispersion of vapours of some halides of elements in the fourth group of the periodic system in the visible region. P. HÖLEMANN and H. GOLDSCHMIDT. VII. Refraction and dispersion of vapours of stannous halides in the visible region. H. GOLDSCHMIDT and P. HÖLEMANN (Z. physikal. Chem., 1934, B, 24, 103—154, 155—176, 177—186, 187—193, 194—198, 199—209, 210—214).—I. In deriving vals. for the refractivity,  $R$ , of free gaseous ions from data for compounds or solutions, account must be taken of the effect on  $R$  of the fields of force of adjacent particles. Fajans and Joos's data for  $R$  for gaseous ions of the inert gas type and for the apparent refraction of ions in aq. solution (A., 1924, ii, 372) have been revised. For  $Na^+$  in aq. solution the most probable val. of  $R_D$  is  $0.25 \pm 0.05$  c.c. The methods used by other authors for calculating  $R$  for ions are reviewed. The vals. calc. by Pauling (A., 1927, 394) and Hassé (A., 1931, 14) for gaseous ions of the He type are more trustworthy than Fajans and Joos' vals. For many ions the latter closely agree with Mayer's vals. (A., 1933, 550). The relative change,  $Q$ , in the refraction,  $R^I$ , of a halogen ion caused by addition of  $H^+$  increases with  $R^I$  from zero when  $R^I$  is zero to a limiting val.,  $0.28$ ,  $Q = 0.2859(1 - e^{-0.2848R^I})$ . This relation can be utilised to derive  $R^I$  from the  $R$  of the product, and also gives acceptable results when used to calculate  $R^I$  for other single-charged gaseous ions, such as  $SH^+$  and  $OH^+$ . The relation is applicable to the addition of  $H^+$  to neutral mols., but for the addition to a doubly-charged anion  $Q$  is  $>$  for addition to a singly-charged anion. The refractometric relations of halides with cations not of the inert gas type (heavy-metal halides) differ from those of halides with cations of the inert gas type, probably because the former class of compounds constitute a transitional type between ideal ionic linking and non-polar linking. The wave-mechanical resonance energy must be responsible for a considerable proportion of the total energy of linking in compounds of this type.

II. The use of a Zehnder interferometer for the measurement of  $n$  for gases and vapours over a wide temp. range is described. Measurement of  $n$  and dispersion,  $D$ , for  $H_2S$  at room temp. and  $D$  for  $H_2O$  vapour at  $130$ — $150^\circ$  gave results agreeing with those of Cuthbertson (A., 1913, ii, 358).

III.  $n$  and  $D$  of  $HgCl_2$ ,  $HgBr_2$ , and  $HgI_2$  vapours at  $340^\circ$  have been measured.  $n$  for  $HgBr_2$  at  $440^\circ$  shows that the effect of temp. on  $n$  is  $<$  0.003% per degree. The mol. refractions of the  $Hg^{II}$  halides are not additively constituted of the  $R$  of the free gaseous ions, and the deviations from additivity do not accord with the relations observed by Fajans and Joos with the H and alkali halides. The same is true of the mol. dispersions. That  $Hg^{II}$  is not of the inert gas type is the probable explanation.

IV. The  $n$  and  $D$  of  $Al_2Cl_6$  and  $Al_2Br_6$  in the vapour state have been measured at  $230^\circ$  and  $300^\circ$ ,

respectively. The fall in  $R$  on formation of the salt from the free gaseous ions,  $\Delta R$ , is greater for  $\text{Al}_2\text{Br}_6$  than for  $\text{Al}_2\text{Cl}_6$ , and the vals. fit in with those for the corresponding effect with other cations of the He type.

V. The  $n$  and  $D$  of  $\text{Al}_2\text{I}_6$  vapour have been measured at  $380^\circ$ .  $\Delta R$  is  $<$  would be anticipated from the vals. for  $\text{Al}_2\text{Cl}_6$  and  $\text{Al}_2\text{Br}_6$  and the regularities observed by Fajans with alkali and H halides, perhaps owing to the relatively complex structure of the double mol.

VI.  $D$  and  $n$  have been measured for the vapours of  $\text{CCl}_4$ ,  $\text{SiCl}_4$ ,  $\text{SnCl}_4$ ,  $\text{SnBr}_4$ , and  $\text{SnI}_4$ . The vals. of  $\frac{1}{4}R_{M\lambda} - R_{\lambda'}$  for the Na  $D$  line become increasingly negative in the order  $\text{SnCl}_4 < \text{SiCl}_4 < \text{CCl}_4$ , and the vals. for infinite wave-length in the order  $\text{SnCl}_4 < \text{SnBr}_4 < \text{SnI}_4$ .

VII.  $D$  and  $n$  have been measured for  $\text{SnCl}_2$ ,  $\text{SnBr}_2$ , and  $\text{SnI}_2$  vapours at  $700^\circ$ .  $\Delta R$  becomes increasingly positive in the order  $\text{SnCl}_2 < \text{SnBr}_2 < \text{SnI}_2$ . With the transition from  $\text{Sn}^{\text{IV}}$  to  $\text{Sn}^{\text{II}}$  the equiv. refractivity of the halide rises considerably by an amount which increases with the size of the anion. R. C.

**Polarisability and molecular refraction of alkali ions.** R. SCHOPPE (Z. physikal. Chem., 1934, B, 24, 259—262).—The mol. refractions and polarisabilities of the alkali ions have been recalcd. by Herzfeld and Wolf's method (A., 1926, 11). The polarisabilities are  $<$  Mayer's vals. (A., 1933, 550) and  $\ll$  those of Fajans and Joos (A., 1924, ii, 372). The mol. refractions of alkali halides have been recalcd. R. C.

**Refractive dispersion of organic compounds.**

IV. *cyclohexene* and *1:3-cyclohexadiene*. C. B. ALLSOPP (Proc. Roy. Soc., 1934, A, 143, 618—630; cf. A., 1931, 1214).—Vals. are given for  $n$  at  $20^\circ$  of *cyclohexene* (I) at 67 wave-lengths from 6708 to 2420 Å., and of  $\Delta^{1:3}$ -*cyclohexadiene* (II) at 48 wave-lengths from 6708 to 2940 Å. Mol. extinction coeffs. are recorded for both compounds in solution in *cyclohexane* (III). The following dispersion equations represent the data for (I) and (II) from 6708 to 3034 Å., and from 6708 to 3700 Å., respectively: (I)  $n^2 = 0.97487 + [1.07441\lambda^2/(\lambda^2 - 0.012226)] + [0.00327\lambda^2/(\lambda^2 - 0.056406)]$ ; (II)  $n^2 = 1.06977 + [0.973295\lambda^2/(\lambda^2 - 0.012226)] + [0.0779625\lambda^2/(\lambda^2 - 0.072900)]$ . Each equation contains a high-frequency term corresponding with the partial refraction of a hypothetical band in the Schumann region, at the same wave-length as that deduced for (III), and a low-frequency term which is the partial refraction of the absorption bands observed in the ultra-violet. The refractive dispersion is correlated with the absorption spectrum of the two compounds. L. L. B.

**Influence of solvents and of other factors on the rotation of optically active compounds.**

XXXII. **Rotation dispersion of esters of dibenzoyl-*d*-tartaric acid in various solvents.** T. S. PATTERSON and D. MCCREATH (J.C.S., 1934, 100—103).—Rotations of  $\text{Bz}_2$  derivatives of Me, Et, Pr<sup>c</sup>, and Bu<sup>c</sup> *d*-tartrates in quinoline,  $\text{C}_5\text{H}_5\text{N}$ , and ethylene bromide (Me ester also in  $\text{MeNO}_2$ ) are tabulated. No definite region of anomalous dispersion was observed. W. R. A.

**Configuration and optical rotation in inorganic complex compounds.** W. KUHN and K. BEIN (Z. anorg. Chem., 1934, 216, 321—348).—Compounds of the type  $[\text{M}(\text{en})_2\text{AB}]X_n$  and  $[\text{M}(\text{C}_2\text{O}_4)_3]K_3$ , where en is  $(\text{CH}_2\text{NH}_2)_2$  or some other base, M is Co, Cr, Rh, or Ir, and A and B are two like or unlike co-ordinate univalent substituents or one bivalent substituent, bear a resemblance in optically active behaviour, *i.e.*, Cotton effect and rotation for the longer waves. The optically active behaviour of a compound is not characterised by a statement of the mol. rotation for a definite wave-length, the same for all compounds, but by the sign of the rotation which analogous absorption bands contribute to the total rotatory power. The long-wave absorption bands of all these substances can be considered as of analogous origin. Measurements of the optical rotation in the long wave, circular dichroism, and absorption of  $[\text{Co}(\text{C}_2\text{O}_4)_3]K_3$  have been made in the spectral region 2600—8000 Å. Agreement with calc. vals. is good. M. S. B.

**Magneto-optical dispersion of organic liquids in the ultra-violet region of the spectrum.** VII. **Magneto-optical dispersion of isobutyl formate, methyl butyrate, and ethyl malonate.** R. H. LAVERY and E. J. EVANS (Phil. Mag., 1934, [vii], 17, 351—369; cf. A., 1931, 24).—Data for the dispersion and magneto-optical dispersion between 3000 and 7000 Å. are tabulated, and represented by equations. Verdet's const. and vals. of  $e/m$  are calc. H. J. E.

**Magnetic rotation of fused organic substances, in connexion with Malleman's molecular theory.** C. SĂLCEANU (Bul. Soc. Fiz. Român., 1933, No. 53, 1—4).—See A., 1932, 215, 561. Deviations from de Malleman's theory are observed for  $1\text{-C}_{10}\text{H}_7\text{Me}$  and phenanthrene. R. T.

**Valency angle of sulphur.** G. M. BENNETT and S. GLASSTONE (J.C.S., 1934, 128—129).—Thi-anthrene has a dipole moment of  $1.50 \times 10^{-18}$  e.s.u. in  $\text{CS}_2$  or  $\text{CCl}_4$  solution. Hence it must have a non-planar configuration; this is discussed, and it is shown that S has valency angle  $< 120^\circ$ . W. R. A.

**Polar molecules and amphoteric ions.** G. DEVOTO (Gazzetta, 1933, 63, 845—848).—Of amphoteric substances, some are polar and others non-polar. A formula which satisfactorily represents the chemical behaviour of a substance does not, therefore, necessarily correspond with the actual structure. H. F. G.

**Chemical and physico-chemical properties of polonium.** I. **Chemical study of certain compounds of polonium.** M. SERVIGNE (J. Chim. phys., 1934, 31, 47—64).—By co-crystallisation of Po compounds with known compounds, confirmation has been obtained that Po has valencies 3 and 4. Po is tervalent in the oxalate, whilst with  $\text{CH}_2\text{Ac}_2$  it forms stable complexes in which it may be ter- or quadri-valent. H. S. P.

**Magnetic susceptibilities at high temperatures.** R. A. FEREDAY (Proc. Physical Soc., 1934, 46, 214—230).—An electromagnet is designed for measurements of small susceptibilities by a method previously described (cf. A., 1932, 678), modified for

use in conjunction with a special furnace up to 450°. Results are given for anhyd.  $\text{NiSO}_4$  and  $\text{Ni}(\text{CN})_2$ .

N. M. B.

**Paramagnetism.** W. J. DE HAAS and E. C. WIERSMA (Rapp. Comm. VI Congr. Int. Froid; Comm. K. Onnes Lab. Univ. Leiden Suppl., 1932, No. 74, 36—70).—At 292—113° abs. van Vleck's formula for the magnetic moment of NO as a function of temp. gives results in accord with experimental vals. to a few tenths of 1%. At 292·10° abs.  $\chi = 49\cdot07 \times 10^{-6}$ ; at 112·77° abs.  $\chi = 87\cdot32 \times 10^{-6}$ . Vals. for  $\text{O}_2$  at 293—155° abs. are summarised. Gaseous  $\text{O}_2$  does not follow the same law as liquid  $\text{O}_2$ . To a first approximation  $\chi(T+1\cdot7)=C$ . Tabulated results for 290—14° abs. are given for  $\text{K}_2\text{SO}_4$ ,  $\text{Cr}_2(\text{SO}_4)_3$ ,  $24\text{H}_2\text{O}$ ,  $\text{CuSO}_4$ ,  $5\text{H}_2\text{O}$ ,  $\text{NiSO}_4$ ,  $7\text{H}_2\text{O}$ ,  $\text{CeF}_3$ ,  $\text{CeCl}_3$ ,  $\text{Nd}_2(\text{SO}_4)_3$ ,  $8\text{H}_2\text{O}$ ,  $\text{Pr}_2(\text{SO}_4)_3$ ,  $8\text{H}_2\text{O}$ , and  $\text{Pr}_2(\text{SO}_4)_3$ . Experimental vals. for the moments of  $\text{V}^{\text{VI}}$ ,  $\text{V}^{\text{VIII}}$ ,  $\text{V}^{\text{VII}}$ ,  $\text{Cr}^{\text{III}}$ ,  $\text{Cr}^{\text{II}}$ ,  $\text{Mn}^{\text{II}}$ ,  $\text{Fe}^{\text{III}}$ ,  $\text{Fe}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ , and  $\text{Cu}^{\text{II}}$  agree in general with the Bose-Stoner predictions. Cryomagnetic anomalies exhibited by  $\text{CuCl}_2$ ,  $\text{CuSO}_4$ , and  $\text{FeCl}_2$  are discussed. CH. ABS.

**Paramagnetism. I. Mechanism of quenching of orbital magnetic moment in paramagnetic ions of the iron group.** S. DATTA (Phil. Mag., 1934, [vii], 17, 585—602).—The magnetic moment of  $\text{Co}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  in co-ordinated compounds (mostly containing  $\text{N}_2\text{H}_4$ ) is lower than in powdered crystals of hydrated and anhyd. salts. Measurements on  $\text{CoCl}_2$  and  $\text{NiCl}_2$  in EtOH and HCl solution from 90° to 390° abs. show a break in the  $1/\chi-T$  diagram, which is correlated with colour changes. At lower temp. the ions exist as hydrated or alcoholated complexes, and at higher temp. as homopolar chlorides. The interpretation is discussed. H. J. E.

**Influence of light on paramagnetic susceptibility.** D. M. BOSE and P. K. RAHA (Nature, 1934, 133, 258—259).—A criticism (cf. A., 1933, 664).

L. S. T.

**Magnetic investigations on insoluble amorphous substances. I. Magnetic susceptibility of different iron salts.** L. N. BHARGAVA and S. PRAKASH (Z. anorg. Chem., 1934, 217, 27—32).—The susceptibilities of amorphous  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  arsenates, phosphates, molybdates, borates, tungstates, oxalates, and benzoates have been measured. On calcination the susceptibility increases to a greater extent than corresponds with the loss in wt. The oxide obtained by calcining  $\text{FeC}_2\text{O}_4$  is strongly paramagnetic, whilst those from  $\text{Fe}_2(\text{C}_2\text{O}_4)_3$  and  $\text{Fe}(\text{OBz})_3$  are ferromagnetic.  $\text{FePO}_4$  is readily sol. in  $\text{H}_2\text{C}_2\text{O}_4$ , and the solution has a much higher paramagnetic val., relatively, than the corresponding solutions in HCl and  $\text{H}_2\text{SO}_4$ , although, for these in turn, the vals. are much > to be expected from Wiedemann's law. M. S. B.

**Covalent radii of atoms and interatomic distances in crystals containing electron-pair linkings.** L. PAULING and M. L. HUGGINS (Z. Krist., 87, 205—238).—The possibility of formation of various sets of covalent linkings (tetrahedral, octahedral, square, etc.) is deduced from quantum-mechanical considerations, and the characteristics distinguishing crystals of covalent from those of ionic or metallic character are described. From

these and measured inter-at. distances sets of radii are deduced corresponding with the different types (tetrahedral etc.) of linkings, and satisfactory agreement with results otherwise obtained is demonstrated, save in the case of Mn, the measured radius of which is much > the calc. The reported structures of several crystals (niccolite, eulytite,  $\text{AsI}_3$ ,  $\text{BiI}_3$ , etc.) are shown to be doubtful (cf. A., 1927, 399; 1931, 670; 1932, 1191).

C. A. S.

**Energetics of oxides of nitrogen, and the structure of nitrous oxide.** L. V. PISARSHEVSKI (Bull. Acad. Sci. U.R.S.S., 1933, 7, 971—974).—A comparison of the heats of formation and decomp. of  $\text{N}_2\text{O}$ , NO,  $\text{NO}_2$ , and  $\text{N}_2\text{O}_3$  leads to the conclusion that  $\text{N}_2\text{O}$  is produced from the ions  $\text{N}_2^{\text{II}}$  and  $\text{O}^{\text{II}}$ .

R. T.

**Quantised Brownian motion.** M. SATÔ (Z. Physik, 1934, 87, 669—673).—Numerical calculations for  $\text{H}_2$  and He show that quantised Brownian motion should be observable in a highly quantised gas.

A. B. D. C.

**Brownian motion in gases.** R. FÜRTH (Z. Physik, 1934, 87, 810—814).—Satô's deductions (A., 1933, 460, 1115) are erroneous. A. B. D. C.

**Space-charge in ice.** G. OPLATKA (Helv. phys. Acta, 1933, 6, 198—209; Chem. Zentr., 1933, ii, 1152).—Pure ice exhibits no space-charge when outgassed, but does so when not completely outgassed.

L. S. T.

**Surface tension of mercury in a vacuum and in the presence of hydrogen.** R. S. BRADLEY (J. Physical Chem., 1934, 38, 231—241).—An apparatus for the determination of the surface tension ( $\gamma$ ) of Hg by the flat-drop method is described. A mean val. of 500·3 dynes per cm. at 16·5° was obtained. The fall of  $\sigma$  with time in  $\text{H}_2$  at pressures 0—100 mm. has been studied and interpreted theoretically. On illumination of the surface of Hg by a Hg-vapour lamp no immediate effect was observed, but  $\gamma$  fell more rapidly than normally.

M. S. B.

**Surface tension of carbon tetrachloride at low temperatures.** T. ALTY and G. F. CLARK (Canad. J. Res., 1934, 10, 129—133).—Measurements by the drop-wt. method at temp. of  $-10^\circ$  to  $12^\circ$  give  $m = 0\cdot022161 - 9\cdot2557 \times 10^{-5}t - 4\cdot896 \times 10^{-8}t^2$ . The calc. vals. of  $\gamma$  are tabulated.

A. G.

**Atomic parachors of carbon and hydrogen.** C. H. CHEESMAN (Chem. and Ind., 1934, 135).—The anomaly reported (Vogel, this vol., 243) is due to an abnormality of the dibasic acids and does not extend to alkyl groups attached thereto.

E. S. H.

**Parachors of some substituted methanes.** D. L. HAMMICK and H. F. WILMUT (J.C.S., 1934, 32—34).—The following have been determined:  $\text{C}(\text{NO}_2)_4$  280·8 (anomaly  $-20\cdot4$ ),  $\text{CH}_2\text{Ph}_2$  419·6,  $\text{CH}(\text{NO}_2)_3$  247·0, as molten substances; and the following solutions:  $\text{CBr}_4$  in  $\text{CCl}_4$  260·1 ( $-16\cdot7$ ),  $\text{C}(\text{NO}_2)_4$  in  $\text{C}_6\text{H}_6$  280·0 ( $-21\cdot2$ ). The parachor of  $\text{CHPh}_3$  evaluated from Przyłuska's data is 578 ( $-13\cdot9$ ). The size of the substituent group may explain the anomalies. Mumford and Phillips' consts. do not give better agreement. W. R. A.

**X-Ray method of distinguishing certain space-groups in the hexagonal system.** W. H. BARNES and A. V. WENDLING (Trans. Roy. Soc. Canada, 1933, [iii], 27, III, 133—140).—There is difficulty in determining to which of two space-groups certain classes of hexagonal crystals belong. This applies to the  $D_{3h}$  class of the hexagonal division and to the  $C_{3v}$ ,  $D_3$ , and  $D_{3h}$  classes of the rhombohedral division, the structures of which are based on a  $T_h$  lattice. By examination of Laue pictures taken along the  $a$ ,  $b$ , and  $c$  axes of the crystal, it is possible to discriminate in the case of seven pairs out of a total of nine. The method has been tested on  $\alpha$ -quartz, and also used to show that  $K_2S_2O_6$  belongs to space-group  $D_{3d}^2$ .

H. S. P.

**Space-group of tourmaline.** W. H. BARNES and A. V. WENDLING (Trans. Roy. Soc. Canada, 1933, [iii], 27, III, 169—175).—The method described in the preceding abstract shows that of the two possible space-groups,  $C_{3v}^1$  and  $C_{3v}^2$ , tourmaline belongs to  $C_{3v}^1$ .

H. S. P.

**Scattering of homogeneous X-rays of 0.25—0.4 Å.** I. BACKHURST (Phil. Mag., 1934, [vii], 17, 321—351).—Scattering by Be, C, Al, S, Fe, Cu, Mo, W, Pb, paraffin wax,  $H_2O$ , turpentine,  $C_6H_6$ , EtOH, and  $COPh_2$  has been measured with a homogeneous incident beam with reference to the angular intensity distribution, the proportion of modified and unmodified scattered radiation, and the abs. vals. of the scattering coeffs. Results agree in general with wave-mechanics equations for scattering from gases.

H. J. E.

**Effect of the divergence of primary X-rays on the valuation of diagrams from reflexion processes.** F. LIHL (Ann. Physik, 1934, [v], 19, 305—334; cf. A., 1932, 1078).—Exact formulæ are derived for calculating the interference angle from the outer and inner edges of the interference lines. A. J. M.

**Barker's determinative method of systematic crystallography.** P. TERPSTRA, J. D. H. DONNAY, J. MÉLON, and W. J. VAN WEERDEN (Z. Krist., 1934, 87, 281—305).—The conclusions of the Conference held at Groningen in August, 1933, to remedy deficiencies in the system are given.

C. A. S.

**Cohesion. V. Cleavage measurements of anhydrite.** H. TERTSCH (Z. Krist., 1934, 87, 326—341; cf. A., 1933, 452).—Cleavability (parallel to crystal faces) increases in the order (100), (010), (001).

C. A. S.

**Madelung constant of cuprite.** J. SHERMAN (Z. Krist., 1934, 87, 342; cf. A., 1933, 12).—The correct val. of the Madelung const. of cuprite is 5.12972; and those of the crystal energies of  $Cu_2O$  and  $Ag_2O$  are 736 and 631 kg.-cal., respectively.

C. A. S.

**Crystal structure of lanthanum, cerium, and praseodymium hydrides.** A. ROSSI (Nature, 1934, 133, 174).—La annealed in a vac. at  $350^\circ$  for several days gives powder photographs of the  $\beta$ -phase, but after removal of a thin outer layer, characteristic photographs of the  $\alpha$ -phase are obtained. The same thermal treatment does not affect Pr. The difficulty of  $H_2$  absorption increases in the order Ce, La, Pr.

The hydrides all have face-centred cubic lattices with sizes  $>$  those of the real or possible  $\beta$ -phases of the pure elements. La has  $a_0$  5.62—5.63 Å., Ce 5.61 $\frac{1}{2}$  Å., and Pr a lattice only slightly  $>$  that of metallic Ce. In one case La gave simultaneously two face-centred cubic phases with  $a_0'$  5.62 Å. and  $a_0''$  5.70 Å.

L. S. T.

**X-Ray investigation of the nature of change of structure in a metal resulting from deformation at high temperatures.** E. F. BAKHMETEV, M. D. VOZDVIZHENSKI, S. I. GURKIN, G. F. KOSOLAPOV, and B. M. ROVINSKI (Mitt. Forschungsinst. Luftfahrtmaterialprüf., U.S.S.R., 1933, No. 1, 131 pp.).—A study of duralumin. When deformation has reached 60—70%, anisotropy is observed. Samples deformed at  $450^\circ$  and at room temp. are similar in structure.

CH. ABS.

**Structure of oxide films on nickel.** G. D. PRESTON (Phil. Mag., 1934, [vii], 17, 466—470).—The thin oxide films on heated Ni have been shown by electron diffraction to have a NaCl type lattice (approx. parameter 4.10 Å.), identical with that of massive NiO.

H. J. E.

**Debye-Scherrer photograph.** G. GREENWOOD (Indian J. Physics, 1933, 8, 269—273).—Kettman's graphical method of evaluation of lattice const. (A., 1929, 629) yields consistent results with specimens of CdO of different origin using both Cu  $K\alpha$  and Fe  $K\alpha$  radiation.

J. W. S.

**Crystal structures and expansion anomalies of MnO, MnS, FeO,  $Fe_3O_4$ , between  $100^\circ$  and  $200^\circ$  abs.** B. S. ELLEFSON and N. W. TAYLOR (J. Chem. Physics, 1934, 2, 58—64).—All structures are cubic, and no major structure changes were apparent in the X-ray patterns. Lattice const. data indicate similarity in the abnormal expansion behaviour of MnS and FeO, and of MnO and  $Fe_3O_4$ . The sp. heat and expansion anomalies are probably due to electron transitions within certain atoms in the crystal lattice.

N. M. B.

**Silver ferrite. IX. Structure of the orthoferric hydroxide from ferrous carbonate.** A. KRAUSE and L. SKORUPSKA (Z. anorg. Chem., 1934, 216, 377—385).—By pptg. aq.  $FeSO_4$  with an equiv. quantity of  $Na_2CO_3$  and adding dil.  $H_2O_2$  in excess, a voluminous, gelatinous, light brown ppt. of ortho- $Fe^{III}$  hydroxide is obtained. Examination by the Ag ferrite method (A., 1932, 481) gives a ratio  $Ag_2O : Fe_2O_3 = 1 : 1.9$ , which indicates a chain mol. containing 6 Fe, or a mixture of higher and lower polymerised mols. The Debye-Scherrer diagram shows no interference. Ageing under aq. NaOH causes the formation of larger polymerides.

M. S. B.

**Crystal structure of ferric oxychloride.** S. GOLDSZTAUB (Compt. rend., 1934, 198, 667—669).— $Fe^{III}$  oxychloride (cf. A., 1890, 1063) has  $a$  3.75,  $b$  7.95,  $c$  3.3 Å., with 2 mols. in the unit cell, space-group  $V_h^a$ — $mnm$ . The structure consists of layers, each made up of two (subordinate) layers of Cl atoms with two each of alternate Fe and O atoms between them, Cl-Cl in the same (principal) layer being 3.3, in different layers 3.75 Å.; the perfect cleavage parallel to (010) is thus explained.

C. A. S.

**Crystal structure of hydrargillite.** (Miss) H. D. MEGAW (Z. Krist., 1934, 87, 185—204; cf. A., 1930, 732).—Hydrargillite,  $\text{Al}(\text{OH})_3$ , is monoclinic with  $a$  8.6236,  $b$  5.0602,  $c$  9.699 Å.,  $\beta$  85° 26', and 8 mols. in the unit cell, space-group  $C_{2h}^{23}-P2_1/n$ . It is neither pyro- nor piezo-electric. The structure is pseudo-hexagonal, and is made up of layers each consisting of two planes of approx. close-packed OH with a plane of Al atoms between; 3 OH in one plane and 3 OH of the other form a distorted octahedron with an Al in the centre, in which Al-O=1.89 Å., and O-O=2.49 and 2.78, whilst O-O in different layers =2.79 Å. The structure explains the thermal expansion (cf. A., 1933, 1237). C. A. S.

**Accurate measurements of rhombohedral lattices:  $\text{NaNO}_3$ .** J. WEIGLE (Arch. Sci. phys. nat., 1933, [v], 15, Suppl., 228—229).—An improved method of calculation gives  $a=6.3108$  Å. and  $\alpha=47^\circ 15' 59''$  at 18° within 1/50,000. R. S.

**Crystal structure of  $\text{BPO}_4$  and  $\text{BaSO}_4$ .** G. E. R. SCHULZE (Z. physikal. Chem., 1934, B, 24, 215—240).—Both compounds have the same structure and 2 mols. in the unit cell.  $\text{BPO}_4$  has  $a$  4.332±0.006,  $c$  6.640±0.008, and  $\text{BaSO}_4$   $a$  4.458±0.006,  $c$  6.796±0.008 Å. The space-group is  $S_6^2-\bar{1}4$ . Both P(As) and B are tetrahedrally surrounded by O. R. C.

**Crystal structure of silver sulphate tetramoniate.** R. B. COREY and R. W. G. WYCKOFF (Z. Krist., 1934, 87, 264—274).— $\text{Ag}_2\text{SO}_4 \cdot 4\text{NH}_3$  is tetragonal with  $a$  8.44,  $c$  6.35 Å., and 2 mols. in the unit cell, space-group  $V_4^2$ . The  $\text{SO}_4^{2-}$  form tetrahedral groups, the  $[\text{Ag}(\text{NH}_3)_2]^+$  are linear; S-O=1.65, Ag-N=1.90 Å. C. A. S.

**X-Ray spectroscopic studies of problems of structure of complex compounds. IV.** O. STELLING (Z. physikal. Chem., 1934, B, 24, 282—292; cf. this vol., 133).—The  $K$ -absorption spectra of Cl in complex compounds of chlorides of bi-, ter-, and quadri-valent metals with org. bases have been studied.  $\text{MnCl}_2$  may combine with up to four mols., e.g., of  $\text{CS}(\text{NH}_2)_2$ , without the Cl being displaced from the complex.  $\text{ZnCl}_2$  additive compounds exhibit only a single absorption edge, possibly consisting, however, of two edges very close together.  $\text{SbCl}_3$  and  $\text{BiCl}_3$  exhibit double edges, and are therefore not ionic compounds.  $\text{ZrCl}_4$  exhibits two edges, and the co-ordination no. of Zr is at least 6, and probably 8.  $(\text{C}_5\text{H}_6\text{N})_2\text{ZrCl}_6$  and  $(\text{C}_5\text{H}_6\text{N})_2\text{CeCl}_6$  each give three absorption edges. R. C.

**Crystal structure of carotenoids.** G. MACKINNEY (J. Amer. Chem. Soc., 1934, 56, 488).—X-Ray powder patterns of carotene (from carrot roots and spinach, cauliflower, and sunflower leaves), leaf xanthophyll, lutein, and lycopene are given; no spacings > 7.53 Å. were observed. H. B.

**X-Ray studies of the structure of hair, wool, and related fibres. II. Molecular structure and elastic properties of hair keratin.** W. T. ASTBURY and H. J. WOODS (Phil. Trans., 1933, A, 232, 333—394; cf. A., 1931, 897).—The X-ray fibre photograph of stretched hair [ $\beta$ -keratin (I)] is analogous to that of natural silk; the former is built of extended, and unstretched hair [ $\alpha$ -keratin (II)] of

folded, polypeptide chains. Intramol. folds of the nature of linked pseudo-diketopiperazine rings which open on extension to produce the normal zigzag protein chain are assigned to (II). The side-chains of (I) unite neighbouring main chains by cross-linkings, including covalent and electrovalent linkings. The (I) structure is of flat polypeptide grids adhering by attraction between CO and NH groups of the main chains of neighbouring grids. Elastic properties may be referred to three phases of the keratin theme associated with intercellular, cell-wall, and intracellular keratin. The side-chain differences of the three phases may be successively eliminated by progressive action of  $\text{H}_2\text{O}$  at rising temp., or by dil. NaOH. Decay of tension, leading to "set" of hair stretched in  $\text{H}_2\text{O}$ , is due to side-chain disturbances arising from hydrolytic modification of (I). Intermediate between side-chain breakdown and recombination is a new phenomenon, "supercontraction," defined by closest approach of acidic and basic side-chains. Irradiation of unstretched keratin by ultraviolet light or X-rays causes intramol. changes analogous to those due to  $\text{H}_2\text{O}$  on stretched keratin. N. M. B.

**Electron diffraction experiments with graphite and carbon surfaces.** R. O. JENKINS (Phil. Mag., 1934, [vii], 17, 457—466).—Polishing a graphite (I) surface reduces the crystal size, and orients them with the main cleavage plane (001) in the plane of the specimen. For "amorphous" C polishing first disintegrates the aggregates of small graphite crystals and then orients them. Fe or Ni, which have been lubricated with oil containing colloidal (I) and then washed with  $\text{C}_6\text{H}_6$ , retains a film of adsorbed (I), the crystals of which are reduced in size and oriented by friction. The inner potential of natural (I) is 10.7 volts. H. J. E.

**Surface lattice interference with electron beams at thin silver layers.** H. LASSEN (Physikal. Z., 1934, 35, 172—175).—The apparatus is described. In some cases the usual Debye-Scherrer rings were obtained, but frequently point interference photographs were produced. Various types of surface lattice interference photographs were obtained. The Ag produced in the manner described is composed of a single crystal with a cube face parallel to the plane of the foil. A. J. M.

**Crystal structure and orientation in zinc oxide films.** G. I. FINCH and A. G. QUARELL (Proc. Physical Soc., 1934, 46, 148—162).—Using a new type of high-precision electron-diffraction camera, partly and completely oxidised Zn films were examined by transmission. The normal type of ZnO is formed by oxidation by way of a ZnO which is basally pseudomorphic with the Zn, and forms a corrosion-resisting coating. N. M. B.

**Electron reflexion of glasses.** K. R. DIXIE (Physikal. Z., 1934, 35, 141).—Seven glasses used all gave a diffuse Debye-Scherrer ring corresponding with a period of 1.5 Å., and inside this, a point, corresponding with 1.55 Å. The 1.55 Å. period is the Si-O separation. A. J. M.

**Investigation of thin films of organic substances by electron diffraction.** C. A. MURISON

(Phil. Mag., 1934, [vii], 17, 201—225).—The investigation of thin films of grease-like mixtures by electron diffraction shows that the mols. are oriented normal to the surface of the film. The orientation is greater with impure substances (e.g., grease), as the mols., being of different lengths, are less likely to crystallise and so form crystals arranged at random. This is probably the cause of the better lubrication by grease than pure substances. H. S. P.

**Determination of size of particles by electronic radiation.** R. BRILL (Z. Krist., 1934, 87, 275—280).—A relation between the width of the electron diffraction ring and the magnitude of the diffracting particle is deduced (cf. A., 1919, ii, 274). C. A. S.

**Intensity of cathode rays scattered by potassium chloride.** S. SHIRAI (Proc. Phys.-Math. Soc. Japan, 1933, 15, 420—427).—The intensities of the Debye-Scherrer diagrams are uniform in all directions. With KCl there is fair quant. agreement between the experimental and the theoretical results. CH. ABS.

**Spreading of waves in crystal lattices.** K. FÖRSTERLING (Ann. Physik, 1934, [v], 19, 261—289).—Mathematical. In the theory of the anomalous dispersion shown by Lippmann colour plates, analogous results are obtained if the Schrödinger equations for electron waves are substituted for the Maxwell equations. A. J. M.

**Crystal structure and electrical properties. VI. Conductivity surfaces in bismuth crystals. I.** O. STIERSTADT (Z. Physik, 1934, 87, 687—699).—Conductivity distribution for a metal crystal in a magnetic field is shown to give a picture of the lattice symmetry. The conductivity surfaces of a Bi crystal without magnetic field are rotation ellipsoids; with a magnetic field these depend in a complicated way on the angle between the field and the crystal axis. A. B. D. C.

**Ferromagnetism of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>.** J. G. KOENIGSBERGER (Naturwiss., 1934, 22, 90).—The magnetic properties of several natural and artificial specimens of Fe<sub>2</sub>O<sub>3</sub>, pure, and mixed with magnetite, were investigated. A ferromagnetic trigonal  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, differing from magnetite in its crit. temp., can be formed under conditions prevailing in nature (temp.  $\leq$  200°; pressure  $\leq$  40 atm.). A. J. M.

**Magnetic anisotropy of graphite.** K. S. KRISHNAN (Nature, 1934, 133, 174—175).—The principal susceptibilities of crystals of Ceylon graphite are  $\chi_1 - 0.4 \times 10^{-6}$  and  $\chi_2 - 22.8 \times 10^{-6}$ . L. S. T.

**Magnetic variations in iron and steel as a function of temperature.** J. SEIGLE (J. Phys. Radium, 1934, [vii], 5, 37—48).—The effect of temp. on magnetic and expansion anomalies is considered from an examination of curves for various types of Fe and steel. Curie points and paramagnetism are discussed. The  $\beta$  form of Fe is regarded as a combination of  $\alpha$  and  $\gamma$  forms, in the temp. range 720—910°, for pure Fe. N. M. B.

**Crystal diamagnetism of bismuth crystals.** A. GOETZ and A. B. FOCKE (Physical Rev., 1934, [ii], 45, 170—199).—The effect on electron configuration in the single crystal lattice of the presence of small

concn. of foreign atoms is investigated. Magnetic anisotropy and susceptibility data for various field strengths are tabulated for several hundred crystals of Bi with small admixtures of Ag, Sn, Pb, Te, Se, and Sb, grown by a modified Goetz method at eight temp. between -185° and 245°. The problem of crystal diamagnetism (I), a property of cryst. matter depending on the presence of large nos. of atoms in the cryst. array, is examined, and the influence on anisotropy, susceptibility, and (I) of concn., type of admixture, and temp. is discussed in detail. N. M. B.

**Magnetostriction and ferromagnetic ellipsoids. I. Theory.** R. BECKER. II. **Measurements with iron and cobalt.** M. KORNETZKI (Z. Physik, 1934, 87, 547—559, 560—579).—I. Dependence of the magnetostriction of an ellipsoid on the ratio of its axes is determined for regions below, at, and above saturation.

II. Longitudinal and vol. magnetostriction were observed in ellipsoids of Fe and Co for fields up to 7000 and 10,000 gauss, respectively; the results agree with Becker's theory. A. B. D. C.

**Magnetic quenching of tellurium (Te<sub>2</sub>).** J. GENARD (Compt. rend., 1934, 198, 816—819; cf. this vol., 1, 2).—With similar methods, but using a more powerful field, Smoluchowski's results are confirmed and amplified (cf. A., 1933, 1095). C. A. S.

**Supposed allotropy of liquid nitrobenzene.** E. COHEN and L. C. J. TE BOEKHORST (Z. physikal. Chem., 1934, B, 24, 241—258; cf. A., 1933, 12).—No criterion for existence of allotropy is found with pure PhNO<sub>2</sub> in the density and viscosity data. R. C.

**Structure and gas content of nickel layers formed by cathodic sputtering.** W. BÜSSEM and F. GROS (Z. Physik, 1934, 87, 778—799).—Ni films sputtered in H<sub>2</sub> are hexagonal I, in N<sub>2</sub> tetragonal and hexagonal II, and the hexagonal I may be transformed into the cubic, the tetragonal into hexagonal II, and then into the cubic structure. A. B. D. C.

**Damping power as an essential property of mica.** E. OROWAN (Z. Physik, 1934, 87, 749—752).—Mica, cut so that it is not flaked, rings like a piece of steel. A. B. D. C.

**Critical field in superconductivity.** D. R. INGLIS (J. Franklin Inst., 1934, 217, 227—228).—A brief discussion.

**Metallic photo-resistance.** Q. MAJORANA (Atti R. Accad. Lincei, 1933, [vi], 18, 184—188; cf. A., 1932, 898).—Practically no variation in resistance of thin films of Al or Na is obtained when they are exposed to intermittent light from a Hg or incandescence lamp. O. J. W.

**Magneto-thermo-electric effects in nickel and iron.** A. PERRIER and (Mlle.) T. KOUSMINE (Compt. rend., 1934, 198, 810—812).—The differences,  $\Delta E$ , between the thermoelectric power of couples consisting of a non-magnetic metal and Ni or Fe unmagnetised, and of couples consisting of the same metal and Ni or Fe magnetised parallel, ||, or perpendicular,  $\perp$ , to the direction of the temp. gradient are plotted against the strength of magnetic field ( $H=55.5-1300$  gauss).  $\Delta E$  is positive, i.e., indic-

ates increase in thermo-electric power, or negative according as  $H$  is  $\parallel$  or  $\perp$ , and much greater when it is  $\parallel$ .  
C. A. S.

**Hall, Nernst, Etingshausen, and Righi-Leduc effects.** N. AKULOV (Z. Physik, 1934, 87, 768—777).—Change of thermo-electric forces of ferromagnetic metals with magnetisation and deformation is shown to be due to anisotropy of the crystals and change in orientation of resultant spin of individual crystal regions.  
A. B. D. C.

**Reflexion of ultrasonic waves.** E. HIEDEMANN and H. R. ASBACH (Z. Physik, 1934, 87, 442—446).—Diffraction of light by ultrasonic waves was used to photograph reflexion from concave and convex cylindrical mirrors.  
A. B. D. C.

**Propagation of supersonic waves through an electrolyte.** S. OKA (Proc. Phys.-Math. Soc. Japan, 1933, 15, 413—419).—Relaxation and electrophoretic forces are taken into account in an extension of Debye's theory.  
CH. ABS.

**Absorption of supersonic waves in mixtures of air and carbon dioxide at different relative humidities.** H. H. ROGERS (Physical Rev., 1934, [ii], 45, 208—211).—The absorption of waves of frequency 409.6 kc. per sec. from a quartz crystal oscillator was measured for the R.H. range 10—75%. The absorption const. is a linear function of the %  $\text{CO}_2$ , and is a max. at 45% R.H., then falling rapidly.  
N. M. B.

**Rendering visible standing ultrasonic waves in liquids: determination of ultrasonic wave velocity.** C. BACHEM, E. HIEDEMANN, and H. R. ASBACH (Z. Physik, 1934, 87, 734—737).—The waves are followed by the variation of light transparency along the direction of the wave, and the wave-lengths thus observed give an accurate measure of the velocity.  
A. B. D. C.

**Rendering visible progressive ultrasonic waves in liquids by means of a high-frequency stroboscope; determination of ultrasonic velocities in liquids.** C. BACHEM (Z. Physik, 1934, 87, 738—740; cf. preceding abstract).  
A. B. D. C.

**Attainment of low temperatures.** F. SIMON (Z. Physik, 1934, 87, 815—818).—A reply to Justi (this vol., 246).  
A. B. D. C.

**Specific heats of real gases.** E. J. HONIGMANN (Z. Physik, 1934, 87, 659—673).—A theoretical deduction of the sp. heats of gases obeying relations of the type:  $d(PV) = (n-1)dU$ ,  $U$  being the internal energy;  $n$  is a term of proportionality of real gases.  
A. B. D. C.

**Specific heats of liquids by a cooling method.** R. W. B. STEPHENS (Phil. Mag., 1934, [vii], 17, 297—312).—The sp. heat in g.-cal. of  $\text{C}_6\text{H}_6$  is 0.399 at 12.5° and 0.402 at 8°, and that of PhMe 0.390 at 12.5° and 0.386 at 7.5°. The accuracy is limited by that for the calibrating liquids, and a method of eliminating this possible source of error is suggested. For bakelite the following data have been determined: thermal conductivity 7.47 and  $7.62 \times 10^{-4}$  cal./cm./sec./° C., at 7.5° and 12.5°, respectively,  $d^{15}$  1.335, linear coeff. of expansion  $2.5 \times 10^{-5}$  per ° C., sp. heat 0.383 g.-cal. ° C.  
H. S. P.

**Heat capacities at low temperatures of the alkaline-earth carbonates.** C. T. ANDERSON (J. Amer. Chem. Soc., 1934, 56, 340—342).—Heat capacities have been determined between 55° and 300° abs. The following entropies at 298.1° abs. (in e.u.) have been calc.: calcite (coarse)  $22.24 \pm 0.4$ , calcite (fine)  $22.40$ , aragonite  $21.18 \pm 0.3$ , strontianite  $23.21 \pm 0.4$ , witherite  $26.75 \pm 0.5$ .  
E. S. H.

**Law of the additivity of specific heats in heteropolar compounds.** F. M. JAEGER (Chem. Weekblad, 1934, 31, 60—61).—The apparent sp. heat ( $C_p$ ) of the O in metallic oxides, calc. additively from recent data, varies from (approx.) 3700 ( $\text{IrO}_2$ ) to 5400 ( $\text{Cu}_2\text{O}$ ) at 0°, and from 5800 ( $\text{Rh}_2\text{O}_3$ ) to 7500 ( $\text{IrO}_2$ ) at 530°. At all temp. the val. in  $\text{Cu}_2\text{O}$  is  $>$  in  $\text{CuO}$ , and falls in  $\text{RhO}$ ,  $\text{Rh}_2\text{O}$ , and  $\text{Rh}_2\text{O}_3$  in the order given.  
H. F. G.

**Heat-capacity curves of the simpler gases. IV. Extension of the "free energy" formula of Giauque and Overstreet to yield reliable approximation formulæ for calculation of entropy and heat capacity from spectroscopic data.** Entropy and heat capacity of carbon monoxide and nitrogen from near 0° K. to 5000° K. H. L. JOHNSTON and C. O. DAVIS (J. Amer. Chem. Soc., 1934, 56, 271—276; cf. A., 1933, 229, 1005).—The calc. vals. of entropy and heat capacity are tabulated for the temp. range indicated.  
E. S. H.

**Discontinuity in thermal behaviour of methane at 20.4° abs. as a phase change of the second order.** K. CLUSIUS and A. PERLICK (Z. physikal. Chem., 1934, B, 24, 313—327).—Ehrenfest's theory (A., 1933, 569) is applied. Phase changes of the second order probably occur in many solidified gases and  $\text{NH}_4$  salts. The transformation of  $\text{CH}_4$  at 20.4° abs. has been studied.  $\text{CH}_4$  crystals become doubly refracting on cooling with liquid  $\text{H}_2$  owing to strain. The sp. heat of the solid has been measured at 15—25°. At the change point there is no heat effect, but the mol. heat changes abruptly from 81 to 13 g.-cal. The val. of  $\Delta(\partial v/\partial T)$  calc. by Ehrenfest's theory from observations of the effect of pressure on the change point agrees with the val. derived from the variation of the mol. vol. with temp., showing that the transformation is a phase change of the second order. The probable reason for the change is that above 20.4°, but not below, the mols. rotate freely in the lattice.  
R. C.

**Heat of dissociation of  $\text{Bi}_2$  determined by the method of molecular beams.** C. C. KO (J. Franklin Inst., 1934, 217, 173—199).—By a modified technique (cf. A., 1931, 542) the ratio of  $\text{Bi}_2$  to Bi in mol. beams has been determined to within 1%. The Bi deposits are stabilised by heating to 60°. The v.p.,  $P_{(\text{mm.})}$ , of the metal between 1100° and 1220° abs. by the Knudsen method is given by  $\log_{10} P = -52.23 \times 195.26/T + 8.56$ , and the heat of dissociation of  $\text{Bi}_2$  is  $77,100 \pm 1200$  g.-cal. The beam at 827° contains approx. 2% of  $\text{Bi}_8$  mols. in addition to Bi and  $\text{Bi}_2$ , but  $\text{Bi}_3$ ,  $\text{Bi}_4$ , and  $\text{Bi}_6$  are absent.  
J. G. A. G.

**Calculation from optical and thermal data of heats of dissociation into atoms of gaseous lithium iodide, and sodium and potassium**



chlorides, bromides, and iodides. Heats of vaporisation of potassium and lithium. H. BEUTLER and H. LEVI (*Z. physikal. Chem.*, 1934, **B**, 24, 263—281).—By means of a cycle combining thermochemical, physical, and optical measurements, heats of dissociation have been calc. with a precision equal to that attainable by direct calculation from data for band spectra. The heats of sublimation of K and Li are calc. from the chemical consts. to be  $21.42 \pm 0.2$  and  $33.3 \pm 0.8$  kg.-cal., respectively, at  $0^\circ$  abs. R. C.

M.p. of  $\text{NF}_3$ . O. RUFF and W. MENZEL (*Z. anorg. Chem.*, 1934, 217, 93—94).—Of the three halts in the heating curve of  $\text{NF}_3$  previously observed (A., 1930, 986) two have been confirmed. The m.p. is  $-208.8^\circ$  and there is a transition point at  $-219^\circ$ . Below this temp.  $\text{NF}_3$  is snow-white and opaque; above, it forms transparent crystals. M. S. B.

Volume of the meniscus at the surface of a liquid. III. A. W. PORTER (*Phil. Mag.*, 1934, [vii], 17, 511—518; cf. *ibid.*, 1932, [vii], 14, 694).—Data are tabulated. H. J. E.

Determination of the thermal conductivity of air between  $0^\circ$  and  $100^\circ$  C. S. W. MILVERTON (*Phil. Mag.*, 1934, [vii], 17, 397—422).—The method, based on the measurement of heat losses from a hot Pt wire, is described, and data are tabulated. H. J. E.

Effect of accommodation on heat conduction through gases. B. G. DICKINS (*Proc. Roy. Soc.*, 1934, **A**, 143, 517—540).—By means of a modification of the "hot-wire" method, the thermal conductivities and accommodation coeffs. have been determined for He, A,  $\text{H}_2$ , CO,  $\text{O}_2$ , air,  $\text{N}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{NH}_3$ , and  $\text{SO}_2$ . Experimental errors have been reduced to a min. The vals. obtained are  $>$  those of previous investigators. L. L. B.

Volume coefficients of expansion of several gases at pressures below one metre. J. B. M. COPPOCK and R. WHYTLAW-GRAY (*Proc. Roy. Soc.*, 1934, **A**, 143, 487—505).—Using a modified Callendar const.-pressure air thermometer and reservoirs of both glass and  $\text{SiO}_2$ , determinations of the vol. coeffs. of expansion of  $\text{C}_2\text{H}_4$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ , NO, CO,  $\text{Me}_2\text{O}$ , and  $\text{SF}_6$  have been made at several pressures over two temp. ranges,  $25$ — $50^\circ$  and  $11$ — $48^\circ$ . The limiting val. for the coeff. at zero pressure, obtained by extrapolation, is  $>$  the accepted val.  $3661 \times 10^{-6}$  for  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{C}_2\text{H}_4$  in glass vessels, but in  $\text{SiO}_2$  vessels it is in close agreement. This discrepancy is due to the greater adsorption on glass than on  $\text{SiO}_2$  surfaces. L. L. B.

Preparation, [vapour] pressures, and densities of pure hydrogen sulphide. (Atomic weight of sulphur.) A. KLEMENC and O. BANKOWSKI (*Z. anorg. Chem.*, 1934, 217, 62—64).—The criticism by Batuecas (A., 1933, 1006) gives no ground for changing the data previously given for  $\text{H}_2\text{S}$  gas (A., 1933, 16). M. S. B.

Isotherms of nitrogen between  $0^\circ$  and  $150^\circ$ , and at pressures up to 400 atmospheres. J. OTTO, A. MICHELS, and H. WOUTERS (*Physikal. Z.*, 1934, 35, 97—100).—Data for the  $\text{N}_2$  isotherms at temp. between  $0^\circ$  and  $150^\circ$ , by  $25^\circ$ , and pressures of

45—400 atm. are given. Empirical formulæ are given connecting  $pv$  with density and with pressure.

A. J. M.

Calculation of thermodynamic quantities from spectroscopic data for polyatomic molecules; free energy, entropy, and heat capacity of steam. A. R. GORDON (*J. Chem. Physics*, 1934, 2, 65—72; cf. this vol., 31).—Mathematical. Data for steam in the temp. range  $298.1$ — $1500^\circ$  abs. are tabulated, and revised vals., in agreement with experiment, for the equilibrium const. of the water-gas reaction are calc. N. M. B.

V.p. of liquid and solid deuterochloric acid. G. N. LEWIS, R. T. MACDONALD, and P. W. SCHUTZ (*J. Amer. Chem. Soc.*, 1934, 56, 494—495).— $\text{H}^2\text{Cl}$  is prepared by reaction of  $\text{H}_2\text{O}$  with  $\text{MgCl}_2$  at  $600^\circ$ . V.p. have been measured at  $152.6$ — $200.9^\circ$  abs. Comparing the v.p. of  $\text{H}^2\text{Cl}$ ,  $p_2$ , with those of  $\text{H}^1\text{Cl}$ ,  $p_1$ , the expression  $\log_{10}(p_1/p_2) = 15.4/T - 0.075$  holds accurately for the liquid state and  $\log_{10}(p_1/p_2) = -57.7/T + 0.387$  holds approx. for the solid state. E. S. H.

Relation between van der Waals' constant  $b$  and the dimensions of molecules and atoms. III. K. JABECZYŃSKI (*Rocz. Chem.*, 1934, 14, 10—13).—The radii  $R$  of mols. and atoms of gases, calc. from a formula based on van der Waals' theoretical equation  $b = 4R^3$ , are in good agreement with experimental vals. for a no. of gases, and for their constituent atoms in cryst. compounds. R. T.

Temperature variation of the orthobaric density of unassociated liquids. A. FERGUSON and J. T. MILLER (*Proc. Physical Soc.*, 1934, 46, 140—147).—A formula is obtained, and tested for thirty org. liquids, connecting orthobaric density and temp. It is applied to the evaluation of expansion coeffs., and to show the variation with temp. of free and total mol. surface energies. N. M. B.

Mercury crystals. E. GRÜNEISEN and O. SCKELL (*Ann. Physik*, 1934, [v], 19, 387—408).—Hg has  $d^{-191} 14.46(9)$ . The sp. resistances parallel and perpendicular to the trigonal axis are  $0.0557 \times 10^{-4}$  and  $0.0737 \times 10^{-4}$ , respectively, at  $-187.5^\circ$ . The mean coeffs. of thermal expansion parallel and perpendicular to the trigonal axis between  $-188^\circ$  and  $-79^\circ$  are  $47.0 \times 10^{-6}$  and  $37.5 \times 10^{-6}$ , respectively; the vol. coeff. of expansion is  $122 \times 10^{-6}$ . There is considerable elastic anisotropy compared with the weak thermal anisotropy. A. J. M.

Thermal expansion of silver measured by X-rays. H. SAINI (*Arch. Sci. phys. nat.*, 1933, [v], 15, Suppl., 229).— $a = 4.07725 \text{ \AA.}$  at  $18^\circ$  and the coeff. of expansion measured between  $20^\circ$  and  $300^\circ$  is  $(19.1 \pm 0.2) \times 10^{-6}$  degree $^{-1}$ . R. S.

Shift of transformation interval of glass by pressure. E. JENCKEL (*Z. anorg. Chem.*, 1934, 216, 349—352).—On heating a glass, there is a narrow temp. range through which the expansion coeff.  $dv/dt$  and sp. heat  $c$  increase very rapidly. The curves of  $dv/dt$  and  $c$  against  $T$  have the same inflexion point at  $T_w$ , which is also the point at which the two branches of the curve of  $v$  against  $T$  and heat content against  $T$  intersect. By modifying the Clausius-Clapeyron expression for the dependence of the m.p. of

a crystal on pressure, the shift of the transformation interval with temp. is:  $dp/dt = (c_1 - c_2)/T_v[(dv/dt)_1 - (dv/dt)_2]$ , where indices 1 and 2 indicate conditions for the highly viscous liquid and the glass, respectively. Calc. vals. of  $dp/dt$  agree satisfactorily with known experimental data for Se, salicin,  $B_2O_3$ , and colophony.

M. S. B.

**Determination of the temperature interval of transformation of glasses by change of viscosity with temperature.** E. JENCKEL (Z. anorg. Chem., 1934, 216, 367—375).—Two methods of determining  $\eta$  by the extension of loaded glass filaments, isothermally at different temp. or as the temp. slowly rises, are described, and data given for  $B_2O_3$  and some silicate glasses. This provides a simple method for determining  $T_v$  with nearly the same degree of accuracy as by determination of  $dv/dt$  or  $c$  (cf. preceding abstract).

M. S. B.

**Compressibility of certain gases at low pressures.** T. BATUECAS (J. Chim. phys., 1934, 31, 65—75; cf. A., 1933, 770).—A criticism of the data used by Cawood and Patterson in deducing mol. wts. from their compressibility measurements. Vals. of the coeffs. of expansion for  $C_2H_4$ ,  $CO_2$ ,  $N_2O$ ,  $SO_2$ ,  $Me_2O$ , and  $MeF$  calc. from their measurements agree satisfactorily with the theoretical vals. deduced by Leduc.

H. S. P.

**Heavy water inert, due to low association.** E. C. BINGHAM and W. H. STEVENS, jun. (J. Chem. Physics, 1934, 2, 107—108).—Fluidity data indicate that the associations of  $H_2O$  and  $D_2O$  are in the ratio 1.34 : 2.50. This and other evidence is in agreement with the observed inertness of  $H_2O$ .

N. M. B.

**Viscosity of liquids. I, II.** E. N. DA C. ANDRADE (Phil. Mag., 1934, [vii], 17, 497—511, 698—732).—I. A theoretical expression has been derived for the viscosity near the f.p., in approx. agreement with experimental vals. for Hg, Pb, Sn, Cu, Sb, Bi, Cl<sub>2</sub>, Br, I, O<sub>2</sub>, and H<sub>2</sub>.

II. Theoretical. The temp. variation of viscosity ( $\eta$ ) is expressed by  $\eta v^{1.3} = Ae^{c/T}$  ( $A$ ,  $c$  are consts.,  $v$  = sp. vol.), in agreement with experimental vals. for associated and non-associated liquids.  $H_2O$  and certain *tert.* alcohols are exceptions.  $c$  shows gradual changes in homologous series of liquids, and for many liquids is proportional to the total internal energy. An expression for the variation of  $\eta$  with  $p$  is derived, agreeing with experimental vals. for  $Et_2O$ ,  $COMe_2$ ,  $EtBr$ , and  $EtI$ .

H. J. E.

**Solubility of vapours in gases.** W. MACFARLANE and R. WRIGHT (J.C.S., 1934, 207—210).—The pressure decreases when a gas is mixed with the vapour of a liquid in which the gas is very sol. Data at 25° are recorded for binary mixtures of  $CO_2$ , air,  $SO_2$ ,  $NH_3$ , and  $HCl$  with  $Et_2O$ ,  $MeOH$ ,  $COMe_2$ , and  $CHCl_3$  vapours.

J. G. A. G.

**X-Ray study of aluminium-zinc alloys.** E. A. OWEN and J. IBALL (Phil. Mag., 1934, [vii], 17, 433—457).—Alloys quenched from 250° consist of (1) an  $\alpha$ -phase (close-packed hexagonal; < 2 wt.-% Al), (2) an  $\alpha + \gamma$  region (2—80% Al), (3) a  $\gamma$ -phase (face-centred cubic; > 80% Al). The parameter of the  $\gamma$ -phase changes from 4.0406 Å. (100% Al) to 4.0345 Å.

(80% Al). Photographs at 290—450° show a transformation temp. at 300—310°. The  $\beta$ -phase is a solid solution (face-centred cubic; 19—45% Al at 375°). The corresponding parameters are 4.016, 4.058 Å. In the  $\beta + \gamma$  region the two face-centred cubic lattices of different parameter co-exist. The solubility range of Zn in Al at higher temp. is < previous vals. indicate.

H. J. E.

**Lattice structure of lithium-cadmium alloys.** Z. ZINTL and A. SCHNEIDER (Z. Elektrochem., 1934, 40, 107).—A criticism of Baroni's results (this vol., 137).

M. S. B.

**Solid phase in the system antimony-bismuth.** W. F. EHRET and M. B. ABRAMSON (J. Amer. Chem. Soc., 1934, 56, 385—388).—X-Ray and microscopical examination reveal the presence of only one phase, indicating a continuous series of solid solutions.

E. S. H.

**Platinum-chromium alloys.** V. A. NEMILOV (Ann. Inst. Platine, 1933, No. 11, 125—134).—The existence of PtCr is suggested by hardness, conductivity, and microcrystallographic data. The thermal diagram, on the other hand, is of the type which corresponds with the formation of solid solutions.

R. T.

**Resistances of copper-palladium alloys.** D. STOCKDALE (Trans. Faraday Soc., 1934, 30, 310—314).—The sp. resistance and temp. coeff.,  $\alpha$ , of annealed alloys with 53.4—60.8 at.-% Pd have been determined over the range 0—148°.  $\alpha$  decreases with rise of temp. and passes through a min. at 56—58 at.-% Pd.

J. G. A. G.

**Electrical conductivity and phase diagram of binary alloys. IX. System magnesium-thallium.** G. GRUBE and J. HILLE (Z. Elektrochem., 1934, 40, 101—106).—The diagram is constructed from electrical conductivity measurements at different temp. and thermal analysis. The existence of  $TlMg_2$  and  $TlMg$  is confirmed, and  $Tl_2Mg_5$  is also shown to be formed. The effect of Mg on the transformation  $\alpha-Tl \rightleftharpoons \beta-Tl$  is indicated.

M. S. B.

**Effect of nickel on transformation point of  $\beta$ -brass and heterogeneous equilibria of the ternary system Cu-Zn-Ni.** K. YAMAGUCHI and K. NAKAMURA (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 89—109).—The transformation point of  $\beta$ -brass near 460° is raised by the addition of Ni.

C. W. G.

**Equilibria in the iron-carbon system.** A. STANSFIELD (Trans. Roy. Soc. Canada, 1933, [iii], 27, III, 177—178).—Fe-C equilibria may be investigated by passing a mixture of CO and  $CO_2$  of known composition over fine turnings of the Fe-C alloy contained in a quartz tube in an electric furnace at known temp., and finding the change in the  $CO_2$  content of the gas.

H. S. P.

**Influence of cathodic hydrogen on the stability of steel.** D. ALEXEEV, P. AFANASIEV, and V. OSTROUMOV (Z. Elektrochem., 1934, 40, 92—98).—The fragility which results when steel is polarised in  $H_2SO_4$  in presence of  $H_2S$ ,  $SO_2$ , or  $As_2O_3$  is apparently due to the entry of  $H_2$  into the inter-cryst. spaces. Neither metallographic nor X-ray examination indicates any structural change in the steel thus satur-

ated with  $H_2$ . The gas is probably present in two forms, a loosely bound form which is easily removed by mechanical working or rise of temp., and a solid solution. The added substances probably act as  $H_2$  carriers. The effect of variation of c.d., loading of steel wire,  $H_2S$  concn., time of polarisation, and temp. has been studied.

M. S. B.

**Crystal structure and ferromagnetism of Mn-Al-Cu alloys.** O. HEUSLER (Z. Metallk., 1933, 25, 274—277).—Debye-Scherrer photographs of quenched  $\beta$ -Mn-Al-Cu alloys show threefold superstructure lines corresponding with a lattice made up of two face-centred cubic lattices making up a lattice of the NaCl type (I) and a body-centred cubic lattice (II) symmetrically disposed in (I). When the composition of the  $\beta$ -phase corresponds with  $Cu_2MnAl$ , the Al and Mn atoms occupy the points of (I) and the Cu atoms the points of (II); with other compositions the element in excess of that necessary to fill one lattice fills the points in the other lattice left vacant by the absence of sufficient of its appropriate atoms. On ageing the quenched alloys no new lines appear in the photographs, but the intensities of the superstructure lines change. This, taken in conjunction with measurements of the electrical conductivity, affords evidence in support of the assumption that completely regular orientation of the lattice structure occurs only on prolonged annealing, the lattice of the quenched alloys containing 20—30% of its atoms in random orientation. Magnetisation experiments lead to the conclusion that the magnetic properties of these alloys are adversely affected by the introduction of foreign atoms into the regularly oriented lattice structure, whether these are introduced by variation of the composition from  $Cu_2AlMn$  or by heat-treatment of the alloy with stoichiometric composition.

A. R. P.

**M.p., b.p., refractive indices, and densities of the system water-1:4-dioxan.** J. GILLIS and A. DELAUNOIS (Rec. trav. chim., 1934, 53, 186—190).—The m.-p. data show a eutectic at  $-14.82^\circ$ . Formation of a hydrate is indicated.

H. J. E.

**Constancy of viscosity of concentrated lithium chloride solutions at low-velocity gradients.** G. W. S. BLAIR and R. K. SCHOFIELD (Phil. Mag., 1934, [vii], 17, 225—229).—Observations made with a rotating cylinder show that the viscosity remains const., even when the max. velocity gradient is only  $0.003 \text{ sec.}^{-1}$ . Previously reported anomalies are explained.

H. S. P.

**Diffusion in molecular dispersions.** R. O. HERZOG, R. ILLIG, and H. KUDAR (Z. physikal. Chem., 1934, 167, 329—342).—The Einstein-Sutherland diffusion equation may be deduced from Riecke's diffusion theory by the methods of hydrodynamics without using the concept of driving force due to osmotic pressure gradient. Equations are derived for the diffusion coeff.,  $D$ , for diffusing mols. having the form of ellipsoids of revolution.  $D$  has been measured for numerous solutions of org. substances in org. solvents, the solute usually being a halogen derivative of the solvent. The val. of the mol. radius deduced from the observed val. of  $D$  is usually  $<$  the val. deduced from space-filling data. This divergence is

ascribed to a reduction in the rotational component of the viscosity (A., 1933, 770) due to attractive forces between the solvent and solute mols., which are probably mainly of a dipole character. It is inferred that the Einstein-Sutherland formula will be valid for the diffusion of spherical dipole-free mols. (saturated hydrocarbon) in a dipole-free solvent (saturated hydrocarbon).

R. C.

**A law of corresponding states for solutions of dipole substances.** A. E. VAN ARKEL and J. L. SNOEK (Physikal. Z., 1934, 35, 187—196).—The examination of twenty-three non-associating dipole liquids shows that the dependence of mol. polarisation on concn., temp., and pressure can be expressed by an equation in which the only parameters are the moment per unit vol. and the temp. Hence for corresponding states the same behaviour is found. A formula is also given for mixtures of two dipole substances. The behaviour of liquids with groups capable of free rotation and of strongly associated substances is described with reference to the dependence of mol. polarisation on concn., temp., and pressure.

A. J. M.

**Internal equilibria and partial vapour pressures of mixtures of primary normal alcohols with normal paraffin hydrocarbons.** G. VON ELBE (J. Chem. Physics, 1934, 2, 73—81).—For mixtures of MeOH, EtOH, Pr<sup>n</sup>OH, and Bu<sup>n</sup>OH with hexane and heptane the heat of mixing at  $10-45^\circ$  is always negative, and heat absorption per mol. of alcohol increases with dilution to a limit of 5800 g.-cal. per mol. The curves of mol. heat absorption-mol. alcohol concn. are identical. It is inferred that the pure liquid primary  $n$ -alcohols are completely associated to double mols., and dissociate to single mols. on mixing with a hydrocarbon. The equilibria between single and double mols. at the same mol. concn. are identical for all primary  $n$ -alcohols in all  $n$ -hydrocarbons. This theory leads to an equation for the partial v.p. of  $n$ -alcohols in  $n$ -hydrocarbons, and for the degree of dissociation and heat of mixing at any temp. and concn.

N. M. B.

**Differences and similarities between azeotropic and heteroazeotropic phenomena, and the relation between composition of heteroazeotrope and temperature.** I. RABCEWICZ-ZUBKOWSKI (Rocz. Chem., 1934, 14, 19—23).—The phenomena of azeotropy are due to changes in the degree of association of the components, whilst those of heteroazeotropy follow from summation of the v.p. of the components according to Dalton's law.

R. T.

**Stability of heterogeneous liquids.** J. L. SYNGE (Trans. Roy. Soc. Canada, 1933, [iii], 27, III, 1—18).—Mathematical. Investigations have been made of the stability of rotating heterogeneous liquids and of the horizontal streaming of such a liquid under gravity.

H. S. P.

**Critical miscibility of liquids.** P. BRUN (J. Chim. phys., 1934, 31, 76—78; cf. A., 1932, 1091).—A reply to the criticisms of Mondain-Monval.

H. S. P.

**Critical solution phenomena.** M. FREED (Trans. Roy. Soc. Canada, 1933, [iii], 27, III, 179—181).—The crit. solution temp. of the system  $MeOH-n-C_6H_{14}$  is

34.6° using synthetic  $C_6H_{14}$  and 29.3° using purified  $C_6H_{14}$  from petroleum. Hand's observation relative to the influence of pressure on the system  $AcOH-C_6H_6-H_2O$  (A., 1930, 1512) is not confirmed. H. S. P.

Solutions of methyl alcohol in cyclohexane, in water, and in cyclohexane and water. E. R. WASHBURN and H. C. SPENCER (J. Amer. Chem. Soc., 1934, 56, 361—364).—Equilibrium data are given for the ternary system at 25°. The f.-p. curve for solutions of MeOH in cyclohexane has been determined. E. S. H.

System carbon tetrachloride-water-methyl alcohol at 30°. H. A. SHOWALTER (Trans. Roy. Soc. Canada, 1933, [iii], 27, III, 183—185).—Bonner's observation that the plait point at 0° is near the  $CCl_4$  end of the binodal curve has been confirmed. The binodal curve and tie lines at 30° have been measured. H. S. P.

Solubility of iodine in the vapour of its solvents. W. BRULL (Z. anorg. Chem., 1934, 216, 353—366).—By a streaming method the saturation concn. at 35° and 46° approx. of pure I in air,  $N_2$ ,  $O_2$ ,  $CH_4$ ,  $CO_2$ , and the vapours of  $CS_2$ ,  $CHCl_3$ ,  $CCl_4$ , and  $C_6H_{14}$  has been determined. In these liquid solvents I gives violet solutions. In all cases the saturation concns. at the same temp. are equal. In  $Et_2O$ , however, the saturation concn. is higher, but the max. is reached only slowly. The results are in good agreement with the supposition that a compound  $I_2 \cdot Et_2O$  is formed with a heat evolution of 3.3 kg.-cal. At a higher concn. of  $Et_2O$  vapour a brown product containing I and  $Et_2O$  separates from the gaseous phase saturated with I. A similar effect is observed in the vapour of other solvents forming brown solutions with I. M. S. B.

Vapour-liquid equilibria in the system nitrogen-water. A. W. SADDINGTON and N. W. KRASE (J. Amer. Chem. Soc., 1934, 56, 353—361).—Data are given for the range 50—250° and pressures up to 300 atm.  $N_2$  has a min. solubility in  $H_2O$  at 70—80°; the effect of pressure is not quantitatively in accordance with Henry's law. The concn. of  $H_2O$  vapour in a given vol. of the compressed gases is considerably > that calc. by the usual methods, especially at higher temp. and pressures. At temp. > 150° an additive rule for the calculation of the compressibility coeff. of the mixture does not hold. E. S. H.

Heptane and its solutions. VII. Solubility of methylamine in heptane. G. O. DOAK (J. Amer. Pharm. Assoc., 1934, 23, 20—21).—The recorded data extend from -13° to 40°. Max. solubility (0.00137 g. per c.c.) is shown at -7°. C. G. A.

Solubility of potassium acid tartrate. I. Tartaric acid and dipotassium tartrate solutions. D. C. CARPENTER and G. L. MACK (J. Amer. Chem. Soc., 1934, 56, 311—313).—Data are given for the range 0—25°. The solubility of K H tartrate is decreased by tartaric acid or  $K_2$  tartrate. Equations have been derived to express the results. E. S. H.

Solubility of potassium acid tartrate. II. Sugar solutions. D. C. CARPENTER and J. J. KUCERA (J. Amer. Chem. Soc., 1934, 56, 324—327).—The solubility of K H tartrate ( $C_1$ ) in solutions of

*d*-glucose, *d*-fructose, invert sugar, or sucrose at 0—20° is given by  $C_1 = C_0 - kC_2^\alpha$ , where  $C_0$  is the solubility of K H tartrate in  $H_2O$ ,  $C_2$  the concn. of sugar, and  $k$  and  $\alpha$  are consts. E. S. H.

Solubility of potassium hydrogen tartrate in solutions of equi-ionic salts. A. WRÓBEL (Rocz. Chem., 1934, 14, 45—52).—The solubility  $L$  of K H tartrate (I) in presence of KCl, KBr, KI, and Na H tartrate is given by  $L = -x/2\gamma + \sqrt{[(L_0\gamma/\gamma_0)^2 + x^2/4\gamma^2]}$ , where  $L_0$  is the solubility of (I) in  $H_2O$ ,  $\gamma_0$  and  $\gamma$  are the dissociation consts. in the saturated aq. solution, and in presence of a concn.  $x$  of  $K'$  or  $C_4H_5O_6'$ .  $L$  increases in presence of K malonate (II), probably owing to association of mols. of (I) and (II). R. T.

Solubility of cupric oxide in salt solutions. J. M. RIGION and H. L. RILEY (J.C.S., 1934, 186—187).—The rate of dissolution and the solubility of  $CuO$  in aq. Na citrate and oxalate are increased by  $CO_2$ , but are diminished by  $OH'$ . The enhanced solubility is attributed to the co-ordinating tendencies of the anions coupled with the neutralisation by  $CO_2$  of the  $OH'$  produced by the dissolution. J. G. A. G.

Solubility in mixtures of solvents, which separately do not dissolve given solutes. A. A. GRÜNBERG and V. M. SCHULMAN (Ann. Inst. Platine, 1933, No. 11, 111—123).—The solubility of  $[Pd_4NH_3][Pt(SCN)_4]$  is at a max. at 0° and 25° in 60%  $COMe_2$ , and at 25° in 60% MeOH. Solvent action is ascribed to the affinity of  $[Pd_4NH_3]''$  for  $H_2O$ , and of  $[Pt(SCN)_4]''$  for  $COMe_2$  or MeOH. R. T.

Distribution of small amounts of substances between liquid and solid crystalline phases. I. Distribution of barium nitrate between saturated aqueous solution and crystals of lead nitrate. A. POLESITSKY (Z. physikal. Chem., 1934, 167, 394—398).—The distribution between saturated  $Pb(NO_3)_2$  solution and  $Pb(NO_3)_2$  crystals of small amounts of  $Ba(NO_3)_2$  at 0°, 25°, and the b.p. is independent of the concn. The distribution ratio increases in favour of the liquid phase as the temp. rises. R. C.

Diffusion with absorption. S. BERNSTEIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 230—234).—Mathematical. H. J. E.

Sorption of hydrogen by reduced nickel. III. Heat-treatment of reduced nickel and its relation to the sorption velocity and to the quantity of hydrogen sorbed. S. IJIMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 23, 164—172).—Heat-treatment at 300—500° shortens the time required for equilibrium to be established in the adsorption of  $H_2$  by reduced Ni at 0° and 20.30 cm. pressure, but diminishes the quantity adsorbed. The velocity of diffusion of  $H_2$  in reduced Ni is unaffected by previous heat-treatment at temp. up to 500°. J. W. S.

Vapour-binding power of active charcoal. I. Dependence of vapour-binding power on the magnitude of the vapour charge of the charcoal. F. KRČZL [with H. WEJROCH] (Kolloid-Z., 1934, 66, 155—163).—The binding power is determined by saturating different kinds of active C with  $C_6H_6$  vapour and measuring the amount of  $C_6H_6$  which can

be subsequently removed in vac. or by the passage of a stream of air. The amount of  $C_6H_6$  thus recovered depends at first on the  $C_6H_6$  content of the C, but later becomes independent at a val. which is characteristic of the kind of C. No relation between adsorptive power and binding power was observed. E. S. H.

**Adsorption of carbon dioxide by activated charcoals in the presence of carbon tetrachloride and hydrogen cyanide.** R. CHAPLIN (Trans. Faraday Soc., 1934, 30, 249—260).—The isothermals at  $25^\circ$  and  $< 0.12$  mm. obtained with air-, steam-, and chemically-activated charcoals show that  $CO_2$  adsorption,  $A$ , is diminished by adsorbed  $CCl_4$  or HCN, but the nature of the process is unchanged; when  $CCl_4$  and HCN are adsorbed together, the irreversible  $A$  is suppressed, and only the reversible  $A$  persists. HCN displaces more bound  $CO_2$  than  $CCl_4$ , but a second displacement of  $CO_2$  always occurs when the second vapour is added, suggesting that neither vapour, when adsorbed singly, can occupy all the active points on the C. J. G. A. G.

**Sorption of gases by minerals. IV. Zeolites and bentonite.** J. SAMESHIMA and H. HEMMI (Bull. Chem. Soc. Japan, 1934, 9, 27—41; cf. A., 1929, 757; 1931, 34, 1120).—The velocity of absorption of  $NH_3$ ,  $CO_2$ ,  $SO_2$ ,  $C_2H_2$ ,  $O_2$ , and  $H_2$  by laumontite (I), stilbite (II), mordenite (III), natrolite (IV), apophyllite (V), analcite (VI), inesite (VII), and bentonite (VIII) has been measured. All except (VI) absorb a large vol. of  $NH_3$ , which combines chemically with (I), (II), (IV), (V), and (VII). (III) absorbs  $NH_3$ ,  $CO_2$ ,  $SO_2$ ,  $C_2H_2$ , and  $O_2$ , and belongs to the chabazite class of sorbent. (VIII) absorbs  $NH_3$ ,  $CO_2$ , and  $SO_2$ , and belongs to the  $SiO_2$  gel class. D. R. D.

**Adsorption of electrolytes on crystalline surfaces. Influence of sign of charge on adsorbent.** L. DE BROUCKÈRE (Compt. rend., 1934, 198, 822—824; cf. A., 1933, 457).— $BaSO_4$  formed by pouring aq.  $H_2SO_4$  rapidly into aq.  $BaCl_2$  is positive, whilst that formed by slowly adding aq.  $BaCl_2$  to aq.  $K_2SO_4$  is negative. The  $\log x$ - $\log C$  curves ( $x$  = electrolyte adsorbed,  $C$  = concn. of solution) for the negative  $BaSO_4$  resemble those previously obtained with the positive, and are consistent with the hypothesis of a unimol. layer. The differences at low concn. are due to the fact that the cations are in contact with the (negative)  $BaSO_4$ . In both cases the adsorption appears to be wholly or partly due to electrostatic action. C. A. S.

**Adsorption of organic substances on crystal surfaces. II. Influence of electrolytes on the adsorption of octyl alcohol on silver sulphide, mercuric sulphide, and barium sulphate, and of nonoic acid on silver sulphide.** N. A. HELD and K. N. SAMOCHVALOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 263—266).—Ions common to the liquid phase and the lattice generally reduce adsorption on the crystal. Adsorption on  $BaSO_4$  is influenced only to a small extent by a common ion. H. J. E.

**Colouring of marble in iodine vapour and the nature of the polish layer.** E. BEUTEL, H. HABERLANDT, and A. KUTZELNIGG (Monatsh., 1934, 64, 53—60).—I is taken up from a dry atm. by marble at room

temp., especially at a surface which has been sawn. The coloration is less when the surface has been etched or sand-blasted, and is much less in the coarsely cryst. material prepared by heating at  $350$ — $500^\circ$ . Adsorption is greater at a polished surface, which is said to consist of crystallites of colloidal dimensions.

E. S. H.  
**Influence of salts on the adsorption of cupric ions by ferric hydroxide.** J. H. HAMENCE (Trans. Faraday Soc., 1934, 30, 299—303).—Equilibrium is reached rapidly, but the adsorption is diminished by rise of temp., and by the presence of  $NH_3$ ,  $NH_4$  and Pb salts, whereas K and Na salts have no effect. The rate of coagulation of  $Fe(OH)_3$  decreases with increasing  $[NH_3]$ . J. G. A. G.

**Adsorption of hydrogen sulphide by activated alumina.** C. H. BAYLEY (Canad. J. Res., 1934, 10, 19—23).—Measurements by static and dynamic methods of the adsorption of  $H_2S$  by activated  $Al_2O_3$  show that this is a max. when the temp. of preheating is  $550^\circ$ . A. G.

**Adsorption and catalysis on alumina.** GUICHARD (Compt. rend., 1934, 198, 573—575; cf. A., 1926, 475).—The adsorption of  $H_2O$ , EtOH, and  $Et_2O$  by  $Al_2O_3$  has been determined at various temp. and pressures. At  $240^\circ$  (the usual temp. for dehydrating EtOH by catalysis with  $Al_2O_3$ ) the adsorption of  $H_2O$  and  $Et_2O$  is practically nil, whilst that of EtOH is still appreciable. C. A. S.

**Adsorption and amount of adsorbent. II. Adsorption of dyes by hydrophilic adsorbents.** T. P. PĀPKOVA-KVITZEL (Kolloid-Z., 1934, 66, 148—155; cf. A., 1933, 346).—The variation of total and sp. adsorption,  $x$ , with the amount of adsorbent,  $m$ , has been studied in the systems acid-violet- $Al(OH)_3$  (positive and negative), acid-violet- $SiO_2$ , Me-violet- $SiO_2$ . The expression  $x = km^{1/n}$  is valid only in presence of sufficiently great amounts of adsorbent. Anomalies when  $m$  is small are traced to the effects of dispersion, dehydration, and coagulation of the adsorbent. E. S. H.

**Absorption of dyes by cellulose. II. Influence of temperature.** W. M. GARVIE, L. H. GRIFFITHS, and S. M. NEALE (Trans. Faraday Soc., 1934, 30, 271—278; cf. A., 1933, 1241).—At const. temp. in the range  $25$ — $100^\circ$ , the rate of diffusion,  $D$ , of heliotrope 2B and fast-red K into sheet viscose (I) passes through a max. with increasing concn. of NaCl, but the absorption equilibria rise continuously. With fixed NaCl concn.  $D$  is approx. doubled by each rise of  $20^\circ$ , but the wt. of dye absorbed at equilibrium is approx. halved for every  $30^\circ$  rise. (I) usually absorbs more dye than cotton, but the difference decreases and is ultimately reversed when the absorption is diminished either by raising the temp. or decreasing  $[NaCl]$ . J. G. A. G.

**Sorption of iodine vapour by fibrous materials. I. Plant fibres.** E. BEUTEL and A. KUTZELNIGG (Monatsh., 1934, 64, 41—52).—Plant fibres take up more I from a wet than from a dry atm. The influence of moisture is due to some non-cellulose material. The sorptive power of cotton is not altered by extracting with EtOH or  $Et_2O$  ( $COMe_2$  produces a

slight effect), but is strongly affected by degreasing with alkali. Flax, ramie, jute, and kapok take up I rapidly when heated with it in a sealed tube at 120°. The resulting material is grey, appearing brown in transmitted light, and has a reduced strength. Under similar conditions cotton becomes brown and its mechanical properties are not impaired. Brown colours are due to thin layers of I, and indicate general adsorption, whilst a chemical change is involved in the production of the blue colours. E. S. H.

**Relation between ascent of colloidal particles in porous substances and their adsorption by such.** A. BOUTARIC and M. PEYRAUD (Compt. rend., 1934, 198, 651—652; cf. this vol., 24).—The velocity,  $v$ , of ascension in vertical strips of filter-paper, and the adsorption-concn. in the paper,  $\sigma$ , have been determined for  $As_2S_3$  sols diluted with  $H_2O$  or aq. NaCl, and  $Fe(OH)_3$  sols diluted with  $H_2O$  or aq.  $FeCl_3$ . For  $As_2S_3$  and  $H_2O$   $\sigma$  is zero, but increases with NaCl concn., whilst  $v$  decreases. In  $Fe(OH)_3$  and  $FeCl_3$   $v$  increases to a max. and then decreases, whilst  $\sigma$  changes in reverse fashion. Colloidal dyes with negative particles behave like  $As_2S_3$ , whilst those with positive particles behave like  $Fe(OH)_3$  in that  $v$  always varies oppositely to  $\sigma$ . C. A. S.

**Adsorption and capillary condensation.** A. A. SCHUCHOVITZKI (Kolloid-Z., 1934, 66, 139—147).—Theoretical. E. S. H.

**Relation between activated and van der Waals adsorption.** J. HOWARD (Trans. Faraday Soc., 1934, 30, 278—287; cf. A., 1933, 1112).—The activated adsorption (I) of  $H_2$  by Cr oxide gel (II) is not due either to impurities (cf. A., 1933, 898) or to diffusion of dissolved gas. The influence of (II) on the velocity of the para- $H_2$  conversion (III) shows a min. in the temp. range where van der Waals adsorption is small and (I) is very slow. This suggests that (III) occurs with mols. which are adsorbed at low temp. by van der Waals forces and at high temp. by (I) (cf. A., 1933, 680). J. G. A. G.

**Theory of adsorption. I. Negative adsorption of solute of dilute electrolytic solution at the free surface.** K. SHIBA (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 109—115).—The connexion between adsorption and the changes of surface tension is discussed. C. W. G.

**Diffusion of hydrogen through metals: fractionating the hydrogen isotopes.** C. G. FINK, H. C. UREY, and D. B. LAKE (J. Chem. Physics, 1934, 2, 105—106).—When electrolysis is carried out with Fe, Ni, or Pd tube cathodes, fractionation results from diffusion through the metal,  $H^1$  diffusing more rapidly than  $H^2$ . Pd gave the best results, and the mixture, on burning, gave  $H_2O$  of  $d$  1.00020. N. M. B.

**Influence of hydrogen-ion concentration on the velocity of diffusion of the chlorine ion through collodion membranes.** K. HRYNAKOWSKI (Rocz. Chem., 1934, 14, 53—59).—The velocity of diffusion of  $Cl^-$  through collodion diminishes with increasing  $p_H$  and  $[Ca^{++}]$ . R. T.

**Shape of the profile of a liquid film draining on a vertical, clean, wetted glass plate and the**

**combined effects of gravity, viscosity, surface tension, and evaporation on the same.** J. SALTERBY and H. GIVENS (Trans. Roy. Soc. Canada, 1933, [iii], 27, III, 145—159).—A theoretical and experimental attempt has been made to ascertain the influence of evaporation and surface tension (I) on the thickness of the film. The influence of (I) is exceedingly small. H. S. P.

**Thin films on a water surface.** B. G. WHITMORE, R. RICHMOND, and H. A. McTAGGART (Trans. Roy. Soc. Canada, 1933, [iii], 27, III, 113—123).—Films of triolein and oleic acid on compression form droplets showing Brownian motion (I). The droplets are probably lens-shaped with a vol. equal to that of a sphere of 0.5  $\mu$  diameter. Films of palmitic and stearic acid show (I) at low, but not at high, pressures. (I) also occurs when a solid film of tripalmitin is heated to its m.p.  $CH_2Ph\cdot OBz$  spreads in an unusual way and the film on compression shows (I). H. S. P.

**Unimolecular films of fatty acids on glass.** K. B. BLODGETT (J. Amer. Chem. Soc., 1934, 56, 495).—The films are formed by withdrawing a glass slide from 0.001N-NaOH covered with a film of stearic acid under slight surface pressure. Orientation phenomena are described. E. S. H.

**Physical chemistry of wetting phenomena and flotation processes. XI. Wettability of aqueous solutions of surface-active substances on paraffin.** P. REHBINDER, M. LIPETZ, and M. RIMSKAJA (Kolloid-Z., 1934, 66, 212—219; cf. this vol., 141).—The influence of several fatty acids, alcohols, phenols, amines, xanthates, and soaps on the boundary paraffin-aq. solution-air has been studied. The increase of wetting power due to the reagent is greater the higher is the surface activity and the greater is the mol. wt. in a homologous series. The wetting effect is determined by the undissociated mols. and not by the ions. E. S. H.

**Phase boundary potential of monolayers of fatty acids on metals.** L. JACOBS (Trans. Faraday Soc., 1934, 30, 303—310; cf. A., 1933, 775).—*n*-Octoic (I) and myristic (II) acids spread uniformly from light petroleum solutions on clean dry Au, Ag, and Pt surfaces. Max. vals. of the phase boundary potential indicate saturation max., and the accessible areas, which depend on the pretreatment of the surfaces, are shown to be 2.7—7.8 times the apparent area. The potential due to (I) increases continuously with concn., but that due to (II) exhibits a discontinuity suggesting a two-dimensional phase change at approx. 39  $\text{\AA}^2$  per mol. The variation of the optical properties of the surface indicates changes of this character at 40—45 and 20—26  $\text{\AA}^2$  per mol. J. G. A. G.

**Lyotropic series and the spreading of proteins.** E. GORTER (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 20—22; cf. A., 1933, 21).—The influence of univalent ions on the spreading of ovalbumin on solutions of  $p_H$  3 increases in the order  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $CNS^-$ . The influence of cations on the spreading of pepsin on solutions of  $p_H$  6 increases in the order  $NH_4^+$ ,  $Li^+$ ,  $K^+$ ,  $Na^+$ . J. W. S.

**Selectivity as exhibited by osmotic diaphragms.** L. L. BURGESS (J. Amer. Chem. Soc.,

1934, 56, 414—419).—Diaphragms have been made by impregnating canvas with (a) Na alginate, (b) soap solution, and (c) casein in aq.  $\text{Na}_2\text{CO}_3$  and subsequent treatment with (a) a solution containing NaCl, NaBr, KCl,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ , and  $\text{MgSO}_4$ , or (b, c) one containing Ca and Mg salts. Diaphragms (a) and (b) retard  $\text{Na}^+$  and favour the passage of  $\text{K}^+$  (or the corresponding salt mols.); (a) favours  $\text{Br}^-$  (at the expense of  $\text{Cl}^-$ ) and to a much smaller extent  $\text{SO}_4^{2-}$  (against  $\text{Cl}^-$ ) and  $\text{Ca}^{2+}$  (against  $\text{Na}^+$  and  $\text{Mg}^{2+}$ ). With (c), the selective action with respect to  $\text{Na}^+$  and  $\text{K}^+$  is reversed. Much greater adsorption of certain ions or salt mols. may occur at the surface of the diaphragm. H. B.

Accumulation of electrolytes. VI. Factors affecting penetration. VII. Molecular versus ionic transport. W. J. V. OSTERHOUT, S. E. KAMERLING, and W. M. STANLEY (J. Gen. Physiol., 1934, 17, 445—467, 469—480).—VI. The relative proportions of the Na and K salts (obtained by shaking aq. KOH and NaOH with a mixture of 70% guaiacol and 30% *p*-cresol) show a change when the salts from one aq. phase are allowed to pass through a non-aq. phase (I) into a second (acid) aq. phase (cf. A., 1932, 977). The observed change depends chiefly on the partition coeffs. (II) and the diffusion consts. in (I). Other factors affecting the ratio are temp., viscosity, rate of stirring, shape and surface of (I), surface forces in (I), outward diffusion from acid aq. layer, movement of  $\text{H}_2\text{O}$  into (I), and the variation of (II) with concn. and  $p_{\text{H}}$ . The observed range of variation in the ratio of K to Na in the above system approximates to that found in *Valonia*.

VII. The order of penetration  $\text{Cs} > \text{Rb} > \text{K} > \text{Na} > \text{Li}$  corresponds with that of the ionic mobilities in  $\text{H}_2\text{O}$ , but is due to the fact that (II) are in the same order, the movement taking place in (I) in the mol. form.  $\text{NH}_4^+$  penetrates more quickly than its (II) would indicate, this being probably due to rapid penetration of  $\text{NH}_3$ . Both observation and calculation indicate that the rate of penetration is not directly proportional to (II), but increases less rapidly. A. L.

Compressibility of aqueous solutions. E. H. LANMAN and B. J. MAIR (J. Amer. Chem. Soc., 1934, 56, 390—393).—The compressibility coeffs. for aq. LiCl, NaCl, KCl, LiOH, NaOH, KOH, HCl, AcOH, and KOAc (1 mol. of solute to 25, 50, and 100 mols. of  $\text{H}_2\text{O}$ ) have been determined at 25° and 100—300 megabars. The compressibility of anhyd. AcOH has also been determined at 25°. The data confirm the linear relation between the apparent mol. compressibility and the sq. root of the concn. E. S. H.

Cryoscopic determination of hydration of ions of nickel chloride. (MLLE.) O. HUN (Compt. rend., 1934, 198, 740—742; cf. this vol., 252).—The hydration in 0.5*M*- and 0.25*M*- $\text{NiCl}_2$  corresponds with  $\text{NiCl}_2 \cdot 28.5\text{H}_2\text{O}$  and  $\text{NiCl}_2 \cdot 33.1\text{H}_2\text{O}$ , respectively. C. A. S.

Cryoscopic determination of hydration of ions of barium chloride. E. ROUYER (Compt. rend., 1934, 198, 742—744; cf. preceding abstract).—The hydration in 0.5*M*- and 0.25*M*- $\text{BaCl}_2$  corresponds with  $\text{BaCl}_2 \cdot 26.1\text{H}_2\text{O}$  and  $\text{BaCl}_2 \cdot 29.1\text{H}_2\text{O}$ , respectively. C. A. S.

Observation of Brownian movement with the unaided eye. N. ANDREEV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 62).—The light reflected from a point source by a ground or oxidised metal plate shows a flickering in its interference colours as observed by the unaided eye when a thin layer of dil. milk or similar substance is smeared over the surface of the plate. This is attributed to Brownian motion of the fat particles in the milk. J. W. S.

Influence of concentration on the velocity of sedimentation of suspensions. T. PIECHOWICZ (Przemysł Chem., 1934, 18, 4—9).—The measured velocities  $v$  of sedimentation of 0.038—0.38% suspensions of  $\text{SiO}_2$  in  $\text{H}_2\text{O}$  are in good agreement with those calc. from the theoretical formula  $v = kr^2(d_s - d_l)(1 - c) \times \{1 - c^{1/3}(r + \alpha)/1.61r\}/\eta$ , where  $r$  is the radius of the particles,  $d_s$  and  $d_l$  the  $d$  of the solid and liquid phases, respectively,  $c$  the concn. of  $\text{SiO}_2$ , and  $k$  and  $\alpha$  are consts. The above equation does not apply to suspensions of  $\text{SiO}_2$  in PhMe,  $\text{CS}_2$ , or  $\text{CCl}_4$ . R. T.

Highly polymerised compounds. LXXXVII. Behaviour of polystyrenes in Svedberg's sedimentation-velocity centrifuge. R. SIGNER and R. GROSS (Helv. Chim. Acta, 1934, 17, 59—77).—Approx. homogeneous fractions of polystyrenes (I) dispersed in org. liquids have been studied in the ultracentrifuge. At the lowest concns. employed the sedimentation const. ( $s$ ) bears a similar relation to mol. complexity as it does to particle size in suspensions of spherical particles. This relationship becomes progressively obscured as the concn. ( $c$ ) is increased, and at 2.75 g. per litre different fractions give almost the same  $s$ . The partial sp. vol. of the dispersed material is independent of  $c$  and of the degree of polymerisation, whence it is inferred that the effect is not due to change of solvation with  $c$ . That it is not caused by elastic forces is clear from the observation that the sedimentation velocity is everywhere  $\propto$  the centrifugal field, and that  $s$  exhibits no drift during sedimentation. The frictional resistance of the mols. in a given fraction of (I) is  $\propto$  the viscosity of the dispersion medium in  $\text{CHCl}_3$ ,  $\text{C}_2\text{H}_4\text{Br}_2$ , PhBr, xylene, and cyclohexanone, indicating that the mols. have the same form in each of the liquids. For five different fractions examined the mol. friction coeff. is  $\propto c$ , and its val. at  $c=0$  (i.e., when there is no mutual interference between the mols.) is a fundamental characteristic of the fraction. The results support Staudinger's view of the mols. of (I) as extended mol. threads. F. L. U.

Mechanical properties of disperse systems. II. Deformation of soils under tension. G. I. POKROWSKI and V. G. BULYTSHEV (Kolloid-Z., 1934, 66, 137—139; cf. A., 1933, 901).—A mathematical relation, expressing the influence of pressure and tension on highly concn. disperse systems, is confirmed by experiments on clays. E. S. H.

Diffusion of rod-shaped colloids. (Determination of molecular dimensions from diffusion.) R. O. HERZOG and H. KUDAR (with R. ILLIG and W. HERZ) (Z. physikal. Chem., 1934, 167, 343—353).—The equation  $D = kT[\log_e(c/a) + 0.69]/6\pi\eta c$  is derived, where  $D$  is the diffusion coeff. of a rod-shaped mol. of

length  $2c$  and radius  $a$ ,  $\eta$  the viscosity, and  $k$  the Boltzmann const. This agrees with experimental data for solutes of low mol. wt. provided that account is taken of slip, and for hemicolloids, for which there is no slip. For eu colloids, where  $D$  is a function of the concn., agreement is also reached by using a mean  $D$  calc. from data afforded by experiments in which diffusion has already progressed for some time. The above equation thus affords a means of determining  $c$  if  $a$  is known.

R. C.

**Dialysis of colloids. II. Colloidal thorium hydroxide.** B. N. DESAI and A. K. DESAI (Trans. Faraday Soc., 1934, 30, 265—271; cf. this vol., 142).—With progressive dialysis of  $\text{ThO}_2$  sols, the stability decreases continuously and the cataphoretic velocity,  $V$ , passes through a max. Although the initial increase of  $V$  with addition of electrolyte occurs only with univalent coagulating ions, coagulation in the presence of other electrolytes begins at about the same  $V$ , in accord with the view that a crit. pptn. potential exists. With progressive dilution,  $V$  passes through a max., and in all cases the viscosity increases with dialysis and increasing concn. of colloid.

J. G. A. G.

**Aggregation of colloidal electrolytes from transport number and conductivity measurements: some benzidine dyes.** C. ROBINSON and J. L. MOILLIET (Proc. Roy. Soc., 1934, A, 143, 630—653).—The transport nos. of benzopurpurin 4B, its isomeride prepared from *m*-tolidine, and Bordeaux-extra have been determined in the moving-boundary apparatus of MacInnes and Brighton (A., 1925, ii, 542) over a range of concns. From these data and concurrent conductivity measurements conclusions are reached as to the micellar constitution of the dyes.

L. L. B.

**Structure of soil colloids. I. Structure of colloidal ferric hydroxide.** A. I. RABINERSON and G. E. FUCHS (Proc. Leningrad Dept. Gedroiz Inst. Fert., 1933, 22, 1—56).—A classification of soil colloids is suggested which depends on (a) slow coagulation with a local lowering of the  $\zeta$  potential [ $\text{Fe}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_3$ ], or (b) expansion of the sheath of hydration (bentonite, solonetz).

A. M.

**Preparation of colloidal ferric oxide and the properties of its hydrosols.** A. VON BUZAGH (Kolloid-Z., 1934, 66, 129—137).—By heating pptd., washed  $\text{Fe}(\text{OH})_3$  in an autoclave with  $\text{H}_2\text{O}$  and filtering, pure  $\text{Fe}_2\text{O}_3$  is obtained, and may be readily dispersed to a brick-red sol by washing with  $\text{H}_2\text{O}$ . The ability to be peptised is retained after drying at low temp. or with  $\text{EtOH}$  or  $\text{Et}_2\text{O}$ . The peptisation of  $\text{Fe}_2\text{O}_3$  is related to the electrophoretic migration velocity and follows the solid-phase rule. The sols are typically hydrophobic; the particles are positively charged, about 20—70  $\mu$  in diameter, and approx. spherical. In sols stabilised by  $\text{FeCl}_3$  a part of  $\text{Cl}^-$  is replaceable by other anions, especially with increasing dilution. Gels are not formed on coagulation.

E. S. H.

**Nature of radiocolloids. Colloidal solutions produced from bismuth nitrate.** M. HAÏSSINSKY (Compt. rend., 1934, 198, 580—583).—The coagulation of the colloidal solutions is its relation to

the  $p_{\text{H}}$  of the solution has been examined in some detail.

C. A. S.

**Cooling curves of sodium stearate solutions in presence of electrolytes.** E. ANGELESCU and M. POPESCU (Kolloid-Z., 1934, 66, 175—183).—Cooling curves have been determined for aq. Na stearate in presence of  $\text{NaCl}$ ,  $\text{NaBr}$ ,  $\text{NaI}$ ,  $\text{NaNO}_3$ ,  $\text{NaOAc}$ ,  $\text{EtCO}_2\text{Na}$ , Na palmitate,  $\text{NaCNS}$ , and the corresponding K salts. Equiv. amounts of the Na salts (excepting palmitate) raise the gelation temp. to the same extent. K salts have a similar, but smaller, effect. The presence of electrolytes also increases the heat of gelation and the thermal conductivity.

E. S. H.

**Influence of unipolar charged air, X-rays, and ultra-violet light on the properties of sols of Congo-rubin and albumin.** B. S. PUTSCHKOVSKY and V. N. NEKLUDOV (Kolloid-Z., 1934, 66, 191—197).—Positively- and negatively-charged air currents have no influence on the colour of Congo-rubin (I) or on the protective properties of albumin (II) sols. X-Rays do not affect the (I) sol, but reduce the protective power of (II). Ultra-violet light discharges the colour of (I), and at first increases, but later decreases, the protective power of (II). The changes are attributed to alterations in dispersity.

E. S. H.

**Variation of the cataphoretic speeds of colloidal particles. VI. Variation with dilution of the colloidal solution and in presence of electrolytes.** J. MUKHERJEE, S. ROYCHOU DHURY, and S. PALIT (J. Indian Chem. Soc., 1934, 10, 713—725; cf. A., 1928, 15).—The electrophoretic velocity (I) of  $\text{As}_2\text{S}_3$  sols varies with dilution according to an S-shaped curve. With sols of  $\text{SiO}_2$  and  $\text{Al}(\text{OH})_3$  (I) increases with dilution. Addition of  $\text{KCl}$  ( $< 0.001N$ ) to  $\text{Al}(\text{OH})_3$  sols increases (I); at higher concns. (I) is decreased, coagulation occurring at 0.1N-KCl.  $\text{K}_2\text{SO}_4$  causes (I) to decrease continuously. Addition of progressively increasing concns. of  $\text{KCl}$ ,  $\text{K}_2\text{SO}_4$ , or  $\text{NaCl}$  to  $\text{Fe}(\text{OH})_3$  sols leads to a continuous fall in (I). The observations are not consistent with a crit. coagulation potential.

E. S. H.

**Electro-osmosis. II. Influence of concentration of electrolyte on electrokinetic potential.** H. ISOBE and S. IMAI (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 3).—Mathematical.

P. G. M.

**Adsorption and swelling of cellulose in electrolyte solutions of varying concentration.** K. KANAMARU (Kolloid-Z., 1934, 66, 163—175).—When cellulose is placed in aq.  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{NaOH}$ ,  $\text{AlCl}_3$ , or  $\text{KCl}$ , the  $p_{\text{H}}$  of the acid solutions increases, whilst in the alkaline region the  $p_{\text{H}}$  decreases. Measurements of swelling indicate max. in the acid and alkaline regions. The swelling min., which does not correspond with the isoelectric point (excepting  $\text{AlCl}_3$ ), is termed the point of hylotropic adsorption. Swelling phenomena are symbatic with the  $\zeta$  potential of cellulose.

E. S. H.

**Complex relationships in lyophilic colloidal systems. I. General introduction.** H. G. B. DE JONG. II. Complex and autocomplex gels. H. G. B. DE JONG and H. J. C. SENGERS (Rec. trav. chim., 1934, 53, 163—170, 171—185).—I. The classification into complex and autocomplex colloidal



systems and the effect of neutral salts on these are discussed.

II. Gels obtained by cooling a mixture of gelatin sol and gum-arabic sol become turbid in dil. AcOH, and have a decreased tendency to swell. They form a complex gel. The turbidity has a max. for a given concn. of acid. Neutral salts restore the swelling tendency, their efficiencies depending on the valencies of anion and cation.  $\text{Fe}(\text{CN})_6'''$  and  $\text{Fe}(\text{CN})_6''''$  are adsorbed and behave abnormally. Gelatin forms complex gels with nucleic acid or agar. Isoelectric gelatin gel, and agar gel + hexol nitrate, are autocomplex gels. H. J. E.

**Paradoxical salt polarity in presence of colloids.** R. KELLER (Kolloid-Z., 1934, 66, 205—211).—Discussion of published work leads to the view that ion antagonism is due to the opposite electric charges acquired by the respective ion-colloid complexes. Thus, in presence of excess of colloid,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{++}$ ,  $\text{SO}_4''$ , and  $\text{PO}_4'''$  retain their usual sign of charge, whilst Rb, Cs, K,  $\text{NH}_4$ , Cl, and Br form part of complexes having a sign opposite to that of the free ion. E. S. H.

**Dielectric constant and conductivity of aqueous solutions of gelatin.** A. PIEKARA and B. PIEKARA (Compt. rend., 1934, 198, 803—805; cf. A., 1929, 646; 1931, 424).—The dielectric const.,  $\epsilon$ , and conductivity,  $\kappa$ , have been determined for 0.81—1.2% gelatin solutions. For these,  $\epsilon$  is  $>$  for  $\text{H}_2\text{O}$ , and the difference increases with concn. and with rise of temp. Vals. of  $\epsilon$  and  $\kappa$  for the sol are  $>$  those for the gel under the same conditions. Both show thermal hysteresis. C. A. S.

**Dielectric constant studies. III. Aqueous gelatin solutions.** A. L. FERGUSON, J. G. MALONE, and L. O. CASE (J. Chem. Physics, 1934, 2, 94—98; cf. this vol., 163).—The variation of the dielectric const. with the gelatin concn. and with  $p_{\text{H}}$  supports the Bjerrum theory of ampholytes. The amount of  $\text{H}_2\text{O}$  fixed by the gelatin and the mol. wt. have been calc. from dielectric absorption data. N. M. B.

**Regularity for periodic reactions in gels.** P. MICHALEV, V. NIKIFOROV, and F. M. SCHEMJAKIN (Kolloid-Z., 1934, 66, 197—200).—In five periodic structures of the Liesegang ring type the product of the distance between successive bands and the velocity of diffusion was found to be const. E. S. H.

**Formation of Liesegang rings by electrolysis.** E. BANDERET (Compt. rend., 1934, 198, 821—822; cf. A., 1933, 786).—The rings produced by the author's electrolytic method obey Veil's law, *i.e.*,  $\sqrt{\delta} = an + b$ , where  $\delta$  is the distance between the  $n$ th and  $(n+1)$ st rings, and  $a$ ,  $b$  are consts. The effect of continued application of electrolysis is illustrated. C. A. S.

**Magnetic study of sols and gels. I.** S. PRAKASH (Indian J. Physics, 1933, 8, 243—258).—The paramagnetic susceptibility (I) of  $\text{FeCl}_3$  and  $\text{CrCl}_3$  solutions is greater at low concns. than at high concns., owing to formation of colloidal  $\text{Fe}(\text{OH})_3$  and  $\text{Cr}(\text{OH})_3$  by hydrolysis. Addition of  $\text{NaOAc}$  to  $\text{FeCl}_3$  and  $\text{CrCl}_3$  decreases (I); in the latter case the reaction is slow, and is accompanied by continuous decrease in

(I). Addition of  $\text{KH}_2\text{AsO}_4$ ,  $\text{K}_2\text{HPO}_4$ ,  $\text{Na}_2\text{WO}_4$ , or  $\text{K}_2\text{MoO}_4$  to excess  $\text{FeCl}_3$  yields the corresponding colloidal  $\text{Fe}^{\text{III}}$  salts, for which (I) is slightly  $>$  for the powdered compounds. No marked change in (I) accompanies the sol-gel change for  $\text{Fe}_2(\text{HPO}_4)_3$ , but the diamagnetic susceptibilities of  $\text{Al}(\text{OH})_3$  and  $\text{Zr}(\text{OH})_4$  sols increase on ageing. J. W. S.

**Cryotropic behaviour of some inorganic jellies.** S. PRAKASH (Indian J. Physics, 1933, 8, 231—242).—Sols of  $\text{Fe}_2(\text{HPO}_4)_3$ ,  $\text{Fe}_2(\text{HAsO}_4)_3$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{Zr}(\text{OH})_4$ , Th molybdate, and Th phosphate are formed when the corresponding gels are cooled in liquid air and allowed to return to room temp. The sols pass into the gel form on keeping. The process can be repeated even with aged gels. The phenomenon is called cryotropy; gels which have developed marked agglomeration tendency are non-cryotropic. Conditions favouring cryotropy and its relation to thixotropy are discussed. J. W. S.

**Emulsions. I. Proteins and allied substances as emulsifiers for phenolic liquids.** R. M. WOODMAN (J.S.C.I., 1934, 53, 57—60T).—In many instances, proteins, protein-containing substances, and their degradation products yield dual types of emulsions with phenolic liquids; the oil-in- $\text{H}_2\text{O}$  type only is formed with a hydrocarbon such as PhMe. Explanatory hypotheses are briefly summarised. Gels are formed in certain systems, rendering verification of type difficult and often impossible. The formation of these gels is discussed, and the notion put forward that some measure of swelling in  $\text{H}_2\text{O}$  is necessary before emulsoid colloids can emulsify; the presence of  $\text{H}_2\text{O}$  may, therefore, be essential to emulsification in such cases.

**Electrokinetic properties of proteins. II. Adsorption of gliadin at a glass-liquid interface as influenced by hydrogen-ion concentration.** W. MCK. MARTIN (J. Physical Chem., 1934, 38, 213—229).—A streaming-potential apparatus for measuring the rate of adsorption at a glass-liquid interface is described. The fritted glass diaphragms used were negatively charged in both acids and alkalis, the magnitude of the charge being a function of the total ionic concn. rather than of  $p_{\text{H}}$ . The electrostatic charge of the double layer at the glass-liquid interface is reversed on adding protein to the streaming liquid if its  $p_{\text{H}}$  is on the acid side of the isoelectric point of the protein. The negatively-charged glass surface apparently adsorbs a layer of positively-charged protein and assumes its electrokinetic properties, the system becoming protein-liquid instead of glass-liquid. The rate of adsorption of gliadin was determined by the sign and magnitude of the difference in the charge of the glass and the protein micelles. In alkaline solutions there should be no adsorption, since both glass and gliadin are negatively charged. The disturbance of the adsorption equilibrium at the isoelectric point of gliadin by changes in  $p_{\text{H}}$  indicates, therefore, either structural transformation of the adsorbed protein micelles or displacement by micelles or fragments with different isoelectric points. M. S. B.

**Surface tension of proteins, a peptone, and amino-acids.** J. ERRERA and E. MILLEAU (J. Chim. phys., 1933, 30, 726—732).—The stalagmometrically

determined surface tension of aq. ovalbumin, serum albumin, and gelatin is min. at the isoelectric point, and for a given change of  $p_H$  the effect of univalent is  $>$  of bivalent acids and bases. Unpurified Witte peptone affords analogous results, but the effect of varying the constitution of the anion of the added org. acid sometimes exceeds that due to changing the valency. Solutions of  $NH_3$ -acids show the same behaviour as that obtained with  $H_2O$ . J. G. A. G.

**Kinetic interpretation of the activity coefficients of non-electrolytes.** J. W. BELTON (Proc. Leeds Phil. Soc., 1934, 2, 499—501).—An expression is deduced kinetically for the activity coeff. in which account is taken of adsorption (I). The agreement with experiment is good at high concns., but poor at low concns., due probably to increase in the index of the (I) isotherm. H. S. P.

**Equilibrium between ammonium thiocyanate and thiocarbamide in solution.** W. URE and F. A. DE LISLE (Trans. Roy. Soc. Canada, 1933, [iii], 27, III, 105—111).—The system  $NH_4CNS \rightleftharpoons CS(NH_2)_2$  has been investigated in glycol solution and vals. of the equilibrium const. have been obtained at 184.4°, 178.3°, and 162.2°. Decomp. of the materials at the higher temp. is considered to explain earlier discrepancies. H. S. P.

**Statistical basis of the theory of electrolytes.** O. HALPERN (J. Chem. Physics, 1934, 2, 85—93).—Mathematical. N. M. B.

**Entropies of aqueous ions.** W. M. LATIMER, P. W. SCHUTZ, and J. F. G. HICKS, jun. (J. Chem. Physics, 1934, 2, 82—84).—A crit. summary of existing thermodynamic data for aq. ions leads to consistent vals. for ionic entropies; vals. for twenty positive and twelve negative ions are tabulated. N. M. B.

**Dissociation constants of organic acids. VIII. Phenylacetic acid.** G. H. JEFFERY and A. I. VOGEL (J.C.S., 1934, 166—168).—According to the conductivities at 25° of 0.0002—0.01N- $CH_2PhCO_2H$  and its Na salt in  $H_2O$ , the limiting mobility of the anion is 34.7 and the thermodynamic dissociation const. of the acid is  $4.884 \times 10^{-5}$ . The classical dissociation const. increases with rise of concn., and for 0.003—0.01N solutions the mean val. is  $5.068 \times 10^{-5}$ . Earlier data are corr. (cf. this vol., 146) J. G. A. G.

**Chemical constitution and dissociation constants of monocarboxylic acids. I. Substituted phenylacetic acids.** J. F. J. DIPPY and F. R. WILLIAMS (J.C.S., 1934, 161—166).—From the conductivities of 0.03—0.0001N-acids and their Na salts in  $H_2O$  at 25°, the classical dissociation consts. and the following thermodynamic dissociation consts. of the acids are evaluated: phenylacetic  $4.88 \times 10^{-5}$ , diphenylacetic  $11.5 \times 10^{-5}$ , *p*-chloro-  $6.45 \times 10^{-5}$ , *p*-bromo-  $6.49 \times 10^{-5}$ , *p*-iodo-  $6.64 \times 10^{-5}$ , and *p*-nitro-phenylacetic acid  $14.1 \times 10^{-5}$ . J. G. A. G.

**Dissociation constant of chloroacetic acid from 0° to 40°.** D. D. WRIGHT (J. Amer. Chem. Soc., 1934, 56, 314—317).—The vals. are derived from e.m.f. data for cells without liquid junctions, using the quinhydrone electrode. Equations are deduced which express the influence of temp. on log  $K$ , the

heat of dissociation, and the difference in the mol. heat capacities of the ions and undissociated acid.

E. S. H.

**Acidity and reducing power of ascorbic acid.** P. KARRER and G. SCHWARZENBACH (Helv. Chim. Acta, 1934, 17, 58—59).—Redetermination of the dissociation const. gives  $K_1$   $3.25 \times 10^{-4}$  and  $K_2$   $7 \times 10^{-12}$ . The reduction potential found by Green (A., 1933, 1015) is too negative. F. L. U.

**Hydrogen-ion concentration of solutions of hydrazine and hydroxylamine hydrochlorides.** A. BERTHOUD and W. EICHENBERGER (Helv. Chim. Acta, 1934, 17, 23—24).—The  $[H^+]$  of aq.  $N_2H_4 \cdot 2HCl$  between 0.05 and 0.0125M, measured with a H electrode at 21°, indicates that the dissociation  $N_2H_4 \cdot 2HCl \rightarrow N_2H_4 \cdot HCl + HCl$  is practically complete. The  $[H^+]$  of aq.  $NH_2OH \cdot HCl$  cannot be determined potentiometrically, but colorimetric measurements indicate that  $[H^+] \propto [NH_2OH \cdot HCl]^{1/2}$ . F. L. U.

**Halide-iodine equilibria in neutral salt solutions.** V. K. LAMER and M. H. LEWINSOHN (J. Physical Chem., 1934, 38, 171—195).—The solubility of I in  $H_2O$  (at  $p_H$  5 to prevent hydrolysis) is  $0.001321 \pm 2 \times 10^{-6}M$ . The vals. for the mass-action expressions for the equilibria:  $XI_2' = I_2 + X'$ , where  $X = Cl, Br, \text{ or } I$ , are a little greater for  $H_2O$  than for 2M- $KNO_3$  and more nearly const. in the presence of the latter.  $KNO_3$  does not appear to combine chemically with I and is used to maintain const. ionic environment. Vals. of  $K_c$  for the tri-iodide equilibrium deviate considerably from  $K_a$  in aq.  $KCl$ , which maintains const. ionic environment, but reacts with I. This contradicts Carter and Hoskin's assumption (A., 1929, 501). The probable influence of the salting-out effect of the different ions on one another is discussed. M. S. B.

**Constitution of hydrobromic acid solutions of cobalt and copper salts.** P. JOB (Compt. rend., 1934, 198, 827—828; cf. A., 1933, 228).—It is found that the respective  $HBr$  solutions contain the ions  $CoBr^+$ ,  $CoBr_3^-$ ,  $CuBr^+$ , and  $CuBr_3^-$ . The equilibrium consts. are respectively  $5 \times 10^{-3}$ ,  $1.1 \times 10^{-5}$ ,  $6.3 \times 10^{-2}$ , and  $6 \times 10^{-4}$ ; those for  $CoCl^-$  and  $CoCl_3^+$  are  $4.5 \times 10^{-3}$  and  $2.9 \times 10^{-4}$ . C. A. S.

**Activity coefficient of silver acetate and silver monochloroacetate in presence of electrolytes.** F. H. MACDOUGALL and J. REHNER, jun. (J. Amer. Chem. Soc., 1934, 56, 368—372).—Solubilities of  $AgOAc$  (I) and of  $CH_2ClCO_2Ag$  (II) have been measured at 25° in aq.  $LiNO_3$ ,  $NaNO_3$ ,  $KNO_3$ ,  $Ca(NO_3)_2$ ,  $Sr(NO_3)_2$ ,  $Ba(NO_3)_2$ , and  $La(NO_3)_3$ . For (I) in presence of  $NaNO_3$  and  $Sr(NO_3)_2$  and for (II) in presence of  $NaNO_3$  and  $LiNO_3$  the activity coeffs. pass through a min. E. S. H.

**Hydrols.** W. D. BANCROFT and L. P. GOULD (J. Physical Chem., 1934, 38, 197—211).—On the assumptions that liquid  $H_2O$  is a mixture of tri-, di-, and mono-hydrol, co-existing in reversible equilibrium, that this equilibrium is differently influenced by different anions, and that the electrolytic solution pressure of  $H_2$  and  $O_2$  is different in the different polymerides, an attempt is made to explain the many phenomena associated with aq. solutions. B.-p. data

have been determined for conc. aq. solutions of NaCl, NaBr, NaI, NaNO<sub>3</sub>, NaSCN, and Na<sub>2</sub>SO<sub>4</sub>. The adsorption by gelatin of NaSCN, NaI, NaCl, and NaNO<sub>3</sub> in EtOH-H<sub>2</sub>O solution has been measured. E.m.f. measurements of the cells H<sub>2</sub>[HX|KCl|Hg<sub>2</sub>Cl<sub>2</sub>]Hg, where X=Cl, Br, or I, have been made for different concns. of acid, and it is found that the vals. are not the same for the same concn. of different acids.

M. S. B.

**Piezochemical studies. XXX. Effect of pressure on chemical equilibrium in condensed systems.** E. COHEN and K. PIEPENBROEK (Z. physikal. Chem., 1934, 167, 365—393).—Planck's equation  $(\partial \log_e K / \partial p)_T = -\Delta V / RT$  for the effect of change in external pressure,  $p$ , on the equilibrium const.,  $K$ , has been verified by a study of the equilibrium  $\text{TlCl}_{\text{solid}} + \text{CNS}' \rightleftharpoons \text{TlCNS}_{\text{solid}} + \text{Cl}'$ . The vals. of  $K$  at high pressures were derived from measurements with the cell  $\text{Tl-Hg} | \text{TlCNS-KCNS} | \text{KCl-TlCl} | \text{Tl-Hg}$  and were checked by measurements of the heat effect and application of the van 't Hoff isochore.

R. C.

**Binary system of flavone and primetin.** T. ASAHINA (Acta Phytchim., 1933, 7, 187—190).—Softening-point and m.-p. curves for mixtures of flavone and primetin (I) (dihydroxyflavone) show that these substances form solid solutions. The natural plant secretion, m.p. 175—180°, contains about 1 mol. of each. Two kinds of crystals exist at 20° when the mixture contains from 40 to 90% of (I). J. H. B.

**Thermodynamics of solid solutions. I. Perfect solutions.** H. SELTZ (J. Amer. Chem. Soc., 1934, 56, 307—311).—Theoretical. The liquidus and solidus curves for binary systems forming solid solutions are deduced from the fugacities or activities of the components. Equations are derived for calculating the liquidus and solidus from the temp. and heats of fusion of two pure solids, assuming that both solutions are perfect.

E. S. H.

**Hydrazine: dissociation pressures of hydrazinium dichloride and dibromide.** B. E. CHRISTENSEN and E. C. GILBERT (J. Amer. Chem. Soc., 1934, 56, 393—395).—Dissociation pressures determined by the dynamic isotherm method show dissociation of N<sub>2</sub>H<sub>4</sub>·2HCl to be practically complete at 197.8° at 1 atm. N<sub>2</sub>H<sub>4</sub>·2HBr decomposes below its m.p., and satisfactory dissociation pressures are obtained only at lower temp.

E. S. H.

**Dynamic comparison between physico-chemical systems.** H. DAMIANOVICH (Anal. Inst. invest. cient. tecn., 1931, 2, 5—14).—Existing data show that the approx. val. of  $Q/T$ , where  $Q$  is the heat of reaction and  $T$  the temp. of the isobar corresponding with a dissociation pressure of 1 atm., is 32 for the systems  $\text{MCl}_{2,y}\text{NH}_3$ , and 38.5 for homogeneous gaseous systems and for the carbonates of Ag, Pb, Mn, Ca, etc. Divergencies from constancy of  $Q/T$  (which is a min. for simple and non-associated systems) serve to indicate the degree of association or polymerisation in a system, or the degree of complexity of the reaction involved.

H. F. G.

**Polyhalides. II. Thermal decomposition of KICl<sub>4</sub>, and the stability of compounds of the**

**type MICl<sub>4</sub> and MICl<sub>2</sub>.** V. CAGLIOTI and G. CENTOLA (Gazzetta, 1933, 63, 907—916).—At 20° KICl<sub>4</sub> decomposes continuously, yielding KCl and ICl<sub>2</sub>; its dissociation pressure is appreciable (0.1 mm.) at 14°. The heat of formation from KCl, ICl (gas), and Cl<sub>2</sub> is -29.5 kg.-cal. CsICl<sub>4</sub> decomposes in two stages; at 28° CsICl<sub>2</sub> is formed, and at 116° this yields CsCl and ICl. The theoretical aspects of the stability of compounds of this type are considered.

H. F. G.

**Compound formation between sodium iodate and sodium iodide.** J. E. RICCI (J. Amer. Chem. Soc., 1934, 56, 295—299).—The double salts 2NaIO<sub>3</sub>·3NaI·20H<sub>2</sub>O, 2NaIO<sub>3</sub>·3NaI·15H<sub>2</sub>O, and 2NaIO<sub>3</sub>·3NaI·10H<sub>2</sub>O exist in the range 20—55°.

E. S. H.

**Ternary systems KIO<sub>3</sub>-KBr-H<sub>2</sub>O and NaIO<sub>3</sub>-NaBr-H<sub>2</sub>O.** J. E. RICCI (J. Amer. Chem. Soc., 1934, 56, 290—295).—Equilibrium data are given for temp. between 5° and 50°. No double salt occurs in the K-salt system. 2NaIO<sub>3</sub>·3NaBr·15H<sub>2</sub>O occurs below 40°, and 2NaIO<sub>3</sub>·3NaBr·10H<sub>2</sub>O at higher temp.

E. S. H.

**Ternary systems involving alkali bromates.** J. E. RICCI (J. Amer. Chem. Soc., 1934, 56, 299—303).—Systems containing H<sub>2</sub>O and the following salt pairs have been studied at 25°: NaBrO<sub>3</sub>-NaCl, NaBrO<sub>3</sub>-NaI, NaBrO<sub>3</sub>-NaNO<sub>3</sub>, NaBrO<sub>3</sub>-Na<sub>2</sub>SO<sub>4</sub>, KBrO<sub>3</sub>-KCl, KBrO<sub>3</sub>-KBr, KBrO<sub>3</sub>-KI, KBrO<sub>3</sub>-KNO<sub>3</sub>, KBrO<sub>3</sub>-K<sub>2</sub>SO<sub>4</sub>. There is no evidence of the formation of double salts.

E. S. H.

**Liquidus and solidus studies. IV. [Nitrates.]** K. LAYBOURN, W. M. MADGIN, and [in part] D. FREEMAN (J.C.S., 1934, 139—146; cf. A., 1933, 465).—The binary systems are of the simple eutectic type; the characteristic eutectic data (% alkali nitrate and temp.) are: Na-Ba, 82.7, 284.0°; Na-Sr, 84.2, 294.9°; Na-Ca, 50.8, 211.3°; K-Ba, 73.0, 285.7°; and K and Sr, 33.8, 274.8°. The graphical thermodynamic treatment is extended to the ternary nitrate systems: (1) Na-Pb-Sr, mixture of lowest m.p.  $M$ , is the binary eutectic Na-Pb, (2) Na-Ca-Sr,  $M$  is the binary eutectic Na-Ca, (3) Na-Ca-Pb,  $M$  (202°) contains 51.8% Na and 3.0% Pb, (4) Na-Ba-Pb,  $M$  (269°) contains 61.5% Na and 36% Pb, and (5) K-Sr-Ba,  $M$  (260°) contains 73.5% K and 3% Ba. M.-p. and f.-p. data are given for (1) and (5).

J. G. A. G.

**Crystallisation of mixtures of acetic acid and normal liquids. The ternary mixture acetic acid-benzene-ethylene dibromide.** L. GAY and P. CARCASSÈS (J. Chim. phys., 1933, 30, 709—712).—The data cover the entire range of concn. The ternary eutectic is -29.3° with 50.89 mol.-% C<sub>6</sub>H<sub>6</sub> and 44.53 mol.-% C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub>.

J. G. A. G.

**Dependence of the equilibrium FeO+Ni  $\rightleftharpoons$  NiO+Fe in the melt on added SiO<sub>2</sub>.** III. **Equilibrium between metals, oxides, and silicates in the melt.** W. JANDER and H. SENF (Z. anorg. Chem., 1934, 217, 48—52).—In presence of SiO<sub>2</sub> up to 12% the val. of  $K = [\text{Fe}][\text{NiO}]/[\text{Ni}][\text{FeO}]$  at 1600° (cf. A., 1933, 352) diminishes, if no distinction is made between combined and uncombined oxide; this indicates that FeO, SiO<sub>2</sub> undergoes less dissociation than NiO, SiO<sub>2</sub>, or, alternatively, that the solvent

has changed the activity of the mols. The dependence of  $K$  on temp., in presence of  $\text{SiO}_2$ , is represented by  $\log K = -6300/T + 1.29$ . M. S. B.

**Formula for reducing experimental heat of combustion to the corresponding isothermic value.** L. J. P. KEFFLER (J. Chim. phys., 1934, 31, 1—8).—The formula applies to most substances containing C, H, O, and N or certain of these elements, but  $\text{H}_2\text{C}_2\text{O}_4$  is an exception. H. S. P.

**Heat of ionisation of some metals.** W. A. ROTH and A. BÜCHNER (Z. Elektrochem., 1934, 40, 87—89).—The heats of dissolution in kg.-cal. of the anhyd. salts  $\text{AlCl}_3$ ,  $\text{GaCl}_3$ ,  $\text{InCl}_3$ ,  $\text{ZnCl}_2$ ,  $\text{CuCl}_2$ , and  $\text{AgCl}$  are, respectively, 78.09,  $45.1 \pm 0.2$ ,  $23.2_5 \pm 0.1$ ,  $16.6_3 \pm 0.01$ ,  $11.9_0 \pm 0.02$ , and  $31.2 \pm 0.1$ . The heats of ionisation calc. from these are Ga 51, In 32.7, Zn 37.0<sub>3</sub>, Cu —16.6, and Ag —24.4<sub>5</sub>. M. S. B.

**Composition and heat of formation of the carbon fluoride mixtures formed from norit and silicon carbide. (Heat of formation of  $\text{CF}_4$  and  $\text{SiC}$ .)** O. RUFF and O. BRETSCHNEIDER (Z. anorg. Chem., 1934, 217, 19—21).—With  $\text{CF}_4$  norit forms about 14% of the higher fluorides, whilst  $\text{SiC}$  gives 43%. On the assumption that the heat evolved by 1 g.-atom of noritic C on forming this mixture is 162 kg.-cal., the heat of formation of  $\text{CF}_4$  is 183.5 kg.-cal., but this assumption cannot be regarded as valid. The combustion in F of C in the form of  $\text{SiC}$  gives 134 kg.-cal. It is not possible to determine the heat of formation of  $\text{SiC}$  from these data. M. S. B.

**Electrolytic transport of water in barium chloride solutions.** J. BABOROVSKÝ and O. VIKTORIN (Chem. Listy, 1934, 28, 2—6).— $\text{H}_2\text{O}$  is transported to the anode in 0.2—2*N*- $\text{BaCl}_2$ , and to the cathode in 0.1*N*- $\text{BaCl}_2$ ; the amount of  $\text{H}_2\text{O}$  transported  $\propto$  [ $\text{BaCl}_2$ ]. The  $\text{Ba}^{++}$  is associated with 11 mols. of  $\text{H}_2\text{O}$  in *N*, and with 97 mols. of  $\text{H}_2\text{O}$  in 0.1*N* solutions. R. T.

**Revised figures for the electrical conductivity of aqueous solutions of sodium and potassium hydroxides, and the limiting mobility of the hydroxyl ion at 25°.** G. H. JEFFERY and A. I. VOGEL (Phil. Mag., 1934, [vii], 17, 582—584; cf. A., 1933, 353).—Results are recalculated. The limiting mobility of  $\text{OH}^-$  at 25° is 210.78. H. J. E.

**Conductivity of aluminium bromide in non-aqueous solutions.** E. WERTYPOROCH and B. ADAMUS (Z. physikal. Chem., 1934, 168, 31—44).— $\text{C}_6\text{H}_6$ , PhMe, and  $\text{C}_6\text{H}_4\text{Me}_2$  dissolve  $\text{AlBr}_3$  readily, forming non-conducting solutions, from which HCl or HBr ppts. a highly conducting oil containing all three components. PhF and PhI, but not PhCl and PhBr, give conducting solutions, for which the mol. conductivity,  $\lambda$ , falls with increasing dilution owing to break-up of the solvates. Addition of EtBr to solutions of  $\text{AlBr}_3$  in various halogenated benzenes (I) greatly increases the sp. conductance. It is concluded that the pseudo-salt solvates of EtBr and  $\text{AlBr}_3$  can add (I) as a whole. In solutions in (I) the H atom is loosened by  $\text{AlBr}_3$  so slightly that ethylation according to the Friedel-Crafts reaction cannot occur. With chloro- and bromo-toluenes as solvents the highest  $\lambda$  is attained with the *m*-isomeride, which agrees with the

general rules for the loosening of nuclear H by substituents.  $\text{PhNO}_2$  and the nitrotoluenes give with  $\text{AlBr}_3$  very stable additive products in which the catalytic action of the  $\text{AlBr}_3$  has disappeared. PhCN and MeCN behave similarly to the  $\text{NO}_2$ -compounds. MeCN dissolves  $\text{ZnCl}_2$  when HCl is passed in, giving highly-conducting solutions containing such acids as  $\text{HZnCl}_3$  and  $\text{H}_2\text{ZnCl}_4$ ;  $\text{C}_6\text{H}_6$  is added and ketone formed by hydrolysis. R. C.

**Conductivities of titanium, tin, and silicon tetrachlorides in non-aqueous solutions.** E. WERTYPOROCH and B. ALTMANN (Z. physikal. Chem., 1934, 168, 1—30).—The mol. conductivity,  $\lambda$ , of these salts in MeOH and EtOH solution shows that the complexes formed by solvation have a salt-like structure. With  $\text{CH}_2\text{Ph}\cdot\text{OH}$  colorations appear, suggesting conjugated double linkings in the solvates. In  $\text{Et}_2\text{O}$  the solvates are salt-like, but only weakly dissociated, and dioxan forms complexes, but gives non-conducting solutions. With alkyl and acyl chlorides there are formed weakly conducting salt-like complexes, which are saturated, and therefore incapable of adding hydrocarbons and loosening H atoms. These metal chlorides do not, therefore, bring about the Friedel-Crafts reaction. MeCHO is decomposed by all three chlorides. With other aldehydes (A) salt-like solvates are formed, and at higher concns. compounds,  $\text{MCl}_4 \cdot 2\text{A}$  separate. For  $\text{COMe}_2$  solutions of  $\text{TiCl}_4$  and  $\text{SnCl}_4$   $\lambda$  does not vary appreciably with the concn., whereas solutions of  $\text{SiCl}_4$  behave as solutions of true salts. For solutions of  $\text{TiCl}_4$  in MeCN  $\lambda$  is large, whilst  $\text{SiCl}_4$  solutions have the same conductivity as the solvent and  $\text{SnCl}_4$  gives a salt-like complex. Solutions in PhCN are coloured and  $\lambda$  is small. In general, the presence of the Ph radical in the solvent involves small  $\lambda$ . R. C.

**Conductivity of solutions of certain substances in fused antimony chloride.** Z. KLEMENSIEWICZ and A. ŻEBROWSKA (Rocz. Chem., 1934, 14, 14—18).—The equiv. conductivity,  $\kappa$ , of HCl and HBr in fused  $\text{SbCl}_5$  (I) is at a max. in 0.25*N* solutions; that of  $\text{SbOCl}$  is given by  $\log \kappa = kC^{1/3}$ , where  $C$  is the concn. The results obtained for solutions of  $\text{H}_2\text{O}$  in (I) are untrustworthy, owing to hydrolysis. The vals. of  $\kappa$  are considerably < for the corresponding aq. solutions. R. T.

**Conductivity and solubility relations in the ternary systems sodium-potassium-ammonia and sodium-lithium-ammonia between —40° and —70°.** F. GRIENGL, F. STEYSKAL, and K. STEYSKAL (Monatsh., 1933, 63, 394—426).—The electrical conductivity of K-Na and Li-Na alloys dissolved in liquid  $\text{NH}_3$  is an additive property, giving no indication of compound formation. The solubility relations show the presence of  $\text{Na}_2\text{K}$ . The limits of the miscibility gaps in the ternary systems have been determined. E. S. H.

**Conductivity of dipyridyl ethylenediaminetetrachloroplatinum.** S. I. CHORUNSHENKOV (Ann. Inst. Platine, 1933, No. 11, 73—75).—Conductivity measurements confirm the structure  $[\text{enCl}_4\text{Pt}](\text{C}_5\text{H}_5\text{N})_2$ . R. T.

**Conductivity titrations in heterogeneous systems.** O. SCHWARZKOPF and J. WEISS (Cellulose-

chem., 1934, 15, 29—31).—When a heterogeneous system consisting of the insol. Na salt of an insol. acid and aq. NaOH is titrated conductometrically with HCl, three types of curve are possible, according to whether  $[\text{OH}^-]$  in equilibrium with the Na salt is  $>$ ,  $=$ , or  $<$   $[\text{OH}^-]$  for  $\text{H}_2\text{O}$ . The titration of Na cellulose in aq. NaOH is discussed. A. G.

**Electrical conductivity of compressed graphite powder.** J. BRUNNER and H. HAMMERSCHMID (Z. Elektrochem., 1934, 40, 60—67).—Measurements have been made on six different graphites for a pressure range of 31—300 atm. by Ryschkewitsch's differential method, and the linear dependence of sp. resistance on  $1/\sqrt{p}$  has been confirmed. The influence of mechanical working on the resistance, on  $d$ , and on compressibility varied very much in 20 graphite powders examined. M. S. B.

**Determination of normal potentials.** (MLLE.) M. QUINTIN (Compt. rend., 1934, 198, 718—720; cf. A., 1933, 781).—The heat of reaction,  $\Delta H$ , derived from e.m.f. data for the cell Cu (amalgam two phases)  $[\text{CuSO}_4(c)|\text{HgSO}_4|\text{Hg}$ , is a linear function of  $c$ . For  $c=0$ ,  $\Delta H=18,640$  g.-cal. per mol. The normal potential,  $E_0$ , is  $0.4042-0.00050T$ . C. A. S.

**Potential of the cobalt electrode.** M. M. HARING and B. B. WESTFALL (Trans. Electrochem. Soc., 1934, 65, 61—72).—Cells of the type  $\text{Co}|\text{CoSO}_4$  solution,  $\text{Hg}_2\text{SO}_4|\text{Hg}$  have been constructed with very finely-divided Co (electrodeposited on a Pt wire at 75—85° and 16 amp. per sq. cm.), and the e.m.f. measured in the absence of  $\text{O}_2$  which has a very considerable influence on the Co potential. From data at 25° the standard electrode potential is  $-0.278 \pm 0.002$ . H. J. T. E.

**Potentials of the lead oxide electrodes in alkaline solution.** L. V. ANDREWS and D. J. BROWN (J. Amer. Chem. Soc., 1934, 56, 388—390).—The following vals. have been obtained:  $\text{PbO}-\text{Pb}_2\text{O}_3|\text{OH}^- + 0.2488 \pm 0.0005$ ,  $\text{Pb}_2\text{O}_3-\text{PbO}_2|\text{OH}^- + 0.1295 \pm 0.001$ ,  $\text{PbO}-\text{PbO}_2|\text{OH}^- + 0.280 \pm 0.001$  volt. The calc. free energies of formation of the oxides at 298° abs. are:  $\text{Pb} + 0.5\text{O}_2 = \text{PbO} - 45,100$ ,  $3\text{Pb} + 2\text{O}_2 = \text{Pb}_3\text{O}_4 - 142,210$ ,  $\text{Pb} + \text{O}_2 = \text{PbO}_2 - 50,600$  g.-cal. E. S. H.

**Electrochemistry of non-aqueous solutions.** IX. **Determination of e.m.f. of silver-silver nitrate concentration cells in nine organic solvents and comparison with the values calculated from conductivity measurements.** R. MÜLLER, H. KUMPFILLER, E. PINTER, and B. VON SEEBACH (Monatsh., 1933, 63, 317—328).—Determinations of e.m.f. in EtOH, MeCN, PhCN,  $\text{NH}_2\text{Ph}$ ,  $\text{C}_6\text{H}_5\text{N}$ , and quinoline agree with vals. calc. from electrical conductivity data. Agreement was not obtained in MeOH, isoamyl alcohol, or  $\text{COMe}_2$ . It is inferred that Nernst's theory of concn. cells is applicable to non-aq. systems. E. S. H.

**Influence of an electric field on the potential at a metal-solution interface.** H. K. McCLAIN and H. V. TARTAR (J. Physical Chem., 1933, 38, 161—170).—The potential of Au or Pt against a solution is only slightly affected by an electric field of moderate strength. The changes of potential

may be due to a current between the electrodes caused by the field, or to a longitudinal movement of the ions through the diffuse double layer at the metal-solution interface. The change has its source at the interface, since addition of a small amount of a substance highly absorbed at the interface, such as tannic acid or gelatin, reduces the change of potential. As the effect diminishes with the size of the electrodes, the potential of an electrode of colloid particle size will probably not be affected, which supports the assumption in cataphoretic measurements that the charge distribution in the double layer is unaffected by the applied field. The electrolytes used were  $\text{H}_3\text{BO}_3$ ,  $\text{KH}_2\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4$ , and  $\text{Al}_2(\text{SO}_4)_3(+\text{HCl})$ .

M. S. B.

**Electrokinetic ( $\zeta$ ) potential of thin metal films.** G. W. SMITH and L. H. REYERSON (J. Physical Chem., 1934, 38, 133—151).—Metallised  $\text{SiO}_2$  gels have been used in streaming potential measurements and a direct comparison of the electrokinetic potential ( $\zeta$ ) with the Nernst thermodynamic potential ( $\epsilon$ ) is thus obtained. Gels covered with Ni or Ag have been prepared by adsorption of  $\text{Ni}(\text{NH}_3)_4$  and  $\text{Ag}(\text{NH}_3)_2$ , respectively, from solution, and reduction by heating in a current of  $\text{H}_2$ .  $\zeta$  is negative for both Ni and Ag, whereas  $\epsilon_{\text{Ag}}$  would normally be positive.  $\zeta$  in the Ni-Ni( $\text{NO}_3$ ) $_2$  system reaches zero at  $N/2000$ . This is characteristic of the effect of bivalent ions on  $\zeta$ . The behaviour of Ag is different from that of other univalent ions. There is an initial sharp decrease followed by a rise and then the usual gradual decrease. The causes of this behaviour are discussed. Variations in  $\zeta$  depend on changes in thickness of the double layer which varies with the concn. of the solution, adsorption of anions, and adsorption of cations.  $\epsilon$  depends only on the osmotic pressure of the ions supplied by the metal. The other factor, the electrolytic solution pressure, is a const. for each metal. M. S. B.

**Decomposition voltages of fused salts. II. Magnesium chloride and sulphate.** Y. KONISHI (J. Soc. Chem. Ind. Japan, 1934, 37, 44—45B).—The decomp. voltages measured at 548—908° ( $\text{MgCl}_2$ ) and 856—968° ( $\text{MgSO}_4$ ) lead to 3.257 and 4.543 volts, respectively, at 15°; the temp. coeffs. are  $-0.000646$  and  $-0.00171$  volt per °C. The decomp. voltages are in accord with the thermal data. A. G.

**Reversibility of oxidation-reduction systems derived from carbohydrates.** R. WURMSER and J. A. DE LOUREIRO (Compt. rend., 1934, 198, 738—740).—The reversibility of such systems consisting of reduced carbohydrates in neutral or alkaline solution, or of ascorbic acid is shown by the agreement between the normal potentials derived, on the one hand, electrometrically, and on the other, by a colorimetric method in which the oxidation of a leuco-compound, e.g., methylene-blue, is determined. The result previously obtained with ascorbic acid appears to have been due to the use of acid which has not been freshly recryst. C. A. S.

**Oxidation-reduction potential of system xanthine  $\rightleftharpoons$  uric acid.** (MLLE.) S. FILITTI (Compt. rend., 1934, 198, 930—932; cf. this vol.,

32).—Determined by a similar method the normal potential of the reaction  $C_5H_4O_2N_4 + H_2O \rightleftharpoons C_5H_4O_3N_4 + H_2$  is  $+0.113 \pm 0.0015$  volt, and  $\Delta F = 5220$  g.-cal. The heat of reaction at const. pressure is  $-12,000$  g.-cal. If the (acid) dissociation of hypoxanthine ( $K_{\text{H}} = 2.12 \times 10^{-12}$ ) be taken into consideration,  $\Delta F$  for the reaction  $C_5H_4ON_2 + 2H_2O \rightleftharpoons C_5H_4O_3N_4 + 2H_2$  is  $5720$  g.-cal. C. A. S.

Optical method for investigation of concentration polarisation during electrolysis. A. G. SAMARCEV (Z. physikal. Chem., 1934, 168, 45—58).—The changes in concn. at the electrodes were deduced from the change in  $n$  of the solution in the diffusion layer and the thickness and structure of the latter studied by means of photographs of the interference images under varying conditions of electrolysis. The electrolyte was mixed by causing it to flow between the electrodes, and the cells  $Cu|CuSO_4, aq.|Cu$  and  $Ag|AgNO_3, aq.|Ag$  were examined. In the immediate vicinity of the electrode the concn. gradient is proportional to the c.d., and increases on approaching the electrode surface. In the above cells the total polarisation is  $>$  the concn. polarisation.

R. C.

Hydrogen overvoltages of iron-chromium alloys in potassium hydroxide solution. M. DE K. THOMPSON and D. M. FLEMING (Trans. Electrochem. Soc., 1934, 65, 73—77).—H overvoltages for c.d. from  $10^{-4}$  to 1 amp. per sq. cm. in  $M$ -KOH have been determined at polished Fe-Cr surfaces of varying composition. The composition of each surface was determined by X-ray analysis. With increasing proportion of Cr the overvoltage remains close to the val. for pure Fe until Cr exceeds 60%, and then rises gradually to that for Cr. An 89.5% Cr alloy prepared by fusion gave results in good agreement.

H. J. T. E.

Theory of passivity. XXIII. Passivity of lead. W. J. MÜLLER and W. MACHU (Monatsh., 1933, 63, 347—367).—Current-time curves, obtained for the anodic polarisation of Pb in  $H_2SO_4$ , are examined in the light of Müller's theory. It is inferred that the normal anodic process consists in  $Pb \rightarrow Pb^{++}$  at  $-0.3$  volt, the p.d. rising to 1.8 volts through film polarisation. At higher p.d. the process  $Pb \rightarrow Pb^{++++}$  occurs, followed by  $Pb^{++++} + 2H_2O \rightarrow PbO_2 + 4H^+$ .

E. S. H.

Unimolecular decomposition at high pressures. L. S. KASSEL (J. Chem. Physics, 1934, 2, 106).—A criticism of Coffin and Geddes' explanation of the decomp. of paraldehyde (cf. this vol., 259).

N. M. B.

Homogeneous first-order gas reactions. IV. Decomposition of para-*n*-butaldehyde and para-isobutaldehyde. C. C. COFFIN (Canad. J. Res., 1933, 9, 603—609).—The thermal depolymerisations of  $(Pr^{\alpha}CHO)_2$  and  $(Pr^{\beta}CHO)_2$  at pressures between 13 and 550 mm. in the range  $215$ — $261^\circ$  are homogeneous first-order reactions of which the velocity coeffs.,  $k$ , are given by  $\log_e k = 33.12 - 42,000/RT$  and  $\log k = 34.06 - 42,800/RT$ , respectively. From these data and those for  $(MeCHO)_2$  (A., 1932, 1094) it is inferred that for a series of reactions with the same energy of activation, an increase in the no. of contributory

internal degrees of freedom of a mol. increases the probability of reaction. J. G. A. G.

Dynamics and mechanism of aliphatic substitution. E. A. MOELWYN-HUGHES (Nature, 1934, 133, 294).—A discussion. L. S. T.

Rates of formation of quaternary phosphonium salts. W. C. DAVIES and S. U. EVANS.—See this vol., 397.

Temperature gradient in flames. O. C. DE C. ELLIS and E. MORGAN (Trans. Faraday Soc., 1934, 30, 287—298).—A technique and a mathematical analysis for determining the sign of the temp. gradient from point to point in spherical flames are given. Only in entire absence of "after-burning" does the gradient fall inwards from the surface throughout the flame period. The experimentally investigated mixtures,  $NH_3 + 3O_2$ , and  $2CO + 2H_2 + xO_2 + 10A$ , conform, in general, to one or the other of two types: the temp. rises inwards from the flame surface (1) throughout the flame period when the reactions lead to equilibria that shift exothermically under conditions of rising temp. and pressure, the gradient becoming steeper as combustion proceeds, or (2) for a considerable portion of the flame period even when the reactions lead to equilibria that shift endothermically under conditions of rising temp. and pressure. The method affords a new and independent demonstration of "after-burning." J. G. A. G.

Speed of "uniform movement" of flame in mixtures of carbon monoxide and oxygen. (A) W. PAYMAN and R. V. WHEELER. (B) W. A. BONE (Nature, 1934, 133, 257, 257—258).—(A) The max. speed (I) of "uniform movement" of flame in moist mixtures of CO and  $O_2$  is obtained with a mixture  $2CO + O_2$ .

(B) (I) is attained with a mixture  $3CO + O_2$ .

L. S. T.

Explosive and non-explosive reactions between oxides of nitrogen and inflammable gases. M. J. VAN DER WAL (Rec. trav. chim., 1934, 53, 97—117).—Explosion limits have been determined in the systems  $CH_4$ -NO,  $CH_4$ - $N_2O$ ,  $CH_4$ - $N_2O$ -NO, CO- $N_2O$ ,  $CH_4$ -CO- $N_2O$ , CO- $N_2O$ -NO,  $H_2$ - $N_2O$ ,  $H_2$ -NO- $N_2O$ ,  $H_2$ -CO- $N_2O$ , and  $H_2$ -CO- $N_2O$ -NO. H. J. E.

Kinetics of the methane-oxygen reaction. G. L. FREAR (J. Amer. Chem. Soc., 1934, 56, 305—307).—In absence of  $SiO_2$  packing, a chain mechanism predominates in the reaction of 76 : 22  $CH_4$ - $O_2$  mixtures in a  $SiO_2$  tube at  $600^\circ$ , the apparent reaction order being 3.5 at 450—575 mm. and increasing rapidly with increasing pressure. In a tube packed with  $SiO_2$  the reaction is approx. unimol., and its rate exceeds that of the reaction in the unpacked tube at  $<$  300 mm.

E. S. H.

Action of condensed spark on mixtures of carbon monoxide and hydrogen. H. LEFEBVRE and M. VAN OVERBÈKE (Compt. rend., 1934, 198, 736—738; cf. A., 1932, 580).—With the same method the condensed spark shows very little change in mixtures of CO and  $H_2$  containing 20—80% of either, at pressures  $>$  9 mm. Hg, unless the products of reaction are immediately removed, e.g., by connecting the reaction tube with one cooled by liquid  $O_2$ . Pressure then

decreases, and ultimately only CO or H<sub>2</sub> remains, the two having interacted as far as possible with formation of H<sub>2</sub>O, CO<sub>2</sub>, and C<sub>2</sub>H<sub>2</sub>, the ratio CO<sub>2</sub> : C<sub>2</sub>H<sub>2</sub> increasing with the initial % of CO. C. A. S.

**Thermal reaction between chlorine trioxide and ozone.** G. K. ROLLEFSON and A. C. BYRNS (J. Amer. Chem. Soc., 1934, 56, 364—367).—The kinetics of the reaction of ClO<sub>3</sub>, formed during the decomp. of O<sub>3</sub> sensitised with Cl<sub>2</sub>, with O<sub>3</sub> have been interpreted in terms of a chain mechanism. The relative efficiencies of Cl<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub> in breaking these chains are of the same order of magnitude. The temp. coeff. of the reaction corresponds with a heat of activation of 10.9 kg.-cal. E. S. H.

**Autoxidation of sodium hypophosphite.** W. BOCKEMÜLLER and T. GÖTZ (Annalen, 1934, 508, 268—297).—Aq. NaH<sub>2</sub>PO<sub>2</sub> is not normally autoxidised in the absence of heavy metals, but in presence of F<sub>2</sub>O or O<sub>3</sub> it readily absorbs O<sub>2</sub>. Velocity of autoxidation in a buffered solution depends not only on the *p*<sub>H</sub> of the solution, velocity being greater and autoxidation more complete with lower *p*<sub>H</sub>, but also on the concn. of the buffer. Phosphate buffer was used. The dependence on NaH<sub>2</sub>PO<sub>2</sub> concn., temp., and partial pressure of O<sub>2</sub> has been studied. An unstable intermediate product, *monoperphosphorous acid*, is formed. CuSO<sub>4</sub> and FeCl<sub>3</sub> are strong stabilisers of this compound and O<sub>2</sub> to a smaller extent. The part played by O<sub>3</sub> or F<sub>2</sub>O is still in doubt. The results are explained by a chain mechanism. The rôle of the heavy-metal ions in bringing about autoxidation (cf. Wieland and Franke, A., 1929, 1309) is discussed. The behaviour of Cu<sup>++</sup> is peculiar, since small quantities increase the velocity of autoxidation, but larger quantities stabilise the per-acid and break the reaction chain. VCl<sub>3</sub> increases the velocity, but brings the reaction to an end at an earlier stage, and very little per-acid is present. Autoxidation of the hypophosphite leads to phosphate, and does not stop at the phosphite. The latter also is autoxidised to phosphate, and in absence of heavy-metal ions requires the presence of O<sub>3</sub> or F<sub>2</sub>O to initiate the reaction. Monoperphosphoric acid is formed. The course of the chain reaction in this case also is discussed. Very little autoxidation of arsenite takes place. M. S. B.

**Kinetics of ethylene polymerisation.** H. H. STORCH (J. Amer. Chem. Soc., 1934, 56, 374—378).—The primary product of polymerisation at 377° and 1415 mm. is butylene, giving propylene as a secondary product. Small amounts of O<sub>2</sub> accelerate the reaction. At 350—400° the heat of activation is about 42,000 g.-cal. E. S. H.

**Kinetics of the thermal isomerisation of cyclopropane.** T. S. CHAMBERS and G. B. KISTIAKOWSKY (J. Amer. Chem. Soc., 1934, 56, 399—405).—The thermal reaction cyclopropane → propylene is homogeneous and unimol. The rate coeffs. depend on the pressure; at high pressure log *K*<sub>∞</sub> = 15.17—65,000/2.3RT. E. S. H.

**Thermal decomposition of *tert.*-butyl and *tert.*-amyl alcohols. Homogeneous unimolecular reactions.** R. F. SCHULTZ and G. B. KISTIAKOWSKY (J. Amer. Chem. Soc., 1934, 56, 395—398).—

The thermal decomp. at 487—555° are homogeneous and unimol., with the activation energies: Bu<sup>o</sup>OH 65,500 g.-cal., *tert.*-amyl alcohol 60,000 g.-cal. The corresponding rate coeffs. are given by 4.8 × 10<sup>14</sup>e<sup>-65,500/RT</sup> and 3.3 × 10<sup>13</sup>e<sup>-60,000/RT</sup>. E. S. H.

**Velocity of decomposition of diazo-compounds in water.** XIII. E. YAMAMOTO, R. GOSHIMA, and J. HASHIMA (J. Soc. Chem. Ind. Japan, 1934, 37, 29—33B).—Decomp. velocity coeffs. at various temps. are given for 1 : 2-, 2 : 1-, and 7 : 2-SO<sub>3</sub>H·C<sub>16</sub>H<sub>6</sub>N<sub>2</sub>Cl. A. G.

**Hydration of unsaturated compounds. I. Rate of hydration of isobutene in dilute nitric acid.** H. J. LUCAS and W. F. EBERZ (J. Amer. Chem. Soc., 1934, 56, 460—464).—Hydration of isobutene (I) (to Bu<sup>o</sup>OH) is catalysed by dil. HNO<sub>3</sub> (II) at 25°. At const. ionic strength the rate of hydration is unimol. with respect to both the concn. of (I) and the concn. of (II). For a fixed concn. of (II), the rate is increased by addition of KNO<sub>3</sub>; this increase is > the increase in the activity of (I) as determined by distribution experiments between CCl<sub>4</sub> and aq. KNO<sub>3</sub>. The sp. rate of hydration of (I) in 0.2N-HNO<sub>3</sub> at 25° is practically unchanged by addition of various metal salts [e.g., CuSO<sub>4</sub>, NiSO<sub>4</sub>, Pb(NO<sub>3</sub>)<sub>2</sub>, Hg(NO<sub>3</sub>)<sub>2</sub>, Th(NO<sub>3</sub>)<sub>4</sub>]. The ratio *k*<sub>35°</sub>/*k*<sub>25°</sub> is about 3.6 [for three concns. of (II)]; the heat of activation is 23.39 kg.-cal. Mixtures of Δ<sup>α</sup>- and Δ<sup>β</sup>-butenes are not hydrated in N-HNO<sub>3</sub> at 25°. H. B.

**Unimolecular reaction velocities and intramolecular energy exchange.** C. C. COFFIN (Trans. Roy. Soc. Canada, 1933, [iii], 27, III, 161—168).—A theoretical discussion is given of results obtained from the preliminary study of the thermal decomp. in the gaseous state of ethylidene diesters and of paraldehydes. H. S. P.

**Raman effect in the study of chemical reactions.** S. PARTHASARATHY (Phil. Mag., 1934, [vii], 17, 471—476).—The reactions between EtOH and AcOH, EtOH and Ac<sub>2</sub>O, and Ac<sub>2</sub>O and H<sub>2</sub>O have been followed by observing the intensity variation of characteristic Raman frequencies. Some new frequencies for chloral, solid chloral hydrate, CH<sub>2</sub>Cl·CO<sub>2</sub>H, and CCl<sub>3</sub>·CO<sub>2</sub>H are recorded. H. J. E.

**Thermal decomposition of organic compounds from the viewpoint of radicals. VI. Mechanism of some chain reactions.** F. O. RICE and K. F. HERZFELD (J. Amer. Chem. Soc., 1934, 56, 284—289).—Theoretical. The observations that (a) the decomp. of C<sub>2</sub>H<sub>6</sub>, COMe<sub>2</sub>, and Me<sub>2</sub>O are unimol. reactions, (b) the decomp. of MeCHO is of the order 1.5, (c) the formation of C<sub>2</sub>H<sub>6</sub> from C<sub>2</sub>H<sub>4</sub> and H<sub>2</sub> is bimol., are consequences of the theory of free radicals (A., 1931, 819; 1933, 930). E. S. H.

**Kinetics of reaction of the thiosulphate ion with the ions of brominated malonic and succinic acids.** M. H. BEDFORD, R. B. MASON, and C. E. MORRELL (J. Amer. Chem. Soc., 1934, 56, 280—283).—Velocity determinations at different concns. cannot be explained by Brönsted's theory, but are explicable in terms of the theory of La Mer and Kammer (A., 1931, 1132). E. S. H.

**Autoxidation of stannous chloride. IV. Effect of some non-aqueous solvents.** R. C. HARING and J. H. WALTON (*J. Physical Chem.*, 1934, **38**, 153—160).—The formation of a complex between  $\text{SnCl}_2$  and  $\text{HCl}$  has been indicated by f.-p. measurements in dioxan. An equimol. compound of  $\text{SnCl}_2$  and dioxan has been identified. The autoxidation of  $\text{SnCl}_2$  in dioxan and  $\text{BzOH}$  increases nearly linearly with  $\text{HCl}$  concn. until the latter approaches the concn. of  $\text{SnCl}_2$ , when the rate becomes practically const. At const.  $\text{HCl}$  concn. the rate also approaches a const val. with increasing concn. of  $\text{SnCl}_2$ . The results confirm the assumption that  $\text{SnCl}_2$  is autoxidised in the form of its complex  $\text{HSnCl}_3$  or  $\text{H}_2\text{SnCl}_4$  (cf. A., 1933, 472). Induced oxidation of the solvents dioxan and  $\text{BzOH}$  also takes place. Several positive and negative catalysts are found to have, qualitatively, the same effect as in aq. solutions (*loc. cit.*).  
M. S. B.

**Kinetics of reaction and adsorption in the system silver-oxygen.** A. F. BENTON and L. C. DRAKE (*J. Amer. Chem. Soc.*, 1934, **56**, 255—263).—Finely-divided  $\text{Ag}$  reacts with  $\text{O}_2$  at  $160^\circ/1$  atm. The no. of c.c. of  $\text{O}_2$  reacting per hr. per mm. pressure is given by  $7.2 \times 10^7 e^{-22,000/RT}$ ; the rate is proportional to the pressure, but independent of the extent of oxidation over the range 0.3—10%. In absence of oxide the initial rate is about four times as great. The rate of decomp. is given by  $1.9 \times 10^{17} e^{-35,600/RT}$ . The difference between the energies of activation of the forward and reverse reactions is equal to the heat of reaction. Two types of adsorption occur below the dissociation pressure of  $\text{Ag}_2\text{O}$ : (a) physical adsorption, which is great at  $-183^\circ$ , but small at  $-78.5^\circ$ , (b) activated adsorption, which is slow at  $0^\circ$ , but increases rapidly at higher temp. The energy of activation for (b) is 12.7 kg.-cal., and for desorption 28.4 kg.-cal. Solubility is not an appreciable factor. Calculation shows that the rate at which  $\text{O}_2$  mols. collide with the surface with energy in excess of the required activation energy is approx. equal to the initial rate of adsorption.

E. S. H.

**Rate of dissolution of electrolytic zinc in acids.** M. CENTNERSZWER and M. STRAUMANTIS (*Z. physikal. Chem.*, 1934, **167**, 421—430).—The rate of dissolution,  $v$ , in  $N\text{-HCl}$  rises as reaction proceeds, and ultimately reaches a steady val.,  $v'$ ; the period of induction is longer than with any other form of pure  $\text{Zn}$ . If the  $\text{Zn}$  is first treated for 3 min. with  $4N\text{-HCl}$ ,  $v$  is a max. at the start and slowly falls towards a limiting val. Rubbing the  $\text{Zn}$  with emery-paper also eliminates the period of induction, and  $v$  ultimately approaches  $v'$ . This mechanical treatment possibly establishes local elements between points deformed to different extents.  $v'$  varies with the acid concn.,  $C$ , according to  $v' = K(C - C_0)$ , where  $C_0$  is the acid concn. for which  $v' = 0$ , and  $K$  is a const. Stirring does not affect  $v'$ , which indicates that the rate of dissolution is determined by the rate of the chemical process. Electrolytic  $\text{Zn}$  dissolves in  $\text{H}_2\text{SO}_4$  far more slowly than in  $\text{HCl}$  of the same  $[\text{H}^+]$ ; rubbing with emery-paper increases  $v$  initially.

R. C.

**Velocity of dissolution of copper in cupric salt solutions.** A. BASIŃSKI (*Rocz. Chem.*, 1934, **14**, 31—44).—The velocity  $v$  of dissolution of  $\text{Cu}$  in aq.  $\text{CuCl}_2$  and  $\text{CuBr}_2$  varies with temp. and rate of stirring in a way characteristic of diffusion processes, and is unaffected by the presence of  $\text{NH}_4\text{Cl}$ , or by variations in the concn. of  $\text{CuCl}_2$ ; the val. of  $v$  for various solutions increases in the order:  $\text{Fe alum} < \text{CuCl}_2 < \text{CuBr}_2$ . Saturating the solutions with  $\text{CO}_2$  slightly increases  $v$ .  
R. T.

**Rate of decomposition of cathode deposits formed on platinum electrodes in presence of helium, nitrogen, and oxygen at low pressure.** J. PIAZZA (*Anal. Inst. invest. cient. tecn.*, 1931, **2**, 33—49).—Isotherms showing the rate of evolution of  $\text{He}$ ,  $\text{N}_2$ , or  $\text{O}_2$  from the deposits at temp. between  $87^\circ$  and  $143^\circ$  have been determined. At low temp. the reaction is partly reversible, but above a certain temp. it becomes completely irreversible; in all cases the decomp. begins at a definite temp. The rate of decomp. varies with the composition. The isotherms indicate the occurrence of autocatalysis. Several compounds appear to be formed in each case between the  $\text{Pt}$  and the gas.  
H. F. G.

**Rate of oxidation of quinol with atmospheric oxygen. I. II. Influence of sodium sulphite.** W. REINDERS and P. DINGEMANS (*Rec. trav. chim.*, 1934, **53**, 209—230, 231—238).—I. At  $p_{\text{H}_2}$  6.9—7.9 the rate is proportional to  $[\text{C}_6\text{H}_4(\text{OH})_2]$ , to the pressure of  $\text{O}_2$  ( $p_{\text{O}_2}$ ) and to  $[\text{OH}]^2$ . No  $\text{H}_2\text{O}_2$  is formed. The reactions are (1)  $\text{C}_6\text{H}_4(\text{OH})_2 + \text{O}_2 = \text{C}_6\text{H}_3(\text{OH})\text{O}_2 + \text{H}_2\text{O}$  (this reaction determines the measured rate), (2)  $\text{C}_6\text{H}_3(\text{OH})\text{O}_2 + \text{C}_6\text{H}_4(\text{OH})_2 = 2\text{C}_6\text{H}_4\text{O}_2 + \text{H}_2\text{O}$  or  $n\text{C}_6\text{H}_3(\text{OH})\text{O}_2 \rightarrow$  polymerides. The reaction is catalysed by  $\text{CuSO}_4$  in proportion to its concn. The catalysed rate is proportional to  $[\text{C}_6\text{H}_4(\text{OH})_2]^{1.05}$  or  $0.6$ , to  $[\text{OH}]$ , and to  $p_{\text{O}_2}$ ;  $\text{MnSO}_4$  is a weak catalyst. The catalytic action of  $\text{CuSO}_4$  is due to a colloidal complex of  $\text{Cu}$  with  $\text{C}_6\text{H}_4(\text{OH})_2$ .

II. The rate has been measured with additions of  $\text{Na}_2\text{SO}_3$  up to 100%, at  $p_{\text{H}_2}$  7.35—8.18. Each substance hinders the oxidation of the other. The  $\text{Na}_2\text{SO}_3$  in a mixture is oxidised before the  $\text{C}_6\text{H}_4(\text{OH})_2$ . The mechanism of inhibition is discussed. An explanation on the chain theory is unsatisfactory.

H. J. E.

**Rate of oxidation of metal with atmospheric oxygen and the influence of sodium sulphite.** W. REINDERS and P. DINGEMANS (*Rec. trav. chim.*, 1934, **53**, 239—245).—At  $p_{\text{H}_2}$  6.0—6.6 the rate is proportional to the concn. of metal, to  $p_{\text{O}_2}$ , and to  $[\text{OH}]$ .  $\text{CuSO}_4$  is a weak catalyst.  $\text{Na}_2\text{SO}_3$  has the same effect as on  $\text{C}_6\text{H}_4(\text{OH})_2$  (cf. preceding abstract). The rate is controlled by the reaction  $\text{NHMe}\cdot\text{C}_6\text{H}_4\cdot\text{O}' + \text{O}_2 = \text{NHMe}\cdot\text{C}_6\text{H}_4\text{O}_3'$ . This is followed by the rapid reaction  $\text{NHMe}\cdot\text{C}_6\text{H}_4\text{O}_3' + \text{H}^+ = \text{NMe}\cdot\text{C}_6\text{H}_4\text{O}_2 + \text{H}_2\text{O}$ .

H. J. E.

**Mechanism of oxidation processes. XXXVIII. [Dehydrogenation] with ethyl peroxide catalysed by iron.** H. WIELAND and K. BOSSERT (*Annalen*, 1934, **509**, 1—18; cf. A., 1930, 890).—The reaction  $\text{RH}_2 + \text{Et}_2\text{O}_2 (\text{I}) \rightarrow \text{R} + 2\text{EtOH}$  is catalysed by  $\text{Fe}^{2+}$ ; the catalysis is not retarded by  $\text{KCN}$ . Thus  $\text{HCO}_2\text{H}$  is dehydrogenated by (I) in presence of a little  $\text{FeSO}_4$ .



to  $\text{CO}_2$  (max. amount at  $p_{\text{H}_2}$  6). Lactic acid (II) affords  $\text{CO}_2$  (best at  $p_{\text{H}_2}$  7), but with high concns. of (II),  $\text{AcCO}_2\text{H}$  (which is oxidised to  $\text{CO}_2$ ) is detected as an intermediate. The following compounds are also dehydrogenated (the products formed are given in parentheses): tartaric acid at  $p_{\text{H}_2}$  5—7 ( $\text{CO}_2$ ); dihydroxymaleic acid; mandelic acid ( $\text{CO}_2$  and  $\text{PhCHO}$ ); *o*- and *m*- $\text{C}_6\text{H}_4(\text{OH})_2$ ; *p*- $\text{C}_6\text{H}_4(\text{OH})_2$  (*p*-benzoquinone); pyrogallol (purpurogallin in dil. solution; cf. Willstätter and Stoll, A., 1918, i, 555); guaiacol; hydrazobenzene; benzidino. Glycine, alanine (III), and phenylalanine react with (I) only in presence of  $\text{Fe}^{++}$  to give  $\text{CO}_2$ ;  $\beta$ -amino- $\gamma$ -hydroxybutane [*H* oxalate, m.p. 164—165° (decomp.); oxalate, m.p. 208° (decomp.); platinichloride, m.p. 190° (lit. 185°)], and  $\text{CH}_2\text{O}$ ,  $\text{MeCHO}$ , and  $\text{CH}_2\text{Ph}\cdot\text{CHO}$ , respectively:  $\text{NH}_2\cdot\text{CHR}\cdot\text{CO}_2\text{H} + 2\text{Et}_2\text{O}_2 \rightarrow \text{RCHO} + \text{CO}_2 + 2\text{EtOH} + \text{NH}_2\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{OH}$ . (III) is dehydrogenated more readily in presence of  $\text{MeCHO}$  probably owing to the suppression of the reaction  $\text{Et}_2\text{O}_2 \rightarrow \text{MeCHO} + \text{EtOH}$ , which is also catalysed by  $\text{Fe}^{++}$  and occurs during the above dehydrogenations. All the reactions are carried out at 20° or 37° in  $\text{N}_2$ .

H. B.

**Effect of methyl substitution on catalysed dehydrogenation of cyclic hydrocarbons with six-membered rings.** A. A. BALANDIN and A. M. RUBINSTEIN (Z. physikal. Chem., 1934, 167, 431—440).—The rates of dehydrogenation of cyclohexane (I), methylcyclohexane (II), and mixtures of the two on Ni supported on  $\text{Al}_2\text{O}_3$  have been determined at 200—270°. At all temp. (II) is dehydrogenated approx. 20% more rapidly than (I). The energy of activation,  $Q$ , is practically the same for (I), (II), and their mixtures, viz., 13,590 g.-cal. The relation previously reported (A., 1933, 234) between  $Q$  and  $k_0$  in Arrhenius' equation  $K = k_0 e^{-Q/RT}$  is confirmed.

R. C.

**Neutral salt action in ion reactions in concentrated salt solutions.** A. VON KISS [with R. KUKAI] (Z. physikal. Chem., 1934, 167, 354—364).—Polemical against Parts (cf. A., 1933, 789) with reference to the effect of neutral salts on the reactions  $\text{CO}_2\text{Me}\cdot\text{CH}_2\cdot\text{CO}_2' + \text{OH}' = \text{OH}\cdot\text{CH}_2\cdot\text{CO}_2' + \text{CO}_2\text{Me}'$  and  $\text{CO}_2\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{CO}_2'' + \text{OH}' = \text{CO}_2\cdot\text{CBr}\cdot\text{CH}\cdot\text{CO}_2'' + \text{Br}' + \text{H}_2\text{O}$  at 25°.  $\log k$ , where  $k$  is the velocity coeff., increases linearly with the neutral salt concn.,  $c$ , from  $N$  upwards. Assuming that  $k = h_r h_m F$  (A., 1925, ii, 681) experimental data show that  $\log F$ , or at least the logarithm of the correspondingly constructed quotients, and  $\log h_m F$  are both linear functions of  $c$ . The applicability of Grube and Schmid's rule (A., 1926, 474) to ion reactions is thus demonstrated. R. C.

**Metallic corrosion. Topochemistry of magnesium.** A. VYSKOČIL (Coll. Czech. Chem. Comm., 1934, 6, 1—16).—Relative adsorbability on the Mg limits the catalysis of corrosion by a mixture of anions. Although  $\text{Cl}'$  alone is more active catalytically than  $\text{SO}_4''$ , the latter is more strongly adsorbed from a mixture and controls the velocity. The adsorbability of  $\text{I}' > \text{Br}' > \text{Cl}'$ , and thus  $\text{I}'$  and  $\text{Br}'$  depress the effect of  $\text{Cl}'$  except in the final stages of corrosion. The catalysis is explained as the formation of complexes between Mg atoms and hydrated anions at discon-

tinuities of the metal surface, the  $\text{H}_2\text{O}$  liberated during complex formation being decomposed by neighbouring Mg atoms. If the exchange of electric charges is especially favoured, a black, unstable substance ("suboxide"), probably a mixture of disintegrated Mg and  $\text{Mg}(\text{OH})_2$ , is formed. J. G. A. G.

**Active oxides. LXXII. Course of reactions in the solid state.** G. F. HÜTTIG [with E. ROSENKRANZ, B. STEINER, and H. KITTEL] (Z. anorg. Chem., 1934, 247, 22—26).—The changes in the catalytic activity of an equimol. mixture of  $\text{MgO}$  and  $\text{Fe}_2\text{O}_3$ , as it is transformed by rising temp. into  $\text{MgFe}_2\text{O}_4$ , have been investigated by its effect on the velocity of oxidation of  $\text{CO}$  to  $\text{CO}_2$ . The max. activity is reached at 625°. The ferromagnetic behaviour and X-ray diagram indicate that at this point the formation of cryst. aggregates of spinel is beginning, but that most of the mixture is still in the stage preceding this formation. Pure  $\text{MgO}$ , formed by the thermal decomp. of  $\text{MgCO}_3$  or  $\text{MgC}_2\text{O}_4$ , also catalyses  $\text{CO}$  oxidation. If the freshly prepared  $\text{MgO}$  be heated at 700°, the activity falls as the time of heating increases. If the  $\text{MgO}$  is prepared from magnesite containing Fe, there is a subsequent rise in activity to a max. which is the same as the activity max. for  $\text{MgFe}_2\text{O}_4$ . M. S. B.

**Two types of activated adsorption of hydrogen on the surface of a promoted iron synthetic ammonia catalyst.** R. W. HARKNESS and P. H. EMMETT (J. Amer. Chem. Soc., 1934, 56, 490—491).—Evidence of two distinct types of activated adsorption and one type of physical adsorption at a catalyst of Fe promoted with 1.3%  $\text{Al}_2\text{O}_3$  and 1.59%  $\text{K}_2\text{O}$  is adduced. The characteristics of the types are described.

E. S. H.

**Catalysts for oxidation of ammonia. I. Chromium catalysts.**—See B., 1934, 236.

**Formation of ammonia on highly-dispersed metals.** D. P. DOBYTSCHIN and A. V. FROST (Z. Elektrochem., 1934, 40, 89—91).—A mixture of finely-divided Fe and NaCl, formed by vaporising the two together at a pressure of 0.06 mm. in  $\text{N}_2$  and  $\text{H}_2$ , adsorbs these gases when cooled in liquid air. Even at 20° the pressure returns to 0.03 mm. only, but, contrary to the observations of Müller and Schwabe (A., 1933, 36), there is no evidence of the production of  $\text{NH}_3$ . The  $\text{N}_2$ - $\text{H}_2$  complex on the Fe is very stable, and cannot be readily destroyed below 100°. The production of  $\text{NH}_3$  by vaporised Pt (cf. Bastow, A., 1931, 1120) has been confirmed. M. S. B.

[Formation of ammonia on highly dispersed metals.] E. MÜLLER and K. SCHWABE (Z. Elektrochem., 1934, 40, 91—92; cf. preceding abstract).—The temp. 175—355° at which the Fe adsorption complex is heated is sufficient to cause the decomp. of any  $\text{NH}_3$  formed. M. S. B.

**Kinetic measurements with concentrated strong acids.** B. BLASER (Z. physikal. Chem., 1934, 167, 441—457).—The reaction  $\text{H}_4\text{P}_2\text{O}_6 + \text{H}_2\text{O} = \text{H}_3\text{PO}_3 + \text{H}_3\text{PO}_4$ , which is catalysed by acids (A., 1933, 1130), has been used to assess the strength of conc. acids. Similar results have been obtained from kinetic measurements on the hydrolysis of  $\text{HSO}_3\text{F}$  and Frey and Elöd's indicator method (A., 1931, 1401). With

the acids studied, except  $\text{HNO}_3$ , the activity rises rapidly with the concn. up to about 70 wt.-%. The strength of  $\text{HNO}_3$  above about 6*N* rises much more slowly than that of other acids; probably the acid begins to change into a weaker tautomeric form. The hydrolysis of  $\text{MeO}\cdot\text{SO}_3\text{H}$  and  $\text{NHPh}\cdot\text{SO}_3\text{H}$  cannot be used to determine the strength of acids owing to intermediate and side reactions. R. C.

**Influence of surface-active substances on the velocity of evaporation of carbon dioxide from supersaturated solutions.** N. A. HELD and A. D. TRATSCHEV (Compt. rend. Acad. Sci. U.R.S.S., 1933, 299—302).—Surface films of *isoamyl*, *n*-butyl, and *n*-heptyl alcohols and *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$  each produce a retardation of the evaporation of  $\text{CO}_2$  from its supersaturated solution, the effect being greatest with concns. corresponding with < a unimol. surface layer. The effect is greatest with *isoamyl* alcohol. With higher concn. the evaporation is less retarded, and may even be accelerated by the film. The phenomena are explained on the basis of the resistance of the film itself, and the effect on the stirring of the surface layer of the aq. solution by the motions in the film. J. W. S.

**Electrolytic concentration of the heavy hydrogen isotope.** B. TOPLEY and H. EYRING (Nature, 1934, 133, 292; cf. this vol., 154).—The electrolytic separation coeff.,  $\alpha$ , defined by the equation  $d \log \text{H}^1 = \alpha d \log \text{H}^2$ , of the metals examined lies between 7.9 and 2.8, the order being: smooth Pt > Pb > Fe > Cu > Ag > Ni > W > Pt-black >  $\text{Ga}_{\text{liq.}}$  > Hg.  $\alpha$  is slightly lower in acid than in alkaline solution, and moderate changes in c.d. have little effect. The over-voltage mechanism proposed by Gurney presents serious difficulties for its acceptance. L. S. T.

**Preparation of heavy hydrogen.** P. HARTECK (Proc. Physical Soc., 1934, 46, 277—280).—Details of a method by the electrolysis of an alkaline solution with Ni electrodes are described. N. M. B.

**Enrichment of the heavy hydrogen isotope [in water].** W. UHLMANN (Naturwiss., 1934, 22, 119—120).—The acid in an old battery of accumulators, which had been in use for 6—10 years and to which only  $\text{H}_2\text{O}$  had been added, afforded  $\text{H}_2\text{O}$  of  $d$  1.000033 (i.e.,  $\text{H}^2 : \text{H}^1 = 1 : 3000$ ). A. J. M.

**Alkaline accumulator. I. Electrolysis of alkali zincate solution.** S. TANAKA. II. S. TANAKA and K. IWASA. III. Alkali zincate accumulator with nickel-mesh cathode. S. TANAKA and T. TOMINAGA (J. Electrochem. Assoc. Japan, 1933, 1, 143—149, 149—153, 220—225).—I. Relative vals. of the current at a Ni electrode and the cathode p.d. were determined in aq. NaOH, or preferably KOH, containing ZnO of various concns. An amalgamated Ni cathode is most effective for prolonged Zn deposition.

II. The solubility of the deposited Zn is low in 7*N*-KOH with  $\text{KOH} : \text{ZnO} = 12$ . Amalgamation of the cathode increases the rate of deposition of the Zn and lowers its solubility.

III. Ni-mesh cathodes give the most compact Zn deposit; the cryst. particles become coarser on repeated charge and discharge. CH. ABS.

**Electrolysis of molten silicates and preparation of silicon and silicides.** L. ANDRIEUX and M. DODERO (Compt. rend., 1934, 198, 753—755; cf. A., 1930, 405).—With a C crucible as anode, an Fe rod as cathode, and a mixture of  $2\text{SiO}_2 + \text{Li}_2\text{O} + 6\text{LiF}$ , at 950° a current of about 25 amp. at 10 volts gave a product containing Si 24.1—46.8%, Si combined with Li 30.7—55.5, Si with Fe 0.7—2.6, Li 17.0—17.8, and Fe 0.7—2.6; with  $\text{H}_2\text{O}$ -cooled cathode and a mixture of  $\text{SiO}_2 + \text{Li}_2\text{O} + 2-4\text{LiF}$  (or  $6\text{LiF} + \text{LiCl}$ ) at 800—920° the corresponding figures were 0—6.4, 48.6—61.8, 0.5—2.5, 26.3—36.4, and 0.5—2.6. In the latter case the product was spontaneously inflammable in air, as also was the gas evolved on contact with  $\text{H}_2\text{O}$ . The Li silicide is violet-coloured, and approx.  $\text{Si}_2\text{Li}_3$  (cf. A., 1902, ii, 452). C. A. S.

**Electrolysis of metals, studied with a scraped electrode.** J. HOEKSTRA (Coll. Czech. Chem. Comm., 1934, 6, 17—36).—Whereas the unscraped Ag electrode (I) in *M*- $\text{AgNO}_3$  gave irregular current-voltage curves, the scraped electrode afforded a rectilinear relationship. The resistance is independent of the pressure on the scraper, is increased by adding gelatin, and has a min. val. for a particular rate of scraping. The resistance decreased with increase of a.c. Cu behaved, qualitatively, like Ag, whilst Hg deposition from  $\text{HgNO}_3$  in  $\text{HNO}_3$  afforded a linear relationship. Scraping eliminated slight irregularities from the curves for the unscraped Pb electrode (II) and had a very large effect on the Zn electrode (III). A close parallelism was found between the polarographic resistances observed with (I), (II), and (III), and the corresponding sp. resistances recorded by Kohlrausch and Holborn. The scraped Ni electrode had no permanent polarisation, and hence the polarograms coincided in both directions, but without scraping coincidence was absent although all of the curves were logarithmic. Photomicrographs of growing deposits of Ag, Cu, Pb, Sn, and Tl are given and rates of spreading are recorded. The c.d. attains high vals. at the many step-edges of the surface, and from the data for scraped electrodes it was inferred that only about 1 in  $10^5$  atoms of the Ag surface was activated during electrolysis. Without scraping, the no. of such active points does not remain const. Existing data are interpreted in terms of activation and adsorption. J. G. A. G.

**Polarographic studies with the dropping mercury cathode. XXXVII. Electrodeposition of gold.** J. HERMAN (Coll. Czech. Chem. Comm., 1934, 6, 37—53).—Current-voltage curves, *C*, have been obtained for the deposition, at the dropping Hg cathode, of Au from  $\text{Au}^{\text{I}}$  and  $\text{Au}^{\text{III}}$  complexes in  $\text{O}_2$ -free alkali hydroxide and cyanide solutions.  $\text{Au}^{\text{III}}$  complexes slowly decompose into, and are always accompanied by,  $\text{Au}^{\text{I}}$  complexes; this change is catalysed by KCN,  $\text{OH}^-$ , and rise of temp. The deposition from  $\text{AuCl}_3$  in 2*N*-KOH at zero voltage decreases with age of the solution owing to slow transformation into more stable complexes, but no mobile equilibrium exists between  $\text{Au}^{\text{III}}$  and  $\text{Au}^{\text{I}}$ . Au is deposited from  $\text{Au}^{\text{III}}$  and  $\text{Au}^{\text{I}}$  at -0.4 and -1.1 volts, respectively, referred to the *N*- $\text{Hg}_2\text{Cl}_2$  electrode. The limiting currents at < 1.4 volts in the complex Au-CN solutions have vals.

characteristic of  $\text{Au}^{\text{I}}$  and  $\text{Au}^{\text{III}}$ , respectively, and are directly proportional to concn. This affords the basis of a polarographic determination of Au in ores and alloys, since in large [KCN], Zn, Cu, Fe, Ag, As, Sb, Pb, and Bi do not interfere. The form of  $C$  indicates that KCN produces with the  $\text{Au}^{\text{III}}\text{-OH}$  complex a  $\text{Au}^{\text{III}}\text{-OH-CN}$  complex (I) which is unaltered by excess of KCN, whilst the addition of KOH does not change the  $\text{Au}^{\text{III}}\text{-CN}$  complex (II).  $C$  for a mixture of (I) and (II) is the sum of the effects of (I) and (II). (II) only is produced by adding  $\text{AuCl}_3$  to a mixture of KOH and KCN, and the  $\text{Au}^{\text{I}}\text{-OH}$  complex is transformed into the  $\text{Au}^{\text{I}}\text{-CN}$  complex by KCN. The general stability of these complexes and their slow response to conditions in solution are emphasised. J. G. A. G.

**Electrolysis of sodium bismuthiodide solutions.** A. E. JURIST and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1934, 23, 15—17).—Electrolysis of  $\text{Na}_2\text{BiI}_5$  in  $(\text{CH}_2\text{OH})_2$  solution causes migration of most of the Bi to the anode, where I is also liberated. About 6% of the Bi is deposited on the cathode.

C. G. A.

**Comparison between cathode deposits of silver and colloidal silver.** J. PIAZZA (Anal. Inst. invest. cient. tecn., 1931, 2, 50—52).—Colloidal Ag is produced when a suspension of pptd.  $\text{Ag}_2\text{O}$  in alcoholic Na tauroglycocholate solution is heated at 50—60°, particularly in presence of  $\text{H}_2$ . The product obtained by filtering and evaporating the solution is readily sol. in  $\text{H}_2\text{O}$  or abs. EtOH, but not in aq. EtOH. If, however, the  $\text{Ag}_2\text{O}$  is projected cathodically (at 860 volts) on to a film of the same salts formed on the walls of the discharge tube, in presence of  $\text{O}_2$  at 0.75 mm. or air at 0.2 mm., it does not possess colloidal properties, even after being warmed with EtOH.

H. F. G.

**Electrolytic manufacture of magnesium.**—See B., 1934, 203.

**Theory of chromium plating.** E. LIEBREICH (Z. Elektrochem., 1934, 40, 73—87).—The current-voltage curve of  $\text{H}_2\text{CrO}_4$  has two branches. Metallic Cr separates when the  $\text{Cr}^{++}$  stage is reached. Four-branched curves are obtained with a Au cathode when an additional acid, e.g., HCl, HF,  $\text{H}_2\text{SiF}_6$ ,  $\text{HClO}_3$ , or  $\text{HClO}_4$ , is present. The position of the curves is practically independent of the nature of the acid. With a Pt cathode there is a further branch showing  $\text{H}_2$  evolution without Cr deposition at zero  $\epsilon_{\text{r}}$ . A Cr oxide film is formed on the Au cathode, but not to an appreciable extent on Pt. As a result there is a considerable  $\text{H}_2$  overvoltage in the former case, but not in the latter. The temporary occurrence of a negative potential is due to a saturation of the cathode with  $\text{H}_2$  and not to a transition resistance as a result of the formation of an oxide film. The nature of the Cr deposit at 20° and 40° for different concns. of a no. of acids and mixed acids has been studied.

M. S. B.

**Rare earths. XLI. Electrolytic preparation of rare-earth amalgams. 3. Amalgams of lanthanum, neodymium, cerium, samarium, and yttrium.** Metallic lanthanum, neodymium, and cerium by thermal decomposition of their amalgams. E. E. JUUKOLA [with L. F. AUDRIETH

and B. S. HOPKINS] (J. Amer. Chem. Soc., 1934, 56, 303—304; cf. A., 1931, 805).—Dil. amalgams of La, Nd, Ce, Sm, and Yt are prepared by electrolyzing concn. solutions of the anhyd. chlorides in EtOH, using a Hg cathode. By distilling in vac. a concn. of 15% has been reached. La, Nd, and Ce have been prepared by thermal decomp. of the amalgams.

E. S. H.

**Texture of cathodic deposits.** A. GLAZUNOV (Z. physikal. Chem., 1934, 167, 399—406).—The deposition of metal in electrolysis is essentially a process of crystallisation (I), but the no. of centres of (I),  $Z$ , and the linear rate of (I),  $G$ , are functions of more factors than in ordinary (I).  $G$  is much greater in the direction of the current lines than perpendicular to this direction. In the deposition of Ag, Pb, Cu, and Cd at 20°  $G$  and  $Z$  increase with the c.d., whilst with increasing concn.  $Z$  and  $G$  in the direction of the current lines fall and  $G$  perpendicular to the current lines rises.

R. C.

**Anodic oxidation of lactic to pyruvic ion.** G. CARPENISEANU (Compt. rend., 1934, 198, 460—462; cf. A., 1923, ii, 298).—This is effected when pure aq. Na lactate is electrolysed with p.d. 1.5—3.5 volts, at low c.d. (about 1 milliamp.). The yield is low, much of the  $\text{AcCO}_2\text{H}$  formed being oxidised to  $\text{CO}_2$  and  $\text{MeCHO}$ . Electrolysis under identical conditions of 0.01M-Na lactate, and of 0.01M- $\text{AcCO}_2\text{Na}$  shows that the anodic oxidation potentials are almost the same. The reactions are:  $\text{OH}\cdot\text{CHMe}\cdot\text{COO}' + 0.5\text{O}_2 = \text{AcCOO}' + \text{H}_2\text{O}$ , and  $2\text{OH}\cdot\text{CHMe}\cdot\text{COO}' + 2\oplus = \text{MeCHO} + \text{CO} + \text{H}_2\text{O} + \text{AcCO}_2\text{H}$ , the former predominating. Presence of diastase has no effect.

C. A. S.

**Electrolytic reduction of camphoric acid imide.** B. SAKURAI and Y. TAMURA (J. Electrochem. Assoc. Japan, 1933, 1, 139—143).—Reduction does not occur in 80%  $\text{H}_2\text{SO}_4$ , or at < 30° whatever the  $\text{H}_2\text{SO}_4$  concn.; it occurs readily at > 80° in 15—30%  $\text{H}_2\text{SO}_4$ .  $\beta$ -Camphidone (I) is formed at high, and  $\alpha$ -camphidone (II) at low,  $\text{H}_2\text{SO}_4$  concn. The yields of both decrease, and of camphidine (III) increases, at high temp. Reduction of (I) to (III) is difficult, and of (II) to (III) easy. The different reducibilities are due to a difference in the properties of the two  $\text{CO}_2\text{H}$  groups in camphoric acid imide.

CH. ABS.

**Electrolytic oxidation of piperidine.** K. YAMAMOTO and M. YOKOYAMA (J. Electrochem. Assoc. Japan, 1933, 1, 160—162).—Piperidine (5.15 g.) in 2N- $\text{H}_2\text{SO}_4$  electrolysed with  $\text{PbO}_2$ -Pb anode and Pt cathode at 0.05 amp. per sq. cm. and 8 faradays per mol. gives  $\delta$ -aminovaleraldehyde,  $\delta$ -aminovaleric acid (0.95 g.), glutaric acid (0.5 g.),  $\text{NH}_3$  (1.9 g. as  $\text{NH}_4\text{Cl}$ ), succinic acid (2.0 g.), and  $\text{HCO}_2\text{H}$  (1.8 g.).

CH. ABS.

**Synthesis of cuprous nitride by cathodic dispersion of copper in nitrogen at low pressure.** G. BERRAZ (Anal. Inst. invest. cient. tecn., 1931, 2, 70—78).—When Cu is dispersed cathodically at 800—1500 volts in an atm. of  $\text{N}_2$  at 0.5—1 mm. pressure, the tube being maintained at room temp., a dark iridescent deposit containing 75% of  $\text{Cu}_3\text{N}$  and 25% of  $\text{Cu}_2\text{N}$  is formed on the walls. The X-ray diagram of the deposit indicates the presence of cryst.  $\text{Cu}_3\text{N}$ , and the absence of free Cu.

H. F. G.

**Preparation of sputtered metal films.** E. O. HULBERT (Rev. Sci. Instr., 1934, [ii], 5, 85—88).—In a cathode sputtering chamber containing residual air, opaque films of Sb, Bi, Cd, Au, Pb, Pt, Ag, and Sn were obtained in about 1 hr., films of Co, Cu, Ir, Fe, Ni, Sc, and Te in about 2 hr., whilst Mo, Ta, and W required several hr. Al, Be, C, Cr, Mg, and Si sputter very slowly under these conditions, but films of Al, Cr, and Si were obtained after a few hr. in residual atm. of Hg, He, or A. Most sputtered particles are of mol. or at. dimensions. Films of Pt, Ta, and Cr have a nearly const. transmission for wave-lengths 0.5—2.2  $\mu$ ; films of Si and C are relatively transparent from 1.0 to 2.2  $\mu$ . E. S. H.

**Cathodic sputtering of metals.** R. K. COWSIK (Indian J. Physics, 1933, 8, 209—229).—The relative rates of cathodic sputtering of a no. of metals, when plotted against their respective total heats of vaporisation, yield a smooth curve, which is not quite a rectangular hyperbola. The results are in accord with the thermal theory of Waran (A., 1931, 405). J. W. S.

**Rôle of oxygen as an inhibitor for the photo-synthesis of hydrogen chloride.** K. B. KRAUSKOPF and G. K. ROLLEFSON (J. Amer. Chem. Soc., 1934, 56, 327—333).—Kinetic measurements at high concns. of  $O_2$  show that as the ratio  $O_2 : Cl_2$  increases the ratio  $H_2O : KCl$  approaches a limit between 1 and 2. The rate of approach to the limit increases slightly with increasing concns. of  $H_2$  and  $HCl$ , and depends slightly on the temp., indicating that the activation energy for the reactions yielding  $HCl$  is  $>$  that for those yielding  $H_2O$ . The existence of the limit shows that the Nernst chains must be ended by a reaction  $H + O_2 = HO_2$  rather than  $Cl + O_2 = ClO_2$ . E. S. H.

**Photochemical union of hydrogen and chlorine.** III. **Effect of wave-length on quantum efficiency.** Experiments with dispersed light. J. B. BATEMAN and A. J. ALLMAND (J.C.S., 1934, 157—161).—The quantum efficiency,  $\gamma$ , is independent of  $\lambda$  between 400 and 490  $m\mu$  and falls slowly on either side of this region, being still appreciable at 550  $m\mu$ . Allmand's earlier statement (A., 1931, 1136), that  $\gamma$  falls considerably in the ultra-violet, was due to the accidental use of a glass window in place of  $SiO_2$ . The results obtained at 492  $m\mu$  (just beyond the convergence limit of the banded spectrum of  $Cl_2$ ) are anomalous, since  $\gamma_{492}/\gamma_{405}$  rises on prolonged irradiation from an initial val. of about 0.6 to a const. val. of about 8. The rate of reaction is proportional to the intensity of illumination at 313  $m\mu$ . D. R. D.

**Photodecomposition of chlorine dioxide.** J. W. T. SPINKS and J. M. PORTER (J. Amer. Chem. Soc., 1934, 56, 264—270).—In presence of  $H_2O$  dark reactions are avoided and 1 mol. disappears from the gaseous phase for each mol. of  $ClO_2$  decomposed by light. The quantum efficiency,  $\gamma$ , is independent of concn. and light intensity for low concns. of  $ClO_2$ . At 3650 Å.,  $\gamma$  is  $> 3$ ; the ratio of  $\gamma$  at 4360 and 3650 Å. is 0.86 : 1. The sensitised reaction in presence of Br at 5460 Å. gives  $\gamma$  equal to that at 3650 Å. With dry gases the reaction is sensitive to temp. changes.

At 15° the pressure decreases during the reaction, and  $Cl_2O_6$  is formed; at 30° the pressure increases and  $Cl_2$  and  $O_2$  are formed. The photolysis of dry  $ClO_2$  is a chain reaction. E. S. H.

**Photodecomposition of gaseous ammonia.** R. A. OGG, jun., P. A. LEIGHTON, and F. W. BERGSTROM (J. Amer. Chem. Soc., 1934, 56, 318—323).—Using ultra-violet light of wave-lengths 2194, 2144, and 2099 Å.,  $NH_3$  is decomposed into  $N_2$  and  $H_2$  stoichiometrically, with a quantum efficiency ( $\gamma$ ) of 0.14 at 20°.  $\gamma$  increases with rise of temp., but is practically independent of pressure of  $NH_3$  or wave-length of light. When  $N_2H_4$  is added the reaction consists in decomp. of  $N_2H_4$  photo-sensitised by  $NH_3$ . A mechanism of the reaction is suggested. E. S. H.

**Photochemical reaction of ammonia with oxygen.** H. E. BACON and A. B. F. DUNCAN (J. Amer. Chem. Soc., 1934, 56, 336—340).—Using the radiation from a Zn spark, the reaction can be represented approx. by  $8NH_3 + 7O_2 \rightarrow 2N_2 + 2NH_4NO_3 + 8H_2O$ . The reaction takes place in several steps, mechanisms for which are discussed. The quantum yield is variable. E. S. H.

**Photographic blackening law for ultra-soft X-rays.** H. BRIOLI and H. KIESSIG (Z. Physik, 1934, 87, 425—431).—At 1.5 Å. the blackening varied almost linearly with time, but at 45 Å. no such relation was observed. Various emulsions were used. A. B. D. C.

**Density surface of [a solid diagram representing] the Villard effect.** II. H. ARENS (Z. wiss. Phot., 1934, 32, 233—238; cf. A., 1931, 1378).—The density surfaces obtained with Agfa-Laue film without and with small and large pre-exposures to X-rays are of similar form. The Villard effect can also be produced by pre-exposure with white light. The differences which occur with increasing pre-exposure are discussed. J. L.

**Photochemical reaction between bromine vapour and platinum.** J. URMSTON and R. M. BADGER (J. Amer. Chem. Soc., 1934, 56, 343—347).—The initial rate of reaction of finely-divided Pt with Br at low pressures, using blue or yellow light, is reduced by 18% when the temp. is lowered by 25°. The acceleration due to illumination is proportional to the light intensity for both colours. A mechanism is not proposed, but it is inferred that the initial step is the same with blue or yellow light, and that a considerable proportion of  $Br_2$  mols. dissociate without collision with other mols. E. S. H.

**Separation of photochemical and thermal action in the photo-bromination of cinnamic acid.** W. H. BAUER and F. DANIELS (J. Amer. Chem. Soc., 1934, 56, 378—385).—The reaction in  $CCl_4$  was followed by means of a monochromator. A chain reaction is involved. The quantum yield,  $\phi$ , is 1—15 or more, varying with the concn. of Br and the temp. over the ranges  $2-8 \times 10^{-3}$  mol.  $Br_2$  per litre and 0—30°. The photochemical reaction consists of (a) a primary photo-reaction of 1 mol. per quantum and (b) a photo-excited thermal reaction measured by  $\phi-1=\theta$ , which is suppressed

at low Br concn. or low temp. Log 0 is nearly a linear function of  $1/T$ .

E. S. H.

**Action of light on vinyl iodide.** G. EMSCHWILLER (Compt. rend., 1934, 198, 464—466; cf. A., 1931, 694; 1933, 706).—When exposed to ultra-violet (Hg) light vinyl iodide decomposes according to:  $C_2H_3I \rightarrow CH_2=C+(H,I) \rightarrow C_2H_2+(H,I)$  and  $C_2H_3I+(H,I) \rightarrow C_2H_4+I_2$ , the solitary H attached to the C to which the I is attached being removed. There is always a relative deficiency of  $C_2H_4$  and a smaller one of  $C_2H_2$  due to I combining therewith. In presence of  $O_2$  in a  $SiO_2$  vessel in ultra-violet light vinyl iodide decomposes with evolution of I and formation (mols. per mol. of  $C_2H_3I$ ) of 0.6—0.65  $HCO_2H$ , 0.2  $CH_2O$ , 0.09 glycolaldehyde, 0.6—0.65 CO, 0.085  $C_2H_2$ , and a little  $CO_2$ . (In glass the reaction is slower with relatively more glycolaldehyde and less  $CH_2O$ , less  $C_2H_2$ , and no  $CO_2$ .) The reactions are:  $2C_2H_3I+7O \rightarrow 2HCO_2H+2CO+H_2O+I_2$ ;  $2C_2H_3I+3O+H_2O \rightarrow 2OH\cdot CH_2\cdot CHO$  (or  $4CH_2O$ ) +  $I_2$  (the  $CH_2O$  may result from photolysis of the  $OH\cdot CH_2\cdot CHO$ ); and  $2C_2H_3I+O \rightarrow 2C_2H_2+H_2O+I_2$ .

C. A. S.

**Piperidine metavanadate, a new light-sensitive compound.** O. BAUDISCH and F. L. GATES (J. Amer. Chem. Soc., 1934, 56, 373—374).—The prep. of  $C_5H_{11}N, HVO_3$  (I) is described. (I) is sensitive to ultra-violet light, but not to visible light. The darkening under ultra-violet light is a reversible reduction; oxidising agents regenerate (I). The ultra-violet absorption spectrum of (I) has been determined; the absorption is much  $>$  that due to  $C_5H_{11}N$ .

E. S. H.

**Influence of light on nitrification in soil.** N. R. DHAR, A. K. BHATTACHARYA, and N. N. BISWAS (J. Indian Chem. Soc., 1934, 10, 699—712).—The amount of  $NO_2'$  formed from  $NH_4$  salts mixed with sterilised or unsterilised soils in presence of air and sunlight is much  $>$  in the dark. A similar observation was made for the amounts of  $NH_3$  and  $NO_2'$  formed on exposing solutions of  $CO(NH_2)_2$  or egg-yolk mixed with soil. Evidence is adduced to support the view that ammonification and nitrification in soil occur actively under the influence of light even in absence of micro-organisms.

E. S. H.

**Influence of sensitisers on chemical reactions produced by  $\gamma$ -radiation.** G. HARKER (Nature, 1934, 133, 378—379).—Radiation from Ra decomposes  $CHCl_3$ , liberating  $Cl_2$ , which then slowly disappears with the formation of  $HCl$  as a secondary product. The apparent rate of decomp. is markedly affected by the presence of the reaction products.  $\gamma$ -Radiation (I) oxidises solutions of ferrous salts, but Berthelot's solution of  $FeCl_3$  and  $H_2C_2O_4$  is not reduced. The Fe in the reduced solution, however, is oxidised, and the addition of small amounts of different org. and inorg. substances modifies the rate of oxidation. The oxidation of  $K_2S_2O_5$  in air is accelerated by (I). The addition of I, KI, or  $KHSO_4$  further increases the rate of oxidation of the irradiated H sulphite solution. The oxidation of glutathione is also accelerated, but the addition of I, KI, or  $KIO_3$  has no further effect in this case.

L. S. T.

**Heavy hydrogen.** (SIR) J. J. THOMSON (Nature, 1934, 133, 281).—A lecture on early work concerning  $H_3$ .

L. S. T.

**Isotopic fractionation of hydrogen.** H. HUNT (J. Chem. Physics, 1934, 2, 106).—The  $H_2$  from electrolysis of  $H_2O$  containing  $H^2 : H^1, 1 : 200$  passed successively over  $CuO$  at  $200^\circ$  and  $600^\circ$  gave  $H_2O$  of which 10 ml. in the first case weighed 6.6 mg.  $<$  10 ml. in the second case. The difference fell to 5.0 mg. on doubling the rate of  $H_2$  flow.

N. M. B.

**Chemical separation of the isotopes of hydrogen.** E. D. HUGHES, C. K. INGOLD, and C. L. WILSON (Nature, 1934, 133, 291—292).—The figures given by A. and L. Farkas (this vol., 264) for the ratio of the sp. rates at which  $H^1$  and  $H^2$  are discharged by the dissolution of metals in  $H_2O$  must not be regarded as characteristic consts. of the metals. The vals. obtained for a given metal appear to depend in an unknown way on the experimental conditions. The authors' val. for Na is 2.9 (2.8—3.0 for media varying from strongly alkaline to strongly acidic), for Ca 1.3—1.6, and Al 4.0—4.9, the higher vals. in these two cases relating to reaction in alkaline solution. Zn containing a trace of C gives 5.6, commercial Zn 6.8, and Zn—Cu couples vals. up to 8.0.

L. S. T.

**Reaction of heavy water with metallic sodium.** J. HORIUTI and A. L. SZABO (Nature, 1934, 133, 327—328; cf. following abstract).—When heavy  $H_2O$  containing 1.81 parts of  $H^2$  (I) to 100 parts of  $H+H^2$  reacts with Na the percentages of (I) in the  $H_2+HH^2$  formed are as follow:  $H_2O$  in excess, at room temp. 0.96, Na in excess at room temp. 0.99, Na in excess at  $-10^\circ$  1.01,  $H_2O$  in excess at room temp. [?] 1.03. Decomp. of  $HH^2O$  by Na apparently can lead to the formation of  $NaOH$  or  $NaOH^2$  alternatively, the latter being preferred, or when  $HH^2O$  comes in contact with Na, the H atom escapes with greater ease to combine with a H atom released by a neighbouring pair of reacting particles  $Na+H_2O$  than does the  $H^2$  atom.

L. S. T.

**Fractionation of the hydrogen isotopes by addition of sodium to water.** C. O. DAVIS and H. L. JOHNSTON (J. Amer. Chem. Soc., 1934, 56, 492—493).—Differences in  $d$  have been observed in the original  $H_2O$ , the  $H_2O$  formed by burning the  $H_2$  liberated by Na, and  $H_2O$  obtained by distillation of the aq.  $NaOH$  formed.

E. S. H.

**Thermal decomposition of deuterium iodide.** D. RITTENBERG and H. C. UREY (J. Chem. Physics, 1934, 2, 106—107).—The difference in the fraction decomposed at equilibrium of pure  $H^1I$  and a sample rich in  $H^2I$  showed that thermal decomp. depends on the concn. of  $H^2$  in the  $HI$ .

N. M. B.

**Introduction of deuterium atoms into acetone.** J. O. HALFORD, L. C. ANDERSON, and J. R. BATES.—See this vol., 394.

**Existence of ammoniates of double salts. II.** G. SPACU and P. SPACU (Z. anorg. Chem., 1934, 217, 80—84; cf. A., 1933, 1128).—Ammoniates of more complex double salts have been prepared at  $-79^\circ$  and

investigated tensimetrically. The existence of the following has been indicated:

$2M^I Cl, M^I_2 Cr_2 O_7, 4HgCl_2, 2H_2O, 10NH_3$  ( $M^I = K$  or  $NH_4$ );  $HgCl_2, Hg_2 Cl_2, 4KCl, 11$  and  $2NH_3$ . The constitution of the salts is discussed. M. S. B.

**Modification of form of crystals grown in solution containing foreign material.** L. ROYER (Compt. rend., 1934, 198, 585—587; cf. this vol., 249).

—Examples of such modifications are [figures in parentheses show the interionic distances in Å. in the (111) plane, in which in all cases the ions in one plane are alternately all metal or all halogen]: the production of octahedral crystals of NaCl (3·97) by addition to its solution of  $CdCl_2$  (3·85),  $ZnCl_2$  (3·77), or  $MnCl_2$  (3·70), whilst these have no effect on KCl (4·43); and of octahedral faces on crystals of both salts by addition of  $NaNO_3$  (5·07) to aq.  $NH_4 I$  (5·09), and to a smaller extent if added to aq. KI (4·97), or KBr (4·70), but not if added to NaCl. C. A. S.

**Hydrolysis of some alkali metallotartrates.**

J. P. MATHIEU (Compt. rend., 1934, 198, 576—578; cf. this vol., 266).—Solutions of  $[TM(OH)_2]$  ( $M = Mn, Fe, Co, Ni, Zn$ ;  $T = C_4H_2O_6$ ) are simply hydrolysed by NaOH. Solutions of  $Na_2[TM(OH)_2]$  are unstable if dil., giving if  $M = Zn$  a ppt. of  $Zn(OH)_2$ , but if  $M = Fe, Mn,$  or  $Co$ , hydrolysis is according to (a)  $Na_2[TM(OH)_2] + 2H_2O \rightleftharpoons H_2[TM(OH)_2] + 2NaOH$ ; and (b)  $2Na_2[TM(OH)_2] + 2H_2O \rightleftharpoons M[TM(OH)_2] + Na_3T + 2NaOH$ . (b) is proved, when  $M = Co$ , by the diminution in the circular dichroism caused by addition of NaOH or  $Na_3T$ , and also by the equilibrium const. of the reaction. C. A. S.

**Interaction of aqueous cupric sulphate and cupric hydroxide.** O. BINDER (Compt. rend., 1934, 198, 653—655).—Mixtures of 5 g. of  $Cu(OH)_2$  and 100 c.c. of aq.  $CuSO_4$  of varying concn. were agitated at 22° until equilibrium was attained. The ratios  $CuO/SO_3$  and  $H_2O/SO_3$  were both invariably 4, and no basic salt other than  $(Cu_4O_3)SO_4 \cdot 4H_2O$  was found. If the relative proportions of  $Cu(OH)_2$  and  $CuSO_4$  were incorrect, one or other of  $Cu(OH)_2$  or  $CuSO_4 \cdot 5H_2O$  accompanied the basic salt. X-Ray investigation confirmed this result (cf. A., 1897, ii, 491; 1926, 246; 1932, 238). C. A. S.

**Prevention of the tarnishing of silver.** F. MARKHOFF (Sprechsaal, 1933, 66, 370—371; Chem. Zentr., 1933, ii, 1245).—The tarnishing of Ag in air can be prevented by varnishing. The action of alkali on Ag passivates the surface. Examples of this process are given. L. S. T.

**Allotropic modifications of calcium.** P. BASTIEN (Compt. rend., 1934, 198, 831—833; cf. A., 1931, 416).—When sublimed Ca is heated and allowed to cool in A, breaks occur in the cooling, thermo-electric power, and dilatation curves, and sudden changes in hardness at 240—265° (with hysteresis) and 430—440°. C. A. S.

**Hydrated calcium aluminates.** J. LEFOL (Ciment, 1933, 38, 322).—In the dehydration by heating of the hydrates of tetra- (I), tri- (II), and di- (III)-Ca aluminates, hydrates with lower  $H_2O$  contents are formed. The mols. of  $H_2O$  in the compounds are: (I) 10·5—11 at 95°, 6 at 175°; (II) 8—8·5 at 135° (from

the needle form), 6 up to 260°, and 1·5 from 260° to 310° (from the cubic form); (III) 5 at 150°.

T. W. P.

**Composition of the black precipitate formed by the action of ammonia on mercurous chloride.** S. AUGUSTI (Gazzetta, 1933, 63, 859—861).—The ppt. consists of Hg with  $Hg_2NCl$ ,  $Hg_2NCl \cdot NH_4Cl$ , or  $HgNCl \cdot 3NH_4Cl$ , according to the quantity of  $NH_3$  present. H. F. G.

**Preparation of mercurous ammonium compounds from mercurous ammonium nitrate.**  
I. Halides. S. AUGUSTI (Gazzetta, 1933, 63, 849—859).—Pptn. of an ammoniacal solution of  $HgNO_3$  with  $NH_4Br$  yields  $Hg_2NBr$ ; if washing is not prolonged the product contains  $Hg_2NBr \cdot NH_4Br$ .  $NH_4Cl$ , KCl, and KI yield, respectively,  $Hg_2NCl \cdot 3NH_4Cl$ ,  $Hg_2NCl \cdot H_2O$ , and  $Hg_2NI \cdot H_2O$ . With  $NH_4F$  no ppt. is formed, but KF yields  $Hg_2NF$ . The properties of the ppts. are described and photomicrographs are reproduced. H. F. G.

**Microscope as aid to study of detonation.** A. MICHEL-LÉVY and H. MURAUOUR (Compt. rend., 1934, 198, 825—826).—Microscopical examination of the result of detonating a minute particle of  $PbN_6$  shows a central space covered with globules of Pb; this is surrounded by an almost continuous ring of Pb, and this again by pulverised Pb arranged radially. A second similar particle placed at a distance of 2—4 mm. is detonated almost simultaneously, i.e., by the explosion wave, and one further off, e.g., 15 mm., after a longer interval, i.e., by the hot gases (cf. A., 1931, 689). C. A. S.

**Concentration of gallium by means of adsorption on hydrated aluminium and iron oxides.** E. WAINER (J. Amer. Chem. Soc., 1934, 56, 348—350).—Hydrated  $Ga_2O_3$  is co-pptd. with  $Al(OH)_3$  and especially with  $Fe(OH)_3$ . The method affords a means of extracting Ga from low-grade ores. E. S. H.

**Carbide hydrolysis.** N. G. SCHMAHL (Z. Elektrochem., 1934, 40, 68—70).—The nature of the reaction products of the hydrolysis of the carbides of the rare earths, Th, and U is discussed from the thermochemical point of view. M. S. B.

**Oxidation of hydrazine by potassium ferricyanide.** I. Influence of gaseous supersaturation on the measurement of reaction velocity. II. Reaction in presence of acetone. T. N. RICHARDSON and K. C. BAILEY (Sci. Proc. Roy. Dublin Soc., 1934, 21, 43—49, 49—56).—I. Oxidation of  $N_2H_4$  by aq. alkaline  $K_3Fe(CN)_6$  is very rapid, but the rate of evolution of  $N_2$  is governed almost entirely by the rate of stirring.

II. The reaction is retarded and eventually inhibited by large amounts of  $COMe_2$  owing to formation of  $(CMe_2 \cdot N)_2$ . R. S. C.

**Interaction of phosphorus bromide and chloride.** IV. A. RENC (Rocz. Chem., 1934, 14, 69—77; cf. this vol., 158).—The products obtained by mixing  $CS_2$  solutions of  $PCl_5$  and  $PBr_5$  in various proportions are the same as those obtained in the absence of a solvent. The Cl content of the products of recrystallisation of  $PCl_4Br_4$  and  $PCl_{0.5}Br_{4.5}$  from  $CS_2$  is  $<$ , and that of  $PCl_4Br_4$  is  $>$ , that of the original crystals.

Crystals containing  $> 3$  atoms of Cl per atom of P lose Br under reduced pressure, yielding products of limiting composition  $\text{PCl}_4\text{Br}$ , whilst those of composition  $\text{PCl}_{0.5-2.55}\text{Br}_{5.6-8.5}$  yield  $\text{PCl}_{0.19-0.31}\text{Br}_{4.7-4.8}$ . The  $d$  of  $\text{PCl}_2\text{Br}$  and  $\text{PClBr}_2$  is  $<$  that of mixtures of  $\text{PCl}_3$  and  $\text{PBr}_3$  in corresponding proportions.

R. T.

**Amphoteric hydrated oxides, their higher molecular compounds, and their solutions.** XXII. Iso- and hetero-polyvanadic acids, purpureo- and luteo-phosphovanadates; explanation of the structure and constitution of heteropoly-compounds. G. JANDER, K. F. JAHR, and H. WITZMANN (Z. anorg. Chem., 1934, 217, 65—79; cf. this vol., 146, and earlier abstracts).—In alkaline or slightly acid vanadate solutions the presence of  $\text{H}_3\text{PO}_4$  has no influence on the aggregation process. Di-, tetra-, penta-, and the unstable octa-vanadic acids are formed. With increase of acidity,  $\text{H}_3\text{PO}_4$  stabilises octavanadic acid. Isopolyvanadates and the double salts, purpureophosphovanadates, are formed. The following compounds have been isolated as reddish-brown crystals:  $3\text{K}_2\text{O}, 2\text{P}_2\text{O}_5, 8\text{V}_2\text{O}_5, \text{aq.}$ ,  $10\text{SrO}, 2\text{P}_2\text{O}_5, 8\text{V}_2\text{O}_5, \text{aq.}$ ,  $4(\text{NH}_4)_2\text{O}, 2\text{P}_2\text{O}_5, 24\text{V}_2\text{O}_5, \text{aq.}$ ,  $5(\text{NH}_4)_2\text{O}, 2\text{P}_2\text{O}_5, 24\text{V}_2\text{O}_5, \text{aq.}$ ,  $11\text{K}_2\text{O}, 2\text{P}_2\text{O}_5, 24\text{V}_2\text{O}_5, \text{aq.}$ ,  $10\text{Na}_2\text{O}, 2\text{P}_2\text{O}_5, 24\text{V}_2\text{O}_5, \text{aq.}$ ,  $10\text{BaO}, 2\text{P}_2\text{O}_5, 24\text{V}_2\text{O}_5, \text{aq.}$  From still more strongly acid solutions, rich in  $\text{H}_3\text{PO}_4$ ,  $p_{\text{H}} < 1$ , greenish-yellow crystals of luteophosphovanadates are formed. These are double salts of alkali and  $(\text{VO})^{\text{III}}$  or  $(\text{VO}_2)^{\text{I}}$  phosphates, and not salts of true heteropolyacids. They are of the general composition  $\text{M}^{\text{I}}_2\text{O}, \text{V}_2\text{O}_5, \text{P}_2\text{O}_5, \text{aq.}$  or  $\text{M}^{\text{I}}_2\text{O}, 2\text{V}_2\text{O}_5, \text{P}_2\text{O}_5, \text{aq.}$ , V being actually present as the phosphate  $(\text{VO})\text{PO}_4$ . From strongly acid solutions poor in  $\text{H}_3\text{PO}_4$  a double octavanadate of Na and  $(\text{VO}_2)^{\text{I}}$  is obtained of the probable composition  $\text{Na}_2(\text{VO}_2)[\text{H}_7\text{V}_8\text{O}_{25}, \text{aq.}]$ . These results do not support the view that the existence of the heteropoly-acids is to be explained on the basis of Werner's co-ordination hypothesis. M. S. B.

**Ammonium arsenates.** C. MATIGNON and A. DE PASSILLÉ (Compt. rend., 1934, 198, 777—779).— $\text{NH}_4\text{H}_2\text{AsO}_4$ , prepared from aq.  $\text{NH}_3$  and  $\text{As}_2\text{O}_5$  in correct proportions, forms non-deliquescent prisms,  $d_4^{20}$  2.340. It loses  $\text{NH}_3$  above  $300^\circ$  to form an almost insol. acid meta-arsenate,  $\text{NH}_4\text{H}(\text{AsO}_3)_2$ , which is unchanged at  $425^\circ$ ; no trace of  $\text{As}_4\text{O}_6$  or As is formed. When boiled with  $\text{H}_2\text{O}$  the meta-arsenate re-forms orthoarsenate.  $(\text{NH}_4)_2\text{HAsO}_4$  is pptd. by EtOH from solution of its constituents. The aq. solution loses  $\text{NH}_3$  to form  $\text{NH}_4\text{H}_2\text{AsO}_4$ , as also does the dry salt on gentle heating, although it is stable in dry air in the cold.  $(\text{NH}_4)_3\text{AsO}_4 \cdot 3\text{H}_2\text{O}$  is pptd. on saturating a solution of  $\text{As}_2\text{O}_5$  or of either acid salt with  $\text{NH}_3$ ; it rapidly loses  $\text{NH}_3$ . The anhyd. salt is formed when either acid salt absorbs  $\text{NH}_3$  under 8 atm. pressure; it also rapidly loses  $\text{NH}_3$ .  $Q_0$  (in  $\log p = -Q_0/4.57T + 1.75 \log T + 3.3$ ) for the  $(\text{NH}_4)_2$  and  $(\text{NH}_4)_3$  salts is, respectively, 15,500 and 13,070. C. A. S.

**Alkali bismuthiodides.** D. MOTARD (Compt. rend., 1934, 198, 655—657).—Varying amounts of alcoholic or aq. MI were added to a mixture of freshly powdered Bi and conc. EtOH-I. After agitation and keeping the cryst. mass was extracted with  $\text{COMe}_2$ , whence the bismuthiodide crystallised out. The only

compounds obtained were, with EtOH-KI,  $\text{KI}, 2\text{BiI}_3$  and  $4\text{KI}, 2\text{BiI}_3$ ; with aq. KI,  $2\text{KI}, 2\text{BiI}_3, 2\text{H}_2\text{O}$  and  $3\text{KI}, 2\text{BiI}_3, 2\text{H}_2\text{O}$ . The methods described by Arppe and Linau (Pogg. Ann., 1845, 64, 237; 1860, 111, 242) yielded no others; the  $6\text{KI}, 2\text{BiI}_3$  claimed by Astre (cf. A., 1890, 1067) seems to have contained BiOI. In similar fashion  $\text{NaI}, \text{BiI}_3, n\text{H}_2\text{O}$  ( $n=0, 1$ , and 2) were prepared. C. A. S.

**Reaction of bismuth [nitrate] with thiocarbamide.** J. V. DUBSKÝ, A. OKAČ, and B. OKAČ (Z. anorg. Chem., 1934, 216, 386—390).—Addition of  $\text{CS}(\text{NH}_2)_2$  to aq.  $\text{Bi}(\text{NO}_3)_3$  acidified with  $\text{HNO}_3$  gives an intense yellow solution, from which can be obtained crystals of varying shades of yellow according to the proportions in which the constituents are mixed. 1Bi : 1CS( $\text{NH}_2$ ) $_2$  gives pale brownish-yellow needles, m.p.  $149^\circ$  (I), 1Bi : 2CS( $\text{NH}_2$ ) $_2$  gives light yellow prisms, m.p.  $153^\circ$  (II), but (I) and (II) appear, on analysis, to have practically the same composition. In (I) Bi : N = 1 : 8.68 and in (II) 1 : 8.38. The proportions 1Bi : 3CS( $\text{NH}_2$ ) $_2$  give bright brownish-yellow needles, m.p.  $151^\circ$ . Analysis gives the composition  $\text{Bi}(\text{NO}_3)_2, \text{CS}(\text{NH}_2)(\text{NH}), 2\text{CS}(\text{NH}_2)_2$ . Acid  $\text{BiCl}_3$  and  $\text{CS}(\text{NH}_2)_2$  give  $\text{BiCl}_3, 3\text{CS}(\text{NH}_2)_2$  in a yellow, cryst., rather labile modification and an orange-red, more stable variety. Possible formulæ are discussed.

M. S. B.

**Preparation of sources of radium-E.** M. HAISSINSKY (J. Chim. phys., 1934, 31, 43—46).—The Ra-E in dil.  $\text{HNO}_3$  solution is pptd. in presence of Sb by means of pyrogallol. The ppt. is dissolved in  $\text{HNO}_3$ ,  $\text{NH}_4$  tartrate and tartaric acid are added, and the solution is electrolysed between Pt electrodes. The Ra-E is deposited at the cathode and the Sb remains in solution. H. S. P.

**Isotope enrichment in technical oxygen fractions.** R. KLAR and A. KRAUSS (Naturwiss., 1934, 22, 119).—A concn. of  $\text{O}^{18}$  in fractions of liquid  $\text{O}_2$  was found ( $\text{O}^{18} : \text{O}^{16} = 1 : 510$ ). The proportion of  $\text{O}^{18}$  in liquid and vapour of the fraction, and the v.p. of the  $\text{O}^{16}\text{O}^{18}$  were derived. The v.p. of  $\text{O}^{16}\text{O}^{18}$  in the neighbourhood of the b.p. is 5%  $<$  that of  $\text{O}^{16}\text{O}^{16}$ .

A. J. M.

**Potentiometric examination of the formation of thiosulphate from alkali sulphide and sulphurous acid.** E. MÜLLER and K. MEHLHORN (Angew. Chem., 1934, 47, 134—139).—Potentiometric titration of  $\text{Na}_2\text{S}$  with aq.  $\text{H}_2\text{SO}_3$  shows the changes  $12\text{Na}_2\text{S} + 12\text{H}_2\text{SO}_3 = 6\text{NaHS} + 9\text{Na}_2\text{S}_2\text{O}_3 + 9\text{H}_2\text{O}$  and  $6\text{NaHS} + 6\text{H}_2\text{SO}_3 = 3\text{Na}_2\text{S}_2\text{O}_3 + 9\text{H}_2\text{O} + 6\text{S}$  to occur successively. Passage of 100% and 7%  $\text{SO}_2$ , respectively, through aq.  $\text{Na}_2\text{S}$  causes the respective reactions,  $6\text{Na}_2\text{S} + 9\text{H}_2\text{SO}_3 = 6\text{Na}_2\text{S}_2\text{O}_3 + 9\text{H}_2\text{O} + 3\text{S}$  and  $6\text{Na}_2\text{S} + 7\text{H}_2\text{SO}_3 = 3\text{Na}_2\text{SO}_3 + 3\text{Na}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O} + 4\text{H}_2\text{S}$  which, in presence of NaOH, become  $6\text{Na}_2\text{S} + 6\text{NaOH} + 12\text{H}_2\text{SO}_3 = 9\text{Na}_2\text{S}_2\text{O}_3 + 15\text{H}_2\text{O}$  and  $6\text{Na}_2\text{S} + 6\text{NaOH} + 10\text{H}_2\text{SO}_3 = 6\text{Na}_2\text{SO}_3 + 3\text{Na}_2\text{S}_2\text{O}_3 + 9\text{H}_2\text{O} + 4\text{H}_2\text{S}$ . The technical prep. of  $\text{Na}_2\text{S}_2\text{O}_3$  from  $\text{Na}_2\text{S}$  and dil.  $\text{SO}_2$  is discussed in the light of these results.

H. W.

**Reactions of chromous acetate.** M. CHATELET and (MME.) P. M. CHATELET (Compt. rend., 1934, 198, 833—834).—Moist  $\text{Cr}(\text{OAc})_2$  (I) in  $\text{C}_6\text{H}_6$  suspension in  $\text{N}_2$  is converted by dry HCl ( $\text{O}_2$ -free) into a

green compound  $\text{Cr}_2\text{OCl}_4 \cdot 5\text{H}_2\text{O}$ , but with  $\text{HCl-O}_2$  mixtures of composition between  $\text{Cr}_2\text{OCl}_4$  and  $\text{CrCl}_3$  are obtained. Pptn. of a solution of dry (I) in  $\text{C}_5\text{H}_5\text{N}$  with  $\text{Et}_2\text{O}$  gives the compound  $[\text{Cr}(\text{OAc})_2]_2 \cdot \text{C}_5\text{H}_5\text{N}$ , and passage of  $\text{NH}_3$  into a dry  $\text{C}_5\text{H}_6$  suspension of (I) gives the compound  $[\text{Cr}(\text{OAc})_2]_2 \cdot \text{NH}_3$ . J. W. B.

**Sodium permolybdate.** K. GLEU (Z. anorg. Chem., 1934, 216, 376; cf. A., 1933, 1258).—In presence of molybdic acid  $\text{H}_2\text{O}_3$  should be titrated iodometrically, and not with  $\text{KMnO}_4$ . The latter method introduces an error of varying size according to conditions (cf. A., 1932, 484). M. S. B.

**X-Ray confirmation of a new type of combination.** I. Tungsten oxides  $\text{W}_4\text{O}_{11}$  and  $\text{W}_8\text{O}_{23}$ . F. EBERT and H. FLASCH (Z. anorg. Chem., 1934, 217, 95—104).—By the action of active H, obtained by the glow discharge in  $\text{H}_2$ ,  $\text{W}_8\text{O}_{24}$  (or  $8\text{WO}_3$ ) is reduced to a readily oxidisable compound  $\text{W}_8\text{O}_{23}$  and a more stable oxide  $\text{W}_4\text{O}_{11}$ . It is shown by X-ray analysis that these are not mixtures of  $\text{WO}_3$  and  $\text{WO}_2$ , but have a definite cryst. structure in which  $\text{W}^{\text{VI}}$  and  $\text{W}^{\text{IV}}$  exist together as structural units. The removal of O in stages results in a deformation of the lattice indicated in the Debye-Scherrer diagram. M. S. B.

**Oxygen fluorides,  $\text{O}_2\text{F}_2$  and OF.** O. RUFF and W. MENZEL (Z. anorg. Chem., 1934, 217, 85—92).—The fluorides were prepared as previously described (A., 1933, 476). V.p. for  $\text{O}_2\text{F}_2$  has been determined for the temp. range  $-132^\circ$  to  $-57^\circ$ . Decomp. into OF begins above  $-100^\circ$ ; b.p. (extrapolated)  $-57^\circ$ , m.p.  $-163.5^\circ$ ,  $d = 2.074 - 0.002917$ . The vol. of the mol. sphere, as determined from the mol. vol. at b.p., is  $41.75 \text{ \AA}^3$  and radius  $2.15 \text{ \AA}$ . OF is distinguished from an equimol. mixture of  $\text{O}_2$  and  $\text{F}_2$  by the fact that it is completely absorbed by HI. Data for v.p. are given for the temp. range  $-201.1^\circ$  to  $-185.4^\circ$  and are represented by  $\log p = 6.897 - 352.7/T$ ; b.p.  $-185.4^\circ$ , m.p.  $-223^\circ$ . There are also two transition temp.,  $-235^\circ$  and  $-226^\circ$ .  $d \ 1.82_3 - 0.00567$  between  $-198.0^\circ$  and  $-190.7^\circ$ ;  $d_{\text{solid}} \ 1.625$  at  $-225^\circ$ . OF is nearly as chemically reactive as  $\text{F}_2$ , but is fairly stable in a quartz vessel at room temp. The vol. of the mol. sphere is  $22.7 \text{ \AA}^3$  and radius  $1.76 \text{ \AA}$ . M. S. B.

**Reaction products of different forms of carbon with fluorine.** II. Carbon monofluoride. O. RUFF and O. BRETSCHNEIDER [with F. EBERT] (Z. anorg. Chem., 1934, 217, 1—18; cf. A., 1930, 1387).—F combines with C either in the form of norit (I) at approx.  $280^\circ/25 \text{ mm.}$  or of graphite (II) at  $420^\circ/760 \text{ mm.}$  to form CF. This is a grey solid,  $d \ 2.39$ , insol. in ordinary solvents, not wetted by  $\text{H}_2\text{O}$  and aq. solutions, but wetted by org. solvents, e.g.,  $\text{C}_6\text{H}_6$ ,  $\text{COMe}_2$ ,  $\text{EtOH}$ , etc., and unattacked by  $\text{H}_2$  at  $400^\circ$  and by aq. HI. Zn dust and  $\text{AcOH}$  reduce it to its original C form, whether (I) or (II). The sp. electrical resistance is  $> 3000 \text{ ohms}$ , whilst that of (II) is  $0.03 \text{ ohm}$ . CF does not adsorb HCl or methylene-blue from  $\text{EtOH}$  solution, but it adsorbs NaOH and PhOH giving, with the former, a brown colloidal solution. X-Ray investigation indicates that F is inserted between the base planes of (II), two F atoms being connected to two C atoms. At higher pressure

and temp. volatile fluorides are formed, the amount and composition varying with conditions. Graphitic CF may decompose explosively. M. S. B.

**Manganese oxides.** M. LE BLANC and G. WEHNER (Z. physikal. Chem., 1934, 168, 59—78).— $\text{MnO}$ , prepared by heating  $\text{MnCO}_3$  in a vac. at  $420\text{--}450^\circ$ , is able to take up  $\text{O}_2$  even at room temp., the sorbed O being active. Up to  $\text{MnO}_{1.13}$  the product is homogeneous, and has the  $\text{MnO}$  lattice, but from  $\text{MnO}_{1.13}$  to  $\text{Mn}_2\text{O}_4$  the X-ray diagram shows the product to be a mixture of  $\text{MnO}$  and  $\text{Mn}_2\text{O}_4$ .  $\text{Mn}_2\text{O}_4$  can take up  $\text{O}_2$  up to  $\text{MnO}_{1.42}$  without change in lattice or appearance of a second solid phase, but with further absorption of  $\text{O}_2$  a new phase, an unstable modification of  $\text{Mn}_2\text{O}_3$ , probably having a tetragonal body-centred lattice, starts to be present. This form, which changes into the ordinary form with the bixbyte structure on tempering, is apparently able to take up  $\text{O}_2$  without change in lattice. The max. amount of  $\text{O}_2$  which can be absorbed by active  $\text{MnO}$  corresponds with  $\text{MnO}_{1.58}$ . No  $\text{O}_2$  can be withdrawn from  $\text{MnO}_2$  without the immediate appearance of the lattice of the stable form of  $\text{Mn}_2\text{O}_3$ , but it seems impossible to achieve complete reversal of evolution or absorption of  $\text{O}_2$ . No evidence of formation of mixed crystals by the various oxides in the course of withdrawal of O from  $\text{MnO}_2$  could be obtained; the systems seem always to be two-phase. The lattice structures of the naturally occurring Mn oxides have been checked. R. C.

**Iodates.** I. Iodates of  $\text{Al}^{\text{III}}$ ,  $\text{Cr}^{\text{III}}$ , and  $\text{Fe}^{\text{III}}$ . A. VON ENDRÉDY (Z. anorg. Chem., 1934, 217, 53—61).—The following iodates have been prepared:  $\text{Al}(\text{IO}_3)_2 \cdot \text{NO}_3 \cdot 6\text{H}_2\text{O}$ , monoclinic;  $\text{Al}(\text{IO}_3)_3 \cdot 6\text{H}_2\text{O}$ ;  $\text{Cr}(\text{IO}_3)_3 \cdot 2\text{H}_2\text{O}$ , dark green;  $\text{Cr}(\text{IO}_3)_3 \cdot 4.5\text{H}_2\text{O}$ , dark green;  $\text{Cr}(\text{IO}_3)_3 \cdot 5\text{H}_2\text{O}$ , green, amorphous;  $\text{Fe}(\text{IO}_3)_3$ ,  $\alpha$ -form, light green, amorphous,  $d_4^{20} \ 4.85$ , and  $\beta$ -form, intense yellow,  $d_4^{20} \ 4.76$ . With increasing ionic radius and falling electroaffinity the stability and solubility of the hydrates diminish. M. S. B.

**Rhenium oxybromides.** A. BRUKL and K. ZIEGLER (Monatsh., 1933, 63, 329—334).—The prep. and properties of  $\text{ReO}_3\text{Br}$  (m.p.  $39.5^\circ$ , b.p.  $163^\circ$ ) and  $\text{ReO}_2\text{Br}$  (decomp.  $60\text{--}70^\circ$ ) are described. E. S. H.

**Rhenium.** III. Reduction of perrhenates with stannous chloride and a potentiometric method of determination for septavalent rhenium. H. HÖLEMANN (Z. anorg. Chem., 1934, 217, 105—112).—The reduction of HCl solutions of perrhenates by  $\text{SnCl}_2$  can be followed potentiometrically, and the method can be used for the potentiometric titration of perrhenates at about  $80^\circ$ .  $\text{Re}^{\text{VII}}$  is reduced to  $\text{Re}^{\text{V}}$ . The end-point is still more definite in presence of  $\text{Re}^{\text{IV}}$  as in a chlororhenate. In presence of CNS' in the cold  $\text{Re}^{\text{VII}}$  is reduced to  $\text{Re}^{\text{IV}}$ , with the establishment of a const. potential. A reddish-brown coloration is observed. M. S. B.

**Structure and ferromagnetism of ferrous ferrites, and the autoxidation of ferrous hydroxide.** A. KRAUSE and J. TUŁECKI (Rocz. Chem., 1934, 14, 60—68).—Dry  $\text{Fe}(\text{FeO}_2)_2$  (I) containing  $\text{Fe}^{\text{II}} : \text{Fe}^{\text{III}} < 1 : 1.13$  cannot be prepared from  $\gamma\text{-FeO}_2\text{H}$  (II) and  $\text{Fe}(\text{OH})_2$  (III) by varying the proportions of (II) and

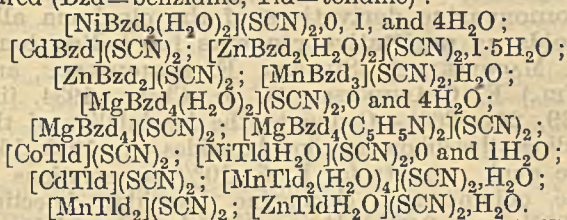


(III), or by excluding atm. O<sub>2</sub> from the reaction mixture; this result is ascribed to adsorption of (III) by (I), with subsequent oxidation to Fe(OH)<sub>3</sub> during drying. The ferromagnetism of (I) is ascribed to the presence of  $\cdot\text{Fe}\langle\text{O}\rangle\text{Fe}\cdot$  groups in the mol. H<sub>2</sub>O<sub>2</sub> is produced during the autoxidation of (III), which is catalysed by BaSO<sub>4</sub>. A structural formula of the spinel type is proposed for (I). R. T.

**Alkoxides of trivalent iron in internal complex union.** B. EMMERT and E. JACOB (Ber., 1934, 67, [B], 286—289; cf. A., 1931, 825).—Passage of O<sub>2</sub> through FeR<sub>2</sub>·2C<sub>6</sub>H<sub>5</sub>N (I) (R=COMe·CH·CO·Me) in EtOH at 35—40° affords the substance R<sub>2</sub>Fe·OEt, m.p. 159·5°, whereas in MeOH at 40—45° the compound, RFe(OMe)<sub>2</sub>, is obtained. With PhOH in C<sub>6</sub>H<sub>6</sub> (I) is oxidised to R<sub>3</sub>Fe·PhOH, m.p. 109°, also obtained from its components in C<sub>6</sub>H<sub>6</sub>. Oxidation of FeR<sub>2</sub>·2C<sub>6</sub>H<sub>5</sub>N (R'=COMe·CH·CO·Ph) leads uniformly to the compounds R'<sub>2</sub>FeOX in which X=Me, m.p. 209·5°, =Et, m.p. 222—223·5°, =Bu<sup>c</sup>, m.p. 200—201°; =Ph, m.p. 219°, =CH<sub>2</sub>·CH<sub>2</sub>·OH, m.p. 212—213°. The substance, R<sub>2</sub>Fe $\langle\begin{smallmatrix} \text{OH}\cdot\text{CH}_2 \\ \text{OH}\cdot\text{CH}_2 \end{smallmatrix}\rangle$ , is described.

H. W.

**Thiocyanammines of benzidine and tolidine.** IV. G. SPACU and C. C. MACAROVICI (Bul. Soc. Stiinte Cluj, 1933, 7, 227—247; Chem. Zentr., 1933, ii, 2225).—The following compounds have been prepared (Bzd=benzidine, Tld=tolidine):—



A. A. E.

**Complex salts with 2 : 2'-dipyridyl.** Complex salts of bivalent nickel. F. M. JAEGER and J. A. VAN DIJK (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 10—15).—On mixing 2·5 g. NiSO<sub>4</sub>·7H<sub>2</sub>O in aq. solution with an EtOH solution of 4·7 g. dipyridyl (dipy); (I) the solution turns deep red and on evaporation on the H<sub>2</sub>O-bath red monoclinic crystals of [Ni(dipy)<sub>3</sub>]SO<sub>4</sub>·7H<sub>2</sub>O (II) are obtained. If a solution of 2 equivs. of NiSO<sub>4</sub>·7H<sub>2</sub>O is added to a solution of (II), the solution turns blue and on evaporation yields triclinic blue crystals of [Ni(dipy)(H<sub>2</sub>O)<sub>2</sub>]SO<sub>4</sub>·4H<sub>2</sub>O (III), which loses 4 mols. of H<sub>2</sub>O at 100°. Addition of powdered NiSO<sub>4</sub>·7H<sub>2</sub>O (2 mols.) to a conc. solution of (II) (1 mol.) followed by heating on the H<sub>2</sub>O-bath, and cooling, yields long hair-like pale blue crystals of a second modification of (III). Details are given of the crystal structures of (I), (II), and (III). The cation of (III) is very stable and is decomposed only by powerful reagents. No di-(I) compound could be obtained.

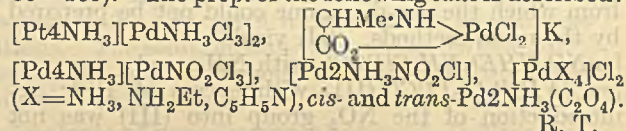
J. W. S.

**New series of rhodammines.** V. V. LEBEDINSKI (Ann. Inst. Platine, 1933, No. 11, 5—12).—(NH<sub>4</sub>)<sub>2</sub>[RhNH<sub>3</sub>Cl<sub>5</sub>] (I) is prepared by adding aq. NH<sub>4</sub>OAc to a saturated solution of Na<sub>2</sub>RhCl<sub>6</sub> and

NH<sub>4</sub>Cl. (I) undergoes hydrolysis in H<sub>2</sub>O to yield (NH<sub>4</sub>)<sub>2</sub>[RhNH<sub>3</sub>Cl(OH)<sub>4</sub>]. Crystallographic and other data are given for (I), and for the corresponding K<sub>2</sub> and [Pt<sub>4</sub>NH<sub>3</sub>] salts. R. T.

**Isomeric pallado-diammines.** A. A. GRÜNBERG and V. M. SCHULMAN (Compt. rend. Acad. Sci. U.R.S.S., 1933, 218—220).—The following isomeric palladodiammines have been prepared: Pd<sub>2</sub>NH<sub>3</sub>Cl<sub>2</sub>, Pd<sub>2</sub>NH<sub>3</sub>Br<sub>2</sub>, Pd<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>N)Cl<sub>2</sub>, and Pd<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>N)Br<sub>2</sub> by the action of NH<sub>4</sub>OAc (or pyridinium acetate) on K<sub>2</sub>[PdCl<sub>4</sub>] or K<sub>2</sub>[PdBr<sub>4</sub>]. These compounds give only AgCl or AgBr when treated with AgNO<sub>3</sub> and none of the brownish ppt. obtained by the action of AgNO<sub>3</sub> on compounds [Pd<sub>4</sub>A][PdX<sub>4</sub>]. They are analogues of the *cis*-platinum diammines, and have the formula [(NH<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub>]. Solubility in H<sub>2</sub>O is greater for *cis*- than for *trans*-diammines of both Pt and Pd. *cis*-[Pd<sub>2</sub>NH<sub>3</sub>Br<sub>2</sub>] in COMe<sub>2</sub> gives an intense red colour with KI, whereas the *trans*-isomeride does not. All the *cis*-compounds give a red colour with KI. W. R. A.

**Complex compounds of bivalent palladium.** A. A. GRÜNBERG (Ann. Inst. Platine, 1933, No. 11, 95—109).—The prep. of the following salts is described:



R. T.

**Complex chloronitrites of iridium.** I. K. PSCHENTSIN and S. E. KRASKOV (Ann. Inst. Platine, 1933, No. 11, 13—19).—HCl and Na<sub>3</sub>[Ir(NO<sub>2</sub>)<sub>6</sub>] yield, amongst other products, the acid H<sub>3</sub>[IrCl<sub>5</sub>NO<sub>2</sub>] (I), which with aq. K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> forms K<sub>3</sub>[IrC<sub>2</sub>O<sub>4</sub>Cl<sub>3</sub>NO<sub>2</sub>]·2H<sub>2</sub>O. The Ag, K, and Cs salts of (I), and the compound [Ir 5NH<sub>3</sub>Cl<sub>3</sub>][IrCl<sub>5</sub>NO<sub>2</sub>] are described. R. T.

**Action of ammonia on Gros' salt.** I. I. TSCHERNIAEV (Ann. Inst. Platine, 1933, No. 11, 55—59).—Gros' salt yields with aq. NH<sub>3</sub> the *pentammine* (NH<sub>3</sub>)<sub>5</sub>ClPtCl<sub>3</sub>, which is readily converted into (NH<sub>3</sub>)<sub>5</sub>(OH)PtCl<sub>3</sub> (I) by excess of NH<sub>3</sub>; a hexammine is not formed in the above reaction. The sulphate of (I) exists in two forms: (NH<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)Pt(SO<sub>4</sub>)<sub>2</sub> and (NH<sub>3</sub>)<sub>5</sub>(OH)Pt(HSO<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. R. T.

**Asymmetrical chloride of the type of Clève's salt.** I. I. TSCHERNIAEV and A. S. SAMSONOVA (Ann. Inst. Platine, 1933, No. 11, 39—43).—The salt [NH<sub>3</sub>RNH<sub>3</sub>ClPt]<sub>2</sub>PtCl<sub>4</sub> (R=NH<sub>2</sub>OH) is obtained by adding K<sub>2</sub>PtCl<sub>4</sub> to aq. NH<sub>3</sub>RNH<sub>3</sub>ClPtCl. C<sub>6</sub>H<sub>5</sub>N and the complex NH<sub>3</sub>RCl<sub>2</sub>Pt yield chiefly NH<sub>3</sub>R(C<sub>6</sub>H<sub>5</sub>N)ClPt, together with NH<sub>3</sub>R(C<sub>6</sub>H<sub>5</sub>N)<sub>2</sub>PtCl<sub>2</sub>. R. T.

**Chemical inertia and activity of the rare gases.** IV. Differences between platinum and the platinum-helium compound. V. X-Ray diagrams. H. DAMIANOVICH (Anal. Inst. invest. cient. tecn., 1931, 2, 15—23, 24—32).—IV. The rate of dissolution (I) in HCl-HNO<sub>3</sub> of Pt containing He is approx. proportional to the He content. If the Pt is heated to remove the He, (I) diminishes. The solubility of Pt deposited in presence of He, O<sub>2</sub>, and N<sub>2</sub> diminishes in the order given. Photomicrographs reveal con-

siderable differences between the structures of electro-deposited Pt containing He and Pt deposited by condensation from the vapour phase. The results afford evidence of the existence of a Pt-He compound.

V. The X-ray diagrams, obtained with a specimen of the Pt-He compound mounted in a manner which obviates the diffuse halo due to the support, exhibit haloes similar to those observed in the case of colloidal Pt and Bi sulphides but not with pure Pt. This fact is regarded as proof of the existence of a Pt-He compound. H. F. G.

**Nitro-compounds of platinum. XI. Ethylamine compounds.** I. I. TSCHERNIAEV and N. V. VALDENBERG. **XII. Diethylamine compounds.** I. I. TSCHERNIAEV and T. B. PEIZNER. **XIII. Reaction of nitration.** I. I. TSCHERNIAEV and L. J. GENNING. **XIV. Determination of nitrogen.** I. I. TSCHERNIAEV (Compt. rend. Acad. Sci. U.R.S.S., 1933, No. 11, 21—32, 33—38, 45—53, 61—62).—XI. The  $\text{NH}_2\text{Et}$  derivatives of  $\text{enPtNO}_2\text{Cl}$  (I) behave in every way analogously to the previously described  $\text{NH}_2\text{Me}$  derivatives (A., 1932, 240).

XII.  $\text{NHEt}_2$  and aq. (I) yield  $[\text{enNO}_2\text{NHEt}_2\text{Pt}]\text{Cl}$ , which with  $\text{Cl}_2$  gives  $[\text{enNO}_2\text{NHEt}_2\text{Cl}_2\text{Pt}]\text{Cl}$  (II), from which the azo-diammine could not be prepared by the usual methods. (II) yields  $[\text{enNO}_2\text{NHEt}_2\text{NH}_3\text{ClPt}]\text{Cl}_2$  with  $\text{NH}_3$ , and  $[\text{enClNHEt}_2\text{Cl}_2\text{Pt}]\text{Cl}$  (III) with excess of  $\text{HCl}$ ; re-introduction of the  $\text{NO}_2$  group into (III) was not possible.

XIII. The reaction of nitration of platinichlorides, nitroplatinichlorides, and tetramines of  $\text{Pt}^{\text{II}}$  is more complex than in the case of non-electrolytic *cis*- $\text{Pt}^{\text{IV}}$  derivatives (A., 1932, 240). Two stereoisomeric forms of the compound  $[(\text{NH}_3)_4\text{Pt}(\text{NO}_2)_2](\text{NO}_3)_2$  have been prepared. The  $\text{NO}_2$  groups of a no. of Pt, Ir, and Rh derivatives are quantitatively eliminated as  $\text{N}_2$  by heating with saturated aq.  $\text{NH}_4\text{Cl}$ , as follows:  $\text{R}\cdot\text{NO}_2 + \text{NH}_4\text{Cl} \rightarrow \text{RCl} + \text{N}_2 + 2\text{H}_2\text{O}$ . This reaction affords a convenient and exact method for determining the  $\text{NO}_2$  content of such compounds.

XIV. The N content of a no. of previously described Pt compounds is given. R. T.

**Chemical evidence for planar configuration of platotetrammines.** H. D. K. DREW and F. S. H. HEAD.—See this vol., 397.

**Kinematic method of quantitative spectral analysis.** A. BETIM (Compt. rend., 1934, 198, 566—569).—A suitable spectral line of the substance to be determined is photographed at fixed intervals, whilst the mineral in which it occurs is steadily heated electrically. The quantity is deduced from the length and rate of diminution in breadth and intensity of the line. C. A. S.

**Quantitative micro-mineral analysis.** F. HECHT (Mikrochem., 1934, 14, 283—285, 286—288). A. A. BENEDETTI-PICHLER (*ibid.*, 285—286, 288).—Polemical. J. S. A.

**New method of preparative microchemistry.** J. WINCKELMANN (Mikrochem., 1934, 14, 171—180).—The prep. of permanent characteristic specimens of microchemical ppts., using a permeable collodion film (I), is described. The undisturbed ppt. is washed

free of precipitant through (I), or may be actually pptd. beneath it. J. S. A.

**Scheme for dilutions in the laboratory.** C. J. LYON (Science, 1934, 79, 60).—A scheme for calculating the amounts of solution and solvent to be used in making up a series of solutions of various concns. from a given stock solution is described. L. S. T.

**Effect of sulphated fatty alcohols in the colorimetric determination of  $p_{\text{H}}$ .** J. E. SMITH and H. L. JONES (J. Physical Chem., 1934, 38, 243—244).—Data are given showing the extent of the errors obtained in the colorimetric determination of the  $p_{\text{H}}$  of buffered solutions containing 0.5% Na lauryl or oleyl sulphate, using a no. of different indicators. M. S. B.

**Volumetric standardisation.** R. H. CURTIS (Chem. and Ind., 1934, 135).—Iceland spar is recommended for standardising  $\text{HCl}$ . The  $\text{CaCl}_2$  solution thus obtained can be pptd. as  $\text{CaC}_2\text{O}_4$  and used to standardise  $\text{KMnO}_4$ . E. S. H.

**Determination of dissolved oxygen in water.**—See B., 1934, 254.

**Nephelometry. I. Analysis of potable waters.**—See B., 1934, 254.

**Silver halides and the potentiometric titration curve.** I. E. ORLOV (Khim. Farm. Prom., 1933, 213—218).—The presence of electrolytes eliminates the retardation of the potential jump. CH. ABS.

**Synthesis in the homoneurine series. III. Homoneurine derivatives of the cinchona alkaloids as qualitative reagents for iodide ions.** E. MACOVSKI, A. SILBERG, E. RAMONTIANU, and (FRL.) E. CRĂCIUNESCU (J. pr. Chem., 1934, [ii], 139, 254—260).—Owing to the insolubility of the iodides the dihomoneurine bromides (A., 1933, 169) are qual. reagents for  $\text{I}^-$ , 5—10% aq. solutions of the quinine and cinchonine bromides detecting 0.05*N*- and 0.025*N*- $\text{I}^-$ , respectively. Sensitivity is increased if the Bz derivatives are used, 3% benzocinchonine dihomoneurine bromide detecting 0.0025*N*- $\text{I}^-$ . J. W. B.

**Colorimetric determination of traces of fluorine.** L. SZEGOE and B. CASSONI (Giorn. Chim. Ind. Appl., 1933, 15, 599—602).—The sample is treated with  $\text{Ca}(\text{OH})_2$  solution, ignited at  $> 550^\circ$ , and fused with Na K carbonate and  $\text{SiO}_2$ . The extract, after removal of  $\text{SiO}_2$ , is treated with  $\text{HCl}$  and  $\text{BaCl}_2$ , and the ppt. dried, mixed with  $\text{SiO}_2$ , and distilled with  $\text{H}_2\text{SO}_4$ . The  $\text{SiF}_4$  is passed into  $\text{H}_2\text{O}$ , 0.025*M*- $\text{Ti}(\text{SO}_4)_2$  and  $\text{H}_2\text{O}_2$  are added, and the coloration is compared with a standard. In an alternative method, the F is separated by distillation of the sample with  $\text{HClO}_4$  at (initially) 100—110°. H. F. G.

**Rapid accurate determination of minute quantities of nitrite.** G. G. RAO and K. M. PANDALAI (Analyst, 1934, 59, 99—100).— $\text{HNO}_2$  is determined by treating it with  $\text{HI}$  and titrating the I liberated:  $2\text{HNO}_2 + 2\text{HI} = 2\text{H}_2\text{O} + \text{I}_2 + 2\text{NO}$ .  $\text{O}_2$  is excluded by bubbling  $\text{CO}_2$  through the solution for 10 min.  $\text{NO}$  is expelled as it is formed by adding  $\text{NaHCO}_3$  and acidifying.  $5.6 \times 10^{-4}$ — $5.6 \times 10^{-5}$  g. of  $\text{NO}_2^-$ -N are determined to within  $\pm 0.7\%$ . E. C. S.

**Sensitivity of diphenylamine as a reagent for nitric acid.** R. KRAUER, jun. (Chimica, 1933, 1, 122—123; Chem. Zentr., 1933, ii, 2297).—0.0002%  $\text{HNO}_3$  in  $\text{H}_2\text{SO}_4$  is detected only after addition of a little  $\text{H}_2\text{O}$ ; 0.00084%  $\text{HNO}_3$  slowly affords a blue coloration without  $\text{H}_2\text{O}$ . A. A. E.

**Oxidation of white phosphorus by iodine. Course of the reaction in the determination by the D.A.B. VI method.** F. VIEBOCK (Arch. Pharm., 1934, 272, 88—100).—The amount of I (as I-KI or in org. solvents) reduced by P in mineral oil varies with the rate of mixing. According to the conditions and amount of MeOH or EtOH used, varying proportions of  $\text{H}_3\text{PO}_4$ ,  $\text{HPO}_3$ ,  $\text{H}_3\text{PO}_3$ , and their esters are formed. The  $\text{PIII}$  compounds, being normally stable to I, are considered to be produced in labile forms. R. S. C.

**Colorimetric determination of phosphoric acid.**—See this vol., 338.

**Reactions of the cyanide ion with tetrathionate and pentathionate ions.** B. FORESTI (Z. anorg. Chem., 1934, 217, 33—47).—It is shown theoretically that the reaction between HCN and  $\text{S}_4\text{O}_6^{2-}$  or  $\text{S}_5\text{O}_6^{2-}$ , giving HCNS, ceases when one third of the reaction is completed, unless a continuous supply of  $\text{OH}^-$  is available. The velocity coeffs.  $K_{s_4o_6}$  and  $K_{s_5o_6}$  have, therefore, been determined at  $p_{\text{H}}$  7.23 and 7.46 at 37° (temp. of human blood; or 7.31 and 7.54 at 18°). Under these conditions the reactions are complete. Assuming constancy of  $\text{OH}^-$ , both reactions are bimol., the decomp. of  $\text{S}_5\text{O}_6^{2-}$  taking place in two stages, the first being the formation of  $\text{S}_4\text{O}_6^{2-}$ . In each case the increase in  $p_{\text{H}}$  doubles  $K$ , and  $K_{s_5o_6}$  is approx. five times  $K_{s_4o_6}$ .  $\text{S}_5\text{O}_6^{2-}$  should therefore be a valuable antidote to HCN poisoning, provided it exercises no unforeseen harmful effect. M. S. B.

**Spot reaction for potassium.** N. S. POLUEKTOV (Mikrochem., 1934, 14, 265—266).—The insol. K salt of hexanitrodiphenylamine is pptd. from slightly alkaline solutions as an orange spot, reddened by addition of HCl. Rb, Cs, and large amounts of  $\text{NH}_4^+$  interfere. J. S. A.

**Microchemical identification of sodium ions by means of picric acid.** G. DENIGÈS (Bull. Soc. Pharm. Bordeaux, 1933, 71, 191—195; Chem. Zentr., 1933, ii, 2427).—Na picrate forms characteristic yellow needles, distinguishable from other alkali picrates. H. J. E.

**[Detection of sodium with uranyl acetate.]** L. ROSENTHALER (Mikrochem., 1934, 14, 267; cf. A., 1933, 583).—A correction. J. S. A.

**Detection and microdetermination of silver, mercury, and iodides.** I. M. KORENMAN (Mikrochem., 1934, 14, 181—188).—The formation of the blue starch-I colour (I) requires the presence of  $\text{I}^-$ , and is hindered by  $\text{Hg}^+$ ,  $\text{Hg}^{2+}$ , and  $\text{Ag}^+$ , which form insol. iodides. By the non-formation of (I), using 0.02% aq. I, limiting concns. of 1 in  $2 \times 10^7$  of  $\text{Ag}^+$ , 1 in  $7 \times 10^6$  of  $\text{Hg}^+$ , and 1 in  $4 \times 10^6$  of  $\text{Hg}^{2+}$  may be detected. Large excesses of Pb, Cu, and Cd do not interfere. The amount of  $\text{I}^-$  necessary to produce (I) is proportional to the amount of Ag or Hg present.  $\text{I}^-$  may be determined by titration with 0.01N-HgCl<sub>2</sub>

until (I) disappears. By use of 0.01N-KI, Ag and Hg may be similarly determined. Large amounts of  $\text{Cl}^-$ , also  $\text{Br}^-$  and  $\text{CNS}^-$ , interfere. J. S. A.

**Reaction differentiating the hydrated calcium aluminates.** A. TRAVERS and P. LEDUC (Compt. rend., 1934, 198, 828—831).—Cubic  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$  (I) (cf. A., 1930, 436) scarcely reacts with boiling  $\text{NH}_4\text{Cl}$ -EtOH, whereas all other hydrated Ca aluminates do so more or less readily, indicating that in (I) the CaO is more firmly combined. It is therefore suggested that (I) is derived from the acid  $\text{H}_2\text{AlO}_3$ , the other Ca aluminates being basic salts of  $\text{HAlO}_2$ , i.e.,  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot n\text{CaO} \cdot \text{aq.}$ , convertible into the former by heat. C. A. S.

**Microchemical contributions. X.** L. ROSENTHALER (Mikrochem., 1934, 14, 268—270; cf. A., 1933, 1262).—The crystal forms of Ba, Sr, and Ca sulphates, under different conditions of pptn., are described. J. S. A.

**Qualitative reaction of radium.** B. A. NIKITIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 19—21).—10 c.c. of 0.1% Ra solution, when heated to boiling and treated with 0.3 c.c. of 50% aq.  $\text{CCl}_3\text{CO}_2\text{H}$  and 0.5 c.c. of 10% aq.  $\text{K}_2\text{CrO}_4$  gives a compact cryst. ppt. on cooling to 0°. Ba gives no ppt. under similar conditions. The solution, however, retains 0.01—0.015% Ra, so the method cannot be applied to the determination of Ra. J. W. S.

**Analysis of magnesium alloys.** L. C. NICKOLLS. —See B., 1934, 240.

**Volumetric determination of lead.** M. N. LU (J. Chinese Chem. Soc., 1933, 1, 139—142).— $\text{Pb}^{2+}$  is pptd. as  $\text{PbO}_2$  by adding excess of NaOCl and NaOH, the ppt. is dissolved in HCl in presence of KI, and the liberated I titrated with  $\text{Na}_2\text{S}_2\text{O}_3$  and starch. The procedure is applicable in presence of any metal that does not ppt. a peroxide when treated with NaOCl. E. S. H.

**Determination of lead dioxide in red lead.**—See B., 1934, 193.

**Colorimetric determination of lead and copper with "dithizon" [dithiocarbazon].** H. FISCHER and (FRL.) G. LEOPOLDI (Angew. Chem., 1934, 47, 90—92).—The use of dithizon (I) as a qual. reagent for metals (A., 1929, 1412) is extended as a quant. method. (I) is purified by extraction from  $\text{CCl}_4$  solution with dil. aq.  $\text{NH}_3$  (1:200), and reprecipitated into fresh  $\text{CCl}_4$  with dil.  $\text{H}_2\text{SO}_4$ . This resultant solution should contain about 20 mg. of (I) per 100 c.c., and is diluted to contain 6 mg. per 100 c.c. for use; it is stored in the dark under a layer of aq.  $\text{SO}_2$ . In determination of Pb, a solution containing 0.006—0.120 mg. of Pb is made alkaline with dil. aq.  $\text{NH}_3$ , holding up other metals with Na K tartrate, and shaken with several successive portions of the reagent until no further red colour is produced. The separated reagent is then shaken with 5 c.c. of 1% aq. KCN to remove excess (I), washed with  $\text{H}_2\text{O}$ , and then shaken with dil. HCl, giving a green colour which is compared with standards made up from known amounts of Pb. Many metals interfere. For Cu, the metal content must lie between 0.004 and 0.050 mg., and it is extracted similarly to Pb from a dil.  $\text{H}_2\text{SO}_4$  solu-

tion, giving a violet colour, excess of (I) being removed by dil.  $\text{NH}_3$ , and the resultant solution compared with standards. Only Hg, Ag, and Au interfere, but excess of  $\text{Fe}^{+++}$  oxidises the reagent. D. R. D.

**Detection of copper by means of *p*-phenylenediamine.** R. J. McILROY (*Analyst*, 1934, 59, 103).—When KCNS and  $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$  are added to a solution of a Cu salt, a black ppt. of Cu thiocyanate-phenylenediamine is formed in the presence of aq.  $\text{NH}_3$  or in neutral solutions. The ppt. is sol. in acid, giving a black solution. No other of the common metals except Ag, which gives a white ppt., is pptd. in aq.  $\text{NH}_3$ . 1 part of Cu in 100,000 can be detected. E. C. S.

**Determination of copper by means of 5:7-dibromo-8-hydroxyquinoline.** J. V. DUBSKÝ and J. CHYTIL (*Chem. Listy*, 1934, 28, 6—7).—Haase's method (A., 1929, 1159) is preferred. R. T.

**Colorimetric determination of copper by precipitation with mercuric thiocyanate.** J. GOLSE (*Bull. Soc. Pharm. Bordeaux*, 1933, 71, 16—24; *Chem. Zentr.*, 1933, ii, 2427—2428).—Pptn. of Cu in presence of Zn by  $\text{K}_2[\text{Hg}(\text{CNS})_4]$  as violet  $\text{CuZn}[\text{Hg}(\text{CNS})_4]_2$  will detect 0.001 mg. Cu. The Zn salt,  $\text{Zn}[\text{Hg}(\text{CNS})_4]$ , pptd. simultaneously, is colourless. H. J. E.

**Magneto-optic Nicol rotation method for the quantitative analysis of copper.** E. R. BISHOP, I. G. OTTO, and L. BAISDEN (*J. Amer. Chem. Soc.*, 1934, 56, 408).—Preliminary observations indicate that the method should be useful for solutions containing  $5 \times 10^{-12}$  to  $1 \times 10^{-4}$  g. Cu per c.c. E. S. H.

**Spectroscopic determination of secondary constituents in copper.**—See B., 1934, 202.

**Determination of very small amounts of copper by measurement of their catalytic action.** F. L. HAHN (*Mikrochem.*, 1934, 14, 280—282; cf. B., 1933, 1062).—The time for decolorisation (I) of  $\text{Fe}(\text{CNS})_3$  by  $\text{Na}_2\text{S}_2\text{O}_3$  varies considerably with minor factors. The ratio (I) in absence of Cu(I) for given Cu concn. is less affected and reproducible with different solutions. Instead of (I), the time to reach a matched shade is advocated. J. S. A.

**Iodometry. I. Micro-determination of iron.** F. RAPPAPORT and E. HOHENBERG (*Mikrochem.*, 1934, 14, 119—128).—The solution containing  $\text{Fe}^{+++}$  is treated with acid KI in a micro-Kjeldahl apparatus, the liberated I being distilled into 2 c.c. of  $\text{NaOH} + \text{Na}_2\text{SO}_3$ . Decomp. of the KI in the hot acid solution is avoided by use of  $\text{KI} + \text{CdSO}_4$  ( $\text{K}_2\text{CdI}_4$ ). The  $\text{NaOH}$  is neutralised, and 3% Br in  $\text{AcOH}$  added, oxidising the I to  $\text{IO}_3'$ , which is determined iodometrically. Excess of Br is removed by  $\text{HCO}_2\text{H}$ .  $\text{Fe}^{++}$  must first be oxidised by  $\text{HNO}_3$ , with subsequent addition of  $\text{CO}(\text{NH}_2)_2$ ,  $\text{PO}_4'''$  and other metals do not interfere. Org. substances are ashed with  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$  in presence of Ti, which serves as catalyst and indicator of excess  $\text{H}_2\text{O}_2$ . Difficultly ashed substances may be treated with  $\text{HNO}_3$ . J. S. A.

**Micro-iodometric determination of iron. (Iron content of thyroid glands.)** J. STRAUB (*Mikrochem.*, 1934, 14, 251—255).—The solution, con-

taining 0.01—0.5 mg. Fe in 10 c.c. is treated with  $\text{KI} + \text{HCl}$ , and titrated with 0.002*N*- $\text{Na}_2\text{S}_2\text{O}_3$  within 2 min. J. S. A.

**Phenanthroline-ferrous ion. III. Silver reducing agent. Direct determination of iron in presence of vanadium.** G. H. WALDEN, jun., L. P. HAMMETT, and S. M. EDMONDS (*J. Amer. Chem. Soc.*, 1934, 56, 350—353; cf. this vol., 257).—The solution is reduced with finely-divided Ag,  $\text{H}_2\text{SO}_4$  is added to give a concn. of 5*M*, and Fe is determined by titration with 0.1*M*- $\text{Ce}(\text{SO}_4)_2$ , using the phenanthroline-ferrous ion as indicator. E. S. H.

**Determination of tin in copper-zinc alloys.**—See B., 1934, 202.

**Potentiometric study of the quinhydrone electrode in the determination of nickel.** B. K. CHATTERJEA and J. B. JHA (*J. Indian Chem. Soc.*, 1934, 10, 727—733).—Ni salt solutions, containing 0.34—0.09 g. Ni in 25 c.c., may be titrated with KCN solution, using the quinhydrone electrode. The change of e.m.f. occurs at the point corresponding with the formation of  $\text{Ni}(\text{CN})_2$ . E. S. H.

**Colorimetric determination of nickel.**—See this vol., 396.

**Reaction of hydrogen peroxide with potassium iodide and its use for the determination of chromium.** E. RUPP [with G. HAMANN and R. MÜLLER] (*Arch. Pharm.*, 1934, 272, 57—60).—Neutral aq.  $\text{H}_2\text{O}_2$  is rapidly decomposed by a little KI, the reaction proceeding by formation and decomp. of HOI, and being accelerated by heat and hindered by alkali. In the determination of aq.  $\text{H}_2\text{O}_2$  by HI it is thus necessary to add the acid before the KI. In the determination of  $\text{Cr}^{+++}$  by oxidation to  $\text{CrO}_4''$  with alkaline  $\text{H}_2\text{O}_2$ , excess of  $\text{H}_2\text{O}_2$  is readily removed in presence of KI, before titration of the liberated I. R. S. C.

**Potentiometric determination of chromium in steel.**—See B., 1934, 240.

**Determination of chromium and vanadium in steel.**—See B., 1934, 240.

**Determination of antimony.** R. I. SHREIDER (*Khim. Farm. Prom.*, 1933, 151—152).—The substance (0.2—0.3 g.) is heated in a Kjeldahl flask with  $\text{K}_2\text{SO}_4$  (2 g.) and conc.  $\text{H}_2\text{SO}_4$  (3 c.c.); after 30 min. the cooled liquid is diluted with  $\text{H}_2\text{O}$  (25 c.c.),  $\text{SO}_2$  is boiled off, 4 c.c. of aq. HCl are added, and Sb is determined by the  $\text{BrO}_3'$  method. CH. ABS.

**Volumetric determination of metals of the platinum group.** A. A. GRÜNBERG and B. V. PIRTSYN (*Compt. rend. Acad. Sci. U.R.S.S.*, 1933, 286—290, and *Ann. Inst. Platine*, 1933, No. 11, 77—94).— $\text{Pt}^{II}$  compounds can be oxidised by  $\text{KMnO}_4$  in presence of  $\text{H}_2\text{SO}_4$ :  $\text{R}\cdot\text{Pt}^{II} + \text{H}_2\text{O} + \text{O} \rightarrow \text{R}\cdot\text{Pt}^{IV}(\text{OH})_2$ , the ease of oxidation varying with the groups co-ordinated to the Pt atom. This reaction is applied to the determination of  $\text{Pt}^{II}$  by potentiometric titration (I) and by visual titration. (I) methods for the determination of  $\text{Ir}^{III}$  with  $\text{KMnO}_4$ , of  $\text{Ir}^{IV}$  with  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ , of  $\text{Pt}^{IV}$  by reduction with  $\text{Cu}_2\text{Cl}_2$  in HCl followed by differential titration with  $\text{KMnO}_4$ , and of  $\text{Pt}^{II}$  and  $\text{Ir}^{III}$  simultaneously

with  $\text{KMnO}_4$  have also been developed. Other methods of volumetric determination of the Pt metals are discussed critically. J. W. S.

**Separation of iridium from rhodium.** B. G. KARPOV and A. N. FEDOROVA (Ann. Inst. Platine, 1933, No. 11, 135—139).—The solution of Ir and Rh chlorides is diluted to 600—800 c.c., and 40 c.c. of conc.  $\text{H}_2\text{SO}_4$ , 3—5 c.c. of saturated aq.  $\text{HgCl}_2$ , and excess of aq.  $\text{VCl}_2$  are added. The solution is filtered through porcelain 2 hr. later, and the ppt. of Rh is dissolved in aqua regia; the solution is evaporated to dryness, and the residue is dissolved in 40 c.c. of conc.  $\text{HCl}$ . The above pptn. is repeated, and the ppt. is ignited, treated with  $\text{HF}$  to remove traces of  $\text{SiO}_2$ , reduced, and weighed. R. T.

**Inexpensive and economical warm room.** G. GRINLING (Analyst, 1933, 59, 103—104). E. C. S.

**Mercury-in-glass thermo-regulator.** C. C. COFFIN (Proc. Nova Scotian Inst. Sci., 1932—1933, 18, 213—214).—A Hg-in-glass thermo-regulator giving control within  $0.001^\circ$  is described. Its advantage lies in various details of construction and in the fact that rapid heat exchange is more important for control than a large coeff. of expansion. R. S. C.

**Improved m.-p. apparatus and comparative study of types of apparatus for m.-p. determinations.** C. L. TSENG (J. Chinese Chem. Soc., 1933, 1, 143—182).—A modification of Mulliken's apparatus is described, and results obtained therewith are compared with those obtained by other methods. Numerous sources of error in m.-p. determinations are discussed, and it is maintained that none of the commonly used types of apparatus based on the capillary tube method can give results trustworthy to  $\pm 1^\circ$ , even under the best conditions. As a rule the initial fusion point, determined by a capillary tube method, is higher than the true m.p. E. S. H.

**Application of the ether calorimeter to measurements of the heat of radiation of feebly radioactive substances.** A. DORABIALSKA (Rocz. Chem., 1934, 14, 24—30).—The results obtained for monazite,  $\text{Sb}_2\text{O}_3$ ,  $\text{Sb}_2\text{S}_5$ , and  $\text{As}_2\text{S}_3$  using an  $\text{Et}_2\text{O}$  calorimeter (I) are of the same order of magnitude as those previously obtained using an adiabatic (I). R. T.

**X-Ray spectroscopy and photography with bent crystal reflectors. II. Description of a focussing spectrograph with point-scattered slit images.** L. VON HÄMOS (Ann. Physik, 1934, [v], 19, 252—260).—A new focussing X-ray spectrograph, using a rock-salt crystal bent into a cylinder as a reflector, is described. A. J. M.

**Photo-electric measurement of absorption and colour change.** R. SEWIG and F. MÜLLER (Chem. Fabr., 1934, 7, 25—27).—The use of metal-vapour discharge lamps, in conjunction with suitable filters, is recommended. The spectral line chosen should correspond approx. with the absorption max. of the indicator used. Thus a Na lamp is satisfactory with bromophenol-blue (absorption max. 5920 Å.) and bromocresol-purple (5910 Å.); a Tl lamp with Me-red (5300 Å.); a Hg lamp with cresol-red (5720

Å.); thymol-blue (5440 Å.), and phenolphthalein (5530 Å.); and a Cd lamp with  $\alpha$ -naphtholphthalein. H. F. G.

**Simple photo-electric colorimeter.** G. A. MILLIKAN (J. Physiol., 1933, 79, 152—157).—A photo-electric colorimeter, especially suitable for measuring the degree of  $\text{O}_2$  saturation of dil. hæmoglobin solutions, is described. Use is made of a differential Cu— $\text{Cu}_2\text{O}$  photo-electric cell (I) and colour filters. The source of light is a Hg arc lamp, and readings are made by means of a galvanometer attached to (I). NUTR. ABS. (m)

**Turbidity and colour measurements. I. Photo-electric cell arrangement for measuring small quantities of certain impurities in reagent chemicals.** R. A. OSBORN (J. Assoc. Off. Agric. Chem., 1934, 17, 135—141).—Appropriate apparatus is described and its use in determining small amounts of Pb, Fe, Cl, and  $\text{SO}_4$  recorded. A. G. P.

**Automatic photo-electric photometer.** E. B. MOSS (Proc. Physical Soc., 1934, 46, 205—213). N. M. B.

**Application of photo-electric cell to nephelometry.** E. CANALS and A. HORTALA (Bull. Soc. Chim. biol., 1933, 15, 1535—1551).—Cheneveau and Audubert's relation between the concn. of suspended particles and light absorption (A., 1920, ii, 327) is confirmed and may be used to determine the concns. of suspensions of mastic, argyrol, and  $\text{AgCl}$ . The optimum  $\lambda$  for the last is 4100 Å., giving a max. error of 4% depending on the mode of prep. of the  $\text{AgCl}$ . H. D.

**Preparation of uniform nephelometric suspensions.** A. F. SCOTT and F. H. HURLEY (J. Amer. Chem. Soc., 1934, 56, 333—335).—A device for effecting the uniform addition of a pptg. agent is described, thus enabling uniform turbidities to be obtained. In suspensions of  $\text{AgCl}$  the  $[\text{Ag}^+]$  before pptn. has no influence on the turbidity at the concns. generally used. Turbidity tests are not vitiated by the presence of  $< 0.6M\text{-KNO}_3$ . E. S. H.

**Vacuum [photo-electric] cells for measurement of weak luminous fluxes.** L. CAPDECOMME (Compt. rend., 1934, 198, 462—464).—To examine the optical properties of opaque minerals a cell is required of great sensitiveness, stability, and strict proportionality to the light flux. For this purpose the best is a vac. Cs cell, but working at p.d.  $< 150$  volts. As the sensitiveness varies with time and previous history, to be strictly comparable measurements must be made immediately after one another, and on the same part of the cathode. C. A. S.

**Photo-electric densitometer for use with suspensions.** T. J. B. STIER, W. ARNOLD, and J. N. STANNARD (J. Gen. Physiol., 1934, 17, 383—392).—The apparatus consists of two photo-electric cells, a light source of high intensity, and a Wheatstone bridge. The suspension of micro-organisms is placed in the path of a beam of light entering one cell whilst another beam falls on the second. The ratio of the magnitude of the two currents set up is then determined. The accuracy obtainable is 1% for

cultures of the same age and comparable optical characteristics. A. L.

**Characteristics of the sodium lamp as influenced by vapour pressure.** G. R. FONDA and A. H. YOUNG (*J. Opt. Soc. Amer.*, 1934, 24, 31—34).—Graphs are given for luminous variation with temp. for various c.d., and variation of voltage characteristics with temp. for a Na lamp containing 1.5 mm. pressure of Ne. Results are explained qualitatively on the energy changes of a Na atom in collision with an electron. Efficiency increases at const. temp. as c.d. is decreased, and max. light output for all c.d. is at a v.p. corresponding with 200°. N. M. B.

**Yellow-blue ratio and personal errors in heterochromatic photometry.** W. S. STILES (*Phil. Mag.*, 1934, [vii], 17, 660—668).—An approx. formula gives the personal error in matching brightnesses of different colour temp., in terms of the yellow-blue ratio of the observer. H. J. E.

**Rapid electro-dialyser.** H. BRINTZINGER [with A. ROTHHAAR and H. G. BEIER] (*Kolloid-Z.*, 1934, 66, 183—188).—The apparatus is described and its performance is compared with that of others. E. S. H.

**Measurement of specific resistance by eddy current shielding.** W. B. KOUWENHOVEN and G. P. DAIGER (*Rev. Sci. Instr.*, 1934, [ii], 5, 94—101).—The method is based on the change in inductance of a solenoid, which occurs when conducting material is brought into the field of the solenoid, owing to eddy currents which are set up in the material by the alternating magnetic field. Experimental results for Cu and some Cu alloys show satisfactory agreement with those obtained by d.c. measurements. E. S. H.

**Combined apparatus for measurement of corrosion and of  $p_H$  and for potentiometric titration for process control and testing of materials.** ANON. (*Chem.-Ztg.*, 1934, 58, 197—198).—The measurement of  $p_H$  and potentiometric titrations are simplified by the use of the twin-tube potentiometer; the galvanometer scale reads directly in  $p_H$  units. A similar apparatus can be used in the determination of corrosion by the direct measurement of current. A. G.

**Conrady system of weighing as an aid to the chemist.** W. H. J. VERNON (*Chem. and Ind.*, 1934, 211—214).—A description is given of the Conrady system of weighing as adapted for routine work. The method can be applied to a balance of robust design carrying loads of 100 or 200 g., with only slight structural modifications; it is capable of yielding an accuracy of  $1 \times 10^{-6}$  of the load on the pan, or 0.001 mg. in 100 g. The underlying principle is an extension of the Gaussian method of exchange, and aims at eliminating, by a process of cancellation, errors that are introduced in a simple double weighing.

**Glass micro-balance.** H. DAMIANOVICH (*Anal. Inst. invest. cient. tecn.*, 1931, 2, 85—90).—The beam is of glass, 0.02 mm. in diam. and 12 cm. long, and carries a mirror at the centre of oscillation. The balance is more sensitive and less difficult to

construct than the usual quartz type. Up to 3 mg. may be weighed to within 0.001 mg. H. F. G.

**Vacuum absorption pipette; its use in the examination and determination of gases and vapours.** R. GROS (*J. Pharm. Chim.*, 1934, [viii], 19, 156—162).—Apparatus and technique are described. E. S. H.

**Horizontal micro-burette.** E. J. CONWAY (*Biochem. J.*, 1934, 28, 283—287).—A simple micro-burette (to deliver 0.1 ml.), easily assembled from Pyrex thermometer and graduated tubing, is described. It may be used for micro-titrations, for the accurate delivery of small vols. if a large vol. of liquid is available, and as an accurate wash-out pipette for very small vols. of blood or serum. A. E. O.

**Gas analysis with modified Orsat apparatus.**—See B., 1934, 175.

**Unitised gas analysis apparatus.**—See B., 1934, 223.

**Micro-Kjeldahl still.** T. P. NASH, jun. (*J. Lab. Clin. Med.*, 1933, 18, 1285—1287). CH. ABS.

**Extraction apparatus.** K. PETERS (*Chem. Fabr.*, 1934, 7, 21—25).—Many forms of apparatus are crit. reviewed; none fulfils satisfactorily the requirements for coal extraction. An apparatus is described which is suitable for extractions with exclusion of air, under reduced pressure, and with solvents of low b.p., together with a condenser operating in any desired atm. In a modification of the apparatus only part of the extract at a time falls into the lower flask, the sudden bursts of vapour occurring when a mixed solvent is used being thus avoided. A further modification renders the apparatus suitable for extraction with liquid  $SO_2$  at 2—3 atm. pressure. A device for ensuring that the whole of the condensate falls on to the material to be extracted (of importance in the extraction of coal) is described. H. F. G.

**Improved equilibrium distillation still and the equilibrium distillation test.** M. MIZUTA (*J. Soc. Chem. Ind. Japan*, 1934, 37, 11B).—The temp. difference between the inside and outside of the glass wall of the upper part of the still is kept const. by electric heating, and condensation prevented. With this still correct vals. were obtained for the b.p. of mixtures of  $C_6H_6$  and PhMe. A. G.

**Apparatus for rectifying small quantities of gas, and the purification of krypton.** H. VAN DIJK, J. MAZUR, and W. H. KEESOM (*Proc. K. Akad. Wetensch. Amsterdam*, 1933, 36, 822—825).—Small quantities of Kr are more easily purified by rectification than by fractional evaporation. The rectifier incorporates Claude's principle of "retour en arrière" and consists of a small heater below a uniform Cu screw fitting snugly in an unsilvered Dewar vessel surrounded by a cooling bath. J. G. A. G.

**Improved vacuum fractionation apparatus.** H. F. J. LORANG and J. KLUIZENAAR (*Chem. Fabr.*, 1934, 7, 66—67).—A single specially constructed tap (illustrated) enables successive fractions to be collected and run out without risk of destroying the vac. accidentally. D. R. D.

**Rapid evaporation of frothing liquids.** E. JANTZEN and H. SCHMALFUSZ (Chem. Fabr., 1934, 7, 61—62).—A simple apparatus for vac. distillation of liquids which foam badly is described. The foam is broken up and thrown back into the evaporator (capacity 1—5 litres) by rapidly rotating vanes.

D. R. D.

**Nickel vessel for storing standard alkali hydroxide solutions.** E. C. RIGHELLATO (Analyst, 1934, 59, 104).

E. C. S.

**Silvering of mirror surfaces by cathodic sputtering.** M. ROMANOVA, A. RUBTSOV, and G. POKROVSKI (Compt. rend. Acad. Sci., U.R.S.S., 1934, 1, 15—18).—Surfaces prepared by cathodic sputtering in  $H_2$  at 0.04—0.05 mm. pressure, using an applied voltage of 1200—1400 volts d.c., and a current of 15—20 milliamp., are very suitable for use in interference gratings.

J. W. S.

**New accessories for a microscope for micro-chemical work (capillary holder, microchemical manipulator), with some notes on qualitative microelectrolysis.** H. ALBER (Mikrochem., 1934, 14, 219—244).—A description of the apparatus. A refinement of the Brenneis electrode (A., 1931, 924), using Pt wires 0.05 mm. diam., sealed through a glass capillary and ground off flush, enables amounts of metal of the order of  $0.01 \times 10^{-6}$  g. to be deposited out of 5—10 c.c. of solution, identification under the microscope following.

J. S. A.

**Modification of Chamberland's autoclave permitting the desiccation of dressings in the same autoclave.** G. HIRT (J. Pharm. Chim., 1934, [viii], 19, 162—168).—After sterilisation at  $134^\circ$  for 45 min., the  $H_2O$  in the autoclave is withdrawn through a tube leading to the bottom, and the contents are dried by a current of hot air.

E. S. H.

**Automatic elementary analysis.** H. REIHLEN and E. WEINBRENNER (Chem. Fabr., 1934, 7, 63—66).—Org. combustions are made automatic by arranging a clock to control the heating by drawing a burner along on rails and turning off the gas.

D. R. D.

**Use of charcoal in maintaining high vacua.** C. H. COLLIE (Proc. Physical Soc., 1934, 46, 252—255).—Measurements were made of the limiting pressures reached by charcoals and  $SiO_2$  gels cooled with liquid air or liquid  $H_2$  when a small const. stream of gas is admitted into the apparatus.

N. M. B.

**High-vacuum leak device.** G. A. WHIPPLE (Proc. Physical Soc., 1934, 46, 281—282).—The device operates on a diffusion principle, and allows continuous variation of pressures in the discharge tube of cold-cathode-ray oscillographs.

N. M. B.

**Valve for the regulation of the rate of gas flow.** K. HAUSCHILD (Chem. Fabr., 1934, 7, 27).—The needle of a needle valve is raised or lowered by a screw operating through a ball and socket joint. Pressures of 30—40 mm. and 5 mm. on either side of the valve may be maintained const. to within 2%.

H. F. G.

**Probable error of sampling sediments for mechanical analysis.** W. C. KRUMBEIN (Amer. J.

Sci., 1934, [v], 27, 204—214).—In beach sands the error varied between 0.75 and 4.51%. C. W. G.

**Apparatus for determination of size distribution of particles in fine powders.**—See B., 1934, 223.

**Hydroclassifier employing motionless liquid.** E. JOUKOWSKY and L. CHARREY (Arch. Sci. phys. nat., 1933, [v], 15, Suppl., 209—211).—An instrument for the determination of the granular structure of ppts. is described. The ppt. is allowed to fall through a column of  $H_2O$  in a thermostat and samples are removed from the bottom at definite intervals.

R. S.

**Correction nomograph for pressure changes supplementary to humidity chart of gases.** S. HATTA (J. Soc. Chem. Ind. Japan, 1934, 37, 38—43B; cf. B., 1933, 735).—A nomograph and the calculations for its construction are given for finding the saturated humidity at any temp. and pressure. The change of heat capacity with pressure may be ignored. Adiabatic cooling lines at different pressures are nearly parallel and the distance between them is equal to the difference in saturated humidity.

A. G.

**Viscosity of basalt glass at high temperatures.** I. K. KANI (Proc. Imp. Acad. Tokyo, 1934, 10, 29—32).—Rice-jelly is employed as standard in a method involving measurement of the relation between load and velocity of revolution of an immersed cylinder.

C. W. G.

**Electromagnetic rotating [cylinder] viscosimeter.** G. BERRAZ (Anal. Inst. invest. cient. tecn., 1931, 2, 79—84).—The force exerted on the inner cylinder by the rotating mass of liquid is balanced by adjusting the current in two bobbins mounted astatically. The balancing current is directly proportional to the viscosity of the liquid. The results obtained are slightly < those given by the Ostwald viscosimeter. The sensitivity is high, but the apparatus is somewhat expensive and requires expert handling.

H. F. G.

**Measurement of abnormal viscosity by the falling-sphere method.** F. HIRATA and K. KUBO (J. Soc. Chem. Ind. Japan, 1934, 37, 11—14B).—The velocities of steel balls falling through 3.83% and 11.88% solutions of caoutchouc in  $C_6H_4Mc_2$  are  $v = kr^{2.85}$ .

A. G.

**Increasing the sensitivity of chemical reactions.** E. W. BLANK (J. Chem. Educ., 1933, 10, 746—747).—The collection of a ppt. at the interface between an aq. solution and an org. solvent, and centrifuging of an opalescent liquid followed by microscopical examination of the point of the centrifuge tube, are aids in the detection of pptn.

CH. ABS.

**"Exergic" and "endergic reactions."** W. BLUM (Science, 1934, 79, 84).—"Exergic" reactions occur with a decrease, and "endergic" reactions with an increase, in free energy.

L. S. T.

**Practical exercises in colloid chemistry.** A. LOTTERMOSER (Kolloid-Z., 1934, 66, 188—191).

E. S. H.

## Geochemistry.

**Composition of air in the stratosphere.** A. F. KAPUSTENSKI (Compt. rend. Acad. Sci. U.R.S.S., 1934, 109).—The observation that the composition of the air is the same on the earth's surface and at a height of 19 km. can probably be explained either by the enrichment of the stratosphere with  $N_2$  by means of gravitational forces or by  $O_2$  enrichment due to thermal diffusion. W. R. A.

**Atmospheric ozone at the Pic du Midi.** J. GAUZIT (Compt. rend., 1934, 198, 492—494).—Measurements of  $O_3$  with the author's spectrophotometer (cf. A., 1933, 45) at the Pic du Midi during August, 1933, are explicable on the supposition that the  $O_3$  is partly (70—92%) collected in a thin layer at heights of 18—45 km. (above the Pic) and partly (8—30%) uniformly diffused throughout the atm. The amount so diffused is equiv. (at normal pressure) to a layer  $35—85 \times 10^{-4}$  cm. thick per km. (cf. A., 1931, 458). C. A. S.

**Radioactivity of air in the Observatory at the Pic du Midi.** H. GARRIGUE (Compt. rend., 1934, 198, 494—496).—Conductivity observations show that the spontaneous ionisation due to radioactivity of the Rn type is approx. 1000 times as great when the Pic is under snow as in summer. C. A. S.

**Soft radiation on the Pic du Midi.** H. GARRIGUE (Compt. rend., 1934, 198, 764—765; cf. preceding abstract).—Determinations with the author's apparatus of the soft radiation of terrestrial radioactive origin in July—Aug., and Nov.—Dec. 1933, show that this is about 4.5 times as strong in winter as in summer. C. A. S.

**Radioactivity of the thermal springs of Mangalia.** T. DONESCU (Bul. Soc. Fiz. Român., 1933, No. 56, 6—8).—The radioactivity of the  $H_2O$  varies from 9 to 144 m $\mu$ c. R. T.

**Variations in the chemical composition of natural waters in relation to atmospheric precipitation.** E. PODA (Annali Chim. Appl., 1933, 23, 581—584).—The electrical resistance of the  $H_2O$  of the Adige runs parallel to the piezometric height of the river. Atm. pptn. produces a proportional and almost immediate effect on the resistance, but with spring  $H_2O$  the effect is delayed and less marked. T. H. P.

**Gold content of the streams of the canton of Geneva.** J. J. PITTARD (Arch. Sci. phys. nat., 1933, [v], 15, Suppl., 232—234).

**Content of dissolved oxygen in water of maritime Seine.** P. CHAUCHARD (Compt. rend., 1934, 198, 594—596; cf. A., 1932, 1227).—The content of  $O_2$  in the  $H_2O$  of the Seine estuary increases on passing from fresh to brackish, to fall slightly in the salt  $H_2O$  of the open sea. It is reduced by the bore and incoming tide which stir up a reducing mud, but is increased by insolation. C. A. S.

**Isotopic composition of sea-water.** E. S. GILLFILLAN, jun. (J. Amer. Chem. Soc., 1934, 56, 406—408).— $H_2O$  obtained by distillation of sea- $H_2O$  had  $d$   $1.0000023 \pm 0.0000002$  at  $0^\circ$  compared with that

obtained by distillation of Cambridge (U.S.A.) tap-water. A method of determining small differences of  $d$  is described. E. S. H.

**Law of variation of the coefficient of carbonation in the world's oceans.** P. T. DANILTSCHENKO and N. S. SPIRO (Bull. Acad. Sci. U.R.S.S., 1933, 1439—1458).—The available data show that the carbonation coeff.,  $100HCO_3/Cl$  ( $=K$ ), varies from 1259 for river- $H_2O$  to 0.79—0.15 for ocean and salt-lake  $H_2O$ . For ocean  $H_2O$   $KS = \text{const.}$ ,  $S$  being the % of total salts present. In general the  $H_2O$  of seas, oceans, rivers, stagnant and salt lakes is saturated with  $CaCO_3$ , the content of which is independent of the salinity and approx. the same in the different parts of the hydrosphere. In certain cases (Black and Caspian Seas) the  $H_2O$  is super-saturated, and in others (Baltic) unsaturated, with  $CaCO_3$ . T. H. P.

**Pink mineral in a serpentine from Bou Oufroh (Morocco).** R. FREY and J. BURGHELLE (Ann. Chim. Analyt., 1934, [ii], 16, 61—62).—Pink veins in a yellowish-green serpentine were round grains of pleochroic, monoclinic plates, showing strong birefringence, hardness 1,  $d$  2.1—2.2. Analysis gave  $2Fe_2O_3, Cr_2O_3, 27MgO, 6CO_2, 54H_2O$ , corresponding with a mixed basic carbonate of Fe, Cr, and Mg or with a mixture of  $Mg(OH)_2$  with a basic carbonate of Fe and Cr. J. G.

**Ægirine-augite hyalo-rhyolite from Tokachi, Hokkaido.** T. NEMOTO (Proc. Imp. Acad. Tokyo, 1934, 10, 21—24).—Analyses are given. The mineral is similar to an average rhyolite. C. W. G.

**Thermal expansion of basaltic hornblende.** S. KÔZU and J. UEDA (Proc. Imp. Acad. Tokyo, 1934, 10, 25—28).—The linear expansions along the three crystal axes have been determined. C. W. G.

**Nickel ore from Petsamontunturit and its examination.** H. VÄYRYNEN (Suomen. Kem., 1934, 7, A, 11—16).—Ores containing 1.6—2.8% Ni and 1.3—1.6% Cu are recorded among intrusive rocks. The Co content is unusually low. A. G. P.

**Rocks of Kenya.** (MLLE.) E. JÉRÉMINE (Compt. rend., 1934, 198, 838—840).—Analyses of the following are given: oceanite from an island in lake Naivasha; a banded spherulitic phonolite containing poikilitic ægyrite and æigmatite, from lake Narasha; a phonolite containing large crystals of nepheline and sphene, with ægyritic augite, hedenbergite, and æigmatite, from between Timboroa and Eldoret; and a similar phonolite with kataforite and soda amphibole in place of hedenbergite, from south of Eldoret. C. A. S.

**Emery [rock] of Samos.** J. DE LAPPARENT (Compt. rend., 1934, 198, 760—761; cf. A., 1933, 928).—The vein of emery rock consists of 4.5 m. of homogeneous steel-blue diaspore with traces of pisolitic structure, and containing white mica and Fe oxides but no corundum; above this is 1.5 m. of ferruginous nodules in an Fe-free matrix, pisolitic and mainly diaspore, but containing mica, chloritoid,



and a little kaolin. It becomes more kaolinic at the top, where there is an argillaceous layer, followed by one of spathic limestone containing mica and kaolin. The emery contains 3.5%  $\text{TiO}_2$  and 24%  $\text{Fe}_2\text{O}_3$ , and is a metamorphosed ferruginous siliceous bauxite. The Naxos emery is similar, but metamorphism has proceeded further with formation of corundum. C. A. S.

**Boracite.** M. MEHMEL (Z. Krist., 1934, 87, 239—264).—Boracite at Stassfurt (I) occurs in nodules associated with pure carnallite, at Luneberg (II) in single crystals in gypsum or anhydrite. The composition of (I) averages  $\text{MgCl}_2 \cdot 5 \cdot 2(\text{MgFe})\text{O} \cdot 6 \cdot 7\text{B}_2\text{O}_3$ ; that of (II)  $\text{MgCl}_2 \cdot 5 \cdot 0(\text{MgFe})\text{O} \cdot 6 \cdot 8\text{B}_2\text{O}_3$ ; it is suggested that the crystals are mixed,  $\text{Mg}_6\text{B}_{14}\text{O}_{26}\text{Cl}_2$  and  $\text{Mg}_7\text{B}_{16}\text{O}_{30}\text{Cl}_2$ . They are rhombic, pseudocubic by reason of polysynthetic twinning (cf. A., 1929, 749). The process of twinning in connexion with the transformation on heating is detailed (cf. A., 1901, ii, 111). C. A. S.

**Rôle of water in basaltic magma.** I. T. C. PHEMISTER (Tsch. Min. Petr. Mitt., 1934, 45, 19—77).—From a consideration of crystallisation in the system  $\text{K}_2\text{SiO}_3\text{—SiO}_2\text{—H}_2\text{O}$  an attempt is made to deduce the probable influence of dissolved  $\text{H}_2\text{O}$  in a basaltic magma on its crystallisation. L. J. S.

**Liparite and obsidian dykes in the Kolymsk district [East Siberia].** W. A. WAKER (Tsch. Min. Petr. Mitt., 1934, 45, 1—18).—Dykes 2—3 m. wide of liparite have a selvage of obsidian. These rocks are ultra-acid, the liparite with 76.87% and the obsidian 72.12%  $\text{SiO}_2$ . L. J. S.

**Minerals of the Niari basin [French Equatorial Africa].** V. LEBEDEF and G. CHOUBERT (Compt. rend., 1934, 198, 484—486).—Deposits of compact or cryst. calamine with smithsonite occur in almost vertically inclined beds of limestone at Mt. Fouati. These minerals are accompanied by willemite, galena, cerussite, Cu glance, malachite, diopside, and other Zn, Pb, or Cu minerals. There also occur well-developed crystals of desclozite (usually growing on vanadinite, which is often covered with a thin crust of pyromorphite), phosgenite, and wulfenite. The earth of rock around these deposits is largely impregnated with vanadates. C. A. S.

**Volcanic rocks west of Lake Rudolph.** (MME.) E. JÉRÉMINE (Compt. rend., 1934, 198, 673—675).—The volcanic rocks west of Lake Rudolph (Kenya) consist of: rhyolites, including comendites and pantellerites (*a*); phonolites with phenocrysts of sanidine and much ægyrite (*a*); nephelinic microsyenites containing solvsbergites and some tinguaites; and basaltic rocks often rich in analcite (*a*), and including ankarmites (*a*) and doleritic basalts, whilst some flows contain large (5—6 cm.) phenocrysts of plagioclase (*a*). A basanitoid basalt resembling ordanichite (*a*) occurs at Lodwar. Holocryst. rocks are found only in dykes or as rounded blocks; they include essexite resembling berondrite, and shonkinite rich in ægyrite and arfvedsonite (*a*). Chalcedony, calcite, analcite, stilbite, heulandite, and mesotype are found in cavities. Eight complete analyses are given of the rocks marked (*a*). C. A. S.

**Constitution and origin of leverrierite.** J. DE LAPPARENT (Compt. rend., 1934, 198, 669—671).—Leverrierite (cf. A., 1900, ii, 86) is an association of muscovite and kaolin in varying relative amounts, probably resulting from decomp. of biotite under humid conditions. The crystals of the two minerals appear to be in definite orientation (epitaxy) (cf. A., 1930, 569). C. A. S.

**Minerals from the Tschetscha deposit (Caucasus).** A. SHAPOVALOV (Min. J., Moscow, 1931, 107, 58—60).—Crude saltpetre contained  $\text{KNO}_3$  10.9,  $\text{NaNO}_3$  41.1%. CH. ABS.

**Chemical and mineralogical composition of the lavas of the Timok basin.** J. TOMIC (Ann. géol. pénins. balkan, 1931, 10, 128—138).—Four analyses of andesites are given. CH. ABS.

**Genetic relations between the crystalline limestones, dolomites, and amphibolites in the rock series at Chynov.** A. ORLOV (Vestn. Král. Ces. Spol. Nauk, 1931, II, 36 pp.).—Analyses are given. CH. ABS.

**Salt layers of the Solikamsk deposit.** E. RAZUMOVSKAYA (Trans. Geol. Prospect. Serv., U.S.S.R., 1931, 54, 1—40).—Halite, sylvite, carnallite, anhydrite, gypsum, hæmatite, clay, and quartz are present. CH. ABS.

**Silicate nickel ores of the Tiulenevsk deposits in the Urals.** E. KUZNETZOVA (Bull. Geol. Prospect. Serv., U.S.S.R., 1931, 50, 265—285).—Analyses are given. CH. ABS.

**Organic minerals. II. Occurrence of chlorophyll derivatives in an oil-shale from the upper Trias.** A. TREIBS (Annalen, 1934, 509, 103—114).—The powdered shale (from Wallgau in the upper Isar) is repeatedly extracted with  $\text{AcOH}$  at  $100^\circ$ , the extract is evaporated to dryness in a vac., the residue washed with  $\text{H}_2\text{O}$  to remove salts, and then extracted with  $\text{CHCl}_3$ . The mixture of oil and porphyrin complex (from the  $\text{CHCl}_3$  extract) is then treated with  $\text{AcOH—HBr}$  at  $50^\circ$  for 4 days. Subsequent washing of the  $\text{Et}_2\text{O}$  extract with 2.5%  $\text{HCl}$  removes the major part of the porphyrin mixture; deoxophylloerythrin, *deoxophylloerythroetioporphyrin*,  $\text{C}_{32}\text{H}_{36}\text{N}_4$ , m.p.  $235^\circ$  (block), and a porphyrin resembling (spectrum) pyrroporphyrin were isolated in small amounts. The nature of the metal in the original complex was not determined. H. B.

**Thermal history of the earth.** J. H. J. POOLE (Sci. Proc. Roy. Dublin Soc., 1934, 21, 9—22).—Some difficulties in the current views relating to a convective layer beneath the earth's crust and the generation of heat due to radioactivity are discussed. L. J. S.

**Actinium-uranium bifurcation ratio.** M. FRANCIS and CHENG DA-CHANG (Compt. rend., 1934, 198, 733—735; cf. A., 1932, 919).—The U and Pa were separated from three samples of Belgian Congo pitchblende and one of Colorado carnotite. The thin layers were prepared by crushing in the ordinary way; by ultrasonic pulverisation; and (for U only) by electrolysis and conversion into  $\text{U}_3\text{O}_8$  at  $700^\circ$ . The ratio of the ionisation currents averaged (with good

agreement) 0.023, giving the bifurcation ratio of 4% (cf. Grosse, A., 1933, 110). C. A. S.

**Radioactive minerals from Shimden, Gifu Prefecture.** S. IIMORI, J. YOSHIMURA, and S. HATA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 23, 209—211).—Analyses and mineralogical descriptions of an allanite and a U-bearing gadolinite are given. C. W. G.

**Working formula for the age determination of a radioactive mineral.** A. F. KOVARIK (Amer. J. Sci., 1934, [v], 27, 193—203).—Successive approximations introducing the Ac series are used. C. W. G.

**Soils of the Pechora Region.** G. A. LIVEROVSKY (Trans. Dokuchaiev Soil Inst., 1933, 8, No. 7, 1—47). A. M.

**Geology and soils of the Koltushi Region.** I. N. IVANOVA, O. P. DOSMANOVA, and N. A. ARCHANGELSKAYA (Trans. Dokuchaiev Soil Inst., 1933, 8, No. 6, 1—107). A. M.

**Soil-climatic facies of the plains of the U.S.S.R. and neighbouring countries.** I. P. GERASIMOV (Trans. Dokuchaiev Soil Inst., 1933, 8, No. 5, 1—38). A. M.

**Soils of Abyssinia and Erythrea.** L. I. PRASSOLOV (Pedology, 1933, 28, 359—373).—Two types, black earths (I) and red earths (II), are distinguished. (I) seems to be most closely related to Indian regur, whilst (II) resembles Mediterranean terra rossa. A. M.

**Soils of the Crimean National Forest.** I. N. ANTIPOV-KARATAIEV and L. I. PRASSOLOV (Trans. Dokuchaiev Soil Inst., 1933, 7, 1—280). A. M.

**Takyr soils and their formation.** I. P. GERASIMOV (Pedology, 1933, 28, 401—403).—A discussion (cf. Sushko, B., 1933, 401). A. M.

**Qualitative composition of organic matter in soils of U.S.S.R.** N. P. REMEZOV (Pedology, 1933, 28, 374—394; cf. A., 1933, 929).—C:N ratio is not const. for all soils, but a characteristic average val. is found for each soil zone. The ratio increases from the serozem zone (1:4.5) northwards to the Siberian chernozem (1:14) and then decreases. In the northern peats it is again wider. Cellulose and hemicellulose are absent from serozem and proteins predominate over ligno-humus complex. In chestnut soils hemicelluloses are present and ligno-humus complex exceeds proteins. In chernozem there is a large increase in ligno-humus. In podsols the ligno-humus complex is again small. A. M.

**Saline and alkaline soils.** F. HARDY (Trop. Agric. [Trinidad], 1933, 10, 35—40).—The classific-

ation and reclamation of these soils and their influence on the mineral intake of plants are discussed. A. G. P.

**Podsols and brown forest soils.** I. K. LUNDBLAD (Soil Sci., 1934, 37, 137—155).—Profile descriptions and characteristics are recorded. The acid-oxalate extraction method (Tamm) for characterising the sesquioxide and SiO<sub>2</sub> of soil colloids differentiates podsols from brown earths. A. G. P.

**Pedology of the soils of France.** V. AGAFONOFF (Ann. Agron., 1933, 3, 587—650).—Classification, chemical composition, and mineral constituents are described (cf. A., 1933, 1269). A. G. P.

**Fossil spores and pollen grains as a thermometer for the process of coal formation.** F. KIRCHHEIMER (Brennstoff-Chem., 1934, 15, 21—25).—Spores and pollen grains show characteristic changes when heated at > 130°. Similar changes have been observed in spores and pollen in samples of coal taken from the neighbourhood of igneous intrusions. The pollen grains in soft brown coals have undergone no thermal change; those of many bright brown coals show changes which indicate a max. temp. of 130—200°. Similarly it has been shown that low-rank bituminous coals cannot have been subjected to a temp. > 200°. The data relating to high-rank bituminous coals are at present insufficient to decide the max. temp. reached during their formation. A. B. M.

**Temperatures reached during the formation of coal.** B. NEUMANN (Brennstoff-Chem., 1934, 15, 25—27).—The appearance of the resin inclusions in a Chinese bright brown coal shows that they have been softened by heat, but have undergone no marked thermal decomp. By comparison with the behaviour of a sample of the resin on being heated it is concluded that the temp. of the coal during its formation must have reached < 265°, but cannot have been > 320°. It has similarly been shown that the max. temp. reached by a German brown coal and a German bituminous coal must lie within the ranges 150—180° and 230—300°, respectively. The significance of these conclusions is briefly discussed. A. B. M.

**Salt domes, gases, and petroleum.** V. I. LUCHITZKI (Min. Suir., 1933, 8, No. 7, 1—2).—Test borings in the Pomen and Isachek regions, N. Poltava, disclosed deposits of rock salt and gases. Domes and the presence of petroleum deposits are indicated. CH. ABS.

**Relationship between porosity and mechanical composition of sands in the Old Grozni area.** S. M. ILINSKI (Neft. Choz., 1933, 24, 24—27).—Sands affording the lowest production have the lowest degree of porosity. CH. ABS.

## Organic Chemistry.

**Catalytic methods in organic chemistry.** J. P. WIBAUT (Chem. Weckblad, 1934, 31, 142—147).—A review.

**Dynamics and mechanism of aliphatic substitution.**—See this vol., 368.

**Elementary organic reactions.** F. O. RICE (J. Amer. Chem. Soc., 1934, 56, 488—490).—The nos. quoted after the following reactions are the activation energies assigned (the evidence is discussed briefly):  
 $H + CH_4 \longrightarrow H_2 + Me > 20$ ;  $H + C_2H_6 \longrightarrow H_2 + Et$   
 17;  $Me + H_2 \longrightarrow CH_4 + H$  23;  $Et + H_2 \longrightarrow C_2H_6 +$

H 25; Me + C<sub>2</sub>H<sub>6</sub> → CH<sub>4</sub> + Et 20; Me + COMe<sub>2</sub> → CH<sub>4</sub> + ·CH<sub>2</sub>·COMe 15; Me + Me<sub>2</sub>O → CH<sub>4</sub> + ·CH<sub>2</sub>·OMe 15; CH<sub>4</sub> → Me + H 100; CH<sub>4</sub> → CH<sub>2</sub> + H<sub>2</sub> 100; Me → CH<sub>2</sub> + H 100; C<sub>2</sub>H<sub>6</sub> → 2Me 79.5; Et → C<sub>2</sub>H<sub>4</sub> + H 49; ·CH<sub>2</sub>·COMe → CH<sub>2</sub>·CO + Me 48; ·CH<sub>2</sub>·OMe → CH<sub>2</sub>O + Me 38; Ac → CO + Me 10. H. B.

**Suitability of alloy skeletons as catalysts for the synthesis of benzene from carbon monoxide and hydrogen.** F. FISCHER and K. MEYER (Ber., 1934, 67, [B], 253—261).—The vol. of the Ni-Mn-Al contacts containing SiO<sub>2</sub> can be reduced to  $\frac{1}{3}$  by protracted grinding without loss of catalytic activity. Alloy skeletons (I) are obtained by fusing Ni and Al together, crushing the cold mass, and removing Al therefrom by aq. NaOH followed by washing with hot H<sub>2</sub>O. Similar (I) are prepared by adding Si to molten Ni or Co and treating the products with NaOH, after which 5—10% of the Si remains. The behaviour of Ni-Al, Ni-Si, Co-Al, Co-Si, and Ni-Co-Si alloys is fully described. Presence of Fe is disadvantageous. The yields of liquid hydrocarbons from CO and H<sub>2</sub> with pptd. contacts (II) are usually 10—20% > with (I). (I) are advantageous in that they operate without additions, whereas an efficient (II) contains a variety of components. (I) are very readily prepared, whilst the prep. of (II) is very tedious. Advantages claimed for (I) are enhanced conductivity for heat, unusually small vol., and ready regeneration by fusion with Si. The theoretical aspects are discussed. H. W.

**Ethane from acetic acid.** H. E. ARMSTRONG (Nature, 1934, 133, 379).—A note on the Kolbe synthesis. L. S. T.

**Rate of hydration of isobutene in dilute nitric acid.**—See this vol., 369.

**Acetylene-mercury complex salt.** E. FERBER and E. RÖMER (J. pr. Chem., 1934, [iii], 139, 277—283).—Contrary to Bilz *et al.* (A., 1905, i, 2) HgCl<sub>2</sub> in abs. EtOH absorbs C<sub>2</sub>H<sub>2</sub> at room temp. to form an amorphous substance HgC<sub>2</sub>H<sub>2</sub>·HgCl<sub>2</sub>·HgCl (I), decomp. 230° (insol. in EtOH), decomposed by dil. HCl to give C<sub>2</sub>H<sub>2</sub> and traces of MeCHO, thus confirming Manchot's views (A., 1913, i, 1009). Addition of H<sub>2</sub>O to the filtrate from (I) gives (with fission of MeCHO) a cryst. complex C<sub>2</sub>H<sub>2</sub>·HgCl<sub>2</sub>·H<sub>2</sub>O, m.p. 93—95°, losing H<sub>2</sub>O by crystallisation from C<sub>6</sub>H<sub>6</sub> to give the Biginelli complex. Saturated Hg(OAc)<sub>2</sub> in AcOH with C<sub>2</sub>H<sub>2</sub> gives an explosive substance 2HgC<sub>2</sub>H<sub>2</sub>·C<sub>2</sub>H<sub>2</sub>·H<sub>2</sub>O which loses its explosive character on keeping. J. W. B.

**Action of light on vinyl iodide.**—See this vol., 375.

**aci-Trinitromethane.** L. W. ANDREW and D. L. HAMMICK (J.C.S., 1934, 244).—Addition of damp (NO<sub>2</sub>)<sub>2</sub>C·NO<sub>2</sub>K to conc. H<sub>2</sub>SO<sub>4</sub> gives (?) aci-trinitromethane, m.p. 50° [with conversion into CH(NO<sub>2</sub>)<sub>3</sub>, m.p. 14°]. H. A. P.

**Tertiary alcohols derived from mesityl oxide.** R. JACQUEMAIN (Compt. rend., 1934, 198, 482—484).—Mesityl oxide and the appropriate Grignard reagent give δ-hydroxy-βδ-dimethyl-Δ<sup>β</sup>-hexene, b.p. 48—50°/3—6 mm., heptene, b.p. 66—68°/5—6 mm., and

octene, b.p. 78.5—80°/3—5.4 mm. The alcohols are dehydrated by cold PhNCO [forming CO(NHPh)<sub>2</sub>] or by short heating at > 6 mm. The pure products are stable at room temp. for 6 months, but, if impure, slowly lose H<sub>2</sub>O. R. S. C.

**Catalytic decomposition of complex alcohols.** M. URION (Ann. Chim., 1934, [xi], 1, 5—87).—Erythrol (γδ-dihydroxy-Δ<sup>c</sup>-butene), b.p. 94—95°/12 mm. (formate, b.p. 86—88°/12 mm.; modified prep., giving a 35% yield), is stable alone at 320°, but with Al<sub>2</sub>O<sub>3</sub> at 310—320° gives a little EtCHO and H<sub>2</sub>O and much crotonaldehyde (I) and its dimeride (Ia), and with Cu at 280° gives a little EtCHO, divinyl, CO, and saturated hydrocarbons, and much α-hydroxy-β-ketobutane (oxime, m.p. 62°; with NHPH·NH<sub>2</sub> in boiling EtOH gives glyoxalosazone), γδ-diketohexane (II), (I), H<sub>2</sub>O, and CO<sub>2</sub>. Divinyl glycol (III) at 300° gives acetaldehyde (IV), EtCHO, cyclopentene-1-aldehyde (V), b.p. 48°/11 mm., m.p. —32° (semicarbazone, m.p. 209°; oxime, an oil; phenylhydrazone, cryst., resinifies readily; NaHSO<sub>3</sub> compound; dibromide, an oil; p-nitrophenylhydrazone, m.p. 198°), formed from adipialdehyde, a little of which is also obtained; with Al<sub>2</sub>O<sub>3</sub> at 280° the same products, including 62% of (V), are formed; with Cu at 300° (III) yields EtCHO, (IV), H<sub>2</sub>O, (II) (25%), (V), and γ-hydroxy-δ-ketohexane (VI), b.p. 57—58°/10 mm. [with NHPH·NH<sub>2</sub> in hot EtOH gives slowly NH<sub>2</sub>Ph and the bisphenylhydrazone of (II)], whereas at 280° (II), (V), (VI), EtCHO, (IV), and 3-methylcyclopentane-1:2-dione (VII) (20%) are obtained. Hydrogenation (Pd-black) of (V) gives a little alcohol and a 60% yield of cyclopentanaldehyde, b.p. 34°/10 mm., 136°/758 mm. (semicarbazone, m.p. 124°), stable to Br·CHCl<sub>3</sub> at —5°, but at 20° giving the 1-Br-derivative. (V) and Ag<sub>2</sub>O give cyclopentene-1-carboxylic acid, m.p. 121°, b.p. 210° (dibromide, m.p. 133°), oxidised by KMnO<sub>4</sub> to CO<sub>2</sub> and CO<sub>2</sub>H·[CH<sub>2</sub>]<sub>3</sub>·CO<sub>2</sub>H. With the appropriate Grignard reagent (V) gives 85—90% yields of α-hydroxy-α-Δ<sup>1</sup>-cyclopentenyl-ethyl, b.p. 165—166°/749 mm., 67—68°/10 mm., n-propyl, b.p. 179—180°/749 mm., 78—79°/10 mm., and n-butyl alcohol, b.p. 197—198°/760 mm., 92—94°/10 mm., dehydrated in 80% yield by Al<sub>2</sub>O<sub>3</sub> at 320° to Δ<sup>1</sup>-cyclopentenyl-ethylene (VIII), b.p. 114—115°/754 mm., Δ<sup>c</sup>-propene, b.p. 142—144°/754 mm., and Δ<sup>c</sup>-butene, b.p. 59—62°/14 mm., respectively. (VIII) is shown by Raman spectra to contain 1% of 1-ethylcyclopentene and ethylidenecyclopentane. (II), b.p. 130°/760 mm., m.p. about —10° [dioxime, m.p. 185°; bisphenylhydrazone, m.p. 161°; (? bis)semicarbazone, m.p. about 270° (decomp.)], with o-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> gives the diethylquinoxaline, m.p. 50.5°, and with H<sub>2</sub>O<sub>2</sub> EtCO<sub>2</sub>H. (VII), m.p. 104.5°, sublimes at 97°/10 mm., +2H<sub>2</sub>O (lost at the m.p.), m.p. 78—79° [dioxime, m.p. (from H<sub>2</sub>O) 148—149° (decomp.), (from EtOH) 175° (decomp.)]; bisphenylhydrazone, m.p. 143°; disemicarbazone (formed slowly), m.p. about 280° (block); quinoxaline derivative, m.p. 73—73.5°, is identical with the compound of Dupont *et al.* (Ann. Off. Combust. Liq., 1929, 3, 467), but not with that of Riley *et al.* (A., 1932, 833), which has now been crystallised and has m.p. 38—40°; it exists in the

enolic form, since it instantly gives a violet-red colour with  $\text{FeCl}_3$ , gives salts,  $\text{C}_6\text{H}_6\text{O}_2\text{Na}_2, 2\text{C}_6\text{H}_8\text{O}_2$  and  $\text{C}_6\text{H}_7\text{O}_2\text{Na}, 2\text{C}_6\text{H}_8\text{O}_2$ , a *phenylurethane*, m.p. 137—138°, and a liquid *dibromide*, which at 20—30° passes into an *isomeride*, m.p. 153—154°; this last gives a violet colour with  $\text{FeCl}_3$ , loses  $\text{HBr}$  with  $\text{NHPh}\cdot\text{NH}_2$ , and with  $\text{Zn}$  in hot  $\text{EtOH}$  regenerates (VII). (VII) reduces Fehling's solution and ammoniacal  $\text{AgNO}_3$ , is stable to  $\text{H}_2\text{SO}_4$  (*d* 1.84), distillation over  $\text{Zn}$ , and fusion with  $\text{S}$ ,  $\text{H}_2$ -Ni at 300°, and  $\text{H}_2$ -PtO<sub>2</sub>; with alkaline  $\text{KMnO}_4$  it gives  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{CO}_2$ , with  $\text{CrO}_3$  or  $\text{H}_2\text{O}_2$  and  $\text{FeSO}_4$  (not without  $\text{Fe}^{++}$ )  $\text{CO}_2$  only.  $\delta\epsilon$ -Dihydroxy- $\Delta^{\beta}$ -octadiene (IX), b.p. 103°/3 mm., with  $\text{Al}_2\text{O}_3$  at 320° gives  $\text{H}_2\text{O}$ , (I), (Ia), and a mixture of *cis*- and *trans*-forms of 1:2-dimethyl- $\Delta^3$ -cyclopentene-3-aldehyde (X), b.p. 64—72°/12 mm. [semicarbazone, m.p. 185—186° (block)], oxidised by  $\text{Ag}_2\text{O}$  to a little  $\text{PrCO}_2\text{H}$  [formed from a little  $\delta\epsilon$ -diketo-octane (XI), present as impurity] and much 1:2-dimethyl- $\Delta^3$ -cyclopentene-3-carboxylic acid, b.p. 105—107°/3 mm., which gives some of the *trans*-form, m.p. 42° (*Ba* salt; *dibromide*, m.p. 160—161°). (IX) with  $\text{Cu}$  at 280° gives (I), (XI), a little (X), b.p. 57—58°/10 mm. [oxime, m.p. 186—187° (block)], 1:2-diketo-4-methyl-3-ethylcyclopentane (XII) (20%), b.p. 106—108°, m.p. 24°, and a mixture of  $\Delta^{\beta\beta}$ -n-octatrienes (XIII), b.p. 137—148°. (XII) shows keto-enolic tautomerism [*dioxime*, m.p. 150—152° (decomp.) (block); *bisphenylhydrazone*, m.p. 132°; sol. in dil. aq.  $\text{KOH}$ ; the 2:5-dibromide, m.p. 142°, can be titrated with  $\text{KOH}$  (phenolphthalein), loses  $\text{HBr}$  to  $\text{NHPh}\cdot\text{NH}_2$ , and regenerates (XII) with  $\text{Zn}$  dust]. (XIII) is separable by distillation into fractions, b.p. 137—143°/764 mm. and 144—148°/764 mm.; the latter yields a *trans-trans*-form, m.p. 52.5°, b.p. 147—148°/764 mm., 43°/10 mm. (exaltation of  $[M]_D$  2.76) (*hexabromide*, m.p. 122°, also obtained from the first fraction), which in air gives (I).

The above results are explained by ionisation, rupture of the linking between  $\text{CO}$  and  $\text{CH}\cdot\text{OH}$ , and relinking of the radicals and  $\text{H}$  atoms thus formed; this is supported by the following evidence. (VI), prepared in 80% yield from  $\text{EtCO}_2\text{Et}$  and  $\text{Na}$  in  $\text{Et}_2\text{O}$ , and  $\text{Al}_2\text{O}_3$  at 320° give  $\text{EtCHO}$ ,  $\text{H}_2\text{O}$ , and (II) (> 45%).  $\text{CH}_2\text{Ac}\cdot\text{OH}$ , b.p. 47—49°/15 mm. (*Ac* derivative, b.p. 64—65°/11 mm.), with  $\text{Al}_2\text{O}_3$  at 325° gives  $\text{MeCHO}$ ,  $\text{Ac}_2$ , and  $\text{CO}_2$ , and with  $\text{Cu}$  at 290° also  $\text{AcCHO}$ . Glycide is stable in  $\text{H}_2\text{O}$  vapour at 300°, but with  $\text{Al}_2\text{O}_3$  at 320° gives  $\text{MeCHO}$  (a little), (IV),  $\text{Ac}_2$ ,  $\text{CH}_2\text{Ac}\cdot\text{OH}$ , glycerol,  $\text{CO}_2$ , and a little  $\text{CO}$ ; with  $\text{Cu}$  at 280° it gives  $\text{H}_2\text{O}$  and (II).  $\text{AcCO}_2\text{H}$  with  $\text{Cu}$  at 300° gives  $\text{MeCHO}$ ,  $\text{Ac}_2$ ,  $\text{AcCHO}$ ,  $\text{H}_2\text{O}$ , and a 70% yield of methylsuccinic acid, m.p. 112.5° (*Ba* salt, +2 $\text{H}_2\text{O}$ , hygroscopic) [formed by elimination of  $\text{CO}_2$  from  $\text{CO}_2\text{H}\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$ ].

R. S. C.

**Determination of glycerol.** E. KATAOKA (J. Biochem. Japan, 1934, 19, 15—20).—The sample (of glycerol or of neutral glyceride) is heated with  $\text{KHSO}_4$  in  $\text{CO}_2$ , the  $\text{CH}_2\cdot\text{CH}\cdot\text{CHO}$  evolved is absorbed in Bertrand's  $\text{Cu}$  solution (A., 1907, ii, 136), and the pptd.  $\text{Cu}_2\text{O}$  determined by  $\text{FeSO}_4$  and  $\text{KMnO}_4$ .

F. O. H.

**Compounds of bivalent carbon. VII. Action of carbon monoxide on sodium ethoxide.** H. SCHEIBLER and G. FRIKELL (Ber., 1934, 67, [B], 312—314; cf. A., 1932, 143).—Freshly prepared,  $\text{EtOH}$ -free  $\text{NaOEt}$  is treated with  $\text{CO}$  at 15—20°/80 atm. during 120 hr. Determination of total  $\text{Na}$ , free alkali, and  $\text{HCO}_2\text{H}$  (sole volatile acid) shows the product to be a mixture of  $\text{NaOEt}$ ,  $\text{HCO}_2\text{Na}$ , and  $\text{OEt}\cdot\text{C}\cdot\text{ONa}$  (I). Preserved specimens evolve  $\text{CO}_2$  when treated with acid, arising probably from  $\text{NaEtCO}_3$  formed by autoxidation of (I).

H. W.

**Glycerophosphoric acid. I. Recognition and separation of  $\alpha$ - and  $\beta$ -glycerophosphates.** J. J. RAE, H. D. KAY, and E. J. KING (Biochem. J., 1934, 28, 143—151).—Methods are described for determining the relative amounts of  $\alpha$ - and  $\beta$ -glycerophosphates, including an enzymic method for small amounts of the  $\beta$ -form in the reputed  $\alpha$ -variety and purification of the  $\alpha$ -form. Attempts to resolve the  $\alpha$ -salt were not successful and the addition of molybdates and tungstates does not increase the rotation to a point where it can be read.

H. G. R.

**Synthesis of ribose-5-phosphoric acid.** P. A. LEVENE and E. T. STILLER (J. Biol. Chem., 1934, 104, 299—306; cf. A., 1933, 1145).—*d*-Ribose,  $\text{COMe}_2$ , and  $\text{MeOH}$  give with  $\text{CuSO}_4$  and  $\text{H}_2\text{SO}_4$  *isopropylidene-methylribofuranoside* (I), b.p. 83—86°/0.05 mm., which is converted by Purdie's reagent into a  $\text{Me}_2$  ether (II) identical with that described (*loc. cit.*). Since (II) is hydrolysed (0.04*N*- $\text{HCl}$ ) to a methylribofuranose identical with 5-methylribofuranose (*loc. cit.*) (*p*-bromophenylosazone, m.p. 175°,  $[\alpha]_D^{25}$  -55.2° in  $\text{EtOH}-\text{C}_5\text{H}_5\text{N}$ , not 161—162° and -48°, respectively, as reported), phosphorylation of (I) with  $\text{POCl}_3$  in  $\text{C}_5\text{H}_5\text{N}$  at -40° is assumed to proceed in the 5-position. The product in the form of its *Ba* salt is hydrolysed (0.5*N*- $\text{H}_2\text{SO}_4$ ) to ribose-5-phosphoric acid,  $[\alpha]_D^{25}$  +16.54° in aq.  $\text{BaCl}_2$ , which was isolated in the form of an amorphous *Ba* salt,  $\text{C}_5\text{H}_9\text{O}_8\text{P}\cdot\text{Ba}\cdot 5\text{H}_2\text{O}$ ,  $[\alpha]_D^{25}$  +5.99° anhyd. in  $\text{H}_2\text{O}$ , and was identical with the natural substance,  $[\alpha]_D^{25}$  +16.09° (A., 1911, i, 408). The correctness of the 5-structure is supported by a comparative study of the hydrolysis of the acid by 0.01*N*- $\text{HCl}$  in sealed tubes at 100°.

W. S.

**Hexosephosphoric acid obtained by hydrolysis of potato starch.** T. POSTERNAK (Compt. rend., 1934, 198, 506—507).—Potato starch and boiling 2%  $\text{H}_2\text{SO}_4$  give glucose-6-phosphoric acid.

R. S. C.

**Polymerisation of unsaturated mercaptans.** J. VON BRAUN and T. PLATE (Ber., 1934, 67, [B], 281—285).— $\Delta^{\beta}$ -Butenyl bromide is converted by  $\text{NH}_2\cdot\text{CS}\cdot\text{SNH}_2$  in  $\text{EtOH}$  into the non-cryst. *dithio-urethane*,  $\text{NH}_2\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CHMe}$ , transformed by  $\text{KOH}$  into  $\Delta^{\beta}$ -butenyl mercaptan, b.p. 99—101°, which rapidly polymerises. Similarly,  $\gamma$ -methyl- $\Delta^{\beta}$ -butenyl bromide, from isoprene alcohol by dehydration by anhyd.  $\text{MgSO}_4$  at 250° and treatment of the distillate with  $\text{AcOH}-\text{HBr}$ , yields  $\gamma$ -methyl- $\Delta^{\beta}$ -butenyl mercaptan, b.p. 125—127°, which polymerises less readily (*Bz* derivative, b.p. 122°/0.2 mm.).  $\Delta^{\gamma}$ -Butenyl mercaptan, b.p. 98—103°, becomes rapidly polymerised at room temp.  $\Delta^{\delta}$ -Pentenyl mercaptan (I), b.p. 135—137°, does not change rapidly at room temp. and relatively

slowly at 100°.  $\Delta^2$ -cycloPentenyl mercaptan, b.p. 116°, closely resembles (I) in its tendency towards polymerisation. cycloPentenyl sulphide, b.p. 112°/16 mm., from cyclopentenyl chloride in PhMe and Na<sub>2</sub>S in EtOH, yields a *sulphinium iodide*, decomp. 204°.

H. W.

**Formation of acids from aldehydes and water vapour.** S. GOLDSCHMIDT, P. ASKENASY, and H. GRIMM (Ber., 1934, 67, [B], 202—213).—Catalytic oxidation of EtOH in presence of Ag leads to MeCHO and a small amount of AcOH which is not increased by a large excess of O<sub>2</sub>. The possibility that acid arises from MeCHO and H<sub>2</sub>O vapour in absence of O<sub>2</sub> is established for many contacts, the most suitable of which is a slightly sintered mixture of CuO and Cr<sub>2</sub>O<sub>3</sub> (7:1) at 280—320°. The only products of the action are AcOH, H<sub>2</sub>, and a little EtOH. PrCHO and PhCHO are similarly converted into acids. The equilibrium is investigated. Owing to side changes, equilibrium from the direction AcOH+H cannot be reached, but the hydrogenation of AcOH to EtOH and MeCHO in presence of the catalyst is established.

H. W.

**Preparation of acid chlorides.** R. H. CLARK and A. BELL (Trans. Roy. Soc. Canada, 1933, [iii], 27, III, 97—104).—Interaction of many acids (I) (1 mol.) with PCl<sub>5</sub> (1 mol.) affords acid chlorides (II), the yield being decreased by ZnCl<sub>2</sub> (0.2 mol.), whereas (I) with PCl<sub>3</sub> gives improved yields with ZnCl<sub>2</sub>. (I) (1 mol.) and SOCl<sub>2</sub> (1.5 mols.) gives the best yields of (II).

J. L. D.

**Dehydrogenation with ethyl peroxide catalysed by iron.**—See this vol., 370.

**Compounds of bivalent carbon. VIII. Action of ethyl formate on sodium triphenylmethyl.** H. SCHLEIBLER and H. COBLER (Ber., 1934, 67, [B], 314—317; cf. this vol., 390).—HCO<sub>2</sub>Et behaves as an enolisable ester towards CPh<sub>3</sub>Na in Et<sub>2</sub>O giving CHPh<sub>3</sub> and a colourless cryst. ppt. hydrolysed by H<sub>2</sub>O to NaOH, HCO<sub>2</sub>Na, and NaHCO<sub>3</sub>. The mechanism of the change is discussed.

H. W.

**Acid iodides. III. Addition of acetyl iodide to unsaturated hydrocarbons.** P. G. STEVENS (J. Amer. Chem. Soc., 1934, 56, 450—452).—Prolonged interaction of CMe<sub>2</sub>:CHMe (I) and AcI at 25° in the dark gives a product, b.p. 25°/1 mm., containing 40.4% I, which with Et<sub>2</sub>O-NPhMe<sub>2</sub> affords a little  $\beta\gamma$ -dimethyl- $\Delta^2$ -penten- $\delta$ -one [*semicarbazone*, m.p. 184—185° (sinters at 183°)]. This is also obtained from (I), AcCl, and SnCl<sub>4</sub> in CS<sub>2</sub> and from COMe<sub>2</sub>, COMeEt, and HCl; in both cases the initial product is treated with NPhMe<sub>2</sub>. cycloHexene and AcI similarly give tetrahydroacetophenone, whilst thiophen at -15° to 0° affords much I, tarry material, and a little 2-acetothienone. C<sub>6</sub>H<sub>6</sub>, stilbene, and  $\Delta^2$ - and *iso*-butenes react with AcI at 25°, but the products could not be identified; cyclohexane and CHCl:CHCl do not react.

H. B.

**Reactions of chromous acetate.**—See this vol., 377.

**Properties of pure deutacetic acid.** G. N. LEWIS and P. W. SCHUTZ (J. Amer. Chem. Soc., 1934, 56, 493—494).—AcOH<sup>2</sup>, prepared by reaction of H<sup>2</sup>Cl

and AcOAg, has m.p. 13.3° and *d* 1.096. The v.p. at 50° is 7.5% > for AcOH, and 3% higher at 90°. No H<sup>2</sup> is attached to the C.

E. S. H.

**Constitution of coccerin.** A. C. CHIBNALL, A. L. LATNER, E. F. WILLIAMS, and C. A. AYRE (Biochem. J., 1934, 28, 313—325).—Coccerin (Liebermann, A., 1885, 1045) is a mixture of waxes. Extraction of the wax with EtOH-C<sub>6</sub>H<sub>6</sub> gives a least sol. fraction, m.p. 106—106.5° (corr.), which on successive hydrolysis with EtOH-KOH in C<sub>6</sub>H<sub>6</sub> and EtOH-NaOEt in C<sub>6</sub>H<sub>6</sub> (the fatty acids must be removed after each treatment as Ca salts) affords cocceryl alcohol, which, contrary to Liebermann and Bergami (A., 1887, 650) and Becker (A., 1931, 1321), is *o*-keto-*n*-tetra-triacontanol (I), m.p. 100.5—100.7° (corr.) [acetate, m.p. 80.9—81.3° (corr.); oxime, m.p. 74.5—75°]. (I) is reduced (Clemmensen) to *n*-tetra-triacontanol, m.p. 91.9—92.2° (corr.), and thence (through the iodide) to *n*-tetra-triacontane. Oxidation (CrO<sub>3</sub>, AcOH) of (I) gives  $\xi$ -keto-*n*-tetra-triacontanoic acid, m.p. 106.5—107° (corr.), the oxime, m.p. 62.5—63°, of which is converted by conc. H<sub>2</sub>SO<sub>4</sub> at 100° and subsequent hydrolysis (conc. HCl at 180°) into *n*-nonadecylamine (II) (*hydrochloride*; benzoate, m.p. 88°), and *n*-eicosanoic (III),  $\nu$ -amino-tetradecic, m.p. 181—182° (*hydrochloride*, m.p. 168°), and tridecamethylene- $\alpha\omega$ -dicarboxylic acids. (I) is reduced (Na, amyl alcohol) to *n*-tetra-triacontane- $\alpha$ -diol, m.p. 98.9—99.1° (corr.) [*diacetate*, molten at 49°, clear at 50—51° (corr.)]. Coccerin acid (*loc. cit.*) is a mixture of *n*-triacontanoic, m.p. 93.6° (corr.), and  $\mu$ -keto-*n*-dotriacontanoic acid (IV), m.p. 104.5—105° (corr.), separable by oximation and fractionation with COMe<sub>2</sub>. The oxime, m.p. 56—57°, of (IV) is converted (as above) into (II), (III), and undecane- $\alpha$ -dicarboxylic and  $\lambda$ -aminododecic acid, m.p. 183° (*hydrochloride*, m.p. 163°). (IV) is synthesised by Robinson's method (A., 1930, 742) from Et sodio- $\alpha$ -ketoundecane- $\alpha\lambda$ -dicarboxylate and *n*-eicosanoyl chloride. The generic relationship between (I), (IV), and *n*-nonacosan- $\alpha$ -ol (A., 1932, 250) is discussed briefly. The conclusions of Schulz and Becker (A., 1931, 975) regarding the acid and alcohol [probably identical with (I)] from the wax of *Pemphigus xylostei* are criticised.

H. B.

**Oxidation of some  $\alpha$ -hydroxy-acids with lead tetra-acetate.** H. ŌEDA (Bull. Chem. Soc. Japan, 1934, 9, 8—14).—The following  $\alpha$ -OH-acids are oxidised to the aldehyde: lactic acid to MeCHO, leucic acid to isovaleraldehyde, mandelic acid to PhCHO,  $\alpha$ -hydroxy- $\beta$ -phenyl- and - $\beta$ -*p*-hydroxyphenyl-propionic acid to CH<sub>2</sub>Ph-CHO and *p*-hydroxyphenylacetaldehyde (*p*-nitrophenylhydrazone, m.p. 165°). F. R. S.

**Micro-determination of acetyl and hydroxyl in fatty acids.** O. FÜRTH, H. KAUNITZ, and M. STEIN (Biochem. Z., 1934, 268, 189—201).—OAc or OH in about 0.1 g. of material (*e.g.*, OH-acids separated from fats by hydrolysis with conc. HCl) is determined by a modification of the method of Friedrich *et al.* (A., 1932, 1051), the process being carried out in N<sub>2</sub>. The vals. for cod-liver oil, dog fat, and human fat are, respectively, 32—33, 9.5—12.3, 25—27.

W. McC.

**Anodic oxidation of lactic to pyruvic ion.**—See this vol., 373.

**Polymerisation and ring formation. XXIII.  $\epsilon$ -Hexolactone and its polymerides.** F. J. VAN NATTA, J. W. HILL, and W. H. CAROTHERS (J. Amer. Chem. Soc., 1934, 56, 455—457).—Crude  $\epsilon$ -hydroxyhexoic acid (I) (obtained as a by-product in the reduction of Et adipate) is converted into  $\epsilon$ -acetoxyhexoic acid, which is hydrolysed to a mixture (A) of (I) (80%) and  $\epsilon$ -hexolactone (II) (20%), b.p. 98—99°/2 mm., m.p. about -5°. When (A) is heated to 150—210°, (I) and a little of the dimeric lactone (III), m.p. 112—113°, are produced; (III) contains a 14-membered ring. (II) polymerises at 150° (sealed tube) to a linear polyester (IV),  $\text{OH}\cdot([\text{C}_6\text{H}_{10}\text{CO}]_n)_n\cdot\text{H}$ , m.p. 53—55°,  $M$  3660, 4300, which is depolymerised to a slight extent at 250°/1—2 mm. (mol. still).  $\epsilon$ -Bromohexoic acid and EtOH-NaOEt (1 equiv.) give (cf. Marvel and Birkheimer, A., 1929, 295) Et  $\epsilon$ -hydroxyhexoate (V), b.p. 104—106°/4 mm., (III), and a polyester (VI), m.p. 51—53°,  $M$  1660, 1980, which resembles (IV). (II)—(VI) are all converted by  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  into  $\epsilon$ -hydroxyhexohydrazide, m.p. 114—115°. H. B.

**Synthesis of succinic acid.** M. S. ROSHDESTVENSKI, E. A. SLASTENINA, and N. O. VALTER (Khim. Farm. Prom., 1933, 117—120).—Technical tartaric acid (960 g.), red P (240 g.), I (144 g.), and 96% AcOH (960 c.c.) are heated slowly, with agitation, to 100—105°. The temp. is then raised to 140°, the mixture refluxed for 3 hr., most of the AcOH distilled off, the mixture dissolved in  $\text{H}_2\text{O}$ , and filtered with active C. Succinic acid which separates on cooling the filtrate is washed with  $\text{H}_2\text{O}$  at 4°. CH. ABS.

**Ready rupture of the carbon chain of a succinic acid derivative.** K. VON AUWERS and O. UNGEMACH (Ber., 1934, 67, [B], 249—252).— $\alpha$ -Acetoxy- $\alpha\beta$ -trimethylsuccino-*p*-tolil (I), m.p. 131°, is converted by NaOH into *isobutyro-p*-toluidide, m.p. 108°, and hydroxytrimethylsuccino-*p*-toluidic acid (II), m.p. 155—156°, showing the structure of the latter to be  $\text{CO}_2\text{H}\cdot\text{CMe}(\text{OH})\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$ . The Ac group of (I) appears very labile, since it is partly removed by the action of 1 mol. of KOH at 0° and (II) results when acetoxytrimethylsuccinic anhydride is treated with excess of *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$  in  $\text{C}_6\text{H}_6$ . H. W.

**Citrate derivatives and their properties.** W. E. DONALDSON and R. F. McCLEARY [with E. F. DEGERING] (J. Amer. Chem. Soc., 1934, 56, 459—460).— $\text{Me}_3$  citrate, b.p. 98°/0.2 mm. (0.1 mol.),  $\text{Bu}^n\text{OH}$  (0.15 mol.), and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$  (I) (0.1 g.) boiled for 24 hr. give about 86% of *Me\_2 Bu^c* citrate, b.p. 111°/0.08 mm.; the *Me\_2 Pr*, b.p. 106°/0.05 mm., and *Me\_2 amyl*, b.p. 121°/0.2 mm., esters are similarly prepared. The catalytic effect of (I),  $\text{PhSO}_3\text{H}$ , and *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$  decreases in the order quoted;  $\alpha$ -naphthol-4-sulphonic acid is inactive. H. B.

**Pyrophosphate of citric acid.** E. WERTYPROOH and H. KICKENBERG (Biochem. Z., 1934, 268, 8—16).— $\text{Et}_2\text{O}$  reacts with  $\text{P}_2\text{O}_5$  to give the anhydride of diethylpyrophosphoric acid  $(\text{OEt})_2\text{PO}\cdot\text{O}\cdot\text{PO}(\text{OH})_2$  (I) [*Ca*, *Na*, and *brucine*, m.p. 215° (decomp.), salts], and a small amount of  $\text{EtOPO}_2$ . (I) heated with citric acid yields an oily citrate (II) (*Ca*, *Ba*, and *brucine*, m.p. 142—143°, salts), H being eliminated from the

OH of (II) and OH from (I). Acid hydrolysis of (II) yields aconitic acid. Tartaric and malic acids appear to yield similar pyrophosphates. W. McC.

**Glucosonic ( $\alpha$ -ketogluconic) acid. III. Constitution of compounds of sugars with *o*-phenylenediamine.** H. OHLE (Ber., 1934, 67, [B], 155—162; cf. A., 1930, 744).—The compound described (*loc. cit.*) as Na  $\alpha$ -ketogluconate (I) is Na glucosaccharonate. (I) crystallises with  $1\text{H}_2\text{O}$ ,  $[\alpha]_D^{20}$  -83.0° to -75.24° in  $\text{H}_2\text{O}$ . *Me*  $\alpha$ -ketogluconate has m.p. 187°,  $[\alpha]_D^{20}$  -80.36° to -70.93° in  $\text{MeOH}\cdot\text{H}_2\text{O}$  (1 : 3). Pure  $\alpha$ -ketogluconates do not immediately reduce cold Fehling's solution and do not decolorise I in acid solution or react with cold KOI.  $\alpha$ -Ketogluconic acid and *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$  in  $\text{H}_2\text{O}$  at 15—20° afford 2-hydroxy-3-*d*-arabotetrahydroxybutylquinoxaline (II),

$\text{N}:\text{C}(\text{OH})\text{C}(\text{OH})_3\cdot\text{CH}_2\cdot\text{OH}$ , m.p. 199—200° (decomp.),  $[\alpha]_D^{20}$  -87.5° in *N*-NaOH (*tetra-acetate*, m.p. 170.5—171.5°,  $[\alpha]_D^{20}$  -17.38° in  $\text{CHCl}_3$ ), oxidised by  $\text{KMnO}_4$  to dihydroxyquinoxaline. The reducing action of (II) is due to fission of the mol. since treatment with  $\text{NHPh}\cdot\text{NH}_2$  in boiling  $\text{H}_2\text{O}$  leads to 2-hydroxyquinoxaline-3-aldehydephenylhydrazone (III), m.p. 278—279°, and glycerol contaminated with the phenylsazone of methylglyoxal or glyceraldehyde. (III) is obtained by condensing dibromopyruvic acid with *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$  in EtOH or  $\text{H}_2\text{O}$  at room temp. to 2-hydroxy-3-dibromomethylquinoxaline, m.p. 250° (decomp.), which is treated with  $\text{NHPh}\cdot\text{NH}_2$  in boiling 50% EtOH. Fructose and *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$  yield 3-*d*-arabotetrahydroxybutylquinoxaline, m.p. 187—188° (decomp.),  $[\alpha]_D^{20}$  -75.2° in 5*N*-HCl, identical with that derived from glucose and behaving qualitatively like (II); the *tetra-acetate* has m.p. 120°,  $[\alpha]_D^{20}$  -30.32° in  $\text{CHCl}_3$ . On the other hand, the product from *l*-arabinose and *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$  is *l*-arabotetrahydroxybutylbenzimidazole,  $\text{C}_6\text{H}_4\text{C}(\text{NH})_2\text{C}(\text{OH})_3\cdot\text{CH}_2\cdot\text{OH}$ , m.p. 234° (decomp.),  $[\alpha]_D^{20}$  -51.96° in 5*N*-HCl, since it is stable towards Fehling's solution, KOI, and  $\text{NHPh}\cdot\text{NH}_2$ ; the *tetra-acetate* has m.p. 141—142°.

H. W.

***d*-Glucosaccharosonic acid, an isomeride of ascorbic acid. I. Preparation and properties.** H. OHLE, H. ERLBACH, and H. CARLS (Ber., 1934, 67, [B], 324—332; cf. A., 1930, 744).—Hydrolysis of *Me*  $\alpha$ -ketogluconate (I) to *d*-glucosaccharosonic acid (II),  $\text{C}_6\text{H}_8\text{O}_6$ , is effected at 60—70° by alkali if added so that the solution is neutral to neutral-red, by alkali carbonate or phosphate, by  $\text{C}_5\text{H}_5\text{N}\cdot\text{H}_2\text{O}$  (not by  $\text{C}_5\text{H}_5\text{N}$  or  $\text{C}_5\text{H}_5\text{N}\cdot\text{EtOH}$ ), or best by  $\text{NaHCO}_3$ . Reaction is confined to (I) and the lactone; (II) is not obtained from  $\alpha$ -ketogluconates and alkali or from  $\alpha$ -ketogluconic acid and  $\text{H}_2\text{O}$  or by hydrolysis of triacetyl- $\alpha$ -ketogluconolactone (III). (II) is obtained in 50% yield from (III) and NaOMe. Na *d*-glucosaccharosonate has  $[\alpha]_D^{20}$  +94° to +100° in  $\text{H}_2\text{O}$ , variations being caused by differences in  $p_{\text{H}}$  of the solution. (II) (cf. Maurer *et al.*, A., 1933, 936) has m.p. 166°,  $[\alpha]_D^{20}$  -18.5° in  $\text{H}_2\text{O}$ ,  $[\alpha]_D^{20}$  +7.66° in  $\text{COMe}_2$ ; the *brucine* salt (?+ $\text{H}_2\text{O}$ ), m.p. 220° (decomp.),  $[\alpha]_D^{20}$  +6.25° in  $\text{H}_2\text{O}$ , *cinchonine* salt, m.p. 221—222° (decomp.), and amorphous *Pb* salt are described.

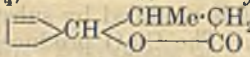
(II) has antiscorbutic action. It gives non-cryst. products when acetylated, and is not esterified by MeOH or EtOH. The oily product with  $\text{CH}_2\text{N}_2$  does not give a cryst. acetate or react with  $\text{COMe}_2$ . (II) does not afford a  $\text{-CPh}_3$  or  $\text{:CMe}_2$  derivative. 5-OH therefore appears to be replaced by cyclic O. (II) is very stable towards acid, but boiling  $5N\text{-HCl}$  or  $\text{-H}_2\text{SO}_4$  causes loss of  $\text{CO}_2$  and production of furfuraldehyde. Reducing power of the Na salt in  $\text{H}_2\text{O}$  towards I at  $20^\circ$  gradually diminishes and ultimately disappears. (II) in  $\text{H}_2\text{O}$  or AcOH or the Na salt in  $\text{H}_2\text{O}$  is not reduced ( $\text{Pd-BaSO}_4$ ). Oxidation by  $\text{H}_2\text{O}_2$  or  $\text{KMnO}_4$  is not sp. According to Willstätter and Schudel, (II) reduces  $2\text{NaOI}$  and then has no action on Fehling's solution. At higher concn. less NaOI is consumed and  $\text{H}_2\text{C}_2\text{O}_4$  is produced. Oxidation with  $\text{Ag}_2\text{O}$  is vigorous, yielding  $\text{CO}_2$ ,  $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , AcOH, and small amounts of a non-reducing, optically active material. H. W.

**Optically active  $\beta$ -thiodipropionic acid.** A. FREDGA (Svensk Kem. Tidskr., 1934, 46, 10—15).—Resolution of *dl*- $\beta$ -thiodipropionic acid,  $\text{S}(\text{CHMe}\cdot\text{CO}_2\text{H})_2$ , is effected by fractional crystallisation of its quinine salt to give the quinine salt,  $+1\cdot25\text{H}_2\text{O}$  and anhyd. (35%), of the *d*-acid,  $[\alpha]_D^{20} +200\cdot5$ , and the quinine salt,  $+1\cdot25\text{H}_2\text{O}$  and anhyd. (49%), of the *l*-acid,  $[\alpha]_D^{20} -204\cdot3$ . J. W. B.

**Amido- and imido-chlorides of non-aromatic acids.** VIII. Preparation of  $\alpha\beta$ -unsaturated aldehydes. J. VON BRAUN and W. RUDOLPH [with H. KRÖPER and W. PINKERNELLE] (Ber., 1934, 67, [B], 269—281; cf. A., 1932, 371).—The unsuitability of imidochlorides of aliphatic acids for further transformations is attributed to the readiness of the change  $\text{:CH}\cdot\text{CCl}\cdot\text{NR} \rightarrow \text{:C}\cdot\text{CCl}\cdot\text{NHR}$  followed by condensations due to NH. With compounds  $\text{:C}\cdot\text{CH}\cdot\text{CCl}\cdot\text{NR}$  such change is impeded by the general difficulty of producing the type  $\text{:C}\cdot\text{C}\cdot\text{CCl}\cdot\text{NHR}$ , and these substances are reduced to  $\alpha\beta$ -unsaturated aldehydes by  $\text{CrCl}_2$ , but not by Dimroth's reagent.  $\text{Cr}(\text{OAc})_2$  washed with MeOH and  $\text{Et}_2\text{O}$  is turbined with  $2\text{—}3N\text{-HCl-Et}_2\text{O}$ , whereby  $\text{CrCl}_2$  is pptd.; the imidochloride in  $\text{Et}_2\text{O}$  or  $\text{C}_6\text{H}_6$  is gradually added to the well-stirred mixture, which is finally treated with dil.  $\text{H}_2\text{SO}_4$  and distilled. Benzanilide- and cinnamyl-anilide-imidochloride yield PhCHO and  $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$  in  $>80\%$  yield.  $\text{BzCl}$  and  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{COCl}$  are unattacked.  $\beta$ -Phenylpropion-anilide and *o*-toluidide, m.p.  $123^\circ$ , are converted by very cautious treatment with  $\text{PCl}_5$  in  $\text{C}_6\text{H}_6$  into the corresponding cryst. imidochlorides [amidine  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{C}(\text{NPh})\cdot\text{NHP}$ , m.p.  $212^\circ$ ], which are not appreciably reduced. Campholyl chloride, campholyl-*N*-ethylimidochloride, b.p.  $125^\circ/12$  mm. (from campholethylamide, m.p.  $88^\circ$ , and  $\text{PCl}_5$ ), and the phenylimidochloride, b.p.  $163^\circ/10$  mm., are resistant.  $\Delta^a$ -Hexenoanilide, m.p.  $109^\circ$ , yields a very unstable imidochloride. The imidochloride, b.p.  $120^\circ/0\cdot07$  mm., of  $\Delta^a$ -hexeno-*o*-toluidide, m.p.  $125^\circ$ , is reduced by  $\text{CrCl}_2$  to  $\Delta^a$ -hexenaldehyde, b.p.  $43^\circ/12$  mm., in 50% yield (*p*-nitrophenylhydrazone, m.p.  $137^\circ$ ; semicarbazone, m.p.  $173^\circ$ ).  $\Delta^a$ -Nonenoic acid [from heptaldehyde and  $\text{CH}_2(\text{CO}_2\text{H})_2$ ] yields successively the corresponding chloride, b.p.  $70\text{—}72^\circ/0\cdot4$  mm.,

anilide, b.p.  $182\text{—}184^\circ/1$  mm., m.p.  $50\text{—}51^\circ$ , non-cryst. imidochloride, and  $\Delta^a$ -nonenaldehyde, b.p.  $92^\circ/12$  mm. (*p*-nitrophenylhydrazone, m.p.  $109^\circ$ ; semicarbazone, m.p.  $163^\circ$ ).  $\Delta^a$ -Nonenoamide is transformed by  $\text{POCl}_3$  in  $\text{C}_6\text{H}_6$  into  $\Delta^a$ -nonenonitrile, b.p.  $100\text{—}102^\circ/12$  mm. (yield 85%), which is indifferent towards  $\text{SnCl}_2 + \text{HCl}$  and  $\text{CrCl}_2$ .  $\alpha$ -Phenylacrylyl chloride, b.p.  $87\text{—}88^\circ/0\cdot35$  mm., is prepared in 75% yield from the acid and  $\text{SOCl}_2$  (2 mols.) or in 40% yield from tropic acid and  $\text{SOCl}_2$  followed by distillation. The corresponding anilide, m.p.  $134^\circ$ , yields the unstable imidochloride, reduced by  $\text{SnCl}_2$  and  $\text{CrCl}_2$  to  $\alpha$ -phenylacetaldehyde (semicarbazone, m.p.  $148^\circ$ ) in 5% and 25—30% yield, respectively. Me  $\delta$ -methylamyl ketone, obtained by reduction of methylheptenone, is converted by Zn and  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$  into *Et*  $\beta$ -hydroxy- $\beta\zeta$ -dimethyloctate, b.p.  $131^\circ/11$  mm. (80% yield); the corresponding OH-acid, b.p.  $172^\circ/11$  mm., is transformed by NaOAc and boiling  $\text{Ac}_2\text{O}$  into  $\beta\zeta$ -dimethyl- $\Delta^a$ -octenoic (dihydrogeronic) acid, b.p.  $145\text{—}147^\circ/11$  mm.  $\beta\zeta$ -Dimethyl- $\Delta^a$ -octenoyl chloride yields the (sterically non-homogeneous) anilide, b.p.  $190\text{—}192^\circ/0\cdot3$  mm., m.p.  $36\text{—}54^\circ$ , and *o*-toluidide, b.p.  $165\text{—}166^\circ/0\cdot1$  mm., m.p.  $60\text{—}74^\circ$ , the cryst. imidochloride of the former being reduced ( $\text{CrCl}_2$ ) to  $\beta\zeta$ -dimethyl- $\Delta^a$ -octenaldehyde, b.p.  $96\text{—}98^\circ/12$  mm. (semicarbazone, m.p.  $141\text{—}145^\circ$ ; *p*-nitrophenylhydrazone, m.p.  $104\text{—}109^\circ$ ).

Chloro- $\Delta^2$ -cyclopentene (from cyclopentadiene and 30%  $\text{HCl-PhMe}$ ) is converted into *Et*  $\Delta^2$ -cyclopentenylacetate, b.p.  $130^\circ/16$  mm., transformed by 10%  $\text{KOH-H}_2\text{O}$  into cyclopentenylacetone (I), b.p.  $67^\circ/12$  mm. (semicarbazone, m.p.  $150^\circ$ ; oxime, m.p.  $86\text{—}87^\circ$ ). (I), Zn, and  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$  yield *Et*  $\beta$ -hydroxy- $\gamma$ - $\Delta^2$ -cyclopentenyl- $\beta$ -methylbutyrate, b.p.  $151^\circ/19$  mm.  $\beta$ -Hydroxy- $\gamma$ - $\Delta^2$ -cyclopentenyl- $\beta$ -methylbutyric acid, b.p.  $170^\circ/0\cdot6$  mm., NaOAc, and boiling  $\text{Ac}_2\text{O}$  afford (sterically non-homogeneous)  $\gamma$ -cyclopentenyl- $\beta$ -methylcrotonic acid (II), b.p.  $160\text{—}161^\circ/13$  mm., from which are prepared the corresponding chloride, b.p.  $82\text{—}85^\circ/0\cdot5$  mm., *Et* ester, b.p.  $123^\circ/13$  mm., amide, b.p.  $157^\circ/0\cdot1$  mm., m.p.  $34\text{—}41^\circ$ , anilide (III), b.p.  $193\text{—}195^\circ/0\cdot35$  mm., and  $\gamma$ -cyclopentenyl- $\beta$ -methylbutyric acid, b.p.  $150^\circ/13$  mm. (II) is unaffected by 70%  $\text{H}_2\text{SO}_4$ , but transformed by conc.

$\text{H}_2\text{SO}_4$  into the lactone , m.p.  $39^\circ$  (*H*<sub>2</sub>-derivative, b.p.  $144^\circ/13$  mm.). (III) is transformed into the imidochloride, reduced ( $\text{CrCl}_2$ ) to  $\gamma$ - $\Delta^2$ -cyclopentenyl- $\beta$ -methyl- $\Delta^a$ -butenal, b.p.  $108\text{—}110^\circ/12$  mm. [semicarbazone, m.p. (indef.)  $139\text{—}145^\circ$ ; *p*-nitrophenylhydrazone, m.p. about  $140^\circ$ ].  $\delta\delta$ -Dimethyl- $\Delta^{\alpha\gamma\eta}$ -decatrienoic acid is converted successively into the chloride, anilide, b.p.  $210^\circ/0\cdot1$  mm., imidochloride, and  $\delta\delta$ -dimethyl- $\Delta^{\alpha\gamma\eta}$ -decatrienal (semicarbazone, m.p.  $125\text{—}150^\circ$ ). The odours of the aldehydes are described. H. W.

**Acidic nature of aqueous formaldehyde solutions.** M. WADANO (Ber., 1934, 67, [B], 191—197).—Potentiometric titration with  $0\cdot02N\text{-NaOH}$  of solutions of  $\text{CH}_2\text{O}$  obtained by subliming paraformaldehyde or  $\alpha$ -polyoxymethylene into conductivity  $\text{H}_2\text{O}$  at  $0^\circ$  shows the presence of  $\text{HCO}_2\text{H}$  in small amount. After making the requisite allowance

for this, the acid dissociation const. of  $\text{CH}_2\text{O}$  is  $1.62 \times 10^{-13}$  at  $23^\circ$ . The basic properties of  $\text{CH}_2\text{O}$  are insufficiently marked to permit potentiometric measurement.

H. W.

**Determination of acetone.** R. GROS (J. Pharm. Chim., 1934, [viii], 19, 214—220).— $\text{COMe}_2$  (I) is determined in aq. solution by distilling the vapour into a modified Nessler solution contained in an absorption pipette; the yellow ppt. is collected in a sintered-glass crucible and weighed. The method is satisfactory for the determination of (I) in urine and blood.

C. G. A.

**Introduction of deuterium atoms into acetone.** J. O. HALFORD, L. C. ANDERSON, and J. R. BATES (J. Amer. Chem. Soc., 1934, 56, 491—492).— $\text{H}^1$  in  $\text{COMe}_2$  is replaced by  $\text{H}^2$  when  $\text{COMe}_2$  is warmed with  $\text{H}_2\text{O}$  containing  $\text{H}_2^{18}\text{O}$  and a small amount of  $\text{K}_2\text{CO}_3$ . The change has been followed by determining the decrease in  $d$  of  $\text{H}_2\text{O}$  and the increase in  $d$  of  $\text{COMe}_2$ .

E. S. H.

**Aliphatic ketyls of metals. II.** I. N. NAZAROV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 123—126).—Di- and tri-ethylpinacolins are converted by Na into  $\text{CMe}_3\text{C}(\text{ONa})\text{CHEt}_2$  and  $\text{CMe}_3\text{C}(\text{ONa})\text{CET}_3$  (I), which slowly associate to yield the corresponding pinacone salts. (I) is comparatively very stable, not being completely associated after 3 months.

R. T.

**Preparation of diethoxyacetone and  $\beta$ -substituted glycerol  $\alpha\gamma$ -diethers.** G. DARZENS and M. MEYER (Compt. rend., 1934, 198, 478—480).— $\text{OEt}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  and  $\text{NaOEt}$  in  $\text{PhMe}$  give a 75% yield of  $\text{OEt}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{OEt})\cdot\text{CO}_2\text{Et}$ , which with hot aq.  $\text{K}_2\text{CO}_3$  gives an 85% yield of diethoxyacetone, b.p.  $195^\circ/760$  mm.,  $94\text{--}95^\circ/15$  mm. (semicarbazone, m.p.  $91^\circ$ ), whence by Grignard reagents are obtained good yields of the following  $\beta$ -substituted glycerol  $\alpha\gamma$ - $\text{Et}_2$  ethers: *Me*, b.p.  $73\text{--}74^\circ/20$  mm., *Bu*, b.p.  $110^\circ/25$  mm., *CH}\_2\text{Ph}*, b.p.  $154^\circ/5$  mm., *p-OEt-C}\_6\text{H}\_4*, b.p.  $149^\circ/2$  mm., and cyclohexyl, b.p.  $160^\circ/15$  mm.

R. S. C.

**Micro-method for detection of monoses in presence of reducing bioses.** H. TAUBER (Mikrochem., 1934, 14, 167—169).—The Barfoed  $\text{Cu}(\text{OAc})_2$  reagent is modified by substitution of lactic acid for  $\text{AcOH}$ . The  $\text{Cu}_2\text{O}$  produced by monoses is treated with  $\text{Na}_2\text{MoO}_4$ , giving a blue coloration proportional to the amount of reducing sugar.

J. S. A.

**Inhibition of oxidation of phenylhydrazine [in the preparation of glucosazone].** R. H. HAMILTON, jun. (J. Amer. Chem. Soc., 1934, 56, 487).—Glucosazone, unaccompanied by tarry material, is obtained from glucose (1 mg.), 50%  $\text{AcOH}$  saturated with  $\text{NaOAc}$  (1 c.c.), 50%  $\text{NaHSO}_3$  (1 c.c.),  $\text{NHPh}\cdot\text{NH}_2$  (0.1 c.c.), and  $\text{H}_2\text{O}$  (8 c.c.); in absence of  $\text{NaHSO}_3$ , the reaction must be carried out in evacuated sealed tubes.

H. B.

**Crystallisation of osazones and hydrazones as a means of identifying different sugars.** M. WAGENAAR (Pharm. Weekblad, 1934, 71, 229—242).—Using a solution of  $\text{NHPh}\cdot\text{NH}_2$  in glycerol- $\text{AcOH}$  (2:1) containing a trace of  $\text{NaHSO}_3$ , crystals suitable for microscopic identification are obtained with

pentoses (I) and hexoses but not with bioses and trioses.  $\text{NPhMe}\cdot\text{NH}_2$  gives a glucosazone with fructose (II) and not with glucose, and cryst. hydrazones with (I), mannose (III), and galactose.  $\text{NPh}_2\cdot\text{NH}_2$  gives hydrazones with (I) and an osazone with rhamnose, but fails with other sugars.

*p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$  and *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}\cdot\text{NH}_2$  react only with (III). Less satisfactory results are obtained if citric or oleic acid is used instead of  $\text{AcOH}$ , but with lactic acid, maltose, cellobiose, melibiose, and raffinose also give phenylosazones. Only (II) and (III) react in the absence of acid.

S. C.

**Nucleic acids. III. Ring structure of ribose in yeast-nucleic acid.** H. BREDERECK (Z. physiol. Chem., 1934, 223, 61—65; cf. A., 1933, 261).—With  $\text{CPh}_3\text{Cl}$  in  $\text{C}_5\text{H}_5\text{N}$ , cytidine (I), adenosine (II), and inosine (III) afford triphenylmethyl-cytidine (IV), m.p.  $255\text{--}257^\circ$  (corr.) (+ $\text{EtOH}$ ),  $[\alpha]_D^{20} -0.7^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ , -adenosine (V), m.p.  $255\text{--}258^\circ$  (corr.),  $[\alpha]_D^{20} -8.7$  in  $\text{CHCl}_3$ , and -inosine, m.p.  $231\text{--}232^\circ$  (corr.). (IV) and (V) are not hydrolysed by  $\text{KOH}$  in  $\text{EtOH}$ , indicating that the  $\text{CPh}_3$  radical is not attached to N. Hence the ribose in (I), (II), and (III) has the furanose structure.

J. H. B.

**Isolation of a crystalline dimethylanhydro-methylhexoside. Characterisation of 3:4:6-trimethylglucose.** W. N. HAWORTH, E. L. HIRST, and L. PANIZZON (J.C.S., 1934, 154—157).—2-*p*-Toluenesulphonyl- $\beta$ -methylglucoside (I) is converted by  $\text{MeI}$  and  $\text{Ag}_2\text{O}$  in  $\text{MeOH}$  into the 3:4:6- $\text{Me}_3$  derivative, m.p.  $67^\circ$ ,  $[\alpha]_D -16^\circ$  in  $\text{CHCl}_3$ , hydrolysed by 4%  $\text{NaOMe}$  at the b.p. to 3:4:6-trimethyl- $\beta$ -methylglucoside, m.p.  $51^\circ$ , b.p.  $95^\circ/0.04$  mm.,  $[\alpha]_D^{20} -20^\circ$  in  $\text{CHCl}_3$ , and further hydrolysed by 5% aq.  $\text{HCl}$  to 3:4:6-trimethylglucose,  $[\alpha]_D^{20} +71^\circ$  in  $\text{H}_2\text{O}$ . This is oxidised by  $\text{Br}\text{--}\text{H}_2\text{O}$  at  $35^\circ$  to (8-)3:4:6-trimethylgluconolactone, b.p.  $140^\circ/0.1$  mm. (phenylhydrazide of the acid, m.p.  $126^\circ$ ). The corresponding acid amide gives a positive Weerman reaction and with  $\text{NaOCl}$  gives 2:3:5-trimethyl-*d*-arabofuranose, identified by oxidation to 2:3:5-trimethyl-*d*-arabonolactone. De-acetylation of the  $\text{Ac}_3$  derivative of (I) with  $\text{NaOMe}$  in  $\text{CHCl}_3$  at  $0^\circ$  gives an anhydro- $\beta$ -methylhexoside,  $[\alpha]_D^{20} -25^\circ$  in  $\text{H}_2\text{O}$  [*Me}\_2* ether, m.p.  $69^\circ$ ,  $[\alpha]_D^{20} +24^\circ$  in  $\text{H}_2\text{O}$ ; this is non-reducing, but with hot 5%  $\text{HCl}$  gives the strongly reducing (?) dimethylanhydrohexose], which with 5%  $\text{HCl}$  at  $95^\circ$  gives a strongly reducing product,  $[\alpha]_D^{20} -77^\circ$ .

H. A. P.

**Action of pyridine-acetic anhydride on aldose oximes. Production of hexa-acetylaldomannoseoxime.** V. DEULOFEU, P. CATTANEO, and G. MENDIVELZUA (J.C.S., 1934, 147—148).—With  $\text{Ac}_2\text{O}\text{--}\text{C}_5\text{H}_5\text{N}$  arabinose-, xylose-, and rhamnose-oximes give only the  $\text{Ac}_4$  derivatives of the corresponding nitriles even at  $0^\circ$ ; glucose- and mannose-oximes at  $0^\circ$  give the  $\text{Ac}_6$  derivatives and at  $>70^\circ$  and  $>30^\circ$ , respectively, only the corresponding penta-acetylnitriles. Hexa-acetylaldomannoseoxime has m.p.  $94^\circ$ ,  $[\alpha]_D^{20} -8.3^\circ$  in  $\text{CHCl}_3$ .

H. A. P.

**Sulphonation of sucrose.** T. SODA (Bull. Chem. Soc. Japan, 1934, 9, 1—8).—Sulphonation of sucrose with  $\text{ClSO}_3\text{H}$  in  $\text{C}_5\text{H}_5\text{N}$  gives a disaccharidesulphonic acid, which examination of the Ba and brucine salts



shows to be a variable mixture of mono-, di-, tri-, and tetra-derivatives. Fermentation of the acid affords a salt,  $C_6H_{11}O_6 \cdot SO_3K$ ,  $[\alpha]_D +26.5^\circ$ , with no mutarotation. The glucose end of the mol. is probably chiefly glucose-6-monosulphonic acid. F. R. S.

**Constitution of picrocrocin and its relationship to the carotene pigments of saffron.** R. KUHN and A. WINTERSTEIN (Ber., 1934, 67, [B], 344—357; cf. Kayser, A., 1885, 59; Winterstein *et al.*, A., 1922, i, 563).—Picrocrocin (I), m.p.  $156^\circ$ ,  $[\alpha]_D^{20} -58^\circ$  in  $H_2O$  (corr.; Berl; decomp.), obtained from *Safran electus* in which lycopene,  $\beta$ - and  $\gamma$ -carotene, zeaxanthin, and hentriacontane are also identified, is  $C_{16}H_{26}O_7$ . Its hydrolysis by acid or alkali occurs without addition of  $H_2O$ , giving exclusively *d*-glucose (identified as the penta-acetate and through its sp. rotation) and *safranal* (II). The reactions of fructose (*loc. cit.*) are attributed to accompanying glucosides. (I) reddens fuchsin- $H_2SO_3$  and reduces  $Ag-NH_3$  solution. Hence it is an aldehyde, and as (II) is also aldehydic, CHO is not involved in the union of the glucose. (I) is transformed by  $Ac_2O-C_5H_5N$  into *picrocrocin tetra-acetate*, m.p.  $142-143^\circ$  (corr.; Berl),  $[\alpha]_D^{20} -31.8^\circ$  in  $CHCl_3$  [*semicarbazone*,  $C_{25}H_{37}O_{11}N_3$ , m.p.  $106^\circ$  (corr.; Berl)], which absorbs  $2H_2$  (Pt- $SiO_2$  in EtOH-AcOH), giving a compound from which glucose is not removed by alkaline hydrolysis. (I) is therefore a derivative of a hydroxycarbonyl compound,  $C_{10}H_{16}O_2$ , in which glucose is involved with OH; it cannot, however, be obtained by acid or alkaline hydrolysis. (II), b.p.  $93^\circ/14$  mm.,  $[\alpha] \pm 0^\circ$  [*semicarbazone*, m.p.  $175^\circ$  (corr.; Berl)], is best obtained from (I) by treatment with boiling 3% Ba(OH) $_2$  in a current of steam. It closely resembles eucarvone (III) and the absorption spectra indicate the presence of the system :C:C:C:C:O. Oxidation of (II) with  $KMnO_4$  affords *as*-dimethylsuccinic acid and AcOH, also obtained from (III). With  $CrO_3$ , (II) and (III) give 1 AcOH. With PhCHO, (III) affords a CHPh: derivative, whereas (II) gives the additive compound  $C_{17}H_{20}O_2$ , m.p.  $135-136^\circ$ , indicating that :CH $_2$  is not vicinal to :CO. Partial catalytic hydrogenation of (II) affords  $\beta$ -cyclocitral (IV) (*semicarbazone*, m.p.  $163-165^\circ$ ), oxidised by air to  $\beta$ -cyclogeranic acid, m.p.  $91^\circ$ . Consideration of the results of oxidative degradation, of mol. refraction, and absorption spectrum proves the double linking saturated by partial hydrogenation to be in conjugation with those of (IV). (II) is therefore 2 : 2 : 6-trimethyl- $\Delta^{4:6}$ -cyclohexadiene-1-aldehyde. Since the absorption spectrum of (I) shows the C:C double linking to be in conjugation with C:O, the 4 : 5-double linking of (II) is solely responsible for the addition of glucose. (I) is therefore  $CHO \cdot C \begin{matrix} \text{CMe-CH}_2 \\ \text{CMe}_2 \cdot \text{CH}_2 \end{matrix} \text{CH} \cdot OGl_u$ . The glucose residue has the pyran form, since (I) does not yield  $CH_2O$  under the influence of  $Pb(OAc)_4$ . The val. of  $[\alpha]_D$  indicates (I) to be a  $\beta$ -glucoside. It is considered that the parent substance is a symmetrical dicyclic carotene pigment with 40 C and that this hypothetical "protocrocin" undergoes oxidative degradation into 1 mol. of crocin (V) and 2 mols. of (I). The pigment therefore is derived from the intermediate polyene chain, the bitter substance from the terminal ring systems. In fresh saffron the mol. ratio

of (V) : (I) = 1.4 : 1. The sensitiveness of (I) is such that it cannot be obtained cryst. from the preserved material. H. W.

**$\beta$ -cycloGeraniol and  $\beta$ -cyclogeraniol- $\beta$ -*d*-glucoside.** R. KUHN and M. HOFFER (Ber., 1934, 67, [B], 357—361).—Reduction of *cyclocitral* (mixture of  $\alpha$ - and  $\beta$ -forms) with  $Al(OPr^i)_3$  and  $Pr^iOH$  affords a mixture of much  $\beta$ - (I) and less  $\alpha$ -cyclogeraniol, from which (I) separates in *crystals*, b.p.  $101-102^\circ/11$  mm., m.p.  $43-44^\circ$ . Treatment of (I) with  $PBr_3$  in  $C_5H_5N$  at  $0^\circ$  affords  $\beta$ -cyclogeranyl bromide (II), b.p.  $96-99^\circ/11$  mm., which with Mg in  $Et_2O$  gives *di*- $\beta$ -cyclogeranyl, m.p.  $116^\circ$  (corr.), but no Grignard reagent. (II) and KI in boiling  $COMe_2$  give probably 1 : 1 : 3-trimethyl-2-methylene- $\Delta^3$ -cyclohexene, b.p.  $48.5-49^\circ/11$  mm., which does not add maleic anhydride and yields  $CH_2O$  when ozonised. (I), acetobromoglucose, and  $Ag_2O$  in anhyd.  $Et_2O$  yield  $\beta$ -cyclogeraniol- $\beta$ -*d*-glucoside tetra-acetate, m.p.  $104^\circ$ ,  $[\alpha]_D^{20} -37.7^\circ$  in 96% EtOH, hydrolysed by aq. Ba(OH) $_2$  to  $\beta$ -cyclogeraniol- $\beta$ -*d*-glucoside, m.p.  $74-75^\circ$ ,  $[\alpha]_D^{20} -35.9^\circ$  in 96% EtOH, which does not reduce Fehling's solution and is not hydrolysed by alkali. H. W.

**Criteria of purity of crystalline digitalin (digitoxoside).** R. CHARONNET (Compt. rend., 1934, 198, 476—478).—Commercial cryst. digitoxin (I) gives by fractionation a product, m.p.  $276^\circ$  (block),  $[\alpha]_D^{20} +17.2^\circ$ ,  $[\alpha]_D^{18} +28^\circ$  in  $CHCl_3$ ,  $[\alpha]_D^{17} -5.7^\circ$  in  $C_5H_5N$ ,  $[\alpha]_D^{16} +22.5^\circ$  in EtOH-HCl, a less sol., less dextro-rotatory (m.p.  $277^\circ$ ), and a more sol. fraction (II), m.p. about  $170^\circ$ . (I) and (II) have similar physiological action. Digitoxigenin has  $[\alpha]_D^{18} +18.1^\circ$  in MeOH and  $-22.7^\circ$  in  $C_5H_5N$ , inversion being thus a function of the lactone group. Commercial residues from (I) gave an inactive oil and flavone and three saponinins having  $[\alpha]_D -64^\circ$  to  $-68^\circ$  and giving a violet-red colour with 85%  $H_3PO_4$  and a little vanillin, with which (I) gives a brown colour. R. S. C.

**Molecular complexity of amylose in potato starch.** J. REILLY, P. P. O'DONOVAN, and (Miss) H. MURPHY (Sci. Proc. Roy. Dublin Soc., 1934, 31, 37—42).—Depression of the f.p. of  $NH_2Ac$  by dry amylose (containing 1% of ash) indicates a formula  $C_{12}H_{20}O_{10}$ . R. S. C.

**Constitution of inulin. Synthesis of 3 : 4 : 6- and 1 : 4 : 6-trimethyl- $\gamma$ -fructose.** T. N. MONTGOMERY (J. Amer. Chem. Soc., 1934, 56, 419—423).— $\beta$ -Disopropylidene-fructose is benzoylated (BzCl,  $C_5H_5N$ ) to the 1-benzoate, m.p.  $82^\circ$ , which is hydrolysed (aq. EtOH- $H_2C_2O_4$ ) to fructose 1-benzoate. This is converted by MeOH-HCl into  $\gamma$ -methylfructoside 1-benzoate, which is methylated (MeI,  $Ag_2O$ ) to 3 : 4 : 6-trimethyl- $\gamma$ -methylfructoside 1-benzoate. Successive hydrolysis of this with aq. EtOH-NaOH and 0.01N-HCl gives 3 : 4 : 6-trimethylfructose (I),  $[\alpha]_D +20.4^\circ$  in  $CHCl_3$ , identical with that obtained by hydrolysis of trimethylinulin (A., 1933, 700). Condensation of (I) with  $COMe_2$  gives (according to time of reaction) products with  $[\alpha]_D +58^\circ$  to  $+80^\circ$ ; partial hydrolysis of the isopropylidene derivative (which is probably a mixture of isomerides) leaves unchanged material of  $[\alpha]_D +32^\circ$ . Complete hydrolysis of all the specimens regenerates (I).  $\alpha$ -Diso-

propylidene-fructose and  $N_2O_5$  in cold  $CHCl_3$  give the 3-nitrate, m.p. 61—62°, hydrolysed (0.1*N*-HCl in  $COMe_2$ ) to 1:2-isopropylidene-fructose 3-nitrate, m.p. 151—152°. This is hydrolysed (aq.  $H_2C_2O_4$ ) to crude fructose 3-nitrate, which when treated successively with  $MeOH-HCl$ ,  $MeI-Ag_2O$ ,  $Na-Hg$  and 50%  $EtOH$ , and 0.01*N*-HCl gives 1:4:6-trimethylfructose,  $[\alpha]_D^{20} +29.7^\circ$  in  $CHCl_3$ , when regenerated from its isopropylidene derivative, b.p. 100° (bath)/0.2 mm.,  $[\alpha]_D^{20} +17.8^\circ$  in  $COMe_2$ . H. B.

**Phosphorus- and nitrogen-free glycogen.** M. SOMOGYI (J. Biol. Chem., 1934, 104, 245—253).—The solubility of glycogen (I) at 22° and 0° in various concn. of  $EtOH$  and  $NaCl$  has been studied. A method for prep. of N- and P-free (I) is described. H. G. R.

**Highly polymerised compounds. LXXXVIII. Constitution of cellulose.** H. STAUDINGER (Chem.-Ztg., 1934, 58, 145—148).—A summary. A. G.

**Action of anhydrous hydrogen chloride under pressure on organic compounds.** H. H. SCHLUBACH, H. ELSNER, and H. KNOOP (Angew. Chem., 1934, 47, 130—131).—Saturated aliphatic hydrocarbons (dicetyl) are not attacked by HCl under pressure. Pure aliphatic alcohols ( $Bu^aOH$ ; glycerol) are not at all or only slightly attacked, whereas impure materials react;  $(-CH_2 \cdot OH)_2$  appears to yield  $(CH_2)_2O$  and thence Cl-compounds. Acids ( $AcOH$ , palmitic acid,  $BzOH$ ) and ethers ( $Et_2O$   $PhOMe$ ) are not attacked. Esters ( $EtOAc$ , fats) are slowly, glucosides ( $\alpha$ - and  $\beta$ -methylglucoside) more rapidly, attacked.  $Ac_2O$  is quantitatively converted into  $AcOH$  and  $AcCl$ . Cellulose occupies a position between ester and anhydride. H. W.

**Mechanism of the degradation of cellulose by hydrogen chloride under pressure.** H. H. SCHLUBACH and V. PROCHOWNICK (Angew. Chem., 1934, 47, 132—133).—With increasing dryness of material reaction occurs with increasing smoothness; augmented  $H_2O$  content causes increase in carbonisation. The intermediate production of 1-chloroglucose (I) during the action of HCl on cellulose is established by treating the product with  $Ag_2CO_3$  and  $H_2O-COMe_2$  or  $Ag_2CO_3$  and  $MeOH$ , whereby glucose (II) and methylglucoside, respectively, are produced. If addition of  $H_2O$  precedes the after-treatment, only (II) results. The yield of (I) is 50—60%, the deficit being attributed to formation of polyglucosans by direct loss of HCl. The intermediate formation of 2:3:6-trimethyl- $\alpha$ -chloroglucose by the action of HCl on trimethylcellulose is established by the isolation of 2:3:6-trimethyl- $\beta$ -methylglucoside. H. W.

**Use of ethyl sulphone diacetate in identification of aliphatic amines.** J. P. ALDEN and B. HOUSTON (J. Amer. Chem. Soc., 1934, 56, 413—414).— $SO_2(CH_2 \cdot CO_2Et)_2$ , b.p. 164—167°/2 mm. [improved prep. of acid described (cf. Lovén, A., 1885, 241)], reacts rapidly with  $NH_2Alk$  (4—5 mols.) to give  $SO_2(CH_2 \cdot CO \cdot NHalk)_2$ . The following are described:  $Alk=Me$ , m.p. 186°,  $Et$ , m.p. 178°,  $Pr^a$ , m.p. 184°,  $Pr^b$ , m.p. 148°,  $Bu^a$ , m.p. 192°,  $Bu^b$ , m.p. 155°,  $n$ -amyl, m.p. 174°, isoamyl, m.p. 152°,  $n$ -heptyl, m.p. 182°, and cyclohexyl, m.p. 170°. Reaction does

not occur with  $NH_2 \cdot CHMeEt$ ,  $NHMe_2$ ,  $NHEt_2$ , or  $NHPr^a_2$ . H. B.

**Reduction of aliphatic cyanides and oximes with sodium and *n*-butyl alcohol.** C. M. SUTER and E. W. MOFFETT (J. Amer. Chem. Soc., 1934, 56, 487).—The cyanide or oxime (1 mol.) in boiling  $Bu^aOH$  (2300 c.c.) is treated with  $Na$  (161 g.) during 10—15 min. The yields of amine from  $Bu^aCN$ ,  $n$ -hexonitrile, heptaldoxime, and a series of  $Me$  alkyl ketoximes are 69—86%. H. B.

**Detection of tri(hydroxyethyl)amine and colorimetric determination of nickel and of tri(hydroxyethyl)amine.** E. JAFFE (L'Ind. Chimica, 1934, 9, 151—153).—When a few drops each of 20% aq.  $N(C_2H_4 \cdot OH)_3$  (I) solution, conc.  $NH_3$ , and 30%  $KOH$  solution are added to 1 c.c. of a solution containing 0.02% of  $Ni$  and the vol. is made up to 6 c.c. (cf. A., 1933, 246), a green colour forms; about 1  $Ni$  in 30,000 is thus detectable. To detect (I) in cosmetics etc., the substance is acidified and treated with  $Et_2O$ , light petroleum, or  $C_6H_6$  to remove fatty acids often present, the aq. solution being made alkaline with 30%  $KOH$  solution and treated with a few drops of a reagent containing 10 g.  $NiSO_4$  and 25 c.c. conc.  $NH_3$  per 100 c.c. This colour reaction serves for the determination of both  $Ni$  and (I). T. H. P.

**Conversion of 2-*p*-toluenesulphonyl- $\beta$ -methylglucoside into methylepiglucosamine.** E. W. BODYCOTE, W. N. HAWORTH, and E. L. HIRST (J.C.S., 1934, 151—154).—2-*p*-Toluenesulphonyl- $\beta$ -methylglucoside or its triacetate is converted by  $NH_3$  in  $MeOH$  at 100° into methylepiglucosamine (cf. A., 1920, i, 420), identified by isolation of its hydrochloride (I) and anhydro-base, and hydrolysis of the former by 0.5%  $HCl$  at the b.p. to epiglucosamine [*phenylosazone*, m.p. 225—227° (decomp.)]. Deamination of (I) with  $AgNO_2$  gives a methylhexoside,  $[\alpha]_D^{20} -52^\circ$  in  $H_2O$  ( $Ac_4$ ,  $[\alpha]_D^{20} -22^\circ$  in  $CHCl_3$ , and  $Me_4$ , b.p. 105°/0.2 mm.,  $[\alpha]_D^{20} -47^\circ$  in  $CHCl_3$ , derivatives), believed to be  $\beta$ -methylaltroside. H. A. P.

**Dehydrogenation of  $\alpha$ -*N*-methylaminoisobutyric acid.** F. BERGEL [with K. BOLZ and R. WAGNER] (Z. physiol. Chem., 1934, 223, 66—70).—*N*-Methylaminoisobutyric acid is slowly oxidised by animal  $C$  and  $O_2$  and unattacked by glucose (cf. Akabori, A., 1933, 263) and *p*-benzoquinone. Apparently for the oxidative degradation of  $NH_2$ -acids paired H atoms must be present at C and N or at N alone. J. H. B.

**New class of hypnotics.** E. FOURNEAU, J. R. BILLETTER, and D. BOVET (J. Pharm. Chim., 1934, [viii], 19, 49—54).— $NH_2$  in aq.  $EtOH$  at 4—6° gives with glycidic esters  $\begin{matrix} CORR' \cdot CH \cdot CO_2Et \\ | \\ O \end{matrix}$  (I) quant. yields of the amides  $\begin{matrix} CORR' \cdot CH \cdot CO \cdot NR''R''' \\ | \\ O \end{matrix}$  (II) ( $R''=R'''=H$ ) (cf. Claisen, A., 1905, i, 286), also obtainable by condensing  $CH_2Cl \cdot CO \cdot NH_2$  with ketones  $CORR'$  in presence of  $NaOEt$  (cf. Darzens, A., 1905, i, 116).  $NH_2Me$  (first method) gives the methylamides (II) ( $R''=Me$ ,  $R'''=H$ ) (poor yields); it does not react with cyclohexylidene-glycidic ester.  $NHMe_2$  only reacts with two of the esters (I), viz.,  $R=Ph$ ,  $R'=Me$ ,

and R=Ph, R'=H, with the former normally, but with the latter giving *NN*-dimethylisoserine (Fourneau, A., 1907, i, 622).  $\text{NH}_2\text{Et}_2$  and  $\text{C}_5\text{H}_{11}\cdot\text{NH}_2$  do not react with (I). The following eight *amides* (II) exercise on mice, rabbits, and fish a feeble narcotic action which presents certain novel features: R=R'=Me, R''=R'''=H, m.p. 85–87°, b.p. 127°/15 mm.; R=R'=Et, R''=R'''=H, m.p. 104° (148° given elsewhere in paper); R=R'=Et, R''=Me, R'''=H, m.p. 48°; R=Ph, R'=R''=R'''=H, m.p. 148°; R=Ph, R'=R''=R'''=Me, m.p. 132°; R=CH<sub>2</sub>Ph, R'=Me, R''=R'''=H, m.p. 133°; (RR')=CH<sub>2</sub> < CH<sub>2</sub>-CH<sub>2</sub> > C, R''=R'''=H, m.p. 139°; R=OPh-CH<sub>2</sub>, R'=Me, R''=R'''=H, m.p. 139°.

W. S.

**Ammonolytic reactions.**—See this vol., 182.

**Reaction of bismuth [nitrate] with thiocarbamide.**—See this vol., 377.

**Rates of formation of quaternary phosphonium salts.** W. C. DAVIES and S. U. EVANS (J.C.S., 1934, 244).—The rate of formation of quaternary salts from  $\text{PPr}_3$  and  $\text{PBu}_3$  and a series of *n*-alkyl bromides in dil.  $\text{CO}_2$  solution at 25° diminishes as the series is ascended and is less with  $\text{PBu}_3$  than with  $\text{PPr}_3$ .  $\text{PPr}_3$  is much more reactive than  $\text{NPr}_3$ .

H. A. P.

**Preparation of organo-magnesium compounds by catalysis.** V. GRIGNARD (Compt. rend., 1934, 198, 625–628).—Formation of  $\text{MgRX}$  is facilitated in many cases by the addition of  $\text{EtBr}$ , which acts by keeping the Mg surface clean and by the formation of a sol.  $\text{MgRX}\text{-MgEtBr}$  complex, rather than insol.  $(\text{MgRX})_2$ .

J. L. D.

**Chemical evidence for planar configuration of platotetrammines.** H. D. K. DREW and F. S. H. HEAD (J.C.S., 1934, 221–226).—Synthesis of the tetrammines  $[\text{Pt am ae ib}]_2\text{Cl}_2$  and  $[\text{Pt ib}_2]_2\text{Cl}_2$  [am=NH<sub>3</sub>, ae=NH<sub>2</sub>Et, and ib=NH<sub>2</sub>·CMe<sub>2</sub>·CH<sub>2</sub>·NH<sub>2</sub> (I)] from the β-diammines gives well-defined *cis*- and *trans*-isomerides; this isomerism is destroyed by use of a chelate *s*-diamine [ $\text{C}_2\text{H}_4(\text{NH}_2)_2$  (II)] or by use of NH<sub>2</sub>Et in place of NH<sub>3</sub>. Both forms of the tetrammines are therefore considered to have a planar structure. The following complex salts are described: α-Pt am ae Cl<sub>2</sub> (from β-[Pt am ae<sub>2</sub>]Cl<sub>2</sub> and conc. HCl); β-Pt am ae Cl<sub>2</sub> (III) (from K[Pt am Cl<sub>3</sub>] and NH<sub>2</sub>Et); α-Pt am ae Cl<sub>4</sub> [from (III), H<sub>2</sub>O<sub>2</sub>, and HCl]; β-Pt am py Cl<sub>2</sub> (IV) (from aq. C<sub>5</sub>H<sub>5</sub>N and Pt am Cl<sub>2</sub> or, better, K[Pt am Cl<sub>3</sub>]); [Pt am py en]Cl<sub>2</sub>, H<sub>2</sub>O [from (II) and (IV) in H<sub>2</sub>O] (+PtCl<sub>2</sub>; anhyd. and +1H<sub>2</sub>O); [Pt am py<sub>3</sub>]Cl<sub>2</sub>, H<sub>2</sub>O (+PtCl<sub>2</sub>, H<sub>2</sub>O); and Pt ib Cl<sub>2</sub> [from (I) and K<sub>2</sub>PtCl<sub>4</sub>]. Interaction of (I) and (III) in H<sub>2</sub>O gives the isomeric salts α (+PtCl<sub>2</sub>) and β-[Pt am ae ib]Cl<sub>2</sub> (+PtCl<sub>2</sub>), but (II) and (III) give only a single [Pt am ae en]Cl<sub>2</sub> (+PtCl<sub>2</sub>). The isomeric salts α (anhyd. and +2H<sub>2</sub>O; +PtCl<sub>2</sub>) and β-[Pt ib<sub>2</sub>]Cl<sub>2</sub> (anhyd., +1H<sub>2</sub>O, +2H<sub>2</sub>O; +PtCl<sub>2</sub>) are similarly formed from (I) and α-Pt am<sub>2</sub>Cl<sub>2</sub>, Pt ib Cl<sub>2</sub>, or K<sub>2</sub>PtCl<sub>4</sub> in H<sub>2</sub>O.

H. A. P.

**Structure of the thio-ether compounds of platinum and palladium chlorides.** E. G. COX, H. SAENGER, and W. WARDLAW (J.C.S., 1934, 182–186).—α- (I) and β-Bisdimethylsulphineplatinous chloride (II) are interconvertible, (I) → (II) being

complete in hot H<sub>2</sub>O, and an equilibrium mixture being formed in (hot) CHCl<sub>3</sub> or on melting. With Cl<sub>2</sub> tetrachlorides, m.p. 219–229° (decomp.), and 215–226° (decomp.), are formed. With Ag<sub>2</sub>O (II) immediately gives AgCl and a yellowish-brown base, reconverted into (II) by HCl, but (I) reacts slowly to give Me<sub>2</sub>S, AgCl, and PtO.<sub>x</sub>H<sub>2</sub>O; similarly, (II) gives a ppt. of AgCl with HNO<sub>3</sub> and AgNO<sub>3</sub> but (I) does not. Crystallographic agree with X-ray data in assigning a planar structure to the isomerides, (I) being the *trans* and (II) the *cis* form; this is supported by the difference in *d*, and by formation of the complex salt  $[\text{Pt en}(\text{Me}_2\text{S})_2]\text{PtCl}_4$  from (II), *s*-C<sub>2</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>, and K<sub>2</sub>PtCl<sub>4</sub> under conditions that with (I) lead only to Me<sub>2</sub>S and  $[\text{Pt en}]_2\text{PtCl}_4$ .

H. A. P.

**Complex compounds of bivalent palladium.**—See this vol., 379.

**Formation of cyclic compounds. I. Relative ease of formation and relative stability of simple carbon rings.** S. SAKO (Bull. Chem. Soc. Japan, 1934, 9, 41–54).—Theoretical. Evidence is brought forward to show that free rotation of the atoms inhibits ring formation.

F. R. S.

**Catalysed dehydrogenation of cyclic hydrocarbons.**—See this vol., 371.

**Stereoisomeric 1-methyl-2-propylcyclopentanes.** G. CHURDOGLU (Bull. Soc. chim. Belg., 1934, 43, 35–48).—Et cyclopentanone-2-carboxylate, Pr<sup>n</sup>I, and Na give *Et* 2-*n*-propylcyclopentanone-2-carboxylate, b.p. 126.0–126.2°/13 mm., m.p. –37.6° (semicarbazone, decomp. 160.2°), hydrolysed in 85% yield to 2-*n*-propylcyclopentanone, b.p. 183.1–183.2°/760 mm., 70.2°/15 mm., m.p. –68.25° (semicarbazone, decomp. 214°), which with MgMeI gives a 90% yield of *trans*- (I), b.p. 84.5–85.0°/18.1 mm., and *cis*- (II), b.p. 91.5–92.0°/18.1 mm., -1-methyl-2-*n*-propylcyclopentan-1-ol, and a small amount of an unstable substance, b.p. 173–177°/15 mm. (I) at 300° gives H<sub>2</sub>O, cyclopentene derivative, and up to 20% of *trans*-1-methyl-2-propylcyclopentane (III). (I) and (II) with HCO<sub>2</sub>H give 1-methyl-2-*n*-propylcyclopentene, b.p. 150.15–150.25°, which is hydrogenated (Pt-black) in AcOH to a mixture of *trans* and *cis* forms of (III), b.p. 146.37–146.38° and 152.58°, sets to a glass and m.p. –104.9°, respectively.

R. S. C.

**Action of hypochlorous acid on [optically] active 1-methyl-Δ<sup>3</sup>-cyclohexene.** M. GODCHOT, M. MOUSSERON, and R. GRANGER (Compt. rend., 1934, 198, 480–482).—3-Methylcyclohexanol and 2% H<sub>2</sub>SO<sub>4</sub> give 1-methyl-Δ<sup>2</sup>- (5%), b.p. 104°/743 mm., [α]<sub>D</sub><sup>20</sup> 80.44°, and -Δ<sup>3</sup>-cyclohexene (I) (95%), b.p. 102.5°/743 mm., [α]<sub>D</sub><sup>20</sup> 106.19° (oxidised to β-methyladipic acid, [α]<sub>D</sub><sup>20</sup> +8.5°). (I) with HOCl gives a mixture, separable by careful fractionation into four forms of 2-chloro-5-methylcyclohexan-1-ol, b.p. 79°/16 mm., 91°/16 mm., 93°/15 mm., and 95°/15 mm., [α]<sub>D</sub><sup>20</sup> +20.14°, –6.32°, +4.21°, and +11.15°, respectively (cf. A., 1905, i, 141). The 5-Cl-2-Me structure is considered improbable. The forms differ widely in *γ*.

R. S. C.

**Side-chain reactions of benzene derivatives.** W. S. NATHAN and H. B. WATSON (Nature, 1934, 133, 379–380).—Theoretical (cf. A., 1933, 1124).

L. S. T.

**Side-chain chlorination of toluene.** H. S. KING and W. B. BEAZLEY (Proc. Nova Scotian Inst. Sci., 1932—1933, 18, 204—212).—The course of the chlorination of boiling PhMe is best followed by the temp. of the boiling liquid. When this is 145° and 155°, the liquid contains 21 and 12% of PhMe, 70% of CH<sub>2</sub>PhCl, and 9 and 13% of CHPhCl<sub>2</sub>, respectively. The relation between *n* and composition is linear.

R. S. C.

**Allyltoluenes.** C. D. HURD and H. T. BOLLMAN (J. Amer. Chem. Soc., 1934, 56, 447—449).—*o*-Allyltoluene (I), b.p. 88—90°/25 mm., 181—181.6°/750 mm. (dibromide, b.p. 166—168°/15 mm.), and *p*-allyltoluene (II), b.p. 58—60°/1.65 mm., 180—181°/750 mm. (dibromide, b.p. 110—112°/0.7—0.9 mm., 186°/34 mm.), are prepared from allyl bromide and *o*- and *p*-C<sub>6</sub>H<sub>4</sub>Me·MgBr, respectively. (I) is not formed by prolonged heating of  $\delta$ -phenyl- $\Delta^a$ -butene (III) at 400°. Pyrolysis of (I) and (II) in quartz (method: A., 1933, 371) gives H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>3</sub>H<sub>6</sub>, showing that fission occurs at all the C-C linkings in the side-chain; aromatic hydrocarbons (PhMe, C<sub>6</sub>H<sub>4</sub>Me<sub>2</sub>) are also formed. (I) and (II) are more stable than (III).

H. B.

**Action of aluminium chloride on isopropyl and butyl chloride in the presence of benzene.** T. FIRLA (Rocz. Chem., 1934, 14, 87—92).—18% yields of C<sub>6</sub>H<sub>5</sub>Pr <sup>$\beta$</sup> <sub>4</sub> (I) are obtained from Pr <sup>$\beta$</sup> Cl, C<sub>6</sub>H<sub>6</sub>, and AlCl<sub>3</sub> at 0°, when the duration of reaction is > 5 min. (I) undergoes decomp. to C<sub>6</sub>H<sub>3</sub>Pr <sup>$\beta$</sup> <sub>3</sub>, C<sub>6</sub>H<sub>4</sub>Pr <sup>$\beta$</sup> <sub>2</sub>, and PhPr <sup>$\beta$</sup>  on leaving at room temp. with AlCl<sub>3</sub> during 2 hr. C<sub>6</sub>H<sub>4</sub>Bu<sub>2</sub> (II) is obtained from BuCl, C<sub>6</sub>H<sub>6</sub>, and AlCl<sub>3</sub> at 0° after 90 sec.; (II) is converted into C<sub>6</sub>H<sub>3</sub>Bu<sub>3</sub>, PhBu, and an unidentified product if the reaction mixture is left at room temp.

R. T.

**Reaction of *o*- and *p*-dichlorobenzene with cuprous oxide and water.** N. N. VOROSHCHEV and P. S. KARLASH (Compt. rend. Acad. Sci. U.R.S.S., 1933, 223).—On warming *o*- or *p*-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> with Cu<sub>2</sub>O and H<sub>2</sub>O at 275°/80 atm. only PhOH is obtained. The reaction proceeds through *p*-C<sub>6</sub>H<sub>4</sub>Cl·OH. Cu<sub>2</sub>O is a sp. reagent for this reaction.

W. R. A.

**Aromatic sulphonates of elements of the second group of the periodic table.** V. ČUPR and J. ŠIRŮČEK (J. pr. Chem., 1934, [ii], 139, 245—253).—The following are described: Mg (+6H<sub>2</sub>O), Zn (+6H<sub>2</sub>O), Cd (+6H<sub>2</sub>O), and Sr (+H<sub>2</sub>O) *p*-ethyl-; Mg (+6H<sub>2</sub>O), Zn (+6H<sub>2</sub>O), Cd (+2H<sub>2</sub>O), Ca, and Sr (+H<sub>2</sub>O) *p*-chloro-; Mg (+6H<sub>2</sub>O), Cd (+3H<sub>2</sub>O and +2H<sub>2</sub>O), and Sr (+2H<sub>2</sub>O) *p*-bromo-; Mg (+6H<sub>2</sub>O), Zn (+6H<sub>2</sub>O), Cd (+6H<sub>2</sub>O), and Sr (+H<sub>2</sub>O) *p*-iodo-; and Cd (+4H<sub>2</sub>O) and Sr (+5H<sub>2</sub>O) *p*-hydroxy-benzene-sulphonate; Mg (+6H<sub>2</sub>O), Zn (+2H<sub>2</sub>O), Cd (+2H<sub>2</sub>O), Ca (+3H<sub>2</sub>O), and Sr (+3.5H<sub>2</sub>O) sulphanilates; Be (+9H<sub>2</sub>O), Mg (+8H<sub>2</sub>O), Zn (+8H<sub>2</sub>O), Cd (+9H<sub>2</sub>O and +5H<sub>2</sub>O), Ca (+6H<sub>2</sub>O), Sr (+2H<sub>2</sub>O), and Ba (+H<sub>2</sub>O) 2-nitro-*p*-toluenesulphonates; Be (+8H<sub>2</sub>O), Mg (+8H<sub>2</sub>O), Zn (+9H<sub>2</sub>O), Cd (+9H<sub>2</sub>O), and Sr (+H<sub>2</sub>O) 6-chloro-3-nitrobenzenesulphonates; Be (+4H<sub>2</sub>O and anhyd.) and Ba (+1.5H<sub>2</sub>O) 1- and Be (+6H<sub>2</sub>O and anhyd.) 2-naphthalenesulphonate. The relative proportions of H<sub>2</sub>O of crystallisation (I) are discussed, (I) being greater the greater is the mol. vol. of the anion.

J. W. B.

**Reduction by magnesium+magnesium iodide.**  
**XII. Reduction of phenyl triphenylmethyl ketone.** W. E. BACHMANN (J. Amer. Chem. Soc., 1934, 56, 449—450).—CPh<sub>2</sub>·CPh<sub>2</sub> is obtained in 92% yield from CPh<sub>3</sub>·COPh, Mg, and MgI<sub>2</sub> in C<sub>6</sub>H<sub>6</sub>-Et<sub>2</sub>O at 80°; about 8% of a viscous product (formed in 70—80% yield at room temp.) is also produced. Small amounts of MgI<sub>2</sub> can effect (slowly) complete reduction: CPh<sub>3</sub>·COPh + Mg + MgI<sub>2</sub> → CPh<sub>2</sub>·CPh<sub>2</sub> + MgO + MgI<sub>2</sub>.

H. B.

**Derivatives of 1:6-dimethylnaphthalene.** F. FEIST (J. pr. Chem., 1934, [ii], 139, 261—268).—1:6-C<sub>10</sub>H<sub>6</sub>Me<sub>2</sub> (I) with Br at 0° gives a Br<sub>2</sub>-derivative, m.p. 134.5°, and an isomeric Br<sub>2</sub>-derivative, m.p. 62—64° (probably the 4:5- and 4:8-derivatives); with Br in CHCl<sub>3</sub> and Fe powder a Br<sub>3</sub>-derivative (II), m.p. 115—116° (also by Br-H<sub>2</sub>O on the mother-liquor from the Br<sub>2</sub>-derivative), is obtained, the mother-liquor giving a Br<sub>3</sub>-derivative, b.p. 227°/10 mm., m.p. 107—108°, which on further bromination gives a Br<sub>4</sub>-derivative (III), m.p. 180—181°. Neither (II) nor (III) condenses with AcCl-AlCl<sub>3</sub> in CS<sub>2</sub> or PhNO<sub>2</sub>, but (I) is thus converted into 1:6-dimethylnaphthyl Me ketone (IV), m.p. 43° (Br<sub>4</sub>-derivative, m.p. 183—184°), converted by Cl<sub>2</sub> (Hg lamp) into an amorphous Cl<sub>9</sub>-derivative C<sub>10</sub>H<sub>5</sub>(CCl<sub>3</sub>)<sub>2</sub>·CO·CCl<sub>3</sub>, b.p. 244—250°/5 mm., which gives only amorphous acids with conc. H<sub>2</sub>SO<sub>4</sub> at 140° and (?) trimellitic acid with KOH at 170°. Oxidation of (IV) with CrO<sub>3</sub>-AcOH gives the corresponding quinone, m.p. 150°.

J. W. B.

**Polyterpenes and polyterpenoids.** LXXXVI.  
**Dehydrogenation of cholesterol, ergosterol, cholic acid, and phytosterols.** L. RUZICKA, G. THOMANN, E. BRANDENBERGER, M. FURTER, and M. W. GOLDBERG (Helv. Chim. Acta, 1934, 17, 200—221).—In part a reply to Diels (A., 1933, 1047; this vol., 288). Dehydrogenation of cholic or cholatrienic acid with Se at 360° affords picene (I), m.p. 354—355° (corr.) [compound with 2:7-dinitroanthraquinone (II), m.p. 292—293°], identical with that from tar, a hydrocarbon C<sub>21</sub>H<sub>16</sub> (III), m.p. 272—274° (corr.), and a small amount of chrysene (IV), identical with that from tar. Dehydrogenation at 420° affords less (I), more (IV), and no (III). Hence the production of (IV) (Diels) results from the higher dehydrogenation temp. employed, at which (III) is either not formed or is destroyed. Absorption and Röntgen spectra show the identity of (I) and (IV) with the specimens from tar, and differentiate them from (III), from the hydrocarbon, m.p. 214—215°, obtained by Se dehydrogenation of ergosterol (C<sub>28</sub>), and from the hydrocarbon C<sub>27</sub>H<sub>28</sub> (V), m.p. 202—203° [compound with (I), m.p. 246—247°] (crystallographic data), obtained by dehydrogenation of phytosterol (from soya bean) with Se at 320°. Contrary to Diels, but in agreement with suggested mechanisms for the production of these hydrocarbons from sterol skeletons, the identity of the hydrocarbons obtained by dehydrogenation of C<sub>27</sub>, C<sub>28</sub>, and C<sub>29</sub> sterols is disproved.

J. W. B.

**Catalytic hydrogenation of decacyclene and rubicene under pressure.** J. VON BRAUN [with G. MANZ and W. KELLER] (Ber., 1934, 67, [B], 214—218).—Addition of H to pure decacyclene (I) in deca-

hydronaphthalene in presence of Ni occurs very slowly at moderate temp. and pressure. Reaction occurs suddenly at about 230°/200 atm., leading immediately to *trisdecahydrodecaacyclene* (II), m.p. 215°, not affected by conc. H<sub>2</sub>SO<sub>4</sub> at 50–60° and oxidised by HNO<sub>3</sub> to mellitic acid. (II) is stable towards heat and is very extensively degraded when distilled over PbO.



Cautious treatment with S at 200°/20 mm. in N<sub>2</sub> leads to the *substance*, C<sub>36</sub>H<sub>38</sub>, m.p. (indef.) 245°, arising from complete dehydrogenation of one of the decahydronaphthalene nuclei. Hydrogenation of (I) containing about 1% of S can be controlled to yield *dodecahydrodecaacyclene*, m.p. 303–306°, with tetrahydronaphthalene rings arranged symmetrically around the C<sub>6</sub>H<sub>6</sub> nucleus. Rubicene (III) is readily reduced to *perhydrorubicene*, C<sub>26</sub>H<sub>40</sub>, m.p. 55–65°, readily dehydrogenated in hot EtOAc at 3 and 3' to the *substance*, C<sub>26</sub>H<sub>28</sub>, m.p. 246–248°. Hydrogenation (Ni) of (III) at about 250°/200 atm. gives a *substance*, m.p. 145–160°, approximating closely to C<sub>26</sub>H<sub>34</sub>. Analogies with the behaviour of fluoranthrene (A., 1930, 1570) are discussed. H. W.

**Internal molecular compounds.** L. DEDE and A. ROSENBERG (Ber., 1934, 67, [B], 147–153).—The optical properties of the nitroanilines (I) are attributed to the mutual action of the two substituents resulting in the formation of “internal mol. compounds.” PhNO<sub>2</sub> and NH<sub>2</sub>Ph yield a coloured mol. compound in solution. Addition of HClO<sub>4</sub> to (I) causes their absorption spectra to become nearly identical with that of PhNO<sub>2</sub>, the smallest concn. of acid to produce the effect being observed with the *m*-derivative. Similarly, acetylation by involving NH<sub>2</sub> hinders the formation of an internal complex, with the expected effect on the absorption band. The optical behaviour of the nitrophenols in presence and absence of acid or alkali or in various media is in harmony with an internal union between NO<sub>2</sub> and O by OH. The inability of *o*- in contrast to *m*- and *p*-OH·C<sub>6</sub>H<sub>4</sub>·NO<sub>2</sub> to yield mol. compounds with NH<sub>2</sub>Ph, *o*-, *m*-, or *p*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>, or  $\alpha$ - or  $\beta$ -C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub> is attributed to the firmness of the union of NO<sub>2</sub> and OH within the mol. The aminobenzoic acids show the band characteristic of internal mol. compounds, and addition of HClO<sub>4</sub> causes their spectra to become identical with that of BzOH. Where little affinity between the radicals exists, the bands are not observed. Thus the nitrotoluenes do not differ markedly from PhNO<sub>2</sub> and *p*-C<sub>6</sub>H<sub>4</sub>Cl·NH<sub>2</sub> and the toluidines closely resemble NH<sub>2</sub>Ph. H. W.

**Nitration of *m*-chloro- and *m*-bromo-aniline derivatives.** M. M. DE MONCHY (Rec. trav. chim., 1934, 53, 141–162).—Interaction of abs. HNO<sub>3</sub> at 0°

with *N*-*m*-chlorophenyl-*N'*-ethylcarbamide (I), m.p. 120° (from *m*-C<sub>6</sub>H<sub>4</sub>Cl·NH<sub>2</sub> and EtNCO), gives the N : 4 : 6-(NO<sub>2</sub>)<sub>3</sub>, m.p. 95°, N : 2 : 6-(NO<sub>2</sub>)<sub>3</sub>, m.p. 85°, and N : 2 : 4-(NO<sub>2</sub>)<sub>3</sub> (not isolated) derivatives. The crude nitration mixture when boiled with MeOH gives *Me* 3-chloro-4 : 6-dinitro-, m.p. 67°, and *Me* 3-chloro-2 : 6-dinitro-phenylcarbamate, m.p. 188°; with EtOH the corresponding *Et* esters, m.p. 70° and 155°, respectively, and (?) *Et* 3-chloro-2 : 4-dinitrophenylcarbamate, m.p. 163° (3-chloro-2 : 4-dinitroaniline, m.p. 100°), are formed. Nitration of (I) with HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> gives the N : 2 : 4 : 6-(NO<sub>2</sub>)<sub>4</sub>-derivative, converted by MeOH into *Me* 3-chloro-2 : 4 : 6-trinitrophenylcarbamate, m.p. 196°, but attempted further nitration of the trinitrocarbamides or dinitrourethanes gave only 1 : 3 : 2 : 4 : 6-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>)<sub>3</sub>. The identity of the above NO<sub>2</sub>-compounds is determined by hydrolysis to amine. Nitration of *Me* *m*-chlorophenylcarbamate, m.p. 81° (from *m*-C<sub>6</sub>H<sub>4</sub>Cl·NH<sub>2</sub> and ClCO<sub>2</sub>Me), gives the 2 : 4- and 2 : 6-(NO<sub>2</sub>)<sub>2</sub>-derivatives. Similar products are obtained by nitration of derivatives of *m*-C<sub>6</sub>H<sub>4</sub>Br·NH<sub>2</sub>, but whilst the carbamide gives only a trace of nuclear (NO<sub>2</sub>)<sub>3</sub>-compound, the urethanes readily yield such derivatives. The following are described: *N*-*m*-bromophenyl-*N'*-ethylcarbamide, m.p. 129° (products of nitration not separated, but converted direct into urethanes); *Me* 3-bromophenylcarbamate [4 : 6-(NO<sub>2</sub>)<sub>2</sub>, m.p. 81°, 2 : 6-(NO<sub>2</sub>)<sub>2</sub>, m.p. 193°, and 2 : 4 : 6-(NO<sub>2</sub>)<sub>3</sub>, m.p. 176°, derivatives]; *Et* 3-bromophenylcarbamate [4 : 6-(NO<sub>2</sub>)<sub>2</sub>, m.p. 110°, 2 : 6-(NO<sub>2</sub>)<sub>2</sub>, m.p. 173°, and 2 : 4 : 6-(NO<sub>2</sub>)<sub>3</sub>, m.p. 230°, derivatives]; and 3-bromo-2 : 6-dinitro-, m.p. 136°, and -2 : 4 : 6-trinitroaniline, m.p. 213°. 3-Chloro-2 : 6-dinitroaniline is dimorphic, m.p. 112°, 136° [*Ac* derivative, m.p. 175° (by nitration of *m*-C<sub>6</sub>H<sub>4</sub>Br·NHAc)]. With NaOMe it gives 2 : 4-dinitro-5-aminoanisole, m.p. 207°, as also does the corresponding Br-compound. Both 3-chloro- and 3-bromo-2 : 6-dinitroaniline give 2 : 4-dinitro-3-aminodiphenylamine, m.p. 200°, with NH<sub>2</sub>Ph.

H. A. P.

**Colour reactions of organic compounds. I. Colour reactions of arylthiocarbamides.** G. M. DYSON (J.C.S., 1934, 174–177).—The colour developed by thiocarbamides, A·NH·CS·NHB, in warm conc. H<sub>2</sub>SO<sub>4</sub> is dependent on group B, which must be aromatic and contain no NO<sub>2</sub> group, and the presence of NO<sub>2</sub> in the aryl residue A. It is due to formation of the corresponding amine, which is oxidised by a trace of HNO<sub>3</sub> produced from the NO<sub>2</sub> group. The following are described: *o*-nitrophenylthiocarbamide, m.p. 74°; *N*-*o*-nitrophenyl-*N'*-propyl-, m.p. 168°; *o*-nitro-, m.p. 188°, 2-nitro-2', m.p. 192°, -3', m.p. 150°, and -4'-methyl-, m.p. 207°, and 4'-bromo-2-nitro-*s*-diphenyl-, m.p. 210°; *N*-*o*-nitrophenyl-*N'*- $\alpha$ -, m.p. 145°, and - $\beta$ -naphthyl-, m.p. 176°; *s*-*di*-*o*-nitrophenyl-, m.p. 160°; 2 : 3', m.p. 116°, and 2 : 4'-dinitro-*s*-diphenyl-, m.p. 153°; *N*-*m*-nitrophenyl-*N'*-propyl-, m.p. 119°; 3-nitro-, m.p. 156°, 3-nitro-2', m.p. 154°, -3', m.p. 158°, and -4'-methyl-, m.p. 157°, 3 : 3'-dinitro-, m.p. 168°, 4'-bromo-3-nitro-, m.p. 173°, 2 : 4'-dichloro-3-nitro-, m.p. 151°, and 3 : 2'-dinitro-6-methyl-*s*-diphenyl-, m.p. 160°; *N*-*m*-nitrophenyl-*N'*- $\alpha$ -, m.p. 156°, and - $\beta$ -naphthyl-, m.p. 164°; 3 : 3', m.p. 136°, and 3 : 4'-dinitro-6'-methyl-, m.p. 158°, 3 : 4'-dinitro-, m.p. 172°, 3 : 3', m.p. 115°,

and 3:2'-dinitro-4'-methyl-s-diphenyl-, m.p. 188°; 4-nitro-, m.p. 175°, 4-nitro-2'-, m.p. 132°, -3'-, m.p. 135°, and -4'-methyl-, m.p. 165°, 4:4'-dinitro-, m.p. 175°, 4'-bromo-, m.p. 164°, and 4'-chloro-4-nitro-, m.p. 179°, and 4-nitro-4'-methoxy-s-diphenyl-, m.p. 155°; N-p-nitrophenyl-N'- $\alpha$ -, m.p. 187°, and - $\beta$ -naphthyl-, m.p. 157°; 4:3'-, m.p. 175°, and 4:4'-nitro-6'-, m.p. 181°, and 4:3'-, m.p. 176°, and 4:2'-dinitro-4'-methyl-s-diphenyl-, m.p. 176°; 4-nitro-o-tolyl-, m.p. 140°; N-4-nitro-o-tolyl-N'-propyl-, m.p. 173°; 5-nitro-, m.p. 171°, and 4'-bromo-5-nitro-2-methyl-, m.p. 183°, 5-nitro-2:2'-, m.p. 149°, 2:3'-, m.p. 156°, and 2:4'-dimethyl-s-diphenyl-, m.p. 161°; N-4-nitro-o-tolyl-N'- $\alpha$ -, m.p. 191°, and - $\beta$ -naphthyl-, m.p. 154°; 3:3'-dinitro-6:6'-dimethyl-s-diphenyl-, m.p. 162°; N-5-nitro-o-tolyl-N'-propyl-, m.p. 157°; 4-nitro-2:2'-, m.p. 154°, -2:3'-, m.p. 152°, and 2:4'-dimethyl-s-diphenyl-, m.p. 150°; N-5-nitro-o-tolyl-N'- $\alpha$ -, m.p. 166°, and - $\beta$ -naphthyl-, m.p. 165°; 2-nitro-p-tolyl-, m.p. 122°; N-2-nitro-p-N'-propyl-, m.p. 147°; 3-nitro-, m.p. 152°, and 4'-bromo-3-nitro-4-methyl-, m.p. 173°, 3-nitro-2':4-, m.p. 147°, -3':4-, m.p. 152°, and -4:4'-dimethyl-s-diphenyl-, m.p. 176°; N-2-nitro-p-tolyl-N'- $\alpha$ -, m.p. 165°, and - $\beta$ -naphthyl-, m.p. 212°; 3-nitro-p-tolyl-, m.p. 138°; N-3-nitro-p-tolyl-N'-propyl-, m.p. 144°; 2-nitro-, m.p. 125°, and 4'-bromo-2-nitro-4-methyl-, m.p. 156°, 2-nitro-2':4-, m.p. 164°, -3':4-, m.p. 156°, and -4:4'-dimethyl-s-diphenyl-, m.p. 162°; N-3-nitro-4-p-tolyl-N'- $\alpha$ -, m.p. 168°, and - $\beta$ -naphthyl-, m.p. 159°; 5-nitro-2-methoxyphenyl-, N-5-nitro-2-methoxyphenyl-N'-propyl-, m.p. 171°; 5-nitro-, m.p. 173°, and 4'-bromo-5-nitro-2-methoxy-, m.p. 180°, 5-nitro-2-methoxy-2'-, m.p. 162°, -3'-, m.p. 168°, and -4'-methyl-, m.p. 162°, 3':5-, m.p. 164°, and 4':5-dinitro-2-methoxy-s-diphenyl-, m.p. 162°; N-5-nitro-2-methoxy-N'- $\alpha$ -, m.p. 178°, and - $\beta$ -naphthyl-, m.p. 175°; 5:5'-dinitro-2:2'-dimethoxy-s-diphenyl-, m.p. 175°; 3-nitro-o-tolyl-, m.p. 171°; 4'-bromo-2-nitro-6-methyl-s-diphenyl-, m.p. 164°; N-3-nitro-o-tolyl-N'- $\alpha$ -naphthyl-, m.p. 171°; 2-nitro-4':6-dimethyl-, m.p. 160°, 4-nitro-, m.p. 158°, 4'-fluoro-, m.p. 154°, and 4'-bromo-4-nitro-3-methyl-s-diphenyl-, m.p. 147°; N-6-nitro-m-tolyl-N'- $\alpha$ -, m.p. 142°, and - $\beta$ -naphthyl-, m.p. 172°; and 4-nitro-3:4'-dimethyl-s-diphenyl-thiocarbimide, m.p. 110°; 3-, m.p. 84°, 4-, m.p. 74°, and 5-nitro-o-, m.p. 92°, 2-, m.p. 68°, and 3-p-, m.p. 67°, and 6-nitro-m-tolyl-, m.p. 77°, and 5-nitro-2-methoxyphenyl-thiocarbimide, m.p. 83°.

F. R. S.

**Inhibitory effect of substituents in chemical reactions. III. Reactivity of the thiocarbimide group in substituted arylthiocarbimides.** D. W. BROWNE and G. M. DYSON (J.C.S., 1934, 178—179).—The rate of reaction between arylthiocarbimides and EtOH has been measured (cf. A., 1932, 154) and indicates that the addition of EtOH is a side-chain reaction favoured by "electron-recession." *m*- and *p*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H and CCl<sub>2</sub> afford respectively 3-, m.p. 163° (decomp.), and 4-carboxyphenylthiocarbimide, m.p. 220° (decomp.). 4-Carbo-propoxy-, m.p. 32°, -*n*-butoxy-, b.p. 180°/5 mm., and -*n*-amyl-oxy-phenylthiocarbimide, b.p. 205°/5 mm., have been prepared from the corresponding *p*-aminobenzoate, and *Et* phenylacetate-, m.p. 58°, *Et* cinnamate-, m.p. 62°, and *Et*  $\beta$ -phenylpropionate-4-thiocarbimide, b.p. 296°, have been similarly obtained. 5-Nitro-1:2:3-trimethoxy-

benzene on reduction and treatment with CCl<sub>2</sub> yields 3:4:5-trimethoxyphenylthiocarbimide, m.p. 65°.

F. R. S.

**Nitration of some  $\alpha$ -naphthalides.** H. H. HODGSON and J. WALKER (J.C.S., 1934, 180—181).—*o-p*-Ratios for nitration of formo-, benzo-, and *o*-carboxybenzo- $\alpha$ -naphthalide (cf. A., 1933, 1155) are respectively 0.4—0.6, 1.1—1.3, and 1.1—1.3. 4-Nitroformo- $\alpha$ -naphthalide, m.p. 182°, is obtained from the nitration mixture with aq. NaOH.  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub> and *p*-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>2</sub>Cl give a mixture of *di-p*-toluenesulphon- $\alpha$ -naphthalide, m.p. 224°, and the mono-compound, which forms a considerable amount of (NO<sub>2</sub>)<sub>2</sub>-derivative under all conditions of nitration. *Di-p*-toluenesulphon-anilide, m.p. 184°, -*o*-toluidide, m.p. 169°, and *p*-toluidide, m.p. 158°, are described.

F. R. S.

**Derivatives of *m*-phenylenediamine.** F. BELL and R. COHEN (J.C.S., 1934, 243).—Addition of Br to the C<sub>6</sub>H<sub>5</sub>N "salt" of 1:3-di-*p*-toluenesulphonamidobenzene (I) gives the 4:6-Br<sub>2</sub>, m.p. 209° [free base, m.p. 134° (Ac<sub>2</sub> derivative, m.p. 257—260°)], and with more Br the 2:4:6-Br<sub>3</sub>-derivative, m.p. 233° (identified by hydrolysis). Fuming HNO<sub>3</sub> in AcOH converts 1:3-di-*m*-nitrobenzenesulphonamidobenzene, m.p. 195°, into 4:6-(NO<sub>2</sub>)<sub>2</sub>, m.p. 235°, and 2:4:6-(NO<sub>2</sub>)<sub>3</sub>, m.p. 218°, -derivatives. Nitration of (I) gives 4:6-(NO<sub>2</sub>)<sub>2</sub>, m.p. 208—210°, and 2:4:6-(NO<sub>2</sub>)<sub>3</sub>, m.p. 223°, -derivatives.

H. A. P.

***p*-Cymene. II. Preparation of an azo-dye [from 2-amino-*p*-cymene] and 5-amino-*p*-cymene.** S. KIMURA (J. Soc. Chem. Ind. Japan, 1934, 37, 4B).—The red dye *p*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>3</sub>H  $\rightarrow$  2-amino-*p*-cymene, reducible to 2:5-diamino-*p*-cymene, which is converted by oxidation into thymoquinone, is described. When diazotised and reduced it gives 5-amino-*p*-cymene.

H. A. P.

**Alleged colour and dyeing properties of some derivatives of tetra-arylmethanes.** A. WEISSBERGER and J. THIELE (J.C.S., 1934, 148—151).—Condensation of pararosaniline (I) with NH<sub>2</sub>Ph, NMe<sub>2</sub>Ph, and some phenolic derivatives (cf. Sen and Banerjee, A., 1931, 840) gives mixtures, the dyeing properties of which are due to the presence of unchanged (I). From PhOH, pp'p''-triamino-p'''-hydr-oxytetraphenylmethane, colourless, m.p. 247° (decomp.), has been isolated. The dyeing properties of the compounds obtained by condensing resorcinol (II) with ketones (cf. Sen *et al.*, A., 1930, 778) are probably due to substances produced by the action of dehydrating agents on (II).

F. R. S.

**Extension of Michael's reaction. III.** T. N. GHOSH and P. C. GUHA (J. Indian Inst. Sci., 1933, 16, A, 103—112).—The Michael condensation takes place with NPh·N·CO<sub>2</sub>Et (I), (N·CO<sub>2</sub>Et)<sub>2</sub> (II), and NHPH·N·C(CO<sub>2</sub>Et)<sub>2</sub> (III), the yields from (I) and derivatives being poor, and the products from (III) unstable. It does not occur with CHPh·NPh or NPh·CH·CO<sub>2</sub>Et, but addition of Na enolates readily occurs to the ·C·N· group of CO<sub>2</sub>Et·NCS. Interaction of (I) in Et<sub>2</sub>O with the Na derivatives of CH<sub>2</sub>Ac·CO<sub>2</sub>Et (IV), CN·CH<sub>2</sub>·CO<sub>2</sub>Et (V), CH<sub>2</sub>Ac<sub>2</sub>, and NH<sub>2</sub>·CO<sub>2</sub>Et (VI), respectively, gives *Et*  $\beta$ -N-carbomethoxyacetylmethyl-, m.p. 103—104°, *Et*  $\beta$ -N-carbomethoxycyanomethyl-, m.p.

69—70°, *Et*  $\beta$ -*N*-diacetylmethyl-, m.p. 130—131°, and *Et*  $\beta$ -*N*-hydroxy-phenylcarbazinate (VII), m.p. 178—179° (decomp.). Hydrolysis of (VII) with *N*-KOH gives a *K* salt, m.p. 135—136°, to which the formula  $\text{NPh} \left\langle \begin{array}{c} \text{N} \\ \text{O} \end{array} \right\rangle \text{C} \cdot \text{OK}$  is assigned as it cannot be esterified,

but with MeI and EtI gives the *Me*, m.p. 128—129°, and *Et*, m.p. 130—131°, derivatives; the free OH-compound (VIII) (+1H<sub>2</sub>O) has m.p. 214—216°. Interaction of *p*-C<sub>6</sub>H<sub>4</sub>Me·N:N·CO<sub>2</sub>Et with the Na derivative of (VI), hydrolysis of the product, and acidification gives the corresponding compound [(VIII), C<sub>6</sub>H<sub>4</sub>Me in place of Ph], m.p. 168—170°. Addition of the Na compound of (IV) to (II) gives *Et*  $\beta$ -*N*-carbethoxyacetylmethylhydrazinedicarboxylate, m.p. 74—75°.

Interaction of the Na derivatives of (IV), (V), and CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub> with (III) and acidification of the product gives in every case *Et H* phenylhydrazinomalonate, m.p. 110—111° (*NHPh*·NH<sub>2</sub> salt, m.p. 124—125°); this is hydrolysed by KOH in EtOH to

*NHPh*·NH·CH<sub>2</sub>·CO<sub>2</sub>H, m.p. 153°, and oxidised by aq. FeCl<sub>3</sub> to *Et H* benzeneazomalonate, m.p. 174—176°. Similarly, from carbethoxythiocarbimide (IX) and ONa·CMc·CH·CO<sub>2</sub>Et (X) acetylcarbethoxythioacetocarbamic acid, CO<sub>2</sub>Et·CHAc·CS·NH·CO<sub>2</sub>H, is obtained; the corresponding *Et*<sub>2</sub> ester does not appear to be cyclised by NaOEt. From (IX) and CHNa(CO<sub>2</sub>Et)<sub>2</sub> is obtained dicarbethoxythioacetocarbamic acid, CH(CO<sub>2</sub>Et)<sub>2</sub>·CS·NH·CO<sub>2</sub>H, m.p. 70—72°, and a compound, m.p. 164—165°; similarly with (X) diacetylthioacetocarbamic acid, CHAc<sub>2</sub>·CS·NH·CO<sub>2</sub>H, m.p. 121—122° (decomp.), and with CN·CHNa·CO<sub>2</sub>Et *Et* carbethoxycyanothioacetocarbamate, CN·CH(CO<sub>2</sub>Et)·CS·NH·CO<sub>2</sub>Et, m.p. 152—153° (decomp.), hydrolysed by cold 0.1*N*-NaOH to the *Et H* ester, m.p. 158—160° (decomp.), is formed.

H. A. P.

**Arylazoforamidoximes.** G. LONGO (Gazzetta, 1933, 63, 923—926).—PhN<sub>2</sub>Cl is converted by KCN into the cyanide, and this treated with NH<sub>2</sub>OH, whereby benzeneazoforamidoxime, *NPh*·N·C(NOH)·NH<sub>2</sub>, m.p. 125—126° [*Ac* and *Bz* derivatives, m.p. 168° and 191—192° (decomp.)], is formed. The *p*-toluene compound has m.p. 164—165° (decomp.) [*Ac* and *Bz* derivatives, m.p. 193—194° and 192—193° (decomp.)].

E. W. W.

**Carbonitrosohydrazines.** II. Hydrazo- and azo-hydroxamic acids. A. QUILICO and R. JUSTONI (Gazzetta, 1933, 63, 862—870; cf. A., 1933, 59).—Carbonitrosohydrazines react with NH<sub>2</sub>OH in EtOH to form compounds of type NHR·NH·C(OH)·NOH, e.g., phenyl-, m.p. 164° (decomp.), *p*-tolyl-, decomp. 165°, *p*-anisyl-, decomp. 162°, and *p*-chlorophenyl-, decomp. 155°. Hydrazinoformhydroxamic acids. These all give a strong reddish-violet FeCl<sub>3</sub> reaction; the last is oxidised by H<sub>2</sub>O<sub>2</sub> in AcOH to *p*-chlorobenzene-azoformhydroxamic acid, m.p. 165° (decomp.). *p*-Anisylcarbonitrosohydrazine has m.p. 136°.

E. W. W.

***o*-Quinonephenylhydrazones.** A. BURAWOY (Annalen, 1934, 509, 60—73; cf. A., 1933, 828, 946).—A reply to von Auwers (A., 1933, 1156). The *o*-quinonephenylhydrazone structure for *o*-hydroxyazobenzenes is supported by the results of bromination and nitration and from refractometric measurements.

The conclusions of von Auwers and Heimke (A., 1928, 688) are criticised.

H. B.

**Action of bromine on 2- and 6-chloro- and 2- and 6-iodo-3-bromophenols.** H. H. HODGSON and J. NIXON (J.C.S., 1934, 137—138).—2-Chloro-3-bromophenol, m.p. 60° [from 3-bromo-2-aminophenol (I)], with Br in CHCl<sub>3</sub> gives 2-chloro-3 : 4 : 6-tribromophenol, m.p. 96°. 2-Chloro-5-bromophenol, m.p. 60° [from 5-bromo-2-aminophenol (II)], similarly gives 6-chloro-2 : 3 : 4-tribromophenol, m.p. 98°, also obtained by chlorination of the tribromophenol obtained from *m*-C<sub>6</sub>H<sub>4</sub>Br·OH (A., 1933, 1045). 3-Bromo-2-, m.p. 85°, and 6-iodophenol, m.p. 55° [from (I) and (II)], with Br in AcOH give 2 : 3 : 4 : 6-tetrabromophenol, the former by less prolonged action also giving 3 : 4 : 6-tribromo-2-iodophenol, m.p. 125°, also obtained through the 2-NH<sub>2</sub>-compound from 3 : 4 : 6-tribromo-2-nitrophenol (*loc. cit.*).

A. A. L.

**Anomalous introduction of nitro-groups into the benzene nucleus through a diazo-compound.** A. CONTARDI and B. CROCCA (Gazzetta, 1933, 63, 878—884).—Action of nitrous fumes on 2 : 6-dibromoaniline-4-sulphonic acid in H<sub>2</sub>O gives an internal diazonium salt, which when treated with aq. NaNO<sub>2</sub> yields 4-bromo-2 : 6-dinitrophenol; 2 : 6-dinitrophenol-4-sulphonic acid is presumably an intermediate product. 2 : 6-Dibromophenol-4-sulphonic acid and aq. NaNO<sub>2</sub> form 2 : 6-dibromo-4-nitrophenol and 2-bromo-6-nitrophenol-4-sulphonic acid. E. W. W.

**Halogenation of phenolic ethers and anilides.** IV. Chlorination of some *p*-substituted anilides. B. JONES (J.C.S., 1934, 210—213).—The velocity coeffs. of the chlorination at 20° of 13 *p*-substituted anilides in AcOH containing 1% of H<sub>2</sub>O have been determined at different consns. With one exception the results show that an increase in the proportion of HCl to anilide decreases the velocity coeff., the relative directive powers varying with the initial consns. of the reactants. In spite of hydrochloride formation the results confirm the previous conclusions (cf. A., 1932, 26). A comparison of the relative directive influences of Br, Cl, CO<sub>2</sub>H, and NO<sub>2</sub> in *p*-substituted phenolic ethers and anilides is made.

F. R. S.

**Displacement of *tert*-butyl by the nitro-group.** G. TIERIE (Rec. trav. chim., 1934, 53, 126—127).—Nitration of *p*-*tert*- ("p-iso-")butylphenol (cf. Schaaf, A., 1932, 378) displaces the Bu<sup>*t*</sup> group and gives *s*-C<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>)<sub>3</sub>·OH, which is similarly obtained by nitration of tyrosine.

H. A. P.

**Substitution in the methyl-4'-nitro- and -4'-acetamido-diphenyl ethers.** H. A. SCARBOROUGH and J. L. SWEETEN (J.C.S., 1934, 52—56).—*p*-C<sub>6</sub>H<sub>4</sub>Cl·NO<sub>2</sub> (I) and *o*-C<sub>6</sub>H<sub>4</sub>Me·OK (II) give 4'-nitro-2-methyldiphenyl ether (III), m.p. 35°, b.p. 225—230°/14 mm., which with HNO<sub>3</sub>, *d* 1.4, gives nitrophenols and 4 : 4'-dinitro-2-methyldiphenyl ether, m.p. 132° [also obtained from K 5-nitro-*o*-tolylloxide and (I)], and on reduction gives 4'-amino-2-methyldiphenyl ether, isolated as the *Ac* derivative (IV), m.p. 110°. (III) with SO<sub>2</sub>Cl<sub>2</sub> in AcOH gives 4-chloro-4'-nitro-2-methyldiphenyl ether, m.p. 65°, b.p. 235—240°/12 mm., reduced and acetylated to the 4'-NHAc-derivative,

m.p. 122°, which on nitration gives 4-chloro-3'-nitro-4'-acetamido-2-methyldiphenyl ether (V), m.p. 128°, changing above 124° to a form, m.p. 133°, also obtained by chlorinating 3'-nitro-4'-acetamido-2-methyldiphenyl ether (VI), m.p. 83°, which results from the nitration of (IV). The 4'-NH<sub>2</sub>-derivative, m.p. 104°, from (V) on deamination gives 4-chloro-3'-nitro-2-methyldiphenyl ether, m.p. 52°, also obtained from *m*-C<sub>6</sub>H<sub>4</sub>·NO<sub>2</sub> (VII) and K 5-chloro-*o*-tolylxide. (VI) similarly gives 3'-nitro-4'-amino-2-methyl-, m.p. 94°, and 3'-nitro-2-methyl-diphenyl ether, b.p. 235°/14 mm., also obtained from (VII) and (II), and converted by Br into the 4-*Br*-derivative (VIII), m.p. 50°. (III) with Br in AcOH gives 4-bromo-4'-nitro-2-methyldiphenyl ether, m.p. 73° [also obtained from (I) and K 5-bromo-*o*-tolylxide], which is converted as above into the 4'-NHAc-derivative, m.p. 144°, also obtained by the bromination of (IV), and nitrated to 4-bromo-3'-nitro-4'-acetamido-2-methyldiphenyl ether, m.p. 147°, which also results from the bromination of (VI), and is converted through the 4'-NH<sub>2</sub>-compound, m.p. 92°, into (VIII). Nitration of (IV) gives 3':4-dinitro-4'-acetamido-2-methyldiphenyl ether, m.p. 137°, hydrolysed to the 4'-NH<sub>2</sub>-compound, m.p. 170°, which is converted into 3':4-dinitro-2-methyldiphenyl ether, m.p. 110°, also obtained from 2-bromo-5-nitrotoluene and *m*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·OK. 4'-Nitro-3-methyldiphenyl ether (IX) with HNO<sub>3</sub>, *d* 1.4, gives nitrophenols and 4:4'-dinitro-3-methyldiphenyl ether, m.p. 120° [also obtained from (I) and K 6-nitro-*m*-tolylxide, and oxidised to the 3-CO<sub>2</sub>H-compound, m.p. 185°], whilst reduction gives 4'-amino-3-methyldiphenyl ether, m.p. 82° [purified through the sulphate; *Ac* derivative (X), m.p. 140°]. Nitration of (X) yields 3'-nitro- (XI), m.p. 81°, or 3':4-dinitro-4'-acetamido-3-methyldiphenyl ether, m.p. 144° [also obtained from (XI)], which gives 3':4-dinitro-3-methyldiphenyl ether, m.p. 87° [also obtained from *m*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·OK and 5-bromo-2-nitrotoluene], after hydrolysis to the 4'-NH<sub>2</sub>-compound, m.p. 140°. (XI) similarly gives a 4-NH<sub>2</sub>-compound, m.p. 52°, yielding 3'-nitro-3-methyldiphenyl ether (XII), m.p. 47°, also obtained from *m*-C<sub>6</sub>H<sub>4</sub>·Me·OK and (VII). Chlorination of (IX) gives 4-chloro-4'-nitro-3-methyldiphenyl ether, m.p. 114° [also obtained from (I) and 6-chloro-*m*-tolylxide], from which the 4'-NH<sub>2</sub>-compound is obtained as the hydrochloride, m.p. 200° (decomp.), through the *Ac* derivative, m.p. 115°. The last-named is also obtained from (X) (together with a little Cl<sub>2</sub>-compound), and on nitration gives 4-chloro-3'-nitro-4'-acetamido-3-methyldiphenyl ether, m.p. 101°, also obtained from (XI) and yielding 4-chloro-3'-nitro-3-methyldiphenyl ether, m.p. 57°, through deamination of the 4'-NH<sub>2</sub>-compound, m.p. 95°. (I) with K 6-bromo-*m*-tolylxide gives 4-bromo-4'-nitro-3-methyldiphenyl ether (XIII), m.p. 96°, also obtained by bromination of (IX), and reduced and acetylated to the 4'-NHAc-compound, m.p. 130° [also obtained by bromination of (X)]. This on nitration gives 4-bromo-3'-nitro-4'-acetamido-3-methyldiphenyl ether, m.p. 102° [also obtained by bromination of (XI)], the 4'-NH<sub>2</sub>-compound, m.p. 111°, from which gives 4-bromo-3'-nitro-3-methyldiphenyl ether, m.p. 59°, also obtained by bromination of (XII). 4'-Nitro-4-methyldiphenyl ether (XIV), m.p. 68° [from (I) and *p*-C<sub>6</sub>H<sub>4</sub>·Me·OK (XV)], on nitration gives 2:4'-dinitro-4-methyldiphenyl

ether, m.p. 104° [also obtained from 4-chloro-5-nitrotoluene and *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·OK], and on reduction gives 4'-amino-4-methyldiphenyl ether, m.p. 125° [*Ac* derivative (XVI), m.p. 135°]. (XVI) on nitration gives 3'-nitro-, m.p. 95° [yielding as above 3'-nitro-4'-amino-4-methyl-, m.p. 91°, and 3'-nitro-4-methyl-diphenyl ether, isolated as a (NO<sub>2</sub>)<sub>2</sub>-derivative, m.p. 86°, similarly obtained from the condensation product of (VII) and (XV)], and 2:3'-dinitro-4'-acetamido-4-methyldiphenyl ether, m.p. 134°, which gives the 4'-NH<sub>2</sub>-compound, m.p. 119°, and 2:3'-dinitro-4-methyldiphenyl ether, m.p. 87°, also obtained from *m*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·OK and 4-chloro-3-nitrotoluene. (XIV) gives a 2-*Br*-derivative, m.p. 82° [also obtained from (I) and K 5-bromo-*p*-tolylxide], which is reduced and acetylated to give 2-bromo-4'-acetamido-4-methyldiphenyl ether, m.p. 142°, yielding a 3'-NO<sub>2</sub>-derivative, m.p. 98°. This gives 2-bromo-3'-nitro-4'-amino-4-methyldiphenyl ether, m.p. 101°, yielding 2-bromo-3'-nitro-4-methyldiphenyl ether, m.p. 47°, which is also obtained from *m*-C<sub>6</sub>H<sub>4</sub>·Cl·NO<sub>2</sub> and K 3-bromo-*p*-tolylxide. (VII) and K 2-bromo-*p*-tolylxide give 3-bromo-3'-nitro-4-methyldiphenyl ether, m.p. 68°. (III) is unattacked by oxidising agents, whilst (IX) with CrO<sub>3</sub> in AcOH gives 3-carboxy-4'-nitrodiphenyl ether, m.p. 183° (small yield). Similarly are obtained 3-carboxy-4-bromo-4'-nitro-, m.p. 157° (*Et* ester, m.p. 76°), 4'-nitro-4-carboxy-, m.p. 245° (*Et* ester, m.p. 78°), and 2-bromo-4'-nitro-4-carboxydiphenyl ether, m.p. 168° (*Et* ester, m.p. 119°). (IX) with AcCl and AlCl<sub>3</sub> in CS<sub>2</sub> gives 4'-nitro-4-acetyl-3-methyldiphenyl ether, m.p. 88°, oxidised to the 4-CO<sub>2</sub>H-compound, m.p. 204°. The position taken on substitution in these compounds is determined by the ethereal O, except in the nitration of the NHAc derivatives. A. A. L.

**Reaction of chlorobenzene with sodium sulphide and hydrosulphide.** N. N. VOROSCHOV, jun., and S. P. MITSSENDLER (*Compt. rend. Acad. Sci. U.R.S.S.*, 1933, 291—295).—The primary product of reaction of PhCl with NaSH or Na<sub>2</sub>S at 350—360° is Ph<sub>2</sub>S, which reacts with excess of Na<sub>2</sub>S, NaSH, or NaOH to yield PhSNa and PhONa; the yield of secondary products increases with increasing temp., duration of reaction, and relative concn. of Na<sub>2</sub>S or NaSH. R. T.

**Action of sodium on 9-methoxy-10-phenylphenanthrene and 3-phenyl-1-diphenyleneindene.** C. F. KOELSCH (*J. Amer. Chem. Soc.*, 1934, 56, 480—484).—Mg *o*-diphenyl iodide (I) and PhCHO give *o*-phenylbenzhydrol, m.p. 69—70°, the *Me* ether, m.p. 72—73°, of which is converted by successive treatment with Na (in Et<sub>2</sub>O and N<sub>2</sub>) and CO<sub>2</sub> into phenyl-*o*-diphenylacetic acid (II), m.p. 171—173°. (I) and BzCO<sub>2</sub>Et afford (after hydrolysis) *o*-phenylbenzylidic acid, m.p. 189—191° (decomp.), oxidised (CrO<sub>3</sub>, AcOH) to *o*-phenylbenzophenone and reduced (I, red P, AcOH) to (II). Successive treatment of (II) with PCl<sub>5</sub> and AlCl<sub>3</sub> in C<sub>6</sub>H<sub>6</sub> gives 9-phenyl-10-phenanthrol, m.p. 142—143° (acetate, m.p. 153—155°; benzoate, m.p. 179—180°; picrate, m.p. 135°), methylated (Me<sub>2</sub>SO<sub>4</sub>, aq. MeOH—NaOH) to 9-methoxy-10-phenylphenanthrene (III), m.p. 189—190°. Treatment of a suspension of (III) in Et<sub>2</sub>O and N<sub>2</sub> with 40% Na—Hg until dissolution occurs affords 10-sodio-9-



phenylphenanthrene, which with EtOH, CO<sub>2</sub>, and PhCHO gives 9-phenylphenanthrene (IV), m.p. 105—106° (*picrate*, m.p. 115°; 10-*Br*-derivative, m.p. 108—110°), 9-phenylphenanthrene-10-carboxylic acid (V), m.p. 185—187° [together with (IV)], and 9-phenyl-10- $\alpha$ -hydroxybenzylphenanthrene (VI), respectively. More prolonged action of (III) and Na-Hg affords the violet 9:10-disodio-9-phenyl-9:10-dihydrophenanthrene, which is hydrolysed to (IV) and 9-phenyl-9:10-dihydrophenanthrene; treatment with CO<sub>2</sub>, ClCO<sub>2</sub>Me, PhCHO, or BzCl also gives (IV). (V) is converted by SOCl<sub>2</sub> in CCl<sub>4</sub> into 1:2:3:4-dibenzfluorenone, m.p. 186—187°, whilst (VI) is dehydrated (AcOH—conc. H<sub>2</sub>SO<sub>4</sub>) to 9-phenyl-1:2:3:4-dibenzfluorene (VII), m.p. 210—211°.

The Na compound (A., 1933, 1042) from 3-phenyl-1-diphenylencindene is 9-sodio-9-phenyl-1:2:3:4-dibenzfluorene (VIII), since it is hydrolysed (H<sub>2</sub>O) to (VII). (VII) is oxidised (CrO<sub>3</sub>, AcOH) to a compound (IX), C<sub>27</sub>H<sub>18</sub>O<sub>3</sub>, m.p. 188—189°, a small amount of a substance, m.p. 207—208°, and a resinous acid. (IX) and HI—AcOH give an I-containing substance, m.p. 185—187° (darkens at 125°), whilst dissolution in boiling 5% EtOH—NaOH and acidification (dil. HCl) affords a compound, C<sub>27</sub>H<sub>16</sub>O<sub>2</sub>, m.p. 184—186°. (VIII) and BzCl give 9-benzoyl-9-phenyl-1:2:3:4-dibenzfluorene, m.p. 228—229°, also prepared by successive treatment of (VII) with 40% Na—Hg and BzCl.

H. B.

***p*-Methoxy- and 3:4-dimethoxy-phenylurethanes.** O. BRUNNER and R. WÖHRL (Monatsh., 1934, 63, 374—384).—From *p*-OMe·C<sub>6</sub>H<sub>4</sub>·NCO (prepared in 80% yield from *p*-OMe·C<sub>6</sub>H<sub>4</sub>·CO·N<sub>3</sub> by the Curtius method) are obtained: *methyl*-, m.p. 90°, *ethyl*-, m.p. 65°, *n*-, m.p. 69°, and *iso-propyl*-, m.p. 63°, *n*-, m.p. 45°, and *iso-butyl*-, m.p. 71°, *n-amyl*-, m.p. 53°, *n-hexyl*-, m.p. 60°, *n-heptyl*-, m.p. 78°, *n-octyl*-, m.p. 77.5°, *n-decyl*-, m.p. 78°, *n-dodecyl*-, m.p. 80°, *n-tetradecyl*-, m.p. 83°, *n-hexadecyl*-, m.p. 88.5°, *n-octadecyl*-, m.p. 92°, *n-docosyl*-, m.p. 98°, *n-tetracosyl*-, m.p. 102°, *allyl*-, m.p. 41°, *phenyl*-, m.p. 151°, *benzyl*-, m.p. 99.5°, and *cholesteryl*-, m.p. 152° (not sharp), *p-methoxyphenylurethane*. Similarly from 3:4-dimethoxyphenylcarbimide, b.p. 142—143°/16 mm. (from the *hydrazide*, m.p. 145°, of veratric acid), the corresponding 3:4-dimethoxyphenylurethanes are obtained, their m.p. being, respectively, 81°, 78.5°, 62°, 88°, 58°, 68°, 67°, 67°, 67.5°, 67°, 73°, 83°, 79.5°, 85°, 87°, 92.5°, 96.5°, 68°, —, 108°, and 160°. *s-Di*-(3:4-dimethoxyphenyl)carbimide has m.p. 215°.

J. W. B.

**Synthesis of pharmacologically important amines. VIII. Substances similar to papaverine.** K. KINDLER and W. PESCHKE [in part with O. BENECKE] (Arch. Pharm., 1934, 272, 60—70; cf. A., 1933, 1288).—Protocatechualdehyde, NaOEt, and EtBr in EtOH at 130° give 3:4-C<sub>6</sub>H<sub>3</sub>(CHO)(OEt)<sub>2</sub> (I), b.p. 158°/16 mm. [also obtained from pyrocatechol Et<sub>2</sub> ether (“ethylguaiaicol”) by Gattermann’s method]. (I) with EtOAc and Na gives Et 3:4-diethoxycinnamate, m.p. 62°, which by hydrogenation (Pd-black) at 18° and hydrolysis affords  $\beta$ -3:4-diethoxyphenylpropionic acid, m.p. 107°; the NH<sub>4</sub> salt of this acid in NH<sub>3</sub> at 200° gives the *amide* (II), m.p.

111°, also obtained from (I) and MeOAc by way of Me 3:4-diethoxy-cinnamate, b.p. 205—207°/15 mm., m.p. 73°, and -phenylpropionate, m.p. 43°, the latter giving (II) by shaking with 25% aq. NH<sub>3</sub>. (I) leads to acetyl-3:4-diethoxymandelonitrile, b.p. 205—207°/15 mm., which is reduced (Pd-black; 2 atm.) in AcOH—H<sub>2</sub>SO<sub>4</sub> to  $\beta$ -3:4-diethoxyphenylethylamine (III), b.p. 162°/13 mm. (*hydrochloride*, m.p. 195° after sintering at 130°; *picrate*, m.p. 142—143°), also obtained from (II) in 61% yield. Hydrogenation (Pd-black; 60°; 2 atm.) of 3:4-dimethoxyphenylacetonitrile in EtOH gives a 92% yield of *di*- $\beta$ -3:4-dimethoxyphenylethylamine (IV), m.p. 55—56° (*hydrochloride*, m.p. 201°). BzCN, veratrole, and AlCl<sub>3</sub> in hot ligroin give 3:4:3':4'-tetramethoxytriphenylacetonitrile, m.p. 124°, which is hydrogenated (Pd-black; 80°; 2 atm.) in AcOH—H<sub>2</sub>SO<sub>4</sub> to  $\beta\beta$ -3:4:3':4'-tetramethoxytriphenylethylamine, (V), m.p. 113—113.5°. Pyrogallol Me<sub>3</sub> ether gives similarly 2:3:4:2':3':4'-hexamethoxytriphenyl-acetonitrile, m.p. 149°, and -ethylamine (VI), m.p. 139—140°. Nine primary, *sec.*, and *tert.*  $\beta$ -alkoxyphenylethylamines, including (III), (IV), (V), and (VI), resemble papaverine in pharmacological action and are highly toxic to paramoecia.

R. S. C.

**Oxidation of isosafrole.** M. IMOTO (J. Soc. Chem. Ind. Japan, 1934, 37, 26—29B).—Oxidation of isosafrole with alkaline KMnO<sub>4</sub> at 80—90° gave 79.5% of piperonylic acid (I), m.p. 226—227.5°. Addition of various “catalysts” diminished the yield. Oxidation with HNO<sub>3</sub> [15% at 75—100°; 25%+Hg(OAc)<sub>2</sub> at 50—100°] gave (I) in poor yield, piperonal, and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.

H. A. P.

**Phthalates of quinol mono-ethers.**—See B., 1934, 187.

**Manufacture of derivatives [phosphates of mono-ethers] of dihydroxybenzenes.**—See B., 1934, 232.

**Rate of oxidation of quinol with atmospheric oxygen.**—See this vol., 370.

**Inositolphosphoric acid compounds II. Compounds of iron inositol phosphate with salts of hydroxy-acids.** S. OTOLSKI (Rocz. Chem., 1934, 14, 78—86).—Na lactate, malonate, and citrate form sol. compounds with Fe<sup>III</sup> inositol phosphate.

R. T.

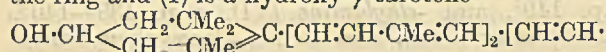
**Molecular rearrangements of optically active radicals.** E. S. WALLIS and P. I. BOWMAN (J. Amer. Chem. Soc., 1934, 56, 491).—When the OH group in *l*-CPhMeEt·CH<sub>2</sub>·OH is replaced by Cl, rearrangement occurs with production of a *d-tert.* chloride.

E. S. H.

**Triphenylmethane series.** I. LIFSCHITZ (Rec. trav. chim., 1934, 53, 191—196).—Polymethoxytriphenylcarbinols, e.g., the 2:4:6:2':4':6'-(OMe)<sub>6</sub>- (*perchlorate*; *cyanide*, m.p. 152—153°) and 2:4:6:2':4':6':4''-(OMe)<sub>7</sub>-derivatives, are conveniently prepared by oxidation of the corresponding triphenylmethane [2:4:6:2':4':6':4''-(OMe)<sub>7</sub>-compound, m.p. 142°] with PbO<sub>2</sub> in AcOH. Exposure to ultra-violet light with quinol in C<sub>6</sub>H<sub>6</sub> gives derivatives of the type 2CAR<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>·2—2.5H<sub>2</sub>O; of these the 4:4':4''-(OMe)<sub>3</sub>-, m.p. 143°, and

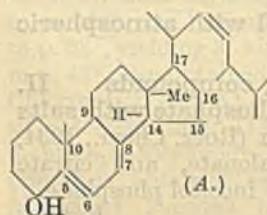
2 : 4 : 6 : 2' : 4' : 6'-(OMe)<sub>6</sub>, m.p. 141°, -compounds are described. H. A. P.

**Rubixanthin, a new xanthophyll C<sub>40</sub>H<sub>56</sub>O.** R. KUHN and C. GRUNDMANN (Ber., 1934, 67, [B], 339—344).—*Rubixanthin* (I), C<sub>40</sub>H<sub>56</sub>O, is present in hips and haws accompanied by considerable amounts of lycopene and carotenes. The ripe fruits of *Rosa rubinosa* are a particularly suitable source. Isolation is effected by chromatographic adsorption using Al<sub>2</sub>O<sub>3</sub> which adsorbs (I) more readily than any of the carotenoids. (I) has m.p. 160° (Berl). Its absorption bands in various media are exactly coincident with those of γ-carotene. In distribution phenomena it very closely resembles kryptoxanthin (II). Catalytic hydrogenation causes union with 12 H<sub>2</sub>. Since O is present as OH, (I) is monocyclic. Degradation with O<sub>3</sub> affords 1 mol. of COMe<sub>2</sub>. Since (I) does not promote growth of rats fed on a diet free from vitamin-A, OH is probably attached to the ring and (I) is a hydroxy-γ-carotene



CH·CMe]<sub>3</sub>·CH<sub>2</sub>·CH<sub>2</sub>·CH·CMe<sub>2</sub>. Although the formula contains asymmetric C, (I) does not appear to be optically active ([α]<sub>D</sub> ± 10° in C<sub>6</sub>H<sub>6</sub>), thus resembling (II). The xanthophyll from *Calendula officinalis* appears identical with (I). H. W.

**Ring-system of sterols and bile acids. V. Constitution of ergosterol and its irradiation products.** O. ROSENHEIM and H. KING (Chem. and Ind., 1934, 196—200; cf. A., 1933, 497).—The structure assigned to ergosterol (I) by Windaus and Langer (this vol., 186) does not contain the ·CH·C< group (which is necessary to account for the production and properties of ergostadienetriol), does not meet the requirements of X-ray analysis or the measurements of unimol. films, and offers no explanation for the intense ultra-violet absorption of (I). Structure (A), which is now assigned to (I), meets the above requirements and explains (a) the reduction of 22 : 23-dihydro-ergosterol to γ- and α-ergosterol by Na+EtOH and Pt+H<sub>2</sub>, respectively, (b) the reduction (H<sub>2</sub>, Pt) of β-ergostadienetriol to ergostenetriol, and (c) reduction (Zn, KOH) of 22 : 23-dihydro-ergosterol peroxide to isoergostenetriol (double linking between C<sub>7</sub> and C<sub>8</sub>). Reductions (as above) involving Pt+H<sub>2</sub> probably involve the formation of an "inert" double linking between C<sub>8</sub> and C<sub>9</sub>, and thus explain the difficulty of reduction (catalytic) of (I) to ergosterol; a similar isomerisation occurs in the change β- → α-pinene (A., 1926, 1148). The close association of the OH with the conjugated system accounts for the absorption of (I); the max. at 280 mμ is also found for oxycholesterilene (C·C·C·C·CO), whilst cholesterilene (C·C·C·C·C), like dihydrobenzene, shows a max. at 250 mμ. The ready loss of H<sub>2</sub>O from (I) (by treatment with POCl<sub>3</sub> or C<sub>6</sub>H<sub>4</sub>Me·SO<sub>2</sub>Cl), the ease of pinacol formation, and catalytic reduction of neoergosterol to a hydrocarbon [and similar reduction (unpublished) of cholestene-3 : 4-diol to cholestan-3-ol and cholestane]



favour the C<sub>4</sub>·OH formulation. The adduct ergosterol-maleic acid can thus undergo γ-lactonisation [which might account for the anomalous titration results (Windaus and Langer, *loc. cit.*)].

The changes (caused by irradiation) (I) → lumisterol (II) → protachysterol (III) → tachysterol (IV) → calciferol (V) may involve the movement of the conjugated system, viz., C<sub>5</sub>·C<sub>6</sub>·C<sub>7</sub>·C<sub>8</sub> (I) → C<sub>6</sub>·C<sub>7</sub>·C<sub>8</sub>·C<sub>9</sub> (II) → C<sub>6</sub>·C<sub>7</sub>·C<sub>8</sub>·C<sub>14</sub> (III) → C<sub>7</sub>·H<sub>8</sub>·C<sub>14</sub>·C<sub>15</sub> (IV) → C<sub>8</sub>·C<sub>14</sub>·C<sub>15</sub>·C<sub>16</sub> (intermediate) → C<sub>14</sub>·C<sub>15</sub>·C<sub>16</sub>·C<sub>17</sub> (V). At the same time, inversion of the OH occurs [in (II)–(V)] and (II)–(V) probably contain C<sub>5</sub>-H and C<sub>10</sub>-Me *cis* to one another (*i.e.*, transition from the steric configuration of the sterols to that of the bile acids). H. B.

**Dehydrogenation of œstrin.** J. W. COOK and A. GIRARD (Nature, 1934, 133, 377—378).—Reduction of the CO< of ketohydroxyœstrin (I) to CH<sub>2</sub>< and dehydrogenation of the "deoxo" compound yielded a non-acidic substance by a secondary change involving the OH. Methylation of the OH before dehydrogenation gave a OMe-compound, m.p. 76—77°, which when heated with Se and distilled over Na in a vac. yielded (from EtOH) colourless needles or plates, the analysis of which corresponded with a methoxycyclopentenophenanthrene (II), m.p. 134.5—136° [orange-red picrate, m.p. 135—136.5°; golden-orange C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>3</sub> complex, m.p. 160—161°]. If the OH and the five-membered ring in the current formula for (I) are correctly oriented, (II) must be 7-methoxy-1 : 2-cyclopentenophenanthrene. L. S. T.

**Marine products. II. Sterols of molluscs.** W. BERGMANN (J. Biol. Chem., 1934, 104, 317—328).—A new sterol, *ostreasterol* (I), m.p. 142—143°, [α]<sub>D</sub><sup>20</sup> -43.57° in CHCl<sub>3</sub>, has been isolated from the unsaponifiable fraction (10%) of the fat from the whole oyster (*Ostrea virginica*) as well as from its individual organs, and from the common round clam (*Venus mercenaria*) and the mussel *Modiola*. It is present with cholesterol (III) in the gastropods *Fulgur carica* and *F. canaliculata*, and is believed to be widely distributed among other mollusca, in which it replaces (III).

(I), C<sub>27</sub>H<sub>46</sub>O or C<sub>27</sub>H<sub>44</sub>O, gives an *acetate*, m.p. 134.5°, [α]<sub>D</sub><sup>20</sup> -45.94° in CHCl<sub>3</sub> (*Br<sub>3</sub>-derivative*, C<sub>29</sub>H<sub>45</sub>O<sub>2</sub>Br<sub>3</sub> or C<sub>29</sub>H<sub>47</sub>O<sub>2</sub>Br<sub>3</sub>, m.p. 122°), *propionate*, m.p. 113—114°, and *benzoate*, m.p. 145—147° to a turbid liquid which then turns blue, green, and again colourless, clearing at 152°; cf. benzoate of (III). Titration with BzO<sub>2</sub>H shows two double linkings. "*Ostreasterol II*," m.p. 122° (*acetate*, C<sub>27</sub>H<sub>45</sub>OAc, m.p. 104—105°, [α]<sub>D</sub><sup>20</sup> -15.9° in CHCl<sub>3</sub>), which is found in the acetylation mother-liquors from (I), does not give insol. Br-derivatives. Both (I) and "II" give positive Liebermann-Burchard and Salkowski reactions. W. S.

**Microciona prolifera.**—See this vol., 316.

**4-Aminocyclohexylacetic acid.** E. FERBER and P. LEONHARDT (Ber., 1934, 67, [B], 245—249).—Treatment of CH<sub>2</sub>Ph·CN with HNO<sub>3</sub> (*d* 1.5) affords *p*-nitrophenylacetonitrile, m.p. 116°, in 60—72% yield, converted by 77% EtOH and HCl into Et. *p*-nitrophenylacetate (I), m.p. 65—66°, in 91% yield. (I) is also obtained by nitration of CH<sub>2</sub>Ph·CO<sub>2</sub>H and esteri-

fication of the crude product. Reduction of (I) by  $\text{SnCl}_2$  and  $\text{HCl}$  in  $\text{EtOH}$  leads to the compound,  $2\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}_2\text{H}_2\text{SnCl}_6$ , whence *Et p-aminophenylacetate*, m.p.  $49.5^\circ$  (*hydrochloride*, m.p.  $215^\circ$ ). Hydrogenation of (I) at  $60^\circ/2.5$  atm. (Skita) leads to a mixture (II) of aminotetrahydro-ester and acid, hydrolysed by  $5\text{N-HCl}$  at  $100^\circ$  to the acid (*Cu salt*). Treatment of (II) with  $\text{BzCl}$  in  $\text{CHCl}_3$  and 5%  $\text{NaOH}$  gives an oil (III) from which *Et 4-benzamidocyclohexylacetate* (IV), m.p.  $142^\circ$ , slowly separates. (IV) is hydrolysed by aq.  $\text{Ba}(\text{OH})_2$  to *trans-4-benzamidocyclohexylacetic acid*, m.p.  $190-191^\circ$  (*Ba salt*, m.p.  $278-279^\circ$ ). Further cooling of (III) causes deposition of crystals, m.p. (indef.)  $35^\circ$ , transformed at  $200^\circ$  into (IV). Treatment of (II) with *d-tartaric acid* in  $\text{EtOH}$  leads to *cis-d-4-aminocyclohexylacetic acid H tartrate*, m.p.  $153-155^\circ$ ,  $[\alpha]_D^{25} +40^\circ$  in  $\text{H}_2\text{O}$ , whence *cis-d-4-aminocyclohexylacetic acid*, m.p.  $289.5^\circ$  (decomp.),  $[\alpha]_D^{25} +11^\circ$  in  $\text{H}_2\text{O}$ . *trans-4-Aminocyclohexylacetic acid*, m.p.  $308-310^\circ$ , is obtained by hydrolysis of (IV) by boiling  $\text{Ba}(\text{OH})_2-50\%$   $\text{MeOH}$ . H. W.

**Phenylcarbimide derivatives and their immunological properties.** III. The amino-acid derivatives and serological inhibition tests. S. J. HOPKINS and A. WORMALL (*Biochem. J.*, 1934, **28**, 228-236).— $\text{PhNCO}$  reacts with  $\alpha$ - (I) and  $\epsilon$ -amino-*n*-hexoic acid (II) to yield  $\alpha$ - and  $\epsilon$ -phenylcarbamido-*n*-hexoic acids, m.p.  $140-141^\circ$  and  $126-127^\circ$ , respectively.  $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{NCO}$  yields with glycine, alanine, leucine, (I), (II), lysine (III), cystine (IV), aspartic acid, and tyrosine the corresponding phenylcarbamido-acids [bis-derivatives of (III) and (IV)], which decompose at  $200-210^\circ$ ,  $181-183^\circ$ ,  $162-164^\circ$ ,  $181-182^\circ$ ,  $170-172^\circ$ ,  $176-177^\circ$ ,  $174-175^\circ$ ,  $175-176^\circ$ , and  $197-199^\circ$ , respectively. The reaction between phenylcarbamido-proteins (cf. A., 1933, 846) and the corresponding antisera in precipitin and complement fixation reactions is inhibited by the phenylcarbamido-acids, but not by the parent  $\text{NH}_2$ -acids. The most highly active are those derived from (II) and (III). It is therefore probable that a large no. of the  $\epsilon\text{-NH}_2$ -groups of the lysine components of the intact protein are free. W. O. K.

**Alkaline halogenation.** I. Chlorination of sodium benzoate. J. C. SMITH (*J.C.S.*, 1934, 213-218).—Chlorination of  $\text{NaOBz}$  by aq.  $\text{NaOCl}$  gives 47% of *o*-, 33% of *m*-, and 20% of *p*-Cl-derivative. It is suggested that the order is due to activation by the negative charge on the  $\cdot\text{CO}_2\cdot$  of the benzoate anion of all positions, the effect falling with distance. Excess of  $\text{BzOH}$  was used, the products were esterified, and the esters fractionally distilled. The regenerated acid mixtures were analysed thermally. F. R. S.

**Perkin reaction.** I. First phase of the reaction. S. ISHIKAWA and R. KOJIMA. II. Condensation of  $\beta$ -methylcrotonic anhydride with aldehydes. S. ISHIKAWA and H. KATOH (*Sci. Rep. Tokyo Bunrika Daigaku*, 1934, **1**, 289-296, 297-305).—I. Determinations of the active H by the Zerevitinov method show that  $\text{Ac}_2\text{O}$ ,  $(\text{PrCO})_2\text{O}$ ,  $(\text{Bu}^t\text{CO})_2\text{O}$  (I),  $(\text{CH}_2\text{Ph}\cdot\text{CO})_2\text{O}$  (II), and  $(\cdot\text{CH}_2\cdot\text{CO})_2\text{O}$ , all of which contain a  $\cdot\text{CO}\cdot$  group adjacent to a  $\text{Me}$  or  $\cdot\text{CH}_2\cdot$  group, react in  $\text{C}_5\text{H}_5\text{N}$  solution giving vals. increasing from 0.14 (40%) for (I) to 1.21 (40%) for (II).

Similar but lower vals. are obtained in anisole and still lower vals. in xylene. Maleic and  $\beta$ -methylcrotonic anhydrides (III), in which the  $\cdot\text{CH}_2\cdot$  group is absent, give no reaction. Thus the primary reaction in the Perkin synthesis is the enolisation of the anhydride.  $\text{CH}_2\text{Ph}\cdot\text{CN}$  acts in the tautomeric form and fluorene also reacts slightly, but  $\text{CH}_2\text{Ph}_2$  has no action.

II. (III) and  $\text{PhCHO}$  in presence of  $\text{NEt}_3$  at  $150^\circ$  give  $\alpha$ -isopropenylcinnamic acid, m.p.  $132^\circ$  (yield 38%), reduced with  $\text{Pd-BaSO}_4$  and  $\text{H}_2$  to  $\beta$ -phenyl- $\alpha$ -isopropylpropionic acid, b.p.  $155-160^\circ/5$  mm. (*chloride*, b.p.  $136-141^\circ/21$  mm.; *anilide*, m.p.  $128.3^\circ$ ). Less satisfactory yields are obtained when other bases or  $\text{KOAc}$  are used as condensing agents. The following are prepared in a similar manner, the appropriate aldehyde being given in parentheses:  $\delta$ -phenyl- $\alpha$ -isopropenyl- $\Delta^{\alpha\gamma}$ -pentadienoic acid, m.p.  $167^\circ$  (cinnamic);  $\alpha$ -isopropenyl-*o*-nitro-, m.p.  $192^\circ$  (*o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ ),  $\alpha$ -isopropenyl-*p*-methoxy-, m.p.  $175.6^\circ$  (*p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ ), and  $\alpha$ -isopropenyl-3 : 4-methylene-dioxy-cinnamic acid, m.p.  $154.8^\circ$  (piperonal);  $\alpha$ -isopropenylfurfurylideneacetic acid, m.p.  $127^\circ$  (furfural). Vanillin gives a resin under these conditions.

S. C.

**Degradation of  $\alpha$ -bromo-acids to aldehydes and ketones.** J. VON BRAUN [with E. ANTON, F. FISCHER, W. KELLER, and G. MANZ] (*Ber.*, 1934, **67**, [B], 218-225).—Reaction follows the course  $\text{CR}_2\text{Br}\cdot\text{CO}_2\text{H} \rightarrow \text{CR}_2\text{Br}\cdot\text{COCl} \rightarrow \text{CR}_2\text{Br}\cdot\text{CO}\cdot\text{N}_3 \rightarrow [\text{CR}_2\text{Br}\cdot\text{CO}\cdot\text{N} <] \rightarrow \text{CR}_2\text{Br}\cdot\text{N}\cdot\text{C}\cdot\text{O} \rightarrow \text{CR}_2\text{Br}\cdot\text{NH}_2 \rightarrow \text{CR}_2\cdot\text{O}$ . The aldehyde or ketone is obtained in about 60% yield. Hexahydrobenzoyl chloride and Br at  $125^\circ$  yield 1-bromohexahydrobenzoyl chloride, readily hydrolysed to 1-bromohexahydrobenzoic acid, b.p.  $120-122^\circ/0.7$  mm., m.p.  $61^\circ$ , whence by  $\text{SOCl}_2$  the pure 1-bromohexahydrobenzoyl chloride (I), b.p.  $105-107^\circ/15$  mm. (I) and  $\text{NaN}_3$  (activated by  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ ) in  $\text{C}_6\text{H}_6$ ,  $\text{PhMe}$ , or  $\text{C}_5\text{H}_5\text{N}$ , react at about  $80^\circ$  and the product is treated successively with cold  $\text{KOH-EtOH}$  and  $\text{HCl}$ , thereby giving cyclohexanone. Bromination of  $\alpha$ -butyl-*n*-hexoic acid smoothly affords  $\alpha$ -bromo- $\alpha$ -butyl-*n*-hexoic acid, b.p.  $168-171^\circ/15$  mm., whence the corresponding chloride, b.p.  $126-127^\circ/15$  mm., and ultimately  $\text{COBu}_2$  (semicarbazone, m.p.  $89^\circ$ ) in 71-77% yield. Dicyclopentylacetic acid (II), P, and Br yield  $\alpha$ -bromodicyclopentylacetic acid, b.p.  $175^\circ/12$  mm., m.p.  $32^\circ$ , whence dicyclopentyl ketone (III), b.p.  $110-112^\circ/12$  mm. (semicarbazone, m.p.  $158-162^\circ$ ). Dicyclopentyl ketoxime, m.p.  $92^\circ$ , is reduced by Na and  $\text{EtOH}$  to dicyclopentylmethylamine (IV), b.p.  $120-122^\circ/14$  mm. [*hydrochloride* (V), m.p.  $193-194^\circ$ ; *picrate*, m.p.  $127^\circ$ ]. (IV) is obtained in 70% yield by treating (II) in conc.  $\text{H}_2\text{SO}_4$  with  $\text{N}_3\text{H}$  or by the action of activated  $\text{NaN}_3$  in  $\text{C}_6\text{H}_6$  on dicyclopentylacetyl chloride, b.p.  $143-144^\circ/13$  mm., followed by  $\text{HCl}$ . Di(dicyclopentylmethyl)carbamide has m.p.  $288^\circ$  after softening at  $280^\circ$ . (V) is transformed by  $\text{NaNO}_2$  into a mixture of  $\text{C}_{11}\text{H}_{19}\cdot\text{OH}$  and  $\text{C}_{11}\text{H}_{18}$ , from which (III) is not obtained by oxidation. (III) is not smoothly prepared by the dry distillation of Ca cyclopentanecarboxylate or from  $\alpha$ -bromodicyclopentylacetamide, Br, and  $\text{KOH}$ . *n*-Hexyl bromide is converted successively into *Et n-hexylmalonate*, b.p.  $150-155^\circ/20$  mm., *n-hexylmalonic acid*, m.p.  $103-105^\circ$ ,  $\alpha$ -bromo-*n*-hexylmalonic acid, m.p.  $119-121^\circ$  (decomp.),

$\alpha$ -bromo-octioic acid, b.p. 118—121°/0.5 mm.,  $\alpha$ -bromo-octoyl chloride, b.p. 112—114°/15 mm., and heptaldehyde mixed with  $\alpha$ -heptylideneheptaldehyde. Et cyclopentylmalonate is hydrogenated and hydrolysed to cyclopentylmalonic acid, m.p. 162°, whence successively  $\alpha$ -bromocyclopentylacetic acid, b.p. 121—123°/0.5 mm., m.p. 50°,  $\alpha$ -bromocyclopentylacetyl chloride, b.p. 130—132°/16 mm., and cyclopentylformaldehyde (semicarbazone, m.p. 124°).  $\alpha$ -Bromo- $\delta$ -phenylvaleryl chloride, b.p. 172°/16 mm., gives  $\gamma$ -phenylbutaldehyde, b.p. 120—122°/16 mm. (semicarbazone, m.p. 105°), in 58.5% yield. H. W.

**1-Methylhydrindene-4-carboxylic acid.** H. HOYER (J. pr. Chem., 1934, [ii], 139, 242—244).—4-Bromohydrindone (in 90% yield by cyclisation of  $o$ -C<sub>6</sub>H<sub>4</sub>Br·CH<sub>2</sub>·CH<sub>2</sub>·COCl with AlCl<sub>3</sub> in CS<sub>2</sub>) with MgMeBr gives 4-bromo-1-hydroxy-1-methylhydrindene, b.p. 135—136°/25 mm., m.p. 33—34°, reduced by red P+HI (*d* 1.7) at 150—160° to 4-bromo-1-methylhydrindene (not pure), b.p. 245°, the Grignard compound of which with CO<sub>2</sub> affords 1-methylhydrindene-4-carboxylic acid, m.p. 138—139°. J. W. B.

**Derivatives of 8-bromo- and 8-chloro-1-naphthoic acids and their orientation by dehalogenation and decarboxylation.** H. G. RULE, W. PURSELL, and (in part) R. R. H. BROWN (J.C.S., 1934, 168—171).—Nitration of 8-bromo-1-naphthoic acid (I) (improved prep.; Et ester, m.p. 52°) gives the 5-NO<sub>2</sub>, m.p. 245° (Me ester, m.p. 97°; Et ester, m.p. 103°), and the 4 : 5-(NO<sub>2</sub>)<sub>2</sub>, (II), m.p. 250—252° (Me ester, m.p. 155°; Et ester, m.p. 127—128°), -derivative. The Br is removed by boiling with Cu in PhMe. Thus (II) gives 4 : 5-dinitro-1-naphthoic acid, m.p. 265° (Et ester, m.p. 143—144°), decarboxylated in boiling quinoline with Cu. Bromination of (I) in AcOH at 150° gives 5 : 8-dibromo-1-naphthoic acid.

F. R. S.

**Constitution of dinitroacenaphthenequinone and of dinitronaphthalic acid. Preparation of a new dinitronaphthalene.** H. G. RULE and R. R. H. BROWN (J.C.S., 1934, 171—174).—Oxidation of 3-nitroacenaphthenequinone to the corresponding dinitronaphthalic anhydride, followed by mercuration and treatment of the product with Br, gives 8-bromo-4-nitro-1-naphthoic acid, m.p. 201—203°; similar treatment of dinitroacenaphthenequinone (I) leads to 8-bromo-4 : 5-dinitro-1-naphthoic acid (preceding abstract), thus establishing (I) as the 3 : 4-(NO<sub>2</sub>)<sub>2</sub>-compound. 3-Nitronaphthalic acid similarly treated yields a mixture, giving a fraction m.p. 240—242°, apparently 8-bromo-3-nitro-1-naphthoic acid (II), since when heated with Cu in PhMe it gave 3-nitro-1-naphthoic acid, m.p. 268—269°. (II) gives a Me ester, m.p. 173°, and Et ester, m.p. 155—156°. Dinitronaphthalic acid yields 8-bromo-3 : 6-dinitro-1-naphthoic acid, m.p. 273—275° (Me ester, m.p. 137—138°; Et ester, m.p. 205—207°), the mercuri-compound being converted by HCl into 3 : 6-dinitro-1-naphthoic acid, m.p. 273.5—274° (Me ester, m.p. 196—197°; Et ester, m.p. 145—146°), decarboxylated to 2 : 7-dinitronaphthalene, m.p. 234°. F. R. S.

**Preparation of naphthastyryl from 8-bromo-1-naphthoic acid.** H. G. RULE and R. R. H. BROWN (J.C.S., 1934, 137).—8-Bromo-1-naphthoic acid with

aq. NH<sub>3</sub>, NH<sub>4</sub>NO<sub>3</sub>, KClO<sub>3</sub>, and a little Cu at 130—150° under pressure gives naphthastyryl, m.p. 181° (yield 82%; less under atm. pressure, or in the absence of the inorg. salts). A. A. L.

**Reactivity of atoms and groups in organic compounds. XIII. Influence of structure on the pyrolysis of esters of triphenylacetic acid.** J. F. NORRIS and A. CRESSWELL (J. Amer. Chem. Soc., 1934, 56, 423—426).—The temp. quoted in parentheses after the following esters of CPh<sub>3</sub>·CO<sub>2</sub>H are those at which signs of decomp. are shown when the esters are heated for 1 hr.: Me (I), m.p. 184—185° (196°), Et, m.p. 116—117° (188°), Pr<sup>α</sup>, m.p. 98—99° (169°), Pr<sup>β</sup>, m.p. 83.5—84.5° (154°), Bu<sup>α</sup>, m.p. 99—99.6° (183°) sec.-Bu, m.p. 101—102° (163°), Bu<sup>β</sup>, m.p. 88—89° (149°), n-amyl, m.p. 76—76.5°, isoamyl, m.p. 77.5—78°, n-hexyl, m.p. 84—84.5°, benzyl (II), m.p. 99—99.5° (179°), and  $\beta$ -phenylethyl, m.p. 92.5—93° (157°). For the first six esters, the effect of the alkyl group on the thermal stability is similar to that of the same alkyl group in CPh<sub>3</sub>·Oalk (A., 1930, 470). The Bu<sup>β</sup>, ·CH<sub>2</sub>Ph, and ·CH<sub>2</sub>·CH<sub>2</sub>Ph groups exert opposite effect in the two series. The above esters [except (I) and (II)] when heated to boiling decompose thus: CPh<sub>3</sub>·CO<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>R → CHPh<sub>3</sub>+CO<sub>2</sub>+CH<sub>2</sub>:CHR; (I) gives 61.9% of CH<sub>2</sub>O and 8% of CO, whilst (II) affords 42.4% of CO. H. B.

**Ring-chain tautomerism of  $\beta$ -*p*-bromobenzoyl-crotonic esters.** R. E. LUTZ and A. W. WINNE (J. Amer. Chem. Soc., 1934, 56, 445—447).—*cis*- $\beta$ -*p*-Bromobenzoylcrotonyl chloride ( $\gamma$ -chloro- $\gamma$ -*p*-bromophenyl- $\beta$ -methyl- $\gamma$ -crotonolactone) (A., 1933, 502) and MeOH give  $\gamma$ -methoxy- $\gamma$ -*p*-bromophenyl- $\beta$ -methyl- $\gamma$ -crotonolactone (cyclic Me  $\beta$ -*p*-bromobenzoylcrotonate) (I), m.p. 64°, also formed (cf. loc. cit.) from *cis*- $\beta$ -*p*-bromobenzoylcrotonic acid (II) and MeOH-HCl. The cyclic Et ester (III), b.p. 165—168°/5 mm., is prepared similarly. (I) and (III) are hydrolysed (EtOH-NaOH) to (II), which is reduced (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>) to  $\beta$ -*p*-bromobenzoylbutyric acid [Me (IV), b.p. 193—194°/20 mm., and Et (V), m.p. 34.5°, esters]. The open-chain Me (VI), m.p. 69° (corr.), and Et, m.p. 42°, esters of (II) are prepared by the Ag salt method and are reduced (Zn, AcOH) to (IV) and (V), respectively. Exposure of Me *trans*- $\beta$ -*p*-bromobenzoylcrotonate (VII) in EtOH to sunlight gives (VI); (VI) in CHCl<sub>3</sub> containing a little I similarly affords (VII). (VI) is converted by MeOH-conc. H<sub>2</sub>SO<sub>4</sub> into (I). It is suggested that the free acid (II) (in the solid state) has the lactone structure, since it dissolves extremely slowly in aq. NaHCO<sub>3</sub>. Preliminary work on the reduction (Zn, AcOH) of (I) and (III) is reported. H. B.

**Amido- and imido-chlorides of non-aromatic acids. VIII. [cyclopentyl and cyclopentenyl derivatives].**—See this vol., 393.

**cycloButane-1 : 2-dicarboxylic acids.** H. BODE (Ber., 1934, 67, [B], 332—335; cf. Kuhn et al., A., 1928, 885).—In agreement with Perkin (J.C.S., 1894, 65, 583), decarboxylation of cyclobutane-1 : 1 : 2 : 2-tetracarboxylic acid at 200° and treatment of the product with AcCl affords *cis*-cyclobutane-1 : 2-dicarboxylic anhydride, m.p. 77—78°, transformed by warm H<sub>2</sub>O into the *cis*-acid (I), m.p. 138—139°. Treatment

of (I) with conc. HCl at 190° gives the *trans*-acid (II), m.p. 130—131°. The dissociation consts. of (I) and (II) have been measured. H. W.

**2-Nitrohomoveratric acid.** K. H. SLOTTA and F. LAUERSON (J. pr. Chem., 1934, [ii], 139, 220—228).—The improved prep. of 2-nitrohomoveratric acid (I) [29% overall yield from vanillin (II)] by the stages, (II) → Ac derivative → 2-NO<sub>2</sub>-derivative, → 2-nitrovanillin → 2-nitro-3:4-dimethoxybenzaldehyde, reduced by Al(OEt)<sub>3</sub> in C<sub>6</sub>H<sub>6</sub> in N<sub>2</sub> or in abs. EtOH to the alcohol (III), which with HCl at room temp. gives the chloride, converted through the nitrile, iminoether, and Me ester into (I), is described. With 50% aq. HBr at 30—40°, (III) gives a 99% yield of the bromide. Similarly Al(OEt)<sub>3</sub> effects quant. reduction of *o*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO to the alcohol. J. W. B.

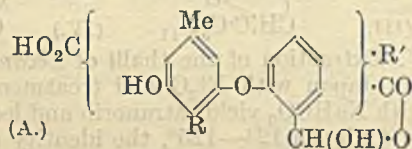
**Preparation of homopiperonylic acid.** K. H. SLOTTA and G. HABERMAN (J. pr. Chem., 1934, [ii], 139, 211—219).—*Me* 3:4-methylenedioxymandelate, m.p. 99° (I) [prep. as for Et ester (Bayer et al., J.C.S., 1909, 95, 552) improved], with SOCl<sub>2</sub> in dry C<sub>6</sub>H<sub>6</sub> gives *Me* α-chloro-3:4-methylenedioxyphenylacetate, b.p. 173°/10 mm., converted by boiling 2% NaOH-MeOH into the corresponding α-*OMe*-acid, m.p. 80°, and reduced (Zn-H<sub>2</sub>O in boiling COMe<sub>2</sub>) to homopiperonylic acid (30—36% yield) and 3:4-methylenedioxymandelic acid (53—60%). 3:4-Methylenedioxymandelonitrile [intermediate in prep. of (I)] with Ac<sub>2</sub>O-AcOH-C<sub>5</sub>H<sub>5</sub>N gives its *O*-Ac derivative, converted by MeOH-HCl into the iminoether hydrochloride, m.p. 131° (decomp.), hydrolysed (H<sub>2</sub>O) to the *O*-Ac derivative, m.p. 102°, of (I). Similarly the *O*-Ac derivative of 3:4:5-trimethoxymandelonitrile (Kindler et al., A., 1932, 1126) gives the iminoether hydrochloride, m.p. 120°, and the *O*-Ac derivative, m.p. 82°, of *Me* 3:4:5-trimethoxymandelate. J. W. B.

**2:5-Dimethoxy-3:4:6-trimethylbenzoic acid.** L. I. SMITH and R. O. DENYES (J. Amer. Chem. Soc., 1934, 56, 475—476).—Diaminodurylic acid, m.p. 221—222° (corr.; decomp.) (lit. 210°), prepared by reduction (Fe powder, aq. AcOH) of the (NO<sub>2</sub>)<sub>2</sub>-acid, is oxidised (FeCl<sub>3</sub>, dil. HCl) to trimethyl-*p*-benzoquinonecarboxylic acid. Reduction (H<sub>2</sub>SO<sub>3</sub>) and subsequent methylation (Me<sub>2</sub>SO<sub>4</sub>, MeOH-KOH) gives the *Me* ester, m.p. 39—41°, of 2:5-dimethoxy-3:4:6-trimethylbenzoic acid (I), m.p. 100—101° (*Ag* salt), oxidised by HNO<sub>3</sub> (*d* 1.4) to nitrotrimethyl-*p*-benzoquinone. (I) could not be prepared by oxidation of 2:5:3:4:6-(OMe)<sub>2</sub>C<sub>6</sub>Me<sub>3</sub>·CHO. H. B.

**Phenylmalonic and nitrophenylmalonic acids and esters.** S. BASTERFIELD and L. A. HAMILTON (Trans. Roy. Soc. Canada, 1933, [iii], 27, III, 125—131).—CHPh(CO<sub>2</sub>Me)<sub>2</sub> (I) (cf. A., 1894, i, 376) in Et<sub>2</sub>O when shaken with 2—4% aq. Na<sub>2</sub>CO<sub>3</sub> during 1 hr. affords the acid (II). Nitration of (I) at 0—10° with H<sub>2</sub>SO<sub>4</sub>-HNO<sub>3</sub> during 3 hr. affords *Me p*-nitrophenylmalonate (III), m.p. 95° (oxidised by KMnO<sub>4</sub> to *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H), and an oil which probably contains the *o*- and *m*-isomerides (cf. A., 1927, 558). Hydrolysis of (III) affords *p*-nitrophenylacetic acid. (II) with fuming HNO<sub>3</sub> at 0° gives *o*- and *m*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H, but with H<sub>2</sub>SO<sub>4</sub>-HNO<sub>3</sub> at 0° gives

*o*-nitrophenylmalonic acid, m.p. 133° (decomp.) (oxidised to *o*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H). *Me p*-carbethoxyaminophenylacetate, Na, and Me<sub>2</sub>C<sub>2</sub>O<sub>4</sub> in dry C<sub>6</sub>H<sub>6</sub> at 60° during 6 hr. afford an oil which when heated loses CO to give *Me p*-carbethoxyaminophenylmalonate (?), b.p. about 110°/5 mm. *Me* 2:4-dinitrophenylmalonate (cf. A., 1916, i, 15) is reduced by (NH<sub>4</sub>)<sub>2</sub>S in boiling EtOH during 2 hr. to *Me* 2-(or 4-)-nitro-4-(or 2-)-amino-, m.p. 131°, and *Me* 4-(or 2-)-nitro-2-(or 4-)-amino-phenylmalonate, m.p. 190°. J. L. D.

**Saxatilis acid.** G. KOLLER and A. KLEIN (Monatsh., 1934, 64, 80—86).—Pptd. by hot H<sub>2</sub>O from COMe<sub>2</sub> solution saxatilis acid (I) gives a monohydrate, becoming anhyd. at 120°/12 mm., analysis of which agrees best with C<sub>18</sub>H<sub>14</sub>O<sub>10</sub>·H<sub>2</sub>O. Reduction of the alcoholysis product C<sub>22</sub>H<sub>22</sub>O<sub>10</sub> of (I) with a weakly active Pd-C catalyst gives a dihydro-compound, m.p. 168° (decomp. in vac.), which no longer reacts with NH<sub>2</sub>Ph (-CHO → ·CH<sub>2</sub>·OH), nor gives atranol with Zn-NaOH. Hence the lactone ring is attached to ring 2. Fusion of (I) with KOH at 300°



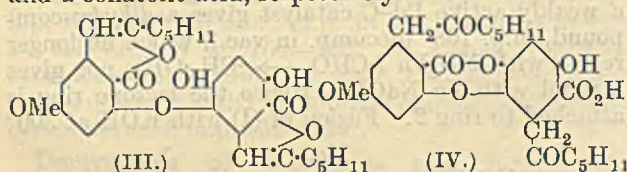
gives orcinol and α-resorcylic acid. Reduction of (I) with a 1% Pd-C catalyst in AcOH affords dihydro-saxatilis acid, C<sub>18</sub>H<sub>16</sub>O (A; R=CH<sub>2</sub>·OH, R'=CH<sub>2</sub>·OH or >CH·OH) (m-bromoanilide), but with a 10% Pd-C catalyst, dideoxydihydro-saxatilis acid, C<sub>18</sub>H<sub>16</sub>O<sub>8</sub> (A; R=Me, R'=Me or >CH<sub>2</sub>) (m-bromoanilide), and with a very active Pd-C catalyst a substance C<sub>18</sub>H<sub>16</sub>O<sub>7</sub>, which no longer reacts with NH<sub>2</sub>Ph (CH·OH of lactone ring → CH<sub>2</sub>). (I) is assigned the partial formula (A; R=·CHO, R'=·CH<sub>2</sub>·OH or >CH·OH). J. W. B.

**Capraris acid.** G. KOLLER and K. PÖPL (Monatsh., 1934, 64, 1—2).—Alcoholysis of capraris acid (I) (introduction of OEt with fission of H<sub>2</sub>O) affords cetraris acid (II), identified as *Me* dimethylcetrarisate (A., 1929, 1459). In (I) the oxide ring is intact, whereas in (II) it has undergone fission with introduction of OEt. J. W. B.

**Ramalis acid.** G. KOLLER, E. KRAKAUER, and K. PÖPL (Monatsh., 1934, 64, 3—5).—Ramalis acid, extracted from *Ramalina farinacea*, is identical with protocetraris acid, since alcoholysis affords cetraris acid, identified as *Me* dimethylcetrarisate and decomposed to atranol. J. W. B.

**Lichen substances. XXXIV. Constitution of alectoronic and α-collatolic acid. XXXV. Identity of α-collatolic acid and lecanorolic acid.** Y. ASAHINA and F. FUJIKAWA (Ber., 1934, 67, [B], 163—168, 169—170; cf. A., 1933, 713).—XXXIV. Treatment of *Me* collatolate Me<sub>2</sub> ether, m.p. 114°, with conc. KOH-EtOH causes loss of two hexoyl groups; CO<sub>2</sub>H is also involved, but its complete elimination requires subsequent treatment with HCO<sub>2</sub>H and leads to alectol Me<sub>3</sub> ether (I), C<sub>17</sub>H<sub>20</sub>O<sub>4</sub>, m.p. 96°, not identical with deoxyhyposalazinol Me<sub>3</sub> ether. (I) is converted by PCl<sub>5</sub> in PhNO<sub>2</sub> at 160° into dichlorolectol

*Me*<sub>3</sub> ether, C<sub>17</sub>H<sub>18</sub>O<sub>4</sub>Cl<sub>2</sub>, m.p. 125°, and by PCl<sub>5</sub> in CHCl<sub>3</sub> at 100° into *trichloroacetol Me*<sub>3</sub> ether, m.p. 185—188°. *Tribromoacetol Me*<sub>3</sub> ether, m.p. 179°, is obtained from (I) and Br in AcOH at room temp. Treatment of (I) with HI (*d* 1.7) and PhOH at 150° leads to orcinol. (I) is transformed by molten KOH into orcinol and  $\alpha$ -resoreylic acid and oxidised by Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in AcOH to 6-methoxy-2-methyl-*p*-benzoquinone, m.p. 151° [obtained by converting orcinol *Me* ether (II) into the NH<sub>2</sub>-derivative which is oxidised by Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> or by oxidation of orcinol *Me*<sub>2</sub> ether]. Treatment of the K derivative of (II) with *bromo-orcinol Me*<sub>2</sub> ether, m.p. 57°, leads to 3 : 4' : 6'-trimethoxy-5 : 2-dimethyldiphenyl ether, identical with (I). Arising from these results, the amended constitutions (III) and (IV) are assigned to collatolone and  $\alpha$ -collatolic acid, respectively :



XXXV. Extraction of the thalli of *Lecanora atra*, Ach., from Japan with Et<sub>2</sub>O and treatment of the extract with NaHCO<sub>3</sub> yields atranorin and lecanorolic acid, m.p. (anhyd.) 124—125°, the identity of which with  $\alpha$ -collatolic acid is proved by determination of mixed m.p. and by conversion by HCO<sub>2</sub>H in glycerol into collatolone. H. W.

Structure of reactants and extent of acetal formation. II. R. E. DUNBAR and H. ADKINS (J. Amer. Chem. Soc., 1934, 56, 442—444).—Equilibrium consts. for the reactions between 1 mol. of hexahydrobenzaldehyde (I), PhCHO (II), CMe<sub>3</sub>CHO (III), and cyclopentylaldehyde (IV) with 5 and/or 11 mols. of (usually) EtOH, Pr<sup>n</sup>OH, octan- $\beta$ -ol, cyclohexanol, and cyclohexylcarbinol in presence of a little HCl are determined and compared with the consts. for other aldehydes (A., 1933, 280). A progressive decrease in the extent of acetal formation is found with MeCHO, Pr<sup>n</sup>CHO, and (III). (IV) resembles (III) in its affinity for acetal formation. The relationship between (I) and (II) is similar to that between tetrahydrofurfuraldehyde and furfuraldehyde (*loc. cit.*); acetal formation occurs to a much greater extent with the saturated aldehyde in each case. There appears to be a fundamental difference between the cyclopentyl and cyclohexyl groups irrespective of whether the group is in the aldehyde or alcohol. The following are described: *hexahydrobenzaldehyde Me*<sub>2</sub>, b.p. 63°/25 mm., 183°/753 mm., Et<sub>2</sub>, b.p. 94—95°/12 mm., 115—117°/20 mm., Bu<sup>n</sup>, b.p. 134—136°/8 mm., 149—150°/22 mm., *diisoamyl*, b.p. 168—169°/8 mm., *di- $\beta$ -octyl*, b.p. 215—217°/8 mm., *di- $\gamma$ -2-tetrahydrofurylpropyl*, b.p. 236—238°/10 mm., *di-cyclohexyl*, b.p. 202—203°/20 mm., and *dicyclohexylmethyl*, b.p. 234—235°/20 mm., -acetals; *trimethyl-acetaldehyde Et*<sub>2</sub>, b.p. 146—148°/742 mm., and *dicyclohexylmethyl*, b.p. 194—195°/22 mm., -acetals.

H. B.

Condensation of aldehydes with hydrazones. IX. A. GIACALONE (Gazzetta, 1933, 63, 870—872).—Condensation of NPhMe·NH<sub>2</sub> with PhCHO yields

pp'-bis-( $\alpha$ -methyl- $\beta$ -benzylidenehydrazino)triphenylmethane, m.p. 163°, different from the compound, m.p. 136°, to which this structure is assigned by Ciusa (A., 1932, 1132). E. W. W.

Basic properties of hydrazones. VIII. R. CIUSA and G. OTTOLINO (Gazzetta, 1933, 63, 884—886; cf. A., 1932, 51).—When the compound CHPh·N·NMe·C<sub>6</sub>H<sub>4</sub>·CPh·C<sub>6</sub>H<sub>4</sub>·NMeCl·N·CHPh (I) is treated with dil. H<sub>2</sub>SO<sub>4</sub> the Cl is replaced by HSO<sub>4</sub>, giving the compound C<sub>35</sub>H<sub>31</sub>N<sub>4</sub>·HSO<sub>4</sub>·2H<sub>2</sub>O (II), m.p. 205°, which is also in part hydrolysed to the compound NH<sub>2</sub>·NMe·C<sub>6</sub>H<sub>4</sub>·CPh·C<sub>6</sub>H<sub>4</sub>·NMe(HSO<sub>4</sub>)·NH<sub>2</sub> (III), which condenses with PhCHO to form (II), and with cinnamaldehyde to form the compound C<sub>39</sub>H<sub>35</sub>N<sub>4</sub>·HSO<sub>4</sub>·2H<sub>2</sub>O, m.p. 197°. E. W. W.

Nitration of 3 : 5-dichlorobenzaldehyde and 3 : 5-dichlorobenzoic acid. F. ASINGER (Monatsh., 1934, 63, 385—393).—3 : 5-C<sub>6</sub>H<sub>3</sub>Cl<sub>2</sub>·CHO is converted by HNO<sub>3</sub> (*d* 1.48) at 0° into its 2-NO<sub>2</sub>-derivative (I), m.p. 91.5° (*oxime*, m.p. 97°; *phenylhydrazone*, m.p. 175°), oxidised (KMnO<sub>4</sub>) to 3 : 5-dichloro-2-nitrobenzoic acid, m.p. 194° (corr.) (*Me*, m.p. 73°, and *Et*, m.p. 69°, esters; *Ca* + 4.5H<sub>2</sub>O, *Ba* + 2.5H<sub>2</sub>O, and *Ag* salts; *chloride*, m.p. 94.5°; *amide*, m.p. 180°), also obtained by nitration of 3 : 5-C<sub>6</sub>H<sub>3</sub>Cl<sub>2</sub>·CO<sub>2</sub>H with HNO<sub>3</sub> (*d* 1.48) at 70°. With PCl<sub>5</sub> in C<sub>6</sub>H<sub>6</sub> (I) affords 3 : 5-dichloro-2-nitrobenzylidene chloride, m.p. 45° (also by nitration of 3 : 5-C<sub>6</sub>H<sub>3</sub>Cl<sub>2</sub>·CHCl<sub>2</sub>), and with Ac<sub>2</sub>O-NaOAc at 180°, 3 : 5-dichloro-2-nitrocinnamic acid, m.p. 227°, is obtained. Reduction of (I) (FeSO<sub>4</sub>-NH<sub>3</sub>-H<sub>2</sub>O-EtOH) gives 3 : 5-dichloro-2-aminobenzaldehyde, m.p. 123° (*oxime*, m.p. 175°; *phenylhydrazone*, m.p. 118°). With 1% NaOH in COMe<sub>2</sub> at -5° to 25°, (I) gives 5 : 7 : 5' : 7'-tetrachloroindigotin. J. W. B.

2-Hydroxy-6-methylbenzaldehydeanil. T. LOVE (J.C.S., 1934, 244).—The prep. of 2-hydroxy-4- and -6-methylbenzaldehydes from *m*-cresol by the Reimer-Tiemann reaction, and their conversion into anils, are described; the *anil* of the latter has m.p. 51.5°. H. A. P.

Condensation products of aromatic hydroxyaldehydes. T. PAVOLINI (Riv. Ital. Ess. Prof., 1933, 15, 171—173; Chem. Zentr., 1933, ii, 2260).—Condensation products of barbituric acid (I) with vanillin (II), dehydrovanillin, and coniferylaldehyde (III) pass from yellow into red in alkaline medium. (I) and lignin (IV) or piperonal (V) afford a yellow, amorphous product unchanged by alkali, owing to blockage of the OH group. The (I) reaction can be carried out with pulverised wood, and can be used for the detection of lignified material. (I) in AcOH has been condensed with PhCHO (light yellow), salicylaldehyde (straw), (V) (yellow), (II) and (III) (orange-red), and dehydrovanillin (crimson) [all 2(I) : 1 aldehyde]. With (IV) (1 : 1) an orange-red powder is obtained. A. A. E.

Lignin. XVII. Tetraconiferaldehyde. P. KLASON (Ber., 1934, 67, [B], 302—303).—Treatment of pine wood with NaHSO<sub>3</sub> at 96—98° followed by HCl leads to a sulphonic acid sol. in H<sub>2</sub>O which with  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub> gives the salt 4(C<sub>10</sub>H<sub>10</sub>O<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>SO<sub>3</sub>·C<sub>10</sub>H<sub>9</sub>N-H<sub>2</sub>O. Contrary to Freudenberg, the individuality of the tetraligninsulphonic

acid is as pronounced as that of the other lignin-sulphonic acids. The composition of this acid considered in conjunction with the acid

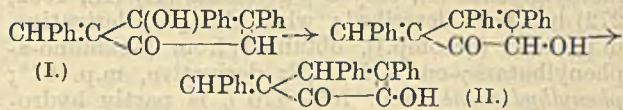
$3(C_{10}H_{10}O_3)_2 \cdot H_2SO_3$  leads to the conclusion that the mol. wt. of  $\alpha$ -lignin corresponds with  $(C_{10}H_{10}O_3)_{12}$  and that of the total lignin of wood is  $> 3640$ . Treatment of wood with 0.2%  $H_2SO_4$  at 96–98° removes hemicellulose, giving a product which with  $\beta$ - $C_{10}H_7 \cdot NH_2$  affords the *anil* ( $C_{10}H_{10}O_{3/3} \cdot C_{10}H_9N \cdot H_2O$ ). Since the action of  $H_2SO_3$  on lignin is similar to that of acids on polysaccharides, tetraconiferaldehyde is regarded as  $OH \cdot R \cdot C_2H_2 \cdot CH(OH) \cdot [O \cdot R \cdot C_2H_2 \cdot CH(OH)]_2 \cdot O \cdot R \cdot C_2H_2 \cdot CHO$  ( $R = \text{anisole residue}$ ). H. W.

**Preparation of cyclic unsaturated ketones and hydrocarbons.** H. BERGS [with C. WITTFELD and, in part, E. WILDY] (Ber., 1934, 67, [B], 238–244; cf. Cook *et al.*, A., 1933, 1042).—I. Phenylacetyl- $\Delta^1$ -cyclohexene (I), b.p. 171–176°/12 mm., m.p. 47°, is obtained from  $CH_2Ph \cdot COCl$ , tetrahydrobenzene, and  $SnCl_4$  in  $CS_2$  at  $-10^\circ$  to  $-5^\circ$ , or with a substance, m.p. 204°, from  $CH_2Ph \cdot MgCl$  and tetrahydrobenzotriazole (II) in  $Et_2O$ . (I) yields a *semicarbazone*, m.p. 175–176°, and an *oxime*, m.p. 124°, transformed by 25%  $H_2SO_4$  at 80–90° followed by addition of Br and loss of HBr into stilbene. (II) and  $MgEtBr$  afford 3:4:5:6-tetrahydrophenyl Et ketone (oxime, m.p. 76°). The *oxime*, m.p. 60–61°, and *dibromide*, m.p. 48°, of 3:4:5:6-tetrahydrophenyl Me ketone are described. 1- $\beta$ -Phenylethylcyclohexan-1-ol, b.p. 168–169°/16 mm., m.p. 56°, from cyclohexanone and  $CH_2Ph \cdot CH_2 \cdot MgCl$ , is converted by  $ZnCl_2$  at 160–165° into  $\beta$ -phenylethylcyclohexene (III), b.p. 136–137°/12 mm. (III) is transformed by  $AlCl_3$  at 40° into 1:2:3:4:9:10:11:12-octahydrophenanthrene, b.p. 149–152°/12 mm. The prep. of  $CH_2Ph \cdot CH_2Cl$  and  $CH_2Ph \cdot CH_2Br$  from  $CH_2Ph \cdot CH_2OH$  and  $PCl_5$  or  $PBr_3$ , respectively, is described.  $CH_2Ph \cdot CH_2 \cdot MgCl$  and the requisite ketone afford 1- $\beta$ -phenylethyl-2-, b.p. 181–183°/20 mm., -3-, b.p. 171–172°/18 mm., and -4-methyl-, b.p. 179°/22 mm., -cyclohexan-1-ol, and 1- $\beta$ -phenylethyl-1:2:3:4-tetrahydro- $\alpha$ -naphthol, b.p. 212–214°/20 mm. H. W.

**Selective catalytic reduction of ketones.** II. N. D. ZELINSKI, K. PACKENDORFF, and L. LEDERPACKENDORFF (Ber., 1934, 67, [B], 300–302; cf. A., 1933, 715).—Hydrogenation of  $\alpha$ -CO or  $\alpha$ -OH-compounds in presence of Pt activated with Pd gives the corresponding  $CH_2$  or Me substances. The following examples are cited: indan-1-one or -1:3-dione to indane; 1:5-diketophenylheptamethylenedicarboxylic ester to the 1:5-(OH) $_2$ -compound; PhCNO and  $CH_2Ph \cdot OH$  to PhMe, furfuraldehyde to silvane; OH-CHPh-CO $_2H$  to  $CH_2Ph \cdot CO_2H$ ; OH-CHPh-CN to Ph-CH $_2$ -CN, and thence in poor yield to  $CH_2Ph \cdot CH_2 \cdot NH_2$ . H. W.

**Ammonolysis of fluorenone and fluorenone-anil.** L. A. PINCK and G. E. HILBERT (J. Amer. Chem. Soc., 1934, 56, 490).—Prolonged interaction of fluorenone and Na-dried liquid  $NH_3$  at room temp. gives fluorenoneimine (I);  $COPh_2$ , 9:9-dichlorofluorene, and  $\alpha\beta$ -dichloro- $\alpha\beta$ -di(diphenylene)ethane do not react under similar conditions. (I) and  $NH_2Ph$  at 120° afford fluorenoneanil, which with  $NH_4Cl$  in liquid  $NH_3$  at 60° for 4 days gives some (I). H. B.

**Anionotropic and prototropic changes in cyclic systems. II. Hydroxy-3:4-diphenyl-5-benzylidenecyclopentenones. III. Isomeric chloro-3:4-diphenylcyclopentenones. IV. Hydroxy-3:4-diphenyl-5-isopropylidenecyclopentenones.** H. BURTON and C. W. SHOPPEE (J.C.S., 1934, 197–201, 201–205, 205–207).—II. The conversion of 4-hydroxy-3:4-diphenyl-5-benzylidene- $\Delta^2$ -cyclopentenone (I) into the 2-hydroxy-compound (II) occurs by successive anionotropic and prototropic changes. Owing to dissymmetry, there are three pairs of theoretically possible alcohols:



The isolation of five of the six possible Me ethers is described. (Ia), m.p. 232° (cf. Gray, J.C.S., 1909, 95, 2138),  $Ag_2O$ , and MeI afford 4-methoxy-3:4-diphenyl-5-benzylidene- $\Delta^2$ -cyclopentenone, m.p. 158° (4-OEt-, m.p. 159°), whilst (Ib), m.p. 213.5°, yields the 4-OMe-compound, m.p. 122°. (IIa), m.p. 216°, is methylated to 2-methoxy-3:4-diphenyl-5-benzylidene- $\Delta^2$ -cyclopentenone, m.p. 112° (2-OEt-, m.p. 122–123°), whilst (IIb), m.p. 223°, gives the 2-OMe-compound, m.p. 124°. (Ia) and  $SOCl_2$  afford 2-chloro- (III), m.p. 175°, and 2:4-dichloro-3:4-diphenyl-5-benzylidene- $\Delta^3$ -cyclopentenone (IV), m.p. 175°. (III) with MeOH and AgOAc yields the 2-OMe-derivative, m.p. 143°, and with AcOH-AgOAc forms the 2-OAc-compound. (IV) with MeOH-AgOAc is converted into 2-chloro-4-methoxy-3:4-diphenyl-5-benzylidene- $\Delta^2$ -cyclopentenone, m.p. 155°, and with AcOH-AgOAc into the 4-OAc-derivative, m.p. 160°, and 3:4-diphenyl-5-benzylidene- $\Delta^2$ -cyclopentene-1:2-dione, m.p. 198–199° [osazone, m.p. 179–180° (decomp.)]. 3:4-Diphenyl- $\Delta^3$ -cyclopentenone and PhCHO-NaOEt give the 2:5-dibenzylidene derivative, m.p. 202°. 4-Hydroxy-3:4-diphenyl-5-benzylidene-2-methyl- $\Delta^2$ -cyclopentenone with  $Ac_2O$  and  $H_2SO_4$  yields 3:4-diphenyl-5-benzylidene-2-methylene- $\Delta^3$ -cyclopentenone (which gives  $CH_2O$  on ozonolysis) and a substance,  $C_{50}H_{38}O_2$ , m.p. 225°.

III. Anhydroacetonebenzil (V) and AcCl give 4-chloro-3:4-diphenyl- $\Delta^2$ -cyclopentenone (VI) and a dimeride,  $C_{34}H_{24}O_2$ ; (VI) and MeOH-AgOAc afford 4-methoxy-3:4-diphenyl- $\Delta^2$ -cyclopentenone, m.p. 123.5°, which is also obtained from (V) by methylation, and with Br yields a compound,  $C_{17}H_{10}OBr_4$ , m.p. 145°. (V) and EtOH-HCl afford 2-chloro-3:4-diphenyl- $\Delta^2$ -cyclopentenone, (VII), m.p. 128–129°, which is reduced (Zn-AcOH) to a substance,  $C_{34}H_{26}OCl$ , m.p. 210° (decomp.). The conclusions of Allen and Spanagel (A., 1933, 67) are shown to be incorrect with regard to (VII). 3:4-Diphenyl- $\Delta^3$ -cyclopentenone with  $SOCl_2$  gives 2-chloro-3:4-diphenyl- $\Delta^3$ -cyclopentenone, m.p. 48°, and with  $Cl_2$  forms a monochlorodimeride (VIII),  $C_{34}H_{23}O_2Cl$ , m.p. 216°. (VIII) is oxidised with NaOBr to diphenylmaleic anhydride.

IV. Mesityl oxide and benzil (cf. Japp and Knox, J.C.S., 1905, 87, 673) give 4-hydroxy-3:4-diphenyl-5-isopropylidene- $\Delta^2$ -cyclopentenone (IX) and a substance, m.p. 251–252° (decomp.). (IX) forms 2-acetoxy-3:4-diphenyl-5-isopropylidene- $\Delta^3$ -cyclopentenone.

tenone (X), reduced (HI) to a ketone, m.p. 171° (*benzylidene* derivative, m.p. 234°). (X) with HCl forms 2-chloro-3 : 4-diphenyl-5-isopropylidene- $\Delta^2$ -cyclopentenone (?), m.p. 188° [which with KOH-EtOH gives the 2-OH-derivative (XI), m.p. 252°], and the 2-OH- $\Delta^3$ -compound (XII), m.p. 207°. The transformation of (IX) into (XI) occurs by successive anionotropic and prototropic stages, the intermediate compound being (XII). F. R. S.

**Dioximes. CIII.** F. S. DE PAOLINI and G. ARMITANO (Gazzetta, 1933, 63, 917—923).—Of benzylmethylglyoxal (I), only a  $\beta$ -glyoxime (II) (A., 1932, 272) has been described; when this [*Bz*<sub>2</sub> derivative, m.p. 167° (decomp.)], obtained from  $\beta$ -oximino- $\alpha$ -phenylbutan- $\gamma$ -one (III), (*Bz* derivative, m.p. 67°; *phenylhydrazone*, m.p. 169—170°), is partly hydrolysed by dil. HCl at 40—50°,  $\gamma$ -oximino- $\alpha$ -phenylbutan- $\beta$ -one (IV), m.p. 94° (*Bz* derivative, m.p. 90°; *phenylhydrazone*, m.p. 144—145°), is formed, but an  $\alpha$ -dioxime cannot be obtained from either (III) or (IV), both of which with N<sub>2</sub>O<sub>4</sub> in Et<sub>2</sub>O yield (I). When, however, the product of further action of N<sub>2</sub>O<sub>4</sub>, 4-benzyl-3-methyl-1 : 2 : 5-oxadiazole 2-oxide (V), m.p. 67°, is reduced by Zn and AcOH,  $\alpha$ -benzylmethylglyoxime, (VI), m.p. 94—95° (*Bz*<sub>2</sub> derivative, m.p. 134°; *Ni* salt insol. in dil. AcOH), is obtained, which is converted into (II) when heated. Reduction of (V) by SnCl<sub>2</sub> gives the *oxadiazole*, b.p. 154°/17 mm.; treatment of (V) with NaOEt yields 4-imino-5-hydroxy-3-benzylisooxazoline, m.p. 141° (*Bz* derivative, m.p. 136—137°). E. W. W.

**Tautomerism of  $\alpha$ -diketones. II. Phenyl benzhydryl diketone.** E. P. KOHLER and N. WEINER (J. Amer. Chem. Soc., 1934, 56, 434—438).— $\alpha$ -Benzoyl- $\beta\beta$ -diphenylethylene oxide (I) is converted by short treatment with MeOH-NaOMe in EtOH and subsequent acidification (dil. H<sub>2</sub>SO<sub>4</sub>) into *Ph benzhydryl diketone* (II), m.p. 49—50° [*quinoxaline*, m.p. 198—199°, from *o*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>; *oxime*, m.p. 135—136], which is completely ketonic, is oxidised (H<sub>2</sub>O<sub>2</sub> in aq. MeOH-NaOH) to BzOH and CHPh<sub>2</sub>·CO<sub>2</sub>H, and readily undergoes the "benzilic acid" rearrangement to  $\alpha$ -hydroxy- $\alpha\beta\beta$ -triphenylpropionic acid (III), m.p. 243—245° (decomp.) (*Me* ester, m.p. 186°), (III) is best obtained from (I) and conc. MeOH-KOH. Methylation (Me<sub>2</sub>SO<sub>4</sub>, aq. MeOH-NaOH) of (II) gives *Ph  $\alpha$ -methoxy- $\beta$ -phenylstyryl ketone*, m.p. 103—104°, whilst benzoylation (BzCl and C<sub>5</sub>H<sub>5</sub>N or aq. NaOH-dioxan) affords *Ph  $\alpha$ -benzoyloxy- $\beta$ -phenylstyryl ketone*, m.p. 161°. (II) is reduced (H<sub>2</sub>, PtO<sub>2</sub>, EtOAc or Zn, acid) to diphenylacetylphenylcarbinol (A., 1931, 354) (*oxime*, m.p. 159°). (I) and HCl in cold AcOH give 1-chloro-1 : 3-diphenylindan-2-one, m.p. 174° (decomp.), oxidised (Na<sub>2</sub>CrO<sub>4</sub>, AcOH) to *o*-C<sub>6</sub>H<sub>4</sub>Bz<sub>2</sub> and converted by EtOH into the 1-*OEt* derivative, m.p. 133°. MgMeI (1 equiv.) and (II) give  $\alpha$ -benzoyl- $\alpha$ -benzhydryl-ethyl alcohol, m.p. 178° (lit. 188°), which with MgPhBr affords  $\alpha\beta$ -dihydroxy- $\alpha\alpha\gamma\gamma$ -tetraphenyl- $\beta$ -methylpropane, m.p. 173°, also prepared from MgPhBr and *Me  $\alpha$ -hydroxy- $\beta\beta$ -diphenyl- $\alpha$ -methylpropionate*, m.p. 87—88° (from MgMeI and CHPh<sub>2</sub>·CO·CO<sub>2</sub>Me). (II) and an excess of MgMeI give  $\alpha$ -diphenylacetyl- $\alpha$ -phenylethyl alcohol, m.p. 72—73°, which is converted by HI into 1 : 3-diphenyl-1-methylindan-2-one, m.p. about 185°

(decomp.), and with MgPhBr affords  $\beta\gamma$ -dihydroxy- $\alpha\alpha\beta\gamma$ -tetraphenylbutane, m.p. 184°. (II) and an excess of MgPhBr give  $\alpha$ -benzoyl- $\alpha\beta\beta$ -triphenylethyl alcohol. H. B.

**4 : 6- and 2 : 4-Diacetyresorcinol.** W. BAKER (J.C.S., 1934, 71—73).—*m*-C<sub>6</sub>H<sub>4</sub>(OAc)<sub>2</sub> and FeCl<sub>3</sub> by an improved process give 4 : 6-diacetyresorcinol (I) (m.p. 182° (yield 32.4%) (*Bz*<sub>2</sub> derivative, m.p. 118° (A., 1933, 155), oxidised by H<sub>2</sub>O<sub>2</sub> in NaOH in the absence of air to 2 : 4 : 5-trihydroxyacetophenone which is isolated as the Me<sub>3</sub> ether, better obtained by similar treatment of the Me ether of (I). Resaceto-phenone with Ac<sub>2</sub>O and NaOAc gives 7-acetoxy-3-acetyl-2-methylchromone, converted by AlCl<sub>3</sub> in PhNO<sub>2</sub> into 7-hydroxy-8-acetyl-2-methylchromone, m.p. 185—186.5°. "Diflavone" (A., 1931, 1305) is shown to be 3 : 3'-dibenzoyldiflavone, and the structures of other products obtained from (I) are discussed. A. A. L.

**Tetramethyl-*o*-benzoquinone.** L. I. SMITH and L. R. HAY (J. Amer. Chem. Soc., 1934, 56, 477—478).—Dinitroprehnitene, m.p. 176° (from prehnitene method, A., 1926, 729) is reduced (SnCl<sub>2</sub>, conc. HCl, EtOH) to diaminoprehnitene (I), m.p. 144°. Treatment of the hydrochloride of (I) with Cl in AcOH-conc. HCl, removal of the pptd. NH<sub>4</sub>Cl and excess of Cl<sub>2</sub> (in a vac.), and subsequent treatment with SnCl<sub>2</sub> and conc. HCl gives *dihydroxyprehnitene*, m.p. 111° (*diacetate*, m.p. 175°; *dibenzoate*, m.p. 157° *Me*<sub>2</sub> ether, m.p. 21°), which is oxidised (dry Ag<sub>2</sub>O in Et<sub>2</sub>O) to tetramethyl-*o*-benzoquinone (*prehnitenequinone*) (II), m.p. 110—111° (darkens at 80°). (II) decomposes when kept for a few hr. even at low temp. in a vac. 1 : 2 : 3 : 4-Tetramethyl-, m.p. 217°, and octamethyl-, m.p. 279°, -phenazines are prepared from (II) and *o*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> and (I), respectively. H. B.

**Quinamines.** K. FRIES, R. BÖCKER, and F. WALLBAUM (Annalen, 1934, 509, 73—102).—The following are prepared from 1 : 5-dibromo-4-keto-1 : 4-dihydro-*m*-xylene (A., 1928, 888) and the requisite NH<sub>2</sub>Ar (2 mols.): 5-bromo-1-*o*- (I), m.p. 120° (decomp.), -*m*- (II), m.p. 110° (decomp.), and -*p*- (III), m.p. 109° (decomp.), -*toluidino*-, -1-*p*-bromoanilino- (IV), m.p. 131° (decomp.), -1-3'-bromo-*p*-toluidino- (V), m.p. 118° (decomp.), -1-3'-chloro-*p*-toluidino- (VI), m.p. 143° (decomp.), -1-3' : 5'-dibromo-*p*-toluidino- (VII), m.p. 118° (decomp.), -1-*m*-4-xylydino- (VIII), m.p. 107° (decomp.), and -1-*o*-carboxyanilino- (IX), m.p. 135° (decomp.), -4-keto-1 : 4-dihydro-*m*-xylene. 3 : 5-Dibromo-1-anilino- (X), m.p. 136° (decomp.) (cf. *loc. cit.*) -1-*o*-, m.p. 126° (decomp.) (lit. 112°), and -*p*- (XI), -*toluidino*-, -1-*m*-*toluidino*- (XII), m.p. 121° (decomp.) (previous blackening), -1-*p*-bromoanilino- (XIII), m.p. 138° (decomp.), -1-*m*-4-xylydino- (XIV), m.p. 111° (decomp.), -1-3'-chloro-*p*-toluidino- (XV), m.p. 146° (decomp.), and -1-*o*-carboxyanilino- (XVI), m.p. 163° (decomp.), -4-keto-1 : 4-dihydro-*toluene* are similarly obtained from 1 : 3 : 5-tribromo-4-keto-1 : 4-dihydro-*toluene* (XVII) (*loc. cit.*). The above quinamines containing no *p*-substituent in the arylamino-group are rearranged by conc. HCl in AcOH or EtOH to (mainly) diphenyl ethers. Thus (X) gives (cf. *loc. cit.*) 2 : 6-dibromo-4'-amino-4-methyldiphenyl ether (XVIII) and a little 5'-chloro-3-bromo-2'-amino-2-



*hydroxy-3-methyldiphenyl* (XIX), m.p. 168° ( $Ac_2$  derivative, m.p. 195°); the amount of (XIX) rises with increased concn. of HCl. (XVIII) is debrominated (Zn dust) to 4'-amino-4-methyldiphenyl ether, m.p. 126° ( $Ac$  derivative, m.p. 131°), also prepared by reduction (Sn, conc. HCl, EtOH) of the 4'- $NO_2$ -derivative, m.p. 68° (obtained from  $p-C_6H_4MeOK$ ,  $p-C_6H_4BrNO_2$ , and  $p-C_6H_4MeOH$  in  $C_{10}H_8$  at 230°). Similarly, (II) and cold EtOH-conc. HCl give 5-bromo-4'-amino-2:4:2'-trimethyldiphenyl ether, m.p. 108° ( $Ac$  derivative, m.p. 155°), whilst (XII) affords 70% of 3:5-dibromo-4'-amino-4:2'-dimethyldiphenyl ether, m.p. 146° ( $Ac$  derivative, m.p. 191°), and 6% of 3:5'-dibromo-2'-amino-2-hydroxy-5:4'-dimethyldiphenyl, m.p. 211° ( $N-Ac$  derivative, m.p. 175°). (I) yields 6-bromo-4'-amino-2:4:3'-trimethyldiphenyl ether, m.p. 131° ( $Ac$  derivative, m.p. 198°), whilst (IX) furnishes 6-bromo-4'-amino-5'-carboxy-2:4-dimethyldiphenyl ether (63%), m.p. 221° (decomp.) ( $Ac$  derivative, m.p. 148°), and 2-chloro-3:5-dimethyldiphenylamine-2'-carboxylic acid (XX) (27%), m.p. 327° ( $Me$  ester, m.p. 163°). Reaction of (IX) with HCl is considered to give  $o-NH_2C_6H_4CO_2H$  and 1-chloro-5-bromo-4-keto-1:4-dihydro-*m*-xylene, which then afford the 1-chloro-5-*o*-carboxyanilino-4-keto-derivative; further addition of HCl to CO and subsequent elimination of HOCl affords (XX). Distillation of (XX) with Zn dust gives (probably) an impure dimethylcarbazole, m.p. about 95°; 6-chloro-2:4-dimethyldiphenylamine-2'-carboxylic acid, m.p. 233° (from 5-chloro-*m*-4-xylidine and  $o-C_6H_4ClCO_2H$ ), similarly affords 2:4-dimethyldiphenylamine, whilst 3:5-, m.p. 205°, and 2:6-, m.p. 204°, -dimethyldiphenylamine-2'-carboxylic acid furnish 3:5-, m.p. 57°, and 2:6-, m.p. 55°, -dimethyldiphenylamine, respectively. (XVI) is converted (EtOH-conc. HCl) into 2:6-dibromo-4'-amino-5'-carboxy-4-methyldiphenyl ether, m.p. 232° ( $Ac$  derivative, m.p. 183°), and a little 6-chloro-5-bromo-3-methyldiphenylamine-2'-carboxylic acid, m.p. 360°.

Diphenyl derivatives are obtained as the main products from several of the quinamines, especially the *p*-substituted-arylamino-derivatives. Thus, (III) gives 2'-amino-2-hydroxy-3:5:5'-trimethyldiphenyl, m.p. 135° ( $Ac_2$  derivative, m.p. 116°), and a compound,  $C_{15}H_{14}ONBr_3$ , m.p. 181° (decomp.); distillation of the former with Zn dust affords 1:3:6-trimethylcarbazole, m.p. 126° ( $NO$ -derivative, m.p. 139°). (XI) gives 3-bromo-2'-amino-2-hydroxy-5:5'-dimethyldiphenyl, m.p. 176° ( $N-Ac$  derivative, m.p. 184°) (converted by Zn dust into 3:5-dimethylcarbazole), and some 6-chloro-5:6'-dibromo-3:4'-dimethyldiphenylamine, m.p. 188°, whilst (IV) yields 70% of 5'-bromo-2'-amino-2-hydroxy-3:5-dimethyldiphenyl, m.p. 148° ( $Ac_2$  derivative, m.p. 94°), and (XIII) furnishes 3:5'-dibromo-2'-amino-2-hydroxy-5-methyldiphenyl, m.p. 205° ( $N-Ac$  derivative, m.p. 110°) [convertible (Zn dust) into 3-methylcarbazole], and some 2:6:5'-tribromo-2'-amino-4-methyldiphenyl ether, m.p. 105° ( $Ac$  derivative, m.p. 204°).

Most of the *op*-substituted-arylamino-compounds give (usually) *O*-free diphenylamines. Thus, (V) affords 2-chloro-2'-bromo-3:5:4'-trimethyldiphenylamine (80%), m.p. 153° [convertible (Zn dust) into 2:4:6-trimethylcarbazole, m.p. 198°]; (VI) yields 2:2'-dichloro-3:5:4'-trimethyldiphenylamine

(80%), m.p. 141°; (XV) furnishes 2:2'-dichloro-3-bromo-5:4'-dimethyldiphenylamine, m.p. 169°. (VIII), however, gives 2'-amino-2-hydroxy-3:5:3':5'-tetramethyldiphenyl, m.p. 98° ( $Ac_2$  derivative, m.p. 117°), and (XIV) similarly affords 3-bromo-2'-amino-2-hydroxy-5:3':5'-trimethyldiphenyl, m.p. 128° ( $N-Ac$  derivative, m.p. 195°), and some 2-chloro-3-bromo-5:2':4'-trimethyldiphenylamine, m.p. 135°. Unlike any of the other quinamines, (VII) yields a derivative of *m*-hydroxydiphenylamine, viz., 4:2':6'-tribromo-3-hydroxy-2:6:4'-trimethyldiphenylamine, m.p. 110° ( $Ac$  derivative, m.p. 141°), which is indifferent to  $FeCl_3$ .  $\alpha-C_{10}H_7NH_2$  and (XVII) in cold EtOH do not give a quinamine but afford the rearrangement product 3:5-dibromo-*p*-tolyl 4-amino- $\alpha$ -naphthyl ether, m.p. 170° ( $Ac_2$  derivative). H. B.

Reaction between duroquinone and sodio-malonic esters. II. Synthesis and reactions of 2:5-dimethoxy-3:4:6-trimethylbenzaldehyde. L. I. SMITH (J. Amer. Chem. Soc., 1934, 56, 472—474).—3:6-Dinitro- $\psi$ -cumene (obtained by deamination of its 5- $NH_2$ -derivative) is reduced ( $SnCl_2$ ; cf. A., 1926, 729) to 3:6-diamino- $\psi$ -cumene stannichloride, which is oxidised ( $FeCl_3$  in dil. HCl) to trimethyl-*p*-benzoquinone ( $\psi$ -cumoquinone), m.p. 29—30° (lit. 11° and 32°). Trimethylquinol, m.p. 168—170° (decomp.) [*dibenzoate*, m.p. 179.5—180.5°; diacetate, m.p. 108.5—110° (lit. 112°)], is methylated ( $Me_2SO_4$ ,  $MeOH-KOH$ ) to the *Me\_2* ether, b.p. 144°/30 mm., m.p. 35.5—36°, which is converted by the method of Adams *et al.* (A., 1924, i, 51, 860) into 2:5-dimethoxy-3:4:6-trimethylbenzaldehyde (A., 1926, 836) [*oxime*, m.p. 134—135° (lit. 129—131°)]. Condensation ( $MeOH-NaOMe$ ) of this with  $CH_2(CO_2Me)_2$  followed by hydrolysis give the -benzylidenemalonic acid, identical with that previously obtained (*loc. cit.*) from duroquinone and  $CHNa(CO_2R)_2$ . H. B.

Santonin series. XIX. Behaviour of santonic acid on oxidative degradation. E. WEDEKIND and I. JACKH (J. pr. Chem., 1934, [ii], 139, 129—140).—Oxidation of santonic acid (I) with alkaline  $H_2O_2$  gives aposantonic acid,  $C_{14}H_{20}O_3$ , m.p. 164—165° [*oxime*, m.p. 185—186°;  $H_2$ -derivative, m.p. 205—206° (*oxime*, m.p. 188—189°)]; Clemmensen reduction gives an oil, a ketomonocarboxylic acid, further oxidised by  $CrO_3-AcOH$  to a diketo-lactone,  $C_{14}H_{18}O_4$ , m.p. 159—160° (*oxime*, decomp. 228°), hydrolysed by alkali to the free acid,  $C_{14}H_{20}O_5$ , decomp. 200—202°. (I) is slowly oxidised by aq.  $KOBr$  at room temp. to hydroxysantonic acid,  $C_{15}H_{20}O_6$ , m.p. 198° (+0.5 $H_2O$ , decomp. 215°) [*Me\_2* ether-ester, m.p. 87—90° (decomp.)];  $Ac_2$  derivative, decomp. 192° (*Me* ester, m.p. 142°)], which appears to be free from CO and lactone groups. No identifiable products were obtained from (I) and  $O_3$ . Distillation of santonic acid (A., 1892, 1352) with  $Ac_2O$  gives a cyclic ketone,  $C_{12}H_{14}O_4$ , m.p. 203—204° [*oxime*, m.p. 223° (decomp.)]. Santolic acid,  $C_{15}H_{20}O_5$ , decomp. 178—180° [lit.  $C_{15}H_{22}O_5$ , m.p. 166—167° (*loc. cit.*)], is conveniently prepared by action of 25%  $H_2SO_4$  on the oxime of (I) and unlike (I) gives a  $H_2$ -derivative, decomp. 160° ( $H_2-PtO_2$ ). Its hydroxamic acid anhydride has m.p. 235° (decomp.) (lit. 226—227°). H. A. P.

**Toad poisons. VI. Ch'an su, the dried venom of the Chinese toad, and the secretion of the tropical toad, *Bufo marinus*.** H. JENSEN and E. A. EVANS (J. Biol. Chem., 1934, 104, 307—316; cf. A., 1930, 1205).—Fresh analyses have necessitated a revision of all empirical formulæ and these now conform with derivatives. Cinobufagin (I),  $C_{25}H_{32}O_6$ , m.p. 222—223° (Ac derivative, m.p. 195—196°), is a lactone, contains two double linkings,  $\cdot CH\cdot OH$ , and  $\cdot OAc$ . (I) gives a *tetrahydro*-derivative, m.p. 230° (Ac derivative, m.p. 238°); on oxidation with  $CrO_3$  it affords a ketone, *cinobufagone*,  $C_{25}H_{30}O_6$ , m.p. 240—241°. *N*-NaOH-EtOH opens the lactone ring and hydrolyses the  $\cdot OAc$ , cinobufagic acid,  $C_{23}H_{32}O_6$  (amorphous), being produced. Bufagin (II),  $C_{24}H_{32}O_5$ , m.p. 212—213° (Ac derivative, m.p. 203—204°), resembles (I) but does not contain  $OAc$ . The formation of  $CH_2O$  by the treatment of (II) with 70%  $H_2SO_4$  and of  $HCO_2H$  with *N*-NaOH-EtOH suggest the presence of  $\cdot CH_2\cdot C(\cdot CH_2)\cdot CH_2\cdot$ ; the latter hydrolysis also opens the lactone ring, *bufagic acid*,  $C_{22}H_{34}O_6$  (amorphous), being produced. (II) forms a *tetrahydro*-derivative, m.p. 210—211° (Ac derivative, m.p. 213—214°), and, with 5%  $H_2SO_4$  in 50% EtOH, gives *dianhydrobufagin* (III),  $C_{22}H_{28}O_3$ , m.p. 245—246°. Marinobufotoxin (IV),  $C_{33}H_{58}O_{10}N_4$ , m.p. 204—205°, and *N*-HCl-EtOH give (III), suberic acid, and arginine. Gamabufagin chloride (V),  $C_{24}H_{32}O_4Cl$ , previously termed bufotalin chloride, is now held to be derived from gamabufogenin,  $C_{24}H_{34}O_5$  (cf. Wieland and Vocke, A., 1930, 1466), since on treatment with  $Ac_2O$ -NaOAc (V) loses HCl and is acetylated to acetylanhydrogamabufagin,  $C_{26}H_{34}O_5$ , m.p. 225—226° (*hexahydro*-derivative, m.p. 180°), and with 25% KOH in MeOH gives *anhydrogamabufagic acid*,  $C_{23}H_{32}O_4$ , m.p. 215°,  $HCO_2H$  and  $Cl^-$  being eliminated. W. S.

**Resins and resin substances. IX.  $\beta$ -Amyrin and manila elemi resin. VI.** A. ROLLETT and R. PETER (Monatsh., 1934, 63, 311—316).—From the  $COMe_2$  mother-liquor of the molozonides of  $\beta$ -amyrin benzoate (I) (A., 1931, 1299), a *cryst. substance*,  $C_{37}H_{52}O_4$  (II), m.p. 333°, is isolated; (II) is a peroxide (I from KI) of an oxy- $\beta$ -amyrin benzoate and on hydrolysis (5% KOH-EtOH) and acetylation of the product gives an Ac derivative, m.p. (indef.) 265—275°, probably identical with oxy- $\beta$ -amyrin acetate (A., 1923, i, 588). With Br vapour in the dark  $\beta$ -amyrin and (I) give indefinite products containing, respectively, approx. 12 and 14 atoms of Br. J. W. B.

**Constitution of hederagenin and oleanolic acid. V.** Z. KITASATO (Acta Phytochim., 1933, 7, 169—186; cf. A., 1933, 612).—With  $CrO_3$  in AcOH, diacetylhederagenin gives ketodiacetylhederagenin lactone, m.p. 197°, hederagenonediacid (I) gives *ketohederagenonediacid monolactone*,  $C_{29}H_{42}O_6$ , m.p. 140° [*dioxime*, m.p. 221° (decomp.)], and the Me ester of (I) gives  *$\gamma$ -ketohederagenonediacid Me ester* (II),  $C_{31}H_{46}O_6$ , m.p. 178° [*dioxime*, m.p. 225° (decomp.)]. Hydrolysis of the monobromolactone of (I) with KOH in EtOH and methylation likewise gives (II), which is also obtained on oxidation of ketohederagenin with Beckmann's mixture. Hederatriacid (III) Me ester by oxidation or the monobromolactone of (III) by hydro-

lysis and methylation affords the  $\gamma$ -*keto*-derivative,  $C_{31}H_{46}O_7$ , m.p. 163° [*oxime*, m.p. 227° (decomp.)]. Oxidation of hederagone Me ester gives the  $\gamma$ -*keto*-derivative, m.p. 237°, whilst oleanolic acid monobromolactone (IV) gives *oleanonic acid monobromolactone* (V),  $C_{30}H_{45}O_3Br$ , m.p. 251° (decomp.) [*oxime*, m.p. 267° (decomp.)]. (V) with Zn-AcOH yields oleanonic acid,  $C_{30}H_{46}O_3$ , m.p. about 190° [*oxime*, m.p. 280° (decomp.)]; Me ester *oxime*, m.p. 246° (decomp.). Acetyloleanolic acid with  $CrO_3$ -AcOH gives as intermediate product (cf. A., 1932, 1035) *ketoacetyloleanolic acid*,  $C_{32}H_{48}O_5$ , m.p. 287° (decomp.). With  $CrO_3$ -AcOH, Me keto-oleanolate (VI) yields *Me keto-oleanolate* (VII), m.p. 175° (*oxime*, m.p. 270°); hydrolysis (KOH in MeOH) and methylation of (IV) affords (VI), which, when dissolved in EtOH and poured into dil.  $H_2SO_4$  gives an *isomeride*, m.p. 198—200° (Ac derivative, m.p. 193—195°). (VII), when poured into dil. HCl, also gives an *isomeride*, m.p. 210° [*oxime*, m.p. 255° (decomp.)]. Oleanolic acid lactonediacid gives a Me ester, m.p. 213°.

J. H. B.

**Convallarin. J.** LINDNER and A. TORGLER (Monatsh., 1934, 63, 335—346).—Repeated extraction of convallarin (I) (Merck) with  $H_2O$  extracts approx. 60%, and with EtOAc approx. 45%, of sol. material. (I) is thus separated into  $H_2O$ -sol. (II) (C 58.4, H 8.17%), EtOAc-sol. (III) (C 60.82, 61.15, H 7.98, 7.92%), and  $H_2O$ - and EtOAc-sol. (IV) portions. The small difference in C and H content of (II) and (III) and other facts render it improbable that the fractions correspond with a neutral, acid, and preformed saponin (Hirschberg), (I) being a complex mixture the composition of which may differ according to its (commercial) source. Hydrolysis of the saponin fraction of (I) with 5%  $H_2SO_4$  gives small yields of *cryst. material* containing at least two different substances (cf. A., 1915, i, 571), and only by examination of these *cryst. products* can the glucosides of the lily of the valley be investigated. J. W. B.

**Caoutchouc. XVI. A. R. Kemp's method of determining iodine values in the case of caoutchouc. R.** PUMMERER and H. STARK (Ber., 1934, 67, [B], 292—294; cf. A., 1933, 1054).—Caoutchouc (I) in pure  $CS_2$  under  $N_2$  is mixed with an excess of 0.2*N*-ICl-AcOH (which may attain 70%) at 0°. After 2—4 hr. the mixture is treated with 10% KI and anhyd. EtOH (to avoid emulsions) and titrated with  $Na_2S_2O_3$ .  $CMe_2\cdot CHMe$  behaves similarly to (I), but  $\gamma$ -ethyl- $\Delta^{\beta}$ -pentene, like the terpenes, cannot be determined thus. H. W.

**Isoprene and caoutchouc. XLI. Hydrogenation of caoutchouc and balata. H.** STAUDINGER and E. O. LEUPOLD (Ber., 1934, 67, [B], 304—311; cf. A., 1932, 1089).—The sp. viscosity (I) of squalene and perhydrosqualene in  $C_6H_6$  is the same; this is true also for hemicolloidal balata and hydrobalata obtained therefrom. This confirms the conclusion that (I) depends only on the length and no. of the mols. and is independent of their chemical nature. Cautious hydrogenation of undegraded balata and euolloidal caoutchouc leads to partly reduced compounds  $(C_5H_9)_x$  and completely hydrogenated polypranes  $(C_5H_{10})_x$  which, in equally conc. solution, have

the same (I) as the non-hydrogenated compounds. Since the size of the particles remains unchanged, all the C atoms which form the colloidal particles are united by normal co-valencies and the particles are mols. in the sense of the classic theory. The mols. of polyprenes and polypranes must necessarily have the same thread formation. The physical properties of the hydrocaoutchoucs, including elasticity, are identical with those of the polymeric-analogous caoutchoucs. Elasticity is not shown by degraded products and hence is conditioned by mol. size; only very complex compounds are elastic. Hydrobalata of mol. wt. 40,000 is as stable as any other paraffin. Eucolloidal hydrocaoutchouc is unaffected by exposure to air and light during many days when solid or in solution.

H. W.

**Reactions of eucalyptol.** L. EKKERT (Pharm. Zentr., 1934, 75, 145).—Colour reactions obtained when eucalyptol and furfuraldehyde, anisaldehyde, salicylaldehyde, vanillin, cinnamaldehyde, piperonal,  $p$ -NMe<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO, or  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·OH in EtOH are treated with conc. H<sub>2</sub>SO<sub>4</sub> are described. S. C.

**Preparation of pure *d*-neomenthol from *l*-menthol.** W. J. GRUBB and J. READ (J.S.C.I., 1934, 53, 52—53T).—When *l*-menthone, prepared by oxidising *l*-menthol (I), is reduced with Ponndorf's reagent (A., 1926, 520) it readily yields a mixture of *d*-neomenthol (II) and (I), containing about 70% of (II). *p*-Nitrobenzoyl chloride reacts 16.3 times as rapidly with (I) as with (II), so that partial esterification leaves a residual menthol containing about 95—98% of (II). One recrystallisation of the *p*-nitrobenzoate of this material yields pure *d*-neomenthyl *p*-nitrobenzoate, from which pure (II) is easily obtained. *l*-Menthone yields about 35% of its wt. of pure (II) in this way.

**Constituents of Indian turpentine from *Pinus longifolia*, Roxb. III (contd.).** A. E. BRADFIELD, E. M. FRANCIS, and J. L. SIMONSEN (J.C.S., 1934, 188—197).—Ozonisation of longifolene (I) in CCl<sub>4</sub> at 0° affords CH<sub>2</sub>O and an ozonide, which when decomposed and treated with H<sub>2</sub>O<sub>2</sub> affords  $\alpha$ -longifolic acid, m.p. 140—142° (labile form, m.p. 121—122°), [ $\alpha$ ]<sub>D</sub><sup>20</sup> —31° in EtOH (Me ester, an oil), stereoisomeric with longifolic (II) and *isolongifolic* acids, which are *cis*-*trans*-isomerides (cf. J.C.S., 1923, 123, 2642). (I) therefore has a vinyl side-chain. (I) with MnO<sub>2</sub> in boiling dil. H<sub>2</sub>SO<sub>4</sub> in 18 hr. affords an acid, decomp. 264—265° (Me ester, m.p. 145—147°), and trimellitic acid, whereas with dil. HNO<sub>3</sub> first at room temp. and then at 100° for 5 days it affords a mixture of solids (III) and an oil from which *as*-dimethylsuccinic acid and CMe<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub> are isolated. CHCl<sub>3</sub> extracts from (III) a dibasic acid, C<sub>11</sub>H<sub>18</sub>O<sub>4</sub>, m.p. 183—185°; the residue is separated by COMe<sub>2</sub> into a very weak tribasic acid, C<sub>14</sub>H<sub>18</sub>O<sub>6</sub>, decomp. 283—285° (from HCO<sub>2</sub>H) and decomp. 272—273° (from MeOH) (Me ester, m.p. 73—74°), stable to KMnO<sub>4</sub>, HBr in AcOH at 180°, and Se at 300°, which indicates that the CO<sub>2</sub>H groups are attached to quaternary C atoms and are derived by oxidation of the CH:CH<sub>2</sub> and two Me groups (one of which comes from the ·CMe<sub>2</sub>· group) not attached to the same C atom, a tribasic acid (IV), C<sub>15</sub>H<sub>20</sub>O<sub>6</sub>, decomp. 222—224° (Me ester, an oil)

[probably formed by addition of H<sub>2</sub>O (or HNO<sub>3</sub>) to CH:CH<sub>2</sub> followed by oxidation to give CH<sub>2</sub>·CO<sub>2</sub>H], stable to similar reagents, and occasionally an *isomeride* of (IV), m.p. 199—200° (sintering at 190°), which with AcCl gives an *anhydride*, m.p. 103°. Longifolamide (V) (prep. described) (cf. *ibid.*, 2656) easily affords *longifonitrile*, b.p. 145—150°/2 mm., which is the main product of the interaction of the acid chloride of (II) and NH<sub>3</sub>, and is hydrolysed to (V) with hot 90% H<sub>2</sub>SO<sub>4</sub>. The urethane from (V) (improved prep.) with Na amyloxide at 160° during 8 hr. affords *l*-amino-1-methyl-longifane (VI), b.p. 150°/18 mm. [*hydrochloride*, decomp. 280—282° (sintering at 258°); *nitrite*, decomp. 132°;  $\alpha$ - and  $\beta$ -Ac derivatives, m.p. 191—192° and 163—165°, respectively; 3 : 5-*dinitrobenzoate*, m.p. 199—200°;  $\alpha$ -, m.p. 258—259°, and  $\beta$ - (VII) -*methiodides* (+1H<sub>2</sub>O, decomp. 184°)]. (VII) with Ag<sub>2</sub>O in H<sub>2</sub>O at 60° during 12 hr. affords an oil which when heated gives 1-dimethylamino-1-methyl-longifane [*hydrochloride* (VIII), m.p. above 280°]. The NH<sub>4</sub> base corresponding with the  $\alpha$ -isomeride affords (VIII) and some NMe<sub>3</sub>. (VI) with NaNO<sub>2</sub> in H<sub>2</sub>O-H<sub>3</sub>PO<sub>4</sub> at 100° during 2 hr. affords a hydrocarbon-alcohol mixture, converted by KHSO<sub>4</sub> at 200° into a hydrocarbon (IX), C<sub>13</sub>H<sub>20</sub>, b.p. 124°/20 mm. (54.8% of unsaturation) (hydrochloride, an oil), and an unchanged alcohol which cannot be dehydrated even by 2-C<sub>10</sub>H<sub>7</sub>·SO<sub>3</sub>H and does not react with *o*-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>O at 100—120°; this indicates it is a *tert*. alcohol and confirms that the CO<sub>2</sub>H in (II) is linked to a quaternary C. (IX) with KMnO<sub>4</sub> in H<sub>2</sub>O-NaOH at 0° during 10 hr. affords a dibasic acid, C<sub>13</sub>H<sub>20</sub>O<sub>4</sub>, m.p. 235—236° (converted by AcCl into an oily anhydride), and a lactone, m.p. 190°, probably obtained by lactonisation of the hydrolytic product of (X) (below). Ozonisation of (IX) in EtOAc below 0°, followed by decomp. of the ozonide with H<sub>2</sub>-Pd (cf. A., 1932, 1113), affords CH<sub>2</sub>O (which indicates ·CH<sub>2</sub>·), an acid, m.p. 166° (converted by NaOH into an acid, m.p. 132°), and an oil, separated into three fractions: 1-methyldehydrolongifane, b.p. 125—127°/25 mm. (liquid *hydrochloride*) (which probably contains a cyclopropane ring), probably longif-1-one (X), identified as its *semicarbazone*, m.p. 208—209°, and liquid OH·CH<sub>2</sub>· derivative (*semicarbazone*, m.p. 199°) (which indicates ·CH<sub>2</sub>·CO), and an unidentified ketone (2 : 4-*dinitrophenylhydrazone*, m.p. 250—251°). Interaction of (VI) in COMe<sub>2</sub> at 30—35° with KMnO<sub>4</sub> affords the  $\alpha$ -NHAc-compound (XI) and an acid, C<sub>16</sub>H<sub>25</sub>O<sub>3</sub>N, m.p. 122—124° (*semicarbazide*, decomp. 179—180°), converted by loss of CO<sub>2</sub> into a substance, m.p. 144°, isomeric with (XI) and converted into (XI) by heating with EtOH-H<sub>2</sub>SO<sub>4</sub>. A mechanism is suggested for these reactions. A formula is proposed for (I).

J. L. D.

**Carvone series. I. Some ketones and amines.** J. READ and R. G. JOHNSTON (J.C.S., 1934, 226—233).—Reduction [Pd(OH)<sub>2</sub>-CaCO<sub>3</sub>-H<sub>2</sub>; cf. A., 1916, ii, 534] of *d*-carvone in MeOH during 2 hr. affords a product, [ $\alpha$ ]<sub>D</sub><sup>20</sup> —30.62° in CHCl<sub>3</sub>; when prepared by Rupe's method (cf. A., 1919, i, 29) this has [ $\alpha$ ]<sub>D</sub><sup>20</sup> —24.9° to —25.1° in CHCl<sub>3</sub> (cf. A., 1926, 1147) and is an equilibrium mixture of *l*- (I) and *l*-*iso*-carvomenthone (II). *d*-Carvomenthol (obtained from *d*-carvomenthylamine and HNO<sub>2</sub>) with Beckmann's reagent (A., 1889,

721) affords *l*-carvomenthone, b.p. 96—96.5°/16 mm.,  $[\alpha]_D^{25}$  —6.0° in  $\text{CHCl}_3$  [oxime, (III), m.p. 99—100°; *semicarbazone*, m.p. 192°]. (II) with conc.  $\text{HCl}$  at room temp., 90%  $\text{H}_2\text{SO}_4$ , or  $\text{Na}$  in cold  $\text{EtOH}$ , formed some (I), although 40%  $\text{NaOH}$  or heat had practically no effect. (I) affords some (II) with cold  $\text{NaOEt-EtOH}$ . (III) with  $\text{Na}$  in boiling  $\text{EtOH}$  affords *d*-carvomenthylamine hydrochloride, m.p. > 250°, converted into the free base, b.p. 89.8—90°/16.5 mm.,  $[\alpha]_D^{25}$  +12.47° in  $\text{CHCl}_3$  [formyl, m.p. 95°; *Ac*, m.p. 160—161°; *propionyl*, m.p. 128—129°; *n*-butyryl, m.p. 123—124°; *n*-hexoyl, m.p. 104°; *n*-octoyl, m.p. 97—98°; *phenylacetyl*, m.p. 177; *Bz* (IV), m.p. 161°, and *d*-camphor-10-sulphonyl derivatives, m.p. 95°; *carbimide*, m.p. 206—207°; *formate*, m.p. 152°; *H d*-tartrate, m.p. 143—144°; *d*-, m.p. 138—140°, and *l*-camphor-10-sulphonate, m.p. 144—145°, together with (V) (below) and possibly another carvomenthylamine (*Bz* derivative, m.p. 151—152°). Interaction of (I) and (II) with  $\text{HCO}_2\text{NH}_4$  at 130° during 48 hr. affords *dicarvomenthylamine*, b.p. 178—179°/11 mm.,  $[\alpha]_D^{25}$  —3.5° in  $\text{CHCl}_3$  (which is probably a mixture of isomerides), and a mixture of formates from which *l*-neocarvomenthylamine (V), b.p. 87.8—88.0°/16 mm.,  $[\alpha]_D^{25}$  —20.13° in  $\text{CHCl}_3$  (*hydrochloride*,  $[\alpha]_D^{25}$  —31.9° in  $\text{H}_2\text{O}$ ; *formyl*, m.p. 50°; *Ac*, m.p. 114°; *propionyl*, m.p. 101°; *n*-butyryl, m.p. 98°; *Bz*, m.p. 126°; *phenylacetyl*, m.p. 81°, and *salicylidene* derivatives, m.p. 36—37°; *formate*, m.p. 131.5—132°; *H d*-tartrate, m.p. 162°), is isolated. Reduction of *d*-carvoxime with  $\text{Na}$  in  $\text{EtOH}$  (cf. A., A., 1893, i, 595) affords a mixture; fractional crystallisation of the formate affords *d*-dihydrocarvylamine formate, m.p. 145°, converted into the free base, b.p. 111°/35 mm.,  $[\alpha]_D^{25}$  +16.4° in  $\text{CHCl}_3$  [*Bz* derivative, m.p. 182°, hydrogenated to (IV); *salicylidene* derivative, m.p. 58°]. Interaction of the appropriate acid chloride with a hydroxyaldehyde in dry  $\text{C}_5\text{H}_5\text{N}$  affords the following: *d*-camphor-10-sulphonyl-*m*-hydroxybenzaldehyde, m.p. 67°; *-vanillin*, m.p. 128°;  $\beta$ -naphthalenesulphonyl-*salicylaldehyde*, m.p. 74—75°; *-vanillin*, m.p. 98°; *-salicylidene-d*-carvomenthylamine, m.p. 104°. A stereochemical analogy between the menthone and carvomenthone series is discussed.

J. L. D.

**Carvone series. II. Some unsaturated alcohols.** R. G. JOHNSTON and J. READ (J.C.S., 1934, 233—237).—Reduction of *d*-carvone with  $\text{Pr}^{\text{OH}}$  and  $\text{Al}(\text{OPr}^{\text{OH}})_3$  at 110° during 8 hr. (cf. A., 1926, 520) affords a carveol; fractional crystallisation of the 3 : 5-dinitrobenzoate gives *d*-trans-, m.p. 111.5°, and *d*-cis-carveyl-3 : 5-dinitrobenzoate, m.p. 92.5°, which are hydrolysed by boiling 5%  $\text{KOH-MeOH}$  to *d*-trans-carveol (I), b.p. 102.2—102.4°/10 mm.,  $[\alpha]_D^{25}$  +213.1° in  $\text{CHCl}_3$  [*p*-nitrobenzoate (II), m.p. 77°; *Ac* derivative, b.p. 106—106.5°/9 mm.] (dehydrated by *d*-camphor-10-sulphonyl chloride to a mixture of a terpene and *p*-cymene), and *d*-cis-carveol (III), m.p. 24—25°,  $[\alpha]_D^{25}$  +23.9° in  $\text{CHCl}_3$  [*p*-nitrobenzoate, m.p. 26.5—28°; *Ac* derivative, b.p. 108—108.5°/10 mm.], respectively. A mixture of (I) and (III) having  $\alpha_D$  +70.74° in  $\text{C}_5\text{H}_5\text{N}$  with *p*- $\text{NO}_2\text{-C}_6\text{H}_4\text{-COCl}$  at 15—30° affords more (II), which supports its *trans*-structure. Similarly, *l*-carvone affords *l*-trans- and *l*-cis-carveol. Equal wts. of *d*- and *l*-trans-carveyl 3 : 5-dinitrobenzoates in hot  $\text{EtOH-EtOAc}$  afford *dl*-trans-carveyl 3 : 5-dinitro-

benzoate, m.p. 119° (*dl*-cis-compound, m.p. 91.5°), hydrolysed to *dl*-trans-carveol, b.p. 108°/16 mm. (*p*-nitrobenzoate, m.p. 101°) (*dl*-cis-compound, b.p. 108°/16 mm.; *p*-nitrobenzoate, m.p. 94°). (I) is unattacked by  $\text{Na}$  in boiling  $\text{EtOH}$ , but  $\text{H}_2\text{-Pd}$  (cf. J.C.S., 1923, 123, 2916) affords a product isolated as *carvotanacetyl* 3 : 5-dinitrobenzoate (?), m.p. 109—110°. Complete hydrogenation of (I) and (III) affords four carvomenthols. Reduction of *d*-carvone with  $\text{Na}$  in  $\text{EtOH}$  affords *d*-dihydrocarveol (cf. A., 1902, i, 630) (*p*-nitro-, m.p. 37°, and 3 : 5-dinitro-benzoate, m.p. 121.5—122°), readily hydrogenated to *d*-carvomenthol, whereas with  $\text{Zn}$  and  $\text{EtOH-KOH}$  it gives *l*-dihydrocarvone (IV), further reduced by  $\text{Al}(\text{OPr}^{\text{OH}})_3$  and  $\text{Pr}^{\text{OH}}$  to a mixture of dihydrocarveols separated by means of 3 : 5-( $\text{NO}_2$ ) $_2\text{C}_6\text{H}_3\text{-COCl}$  into a *dihydrocarveol*, b.p. 99—100°/13 mm. (*p*-nitro-, m.p. 83—84°, and 3 : 5-dinitro-benzoate, m.p. 106—107°), and *l*-neodihydrocarveol, b.p. 101—102°/18 mm. (3 : 5-dinitro-, m.p. 138—138.5°, and *p*-nitrobenzoate, m.p. 107°; *d*-camphor-10-sulphonate, m.p. 91—93°, decomposed at 125° into  $\alpha$ -phellandrene and *d*-camphor-10-sulphonic acid), hydrogenated to *l*-neocarvomenthol. (IV) with hot dil.  $\text{H}_2\text{SO}_4$  (cf. A., 1895, i, 621) affords *dl*-carvenone, reduced by  $\text{Al}(\text{OPr}^{\text{OH}})_3$  to *dl*-carvenol (3 : 5-dinitro-, m.p. 75—76°, and *p*-nitro-benzoate, m.p. 65°).  
J. L. D.

**Catalytic hydrogenation of diosphenol.** J. WALKER and J. READ (J.C.S., 1934, 238—242; cf. A., 1924, i, 862).—Reduction of diosphenol (I) (cf. A., 1922, i, 667) with  $\text{Pd-H}_2$  affords dihydrodiosphenol (II), b.p. 108—115°/12 mm. [*semicarbazone*, m.p. 210—211° (decomp.); *p*-toluenesulphonate, m.p. 106—107°; *d*-camphor-10-sulphonate (III), an oil]. (III) at 150° in vac. affords *dl*-piperitone and *dl*- $\Delta^4$ -menthenone-3, b.p. 90—97°/10 mm. [oxime identical with the product of Richtmann and Kremers (cf. A., 1897, i, 84)], which indicates that (II) is 2-hydroxymenthone. The *p*-toluenesulphonate of (I), m.p. 76°, or of (II), is unattacked by  $\text{H}_2\text{-Pd}$  or  $\text{H}_2\text{-Adams'}$  catalyst. *dl*-Piperitone oxide with  $\text{H}_2\text{-Pd}$  affords *l*-hydroxymenthone (?), m.p. 88.5—90.5°. Similarly, *dl*-carvenone oxide affords 4-hydroxycarvomenthone (?), m.p. 72.5—74°.  
J. L. D.

***d*- $\Delta^{3,8(9)}$ -*p*-Menthadiene from *d*-pulegone.** W. J. GRUBB and J. READ (J.C.S., 1934, 242—243; cf. A., 1931, 230).—Reduction of *d*-pulegone with  $\text{Al}(\text{OPr}^{\text{OH}})_3$  in dry  $\text{Pr}^{\text{OH}}$  (cf. A., 1926, 520) affords *p*-pulegol, but *d*- $\Delta^{3,8(9)}$ -*p*-menthadiene (cf. J.C.S., 1906, 89, 848; 1911, 99, 537), b.p. 69°/14 mm.,  $[\alpha]_D^{25}$  +140.6° in  $\text{CHCl}_3$  (which gives no solid derivatives, but adds on 2 Br), oxidised ( $\text{KMnO}_4\text{-COMe}_2$  at 0°) to  $\beta$ -methyladipic acid.  
J. L. D.

**Optical resolution of externally compensated alcohols.** J. WALKER and J. READ (J.S.C.I., 1934, 53, 53—54T).—Chloromethylene-*d*-camphor, prepared from hydroxymethylene-*d*-camphor, reacts with  $\text{Na l}$ - and  $\text{dl}$ -menthoxide to yield *cryst. l*-, m.p. 74—75°,  $[\alpha]_D^{25}$  +109.3° in  $\text{EtOH}$ , and *dl*-, m.p. 75—76°,  $[\alpha]_D^{25}$  +150.0° in  $\text{EtOH}$ , *-menthoxymethylene-d*-camphor; the *dl*-compound is a partial racemate. The corresponding *dl*-3-methylmenthyl and *dl*-*m*-methylcyclohexyl ethers do not crystallise. The pos-

sible application of such derivatives to the optical resolution of suitable *dl*-alcohols is pointed out.

**Constituents of campherol.** Y. ASAHINA and M. ISHIDATE (Proc. Imp. Acad. Tokyo, 1933, 9, 596—598; cf. this vol., 79).—The 5- is more reactive than the 2-CO group in 5-ketocamphor (I), since (I) adds HCN exclusively to the former and its monosemicarbazone, m.p. 238—240°, gives (Wolff-Kishner) *d*-borneol. Similarly (I) with cold Na-Hg in presence of CO<sub>2</sub> gives 5-hydroxycamphor, m.p. 210°,  $[\alpha]_D^{25} +47.4^\circ$  (*Ac* derivative), the *semicarbazone* of which (Wolff-Kishner) gives probably impure *epiborneol* and may thus be a mixture of isomerides. Me *trans*- $\pi$ -apocamphor-7-carboxylate semicarbazone, when reduced (Na-EtOH) and then hydrolysed by HCl, gives *trans*- $\pi$ -hydroxycamphor, m.p. 233°,  $[\alpha]_D^{25} +62.2^\circ$ . The corresponding *cis*-ester gives similarly *cis*- $\pi$ -hydroxycamphor, m.p. 233°,  $[\alpha]_D^{25} +40.68^\circ$ .

R. S. C.

**Determination of configuration in the terpene and camphor series.** VI. J. VON BRAUN and P. KURTZ (Ber., 1934, 67, [B], 225—230; cf. A., 1932, 43).—(+)-Camphor is transformed by two treatments with NaNH<sub>2</sub> and MeI into dimethylcamphor and thence by NaNH<sub>2</sub> into dimethylcampholamide (I). Treatment of (I) with Br and KOH leads to the

*carbimide*  $\begin{matrix} \text{CH}_2 & \text{---} & \text{CH}_2 \\ \text{CHPr}^\beta & \text{---} & \text{CMe}_2 \end{matrix} > \text{CMe} \cdot \text{N} : \text{C} : \text{O}$ , b.p. 109—112°/14 mm.,  $[\alpha]_D^{25} +16.5^\circ$  in EtOH [*di*(dimethylcamphelyl)-*carbamide*, m.p. 154°], hydrolysed by HCl to *dimethyl-*

*camphelylamine* (II),  $\begin{matrix} \text{CH}_2 & \text{---} & \text{CH}_2 \\ \text{CHPr}^\beta & \text{---} & \text{CMe}_2 \end{matrix} > \text{CMe} \cdot \text{NH}_2$ , b.p. 90°/14 mm.,  $[\alpha]_D^{25} +22.31^\circ$ ,  $[\alpha]_D^{25} +33.06^\circ$  in EtOH [*picrate*, m.p. 202°; *hydrochloride*; *sulphate*; *phosphate* (III)]. (I) is hydrolysed by conc. HCl at 150° to dimethylcampholic acid (III), b.p. 137—140°/0.5 mm.,  $[\alpha]_D^{25} +47.8^\circ$  in EtOH (re-converted into the amide by action of NH<sub>3</sub> on the *chloride*, b.p. 100°/0.5 mm.). Treatment of (III) in H<sub>2</sub>SO<sub>4</sub> with NH<sub>3</sub>-CHCl<sub>3</sub> gives partly racemised (II). Dry distillation of (III) gives a smaller amount of somewhat racemised (II) and a larger quantity of 1 : 2 : 2-trimethyl-3-isopropyl- $\Delta^5$ -cyclopentene (IV), b.p. 168—170°,  $[\alpha]_D^{25} -15.49^\circ$ , probably containing a small amount of a semicyclic impurity. Ozonisation in AcOH of (IV) followed by treatment with Zn dust leads to  $\delta$ -*keto*- $\gamma\gamma$ -dimethyl- $\beta$ -isopropylhexaldehyde (V), b.p. 117—120°/12 mm.,  $[\alpha]_D^{25} +43.39^\circ$  (*p*-nitrophenylhydrazone, m.p. 179—180°; *semicarbazone*, m.p. 218°), with a small proportion of (?) 2 : 2-dimethyl-3-isopropylcyclohexanone (*semicarbazone*, m.p. 200°). (V) is the first example of an open-chain, optically active degradation product of camphor in which C<sub>1</sub> of camphor has been inactivated, whereas C<sub>4</sub> retains its original configuration.

H. W.

**Electrolytic reduction of camphoric acid imide.**—See this vol., 373.

**Fenchene series.** V. *sec.*- and *tert.*-Fenchyl chlorides. G. KOMPPA and S. BECKMANN (Annalen, 1934, 509, 51—60).—The rate of elimination of HCl (by 0.5*N*-KOH-EtOH at 20—24°) from the following is: *dl*- $\alpha$ -fenchene hydrochloride (I) > *dl*-cyclofenchene hydrochloride > *dl*- $\beta$ -fenchene hydrochloride >> “*isofenchyl chloride*” (II) > “*fenchyl chloride*”

(III). (I) thus regenerates  $\alpha$ -fenchene; careful hydrolysis gives methyl- $\alpha$ -fenchocampherol. (III), prepared from *dl*-fenchyl alcohol and PCl<sub>5</sub>, is a mixture of *sec.*- and *tert.*-chlorides; the composition varies according to the method of prep. Thus, rapid treatment with PCl<sub>5</sub> gives 20—30% of  $\beta$ -fenchene [and (probably) some  $\gamma$ -fenchene], which then adds HCl to give the *tert.*-chloride. When (III) is kept in contact with the acid reaction mixture for a relatively long time, *isofenchyl chloride* results; elimination of HCl from this gives (mainly)  $\beta$ -fenchene (cf. Qvist, A., 1919, i, 165). Treatment of (III) with aq. Ca(OH)<sub>2</sub> at 50—60° gives unchanged *sec.*-chloride (*i.e.*, true *sec.*-fenchyl chloride or its rearrangement product *isofenchyl chloride*) and  $\beta$ -fenchene hydrate (A., 1933, 830); similar results are obtained using AgOAc (and subsequent hydrolysis). (II) is also a mixture containing a considerable amount of *tert.*-chloride. *dl*-*isofenchyl H phthalate* has m.p. 153—154°. H. B.

**Super-aromatic properties of furan.** III. Nitration. H. GILMAN and R. V. YOUNG (J. Amer. Chem. Soc., 1934, 56, 464—466).—Ph 2-furyl ketone and HNO<sub>3</sub> (*d* 1.5) in Ac<sub>2</sub>O at < -8° give Ph 5-nitro-2-furyl ketone, m.p. 111°, also prepared from 5-nitro-2-furoyl chloride (improved prep.), C<sub>6</sub>H<sub>6</sub>, and AlCl<sub>3</sub>, which is oxidised (KMnO<sub>4</sub>) to 5-nitro-2-furoic acid and a little BzOH. 2-Furyl 2-thienyl ketone (*semicarbazone*, m.p. 150°) similarly affords 5-nitro-2-furyl 2-thienyl ketone, m.p. 161°, which when heated with 10% NaOH (to effect destruction of the nucleus containing the NO<sub>2</sub>-group) and then oxidised (KMnO<sub>4</sub>) gives 2-thienoic acid. These and previous results (A., 1933, 1300) show that 2-furyl, 2-thienyl, and Ph are decreasingly aromatic. *Fur*-2' : 4' : 6'-tribromoanilide, m.p. 164°, and *N*-methylanilide, m.p. 125°, and 5-nitro-2-fur-2' : 4' : 6'-tribromoanilide, m.p. 191—192°, are described; attempted nitration gives resinous products.

H. B.

**Decarboxylation temperatures of furoic acids.** H. GILMAN, A. M. JANNEY, and C. W. BRADLEY (Iowa State Coll. J. Sci., 1933, 7, 429—431).—M.p. and decarboxylation temp. (determined by Norris' graphical method) are: 2-furoic acids: unsubstituted 132°, 158°; 5-Me 107°, 122—125°; 5-Bu' 105°, 125—127°; 5-Cl 175°, 180—182°; 5-Br 185°, 177—179°; 3 : 5-Cl<sub>2</sub> 156—157°, 168—170°; 3 : 5-Br<sub>2</sub> 168—168.5°, 174°; 5-I 193°, —; 5-NO<sub>2</sub> 186°, 201—203°. 3-Furoic acids: unsubstituted 122°, 152°; 2-Me 101°, 101—103°; 2 : 4-Me<sub>2</sub> 114°, 129°; 5-NO<sub>2</sub>-2-Me 154.5°, 172°; 5-NO<sub>2</sub>-2 : 4-Me<sub>2</sub> 182°, 185—186°. *o*-Anisic acid 98°, 213—215°; *p*-anisic acid 106—107°, 243—245°.

CH. ABS.

**Synthesis of 6- $\beta$ -*d*-glucosidokojic acid.** R. M. HANN (J. Amer. Chem. Soc., 1934, 56, 485—486).—Acetobromoglucose, kojic acid, and EtOH-KOH in CHCl<sub>3</sub> give 5- $\beta$ -tetra-acetyl-*d*-glucosidoxy-2-hydroxymethyl-1 : 4-pyrone, m.p. 201° (corr.),  $[\alpha]_D^{25} -88.3^\circ$  in CHCl<sub>3</sub>, de-acetylated (MeOH-NaOMe in cold CHCl<sub>3</sub>) to 5- $\beta$ -*d*-glucosidoxy-2-hydroxymethyl-1 : 4-pyrone (5- $\beta$ -*d*-glucosidokojic acid), m.p. 197—198° (corr.),  $[\alpha]_D^{25} -107.3^\circ$  in H<sub>2</sub>O.

H. B.

**Natural coumarins.** X. Synthesis of osthol. E. SPATH and H. HOLZEN (Ber., 1934, 67, [B], 264—265; cf. A., 1933, 614).—2-Hydroxy-4-methoxybenz-

aldehyde is transformed by successive treatment with Na in  $C_6H_6$  at  $80^\circ$  and  $\gamma$ -methyl- $\Delta^{\beta}$ -butenyl bromide into 2-hydroxy-4-methoxy-3- $\gamma$ -methyl- $\Delta^{\beta}$ -butenylbenzaldehyde, b.p.  $118-122^\circ/0.6$  mm., converted by NaOAc and  $Ac_2O$  at  $155-160^\circ$  into 7-methoxy-8- $\gamma$ -methyl- $\Delta^{\beta}$ -butenylcoumarin, m.p.  $82-83^\circ$ , identical with osthol (I). Immediately after distillation (I) has m.p.  $62-63^\circ$ , but passes slowly when preserved, rapidly when heated at  $50-60^\circ$  and seeded or crystallised from ligroin or  $Et_2O$ , into the modification, m.p.  $83-84^\circ$ .

H. W.

**Synthesis of dihydro-osthol from a degradation product of rotenone.** E. SPATH, S. TAKEI, and S. MIYAJIMA (Ber., 1934, 67, [B], 262-263).—2-Hydroxy-4-methoxy-3- $\gamma$ -methylbutylbenzoic acid (tetrahydro tubaie acid Me ether) is decarboxylated at  $220-230^\circ/vac.$  to 3-methoxy-2- $\gamma$ -methylbutylphenol (tetrahydro tubanol Me ether), b.p.  $120^\circ/7$  mm., converted by malic acid (I) and conc.  $H_2SO_4$  into 7-methoxy-8- $\gamma$ -methylbutylcoumarin (dihydro-osthol), m.p.  $85-85.5^\circ$ , identical with the substance obtained by hydrogenation of osthol (Pd-C in AcOH). 1:3-Dihydroxy-2- $\gamma$ -methylbutylbenzene and (I) give 8- $\gamma$ -methylbutylumbelliferone in poor yield. H. W.

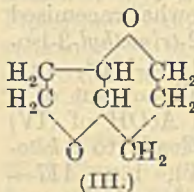
**Constitution of tannins. I. Reduction products of chalcones and the synthesis of a typical phlobatannin.** A. RUSSELL (J.C.S., 1934, 218-221).—Gallacetophenone 3:4-Me<sub>2</sub> ether (I) with piperonal affords 2-hydroxy-3:4-dimethoxy-3':4'-methyleneedioxy-chalkone, m.p.  $175^\circ$ . Similarly (I) and  $p$ -OH-C<sub>6</sub>H<sub>4</sub>-CHO give 2:4'-dihydroxy-3:4-dimethoxychalkone, m.p.  $106^\circ$ . Gallacetophenone Me<sub>2</sub> ether and anisaldehyde afford 2:3:4:4'-tetramethoxychalkone (II), m.p.  $94^\circ$ . 2-Hydroxy-3:4:4'-trimethoxychalkone in boiling EtOH-AcOH containing Zn during 1 hr. affords 4-hydroxy-7:8:4'-trimethoxyflavan, decomp.  $> 85-95^\circ$ . Similarly prepared, 4-hydroxy-7:8:3':4'-tetramethoxy-, 4-hydroxy-7:8-dimethoxy-3':4'-methylenedioxy-, and 4:4'-dihydroxy-7:8-dimethoxy-flavan have m.p.  $90-110^\circ$ ,  $110-125^\circ$ , and  $120-125^\circ$ , respectively. These flavans closely resemble the methylated natural phlobatannins. Reduction of chalkone (as above), 4'-hydroxychalkone, and (II) gives compounds, m.p.  $192^\circ$ ,  $204-205^\circ$ , and  $168^\circ$ , respectively. Resacetophenone dibenzoate and protocatechualdehyde dibenzoate in dry EtOAc containing HCl at  $0^\circ$  during many hr. afford, after treatment with boiling KOH, 2:4:3':4'-tetrahydroxychalkone, m.p.  $212^\circ$  [identical with butein (cf. J.C.S., 1904, 85, 1459; A., 1912, i, 30)], reduced (Zn-AcOH) to 4:7:3':4'-tetrahydroxyflavan (or the 4:4-bis-compound), indistinguishable from natural phlobatannins. J. L. D.

**Synthetic experiments with methyltrihydroxybenzenes. I. Synthesis of 2:6-dimethylpolyhydroxyflavones.** S. FUJISE and S. MITUI (Bull. Chem. Soc. Japan, 1934, 9, 24-26).—2:4-Dimethylphloroglucinol with piperonylacrylyl chloride and  $AlCl_3$  gives 5:7-dihydroxy-3':4'-methyleneedioxy-6:8-dimethylflavone, m.p.  $207^\circ$  (chalkone, m.p.  $222-223^\circ$ ), and with carbethoxyferulyl chloride yields the 3'-methoxy-4'-hydroxy-flavone, m.p.  $254.5-255.5^\circ$ . Absorption spectra are given. F. R. S.

**Pigments of the benzopyrylium type. II. Absorption spectra of flavylum chlorides. K.**

HAYASHI (Acta Phytochim., 1933, 7, 143-168; cf. A., 1933, 832).—Absorption curves were obtained for the following flavylum chlorides prepared by cold hydrolysis of the 5-Bz derivatives with 10% aq. NaOH: 5:7-dihydroxy-, 5:7-dihydroxy-2'-methoxy-(+2H<sub>2</sub>O), 5:7:3'- and 5:7:4'-trihydroxy-, 5:7-dihydroxy-2':4'-dimethoxy-, m.p.  $> 290^\circ$  (+H<sub>2</sub>O), 5:7:4'-trihydroxy-3'-methoxy-, m.p.  $> 290^\circ$  (+1.5H<sub>2</sub>O), 5:7-dihydroxy-3':4'-methylenedioxy-not decomp.  $< 290^\circ$  (+1.75H<sub>2</sub>O), 5:7-dihydroxy-2':5'-dimethoxy-, m.p.  $< 290^\circ$  (+1.75H<sub>2</sub>O), 5:7-dihydroxy-2':6'-dimethoxy-4'-methyl-, brown prisms (+H<sub>2</sub>O), orange needles (+1.75H<sub>2</sub>O), m.p.  $< 270^\circ$ , 5:7-dihydroxy-2':3':4'-trimethoxy- (+0.5H<sub>2</sub>O), decomp.  $< 260^\circ$ , 5:7-dihydroxy-3':4':5'-trimethoxy- (+2H<sub>2</sub>O), m.p.  $> 270^\circ$ , 5:7-dihydroxy-2':4':6'-trimethoxy- (+2.5H<sub>2</sub>O), not decomp. at  $270^\circ$ , 5:7-dihydroxy-2':4':5'-trimethoxy- (+1.5H<sub>2</sub>O), decomp.  $260^\circ$ , 5:7-dihydroxy-2':3':4':6'-tetramethoxy- (+3H<sub>2</sub>O), decomp.  $> 270^\circ$ , 3:5:7:4'-tetrahydroxy- (+H<sub>2</sub>O), 3:5:7-trihydroxy-4'-methoxy- (5-Bz derivative from  $\omega$ -acetoxy-4-methoxyacetophenone, m.p.  $60-61^\circ$ ). The observations on the influence of OH-substitution in the Bz compounds are here confirmed. A band at frequency 3000-3300 is characteristic of 4'-substitution (OH or OMe), but may be neutralised by 3'-substitution. Other bands are sp. for 2':5'-dimethoxy- (or methylenedioxy-) and pelargonidin derivatives. J. H. B.

**Hydrogenation and hydrogenolysis of furan derivatives.** H. E. BURDICK and H. ADKINS (J. Amer. Chem. Soc., 1934, 56, 438-442).— $\beta$ -2-Furylacetaldehyde (I) is reduced [ $H_2$  (100-200 atm.), Niekelselguhr catalyst (a),  $160^\circ$ ] to 2-ethyltetrahydrofuran (3%), b.p.  $105-107^\circ/740$  mm.,  $\gamma$ -2-tetrahydrofurylpropyl alcohol (II) (38%), b.p.  $105-106^\circ/10$  mm., 221-224<sup>o</sup>/741 mm., and 1:5-dioxaoctahydroindene (III) (33%), b.p.  $49-50^\circ/10$  mm.,  $156-157^\circ/740$  mm. Reduction [ $H_2$ , Raney Ni (b), EtOH at  $23^\circ$ ] of (I) affords  $\beta$ -2-furylpropylaldehyde (IV) (46%), b.p.  $69-70^\circ/14$  mm.,  $179-180^\circ/740$  mm., and some  $\gamma$ -2-furylpropyl alcohol, b.p.  $93^\circ/10$  mm. (II) and (III) are also produced from (IV) (method a). Small amounts of (III) are also formed from (I) using Cu-Cr oxide in EtOH; at  $200^\circ$  (no solvent) (II) (22%),  $n$ -heptyl alcohol (4%), heptane- $\alpha\delta$ -diol (V) (29%), b.p.  $127-130^\circ/6$  mm., and heptane- $\alpha\eta$ -diol (VI) (20%), b.p.  $148-149^\circ/11$  mm., are produced. (V) and (VI) are further reduced (method b at  $250^\circ$ ) to hexan- $\gamma$ -ol, b.p.  $130-132^\circ/740$  mm., and  $n$ -pentane (21%), respectively; (II) similarly affords H<sub>2</sub>O,  $n$ -pentane (1%), and 2-ethyl- (60%) and 2- $n$ -propyl-tetrahydrofuran (1%), b.p.  $132-133^\circ/739$  mm. (also prepared by reduction of Mg  $\gamma$ -2-tetrahydrofurylpropyl chloride). Furfurylidene acetate is reduced (method a) to 2-methyltetrahydrofuran (10%), b.p.  $78-79^\circ/740$  mm., tetrahydrofurfuryl acetate (41%), b.p.  $88-90^\circ/18$  mm.,  $192-194^\circ/740$  mm., and tetrahydrofurfurylidene acetate (24%), b.p.  $134-136^\circ/16$  mm. (lit.  $133^\circ/29$  mm.). Similarly, furfuryl alcohol gives 85% of tetrahydrofurfuryl alcohol, b.p.  $80-82^\circ/20$  mm.; fur-



furoin affords a mixture of  $\alpha\beta$ -dihydroxy- $\alpha\beta$ -di-2-tetrahydrofurylethanes (Kaufmann and Adams, A., 1924, i, 197); furfurylideneacetone yields 89% of  $\gamma$ -hydroxy- $\alpha$ -2-tetrahydrofurylbutane, b.p. 95°/6 mm.; furfurylideneacetophenone furnishes  $\gamma$ -phenyl- $\alpha$ -2-tetrahydrofurylpropane (VII) (31%), b.p. 160°/28 mm., and its  $\gamma$ -OH-derivative (25%), b.p. 177—181°/12 mm.; (VII) gives  $\gamma$ -cyclohexyl- $\alpha$ -2-tetrahydrofurylpropane, b.p. 121—122°/6 mm., 150—151°/28 mm.; Et  $\beta$ -2-furylacrylate, b.p. 132—133°/18 mm., yields Et  $\beta$ -2-tetrahydrofurylpropionate, b.p. 115—116°/18 mm.; (III) affords some (II).

(III) and 48% HBr give (probably) 3-bromo-2- $\gamma$ -bromopropyltetrahydrofuran, b.p. 142°/5 mm., which with Zn-Cu and aq. EtOH regenerates (III). (III) and HI afford a compound,  $C_7H_{12}OI_2$ , m.p. 45°.  $\gamma$ -2-Furylallyl alcohol has b.p. 85—87°/4 mm. (cf. Bray and Adams, A., 1927, 973). H. B.

Piperidine metavanadate.—See this vol., 375.

Electrolytic oxidation of piperidine.—See this vol., 373.

Introduction of pyridine into the inner sphere of quadrivalent platinum. I. I. TSCHERNIAEV and A. M. RUBINSCHTEIN (Ann. Inst. Platine, 1933, No. 11, 63—71).—The product of reaction of  $enPtCl_4$  (I) and  $C_5H_5N$  at room temp. is  $[enCl_4Pt](C_5H_5N)_2$  and not, as Schleicher *et al.* (A., 1923, i, 1120) supposed,  $[en(C_5H_5N)_2Cl_2Pt]Cl_2$ ; at 100° the product is  $[enCl_3(C_5H_5N)Pt]Cl$ . Schleicher *et al.* based their supposition on the observation that the salt obtained by treating (I) successively with  $C_5H_5N$  and  $en$  had the composition  $en_2PtCl_4$ ; in reality, a 1 : 1 mixture of  $en_2PtCl_4$  and  $enPtCl_4$  is obtained. R. T.

Derivatives of 2-aminopyridine. K. FEIST [with W. AWE, J. SCHULTZ, and F. KLATT] (Arch. Pharm., 1934, 272, 100—113).—2-Aminopyridine (I), m.p. 57° (modified prep.; dibromide, m.p. 195—197°), with  $o$ -OH- $C_6H_4$ -CHO (0.5 mol.) in cold EtOH (not with other proportions or in presence of dehydrating agents) gives the salicylidene derivative, m.p. 65° (dibromide, m.p. 170°; blue  $FeCl_3$  colour), which is hydrogenated (Pd-black) in  $Et_2O$  to the  $N$ - $o$ -hydroxybenzyl derivative, m.p. 105° (picrate, m.p. 185°;  $HgCl_2$ -derivative, +6H<sub>2</sub>O, m.p. 134°; does not give a colour with  $FeCl_3$  and thus probably exists in the betaine form). (I) with  $CCl_3$ -CHO (II) (1.5 parts) in cold  $CHCl_3$  yields 2-pyridyl-( $\beta\beta\beta$ -trichloro- $\alpha$ -hydroxyethyl)amine (III), m.p. 106°, but with 0.75 part of (II) in  $CHCl_3$  without cooling gives  $\alpha\alpha\alpha$ -trichloro- $\beta\beta$ -di-(2-pyridylamino)-ethane,  $CCl_3$ -CH(NH- $C_5H_4N$ )<sub>2</sub>, m.p. 172° (lit. 160°) [picrate, m.p. 185° (decomp.)], also obtained from (III) at 110°. When heated with the appropriate thiocarbimide (I) gives substituted 2-pyridylthiocarbamides,  $C_5H_4N$ -NH-CS-NHR, in which R is *allyl*, m.p. 98°, b.p. 201—205°/18 mm. (picrate, m.p. 144°), *Me*, m.p. 146°, and *Bu*<sup>o</sup>, m.p. 97°, whence by NaOH-EtOH-Pb(OAc)<sub>2</sub>-H<sub>2</sub>O were obtained the corresponding carbamides, m.p. 102°, 148°, and 102°, respectively. *N*-Phenyl-*N'*-2-pyridylcarbamide, m.p. 187° (lit. 180°), was similarly prepared. (I) and CS<sub>2</sub> in cold  $Et_2O$  yield slowly an iso-form, m.p. 147°, of *s*-di-2-pyridylaminothiocarbamide; this and its isomeride, m.p. 163°, give the same carbamide, m.p. 175°, and thus are probably

CS(NH- $C_5H_4N$ )<sub>2</sub> and  $C_5H_4N$ -NH-C(SH)-N- $C_5H_4N$ , or *vice versa*.  $\omega$ -Chloro-3 : 4-dihydroxyacetophenone, m.p. 173°, and (I) (2 mols.) in hot EtOH give 3 : 4-dihydroxy- $\omega$ -2-pyridylaminoacetophenone, an unstable oil with no sympathomimetic action [hydrochloride, +4H<sub>2</sub>O, decomp. 300° after darkening at 250°, and anhyd.; picrate, m.p. 231° (decomp.);  $HgCl_2$ -derivative, +17H<sub>2</sub>O, m.p. 209° after sintering at 190°, and anhyd.; sulphate, sinters at 160°; Ac<sub>2</sub> derivative, cryst. (hydrochloride, +2H<sub>2</sub>O, m.p. 199° after previous sintering, and anhyd.)], which is hydrogenated (Pd-C) to 2-( $\beta$ -hydroxy- $\beta$ -2' : 4'-dihydroxyphenylethylamino)pyridine (hydrochloride, m.p. 300—301°). 2 : 3 : 4-Trihydroxy- $\omega$ -2-pyridylaminoacetophenone, an unstable oil [hydrochloride, +H<sub>2</sub>O, m.p. 265° after sintering, and anhyd.; picrate, m.p. 190° (decomp.);  $HgCl_2$ -derivative, +8H<sub>2</sub>O, m.p. 231°, and anhyd.], was similarly prepared. R. S. C.

Acyl derivatives of polymeric indoles and [precaution in] determination of active hydrogen. O. SCHMITZ-DUMONT and K. HAMANN (J. pr. Chem., 1934, [ii], 139, 167—179).—Treatment of polymeric indoles (I) with acid anhydrides or chlorides gives  $\alpha$ - (II) or  $\beta$ -acyl derivatives (III); (III) are generally formed at higher temp., but not by rearrangement of (II). (II) contain 1 active H < (I) and are true *N*-acyl derivatives, being readily hydrolysed to (I) by hot aq. EtOH-KOH. (III) are produced without loss of active H and with certain exceptions (*e.g.*, the  $\beta$ -Ac and Bz derivatives of tri-indole) do not regenerate (I) with alkali; they do not seem to be *C*-derivatives, however, as they do not give CO reactions, even with MgMeI. Many of these derivatives are, however, affected by MgMeI, and Zerevitinov determinations need to be conducted with care, and should be checked by regeneration of the compound. The following are described:  $\alpha$ -Ac, m.p. 158.5°,  $\alpha$ -CO<sub>2</sub>Et, m.p. 130—131°,  $\alpha$ -Bz, m.p. 178—179°,  $\beta$ -Bz, m.p. 197—198°, and (? $\alpha$ )p- $C_6H_4$ MeSO<sub>2</sub>, m.p. 186—187°, derivatives of di-indole;  $\alpha$ -Bz, m.p. 212°,  $\alpha$ -CO<sub>2</sub>Et, m.p. 155—156°, and  $\alpha$ -p- $C_6H_4$ MeSO<sub>2</sub>, m.p. 188—189°, derivatives of diskatole; and  $\beta$ -carbethoxytri-indole, m.p. 163—164°. H. A. P.

Derivatives of 8-aminoquinoline as anti-malarials. III. Influence of branching of the chain in position 8. O. J. MAGIDSON, N. M. DELEKTORSKAYA, and I. M. LIPOVITSCH (Arch. Pharm., 1934, 272, 74—84; cf. this vol., 82).—Branching of the chain in position 8 in five cases greatly depresses the toxic index of this type of substance. 8-Amino-6-methoxyquinoline (I), NaNH<sub>2</sub>, and isoamyl bromide in  $Et_2O$  give the 8-isoamyl-amino- and 8-diisoamylamino-derivatives, b.p. 163—165°/4 mm. and 172—183°/4 mm., respectively (hydrochlorides, m.p. 205° and 136—138.5°, respectively). (I) with NEt<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>Cl, HCl at 125—130° gives the 8- $\beta$ -diethylaminoethylamino-derivative, b.p. 197—203°/4 mm.,  $D_{tot.}/D_{cur.}=6$ . Et  $\alpha$ -bromoiso-valerate, NHEt<sub>2</sub>, and NaI (not without NaI or with Cu, with or without solvents) at 60° give slowly Et dimethylacrylate and Et  $\alpha$ -diethylaminoisovalerate, b.p. 80—85°/10—11 mm., reduced (Na-EtOH) to  $\beta$ -diethylaminoisoamyl alcohol, b.p. 87—93°/14 mm., which with SOCl<sub>2</sub> in  $CHCl_3$  gives the chloride, b.p.

85—88°/14 mm., the hydrochloride of which with (I) at 125—130° gives 8-N- $\beta$ -diethylaminoisoamylamino-6-methoxyquinoline, b.p. 198—205°/1 mm.,  $D_{\text{tol.}}/D_{\text{cur.}}=4$ . isoAmylene and cold aq. Ca(OCl)<sub>2</sub> give  $\alpha$ -chloro- $\gamma$ -methylbutan- $\beta$ -ol (35% yield), b.p. 140—145°, which with boiling aq. NH<sub>4</sub>Et<sub>2</sub> gives  $\alpha$ -diethylamino- $\gamma$ -methylbutan- $\beta$ -ol (39% yield), b.p. 181—184°.  $\alpha$ -Nitro- $\gamma$ -methylbutan- $\beta$ -ol (obtained in 70% yield from MeNO<sub>2</sub> and Pr <sup>$\beta$</sup> CHO), b.p. 78—82°/2—3 mm., with Al-Hg and EtOH (not Zn-AcOH) (8% yield), Zn and HCl (41% yield), or Fe and HCl (53% yield) gives  $\alpha$ -amino- $\gamma$ -methylbutan- $\beta$ -ol, b.p. 79°/6—7 mm., m.p. 34—35° (oxalate, m.p. 223°; carbonate, cryst.), which yields the  $\alpha$ -diethylamino-alcohol, b.p. 181—184°/760 mm., 84—88°/24 mm., and thence by SOCl<sub>2</sub> in C<sub>6</sub>H<sub>6</sub>  $\beta$ -chloro- $\alpha$ -diethylamino- $\gamma$ -methylbutane, b.p. 70—72°/12 mm. The hydrochloride of the last-mentioned base and (I) at 125—130° give 8-( $\alpha$ -diethylaminomethyl- $\beta$ -methyl)propylamino-6-methoxyquinoline, b.p. 187—191°/3 mm., non-curative.  $\alpha'$ -Bromoneopentanol, b.p. 184—187° (obtained from the Ac derivative by KOH-EtOH, not by NH<sub>4</sub>Et<sub>2</sub>), and NH<sub>4</sub>Et<sub>2</sub> at 140—150° form the  $\alpha'$ -NEt<sub>2</sub>-compound, b.p. 88—89°/8 mm. (41% yield), giving with SOCl<sub>2</sub> in hot C<sub>6</sub>H<sub>6</sub>  $\alpha$ -chloro- $\alpha'$ -dimethylaminoneopentane, b.p. 69—71°/11 mm., the hydrochloride, m.p. 105°, of which with (I) at 125—130° gives 8- $\gamma$ -diethylamino-neopentylamino-6-methoxyquinoline, b.p. 196—200°/1—1.5 mm.,  $D_{\text{tol.}}/D_{\text{cur.}}=2$  (hydrochloride, an oil; meconate, m.p. 134—136°). N-Diethyl-leucine Et ester gives (Na-EtOH) a 75% yield of  $\beta$ -diethylamino- $\delta$ -methylpentan- $\alpha$ -ol, which led to the chloride, b.p. 69—75°/15 mm. (hydrochloride, cryst.), and 8- $\beta$ -diethylamino- $\delta$ -methyl-n-amylamino-6-methoxyquinoline, b.p. 200°/1.5 mm.,  $D_{\text{tol.}}/D_{\text{cur.}}=4$  [meconate, m.p. 153—154° (decomp.)].  
R. S. C.

**Hydroxyquinolines. I. Iodo-derivatives of 8-hydroxyquinoline.** F. PIRRONI and A. CHERUBINO (Atti R. Accad. Lincei, 1933, [vi], 18, 311—313).—Treatment of boiling EtOH solution of 8-hydroxyquinoline (I) with I in EtOH yields the hydriodide of (I), m.p. 174—175° (decomp.), and 5-iodo-8-hydroxyquinoline, m.p. 114—116° or 124—126° (+aq.), which forms a hydrochloride, m.p. 206—208° (decomp.), picrate, m.p. 162—163°, sulphate, m.p. 208—209°, 1-MeI derivative, m.p. 136—137°, pale yellow Cu and greenish-yellow Ni salts (cf. Matsumura, A., 1927, 467).  
T. H. P.

**isoQuinoline derivatives. III. isoQuinoline-3-carboxylic acids.** H. J. HARWOOD and T. B. JOHNSON (J. Amer. Chem. Soc., 1934, 56, 468—469).—Me  $\alpha$ -benzamido- $\beta$ -3:4-dimethoxyphenylpropionate (Hartmann and Kagi, A., 1923, i, 604) and P<sub>2</sub>O<sub>5</sub> in boiling xylene give the Me ester (I), m.p. 120.5—121.5°, of 6:7-dimethoxy-1-phenyl-3:4-dihydroisoquinoline-3-carboxylic acid (II) [the Et ester, an oil, is similarly prepared from Et  $\alpha$ -benzamido- $\beta$ -3:4-dimethoxyphenylpropionate, m.p. 100—101°, which is obtained by reduction (H<sub>2</sub>, PtO<sub>2</sub>) of Et veratrylidenehippurate, m.p. 118—119°]. (II) heated in C<sub>6</sub>H<sub>6</sub> gives 6:7-dimethoxy-1-phenyl-3:4-dihydroisoquinoline, m.p. 120.5—121.5°, also obtained from benz- $\beta$ -3:4-dimethoxyphenylethylamide, m.p. 90—91°, and POCl<sub>2</sub> in PhMe. Successive treatment of (II) with SOCl<sub>2</sub>

and MeOH affords the Me ester (III), m.p. 172—173°, of 6:7-dimethoxy-1-phenylisoquinoline-3-carboxylic acid, m.p. 216—216.5° (the  $\beta$ -diethylaminoethyl ester, m.p. 158.5—159°, is similarly prepared). (III) is also formed when (I) is oxidised by Pictet and Kay's method (A., 1909, i, 513). Successive treatment of (II) with PCl<sub>5</sub> (in C<sub>6</sub>H<sub>6</sub>) and MeOH gives (I).

H. B.

**Synthesis of cincophens [2-phenylquinoline-4-carboxylic acids] from phenacylideneoxindoles.** R. N. DUPUIS and H. G. LINDWALL (J. Amer. Chem. Soc., 1934, 56, 471—472).—3-Phenacylideneoxindole (A., 1933, 164) is converted by warm aq. EtOH-HCl into 2-phenylquinoline-4-carboxylic acid (4'-Cl-, m.p. 243—245°, 4'-Br-, and 4'-Me derivatives, all similarly prepared).  
H. B.

**Quinoline derivatives. XLIII.  $\alpha$ -Alkylated  $p$ -2-quinolylanilinoacetic acids.** H. JOHN (J. pr. Chem., 1934, [ii], 139, 183—188).— $p$ -2-Quinolylanilinoacetic acid, m.p. 218° (Me, m.p. 152°, and Et, m.p. 144°, esters), is prepared by gradual addition of aq. CH<sub>2</sub>O to NaCN and 4'-amino-2-phenylquinoline (I) in abs. EtOH. It is decarboxylated at > its m.p. to 2- $p$ -methylaminophenylquinoline, m.p. 82° (hydrochloride, m.p. 186°). The following are prepared from (I) and the appropriate  $\alpha$ -Br-acid at 140°:  $\alpha$ - $p$ -2-quinolylanilino-propionic, m.p. 215—217° (Et ester, m.p. 86°; 2- $p$ -ethylaminophenylquinoline, m.p. 110°), -n-, m.p. 187°, and -iso-butyl-, m.p. 192—195°, -n-, m.p. 163—165° (Et ester, m.p. 108°), and -iso-valeric, m.p. 180—182°, and -stearic acid, m.p. 127—128° (Et ester, m.p. 65°).  
H. A. P.

**Quinoline derivatives. XLIV. Synthesis of  $\alpha$ -aryl- $p$ -2-quinolylanilinoacetic acids.** H. JOHN and (in part) E. PIETSCH. XLV. Derivatives of 2-phenyl-4-quinolylaminoacetic acid. H. JOHN and G. BEHMEL (J. pr. Chem., 1934, [ii], 139, 237—241, 284—288).—XLIV. By the action of the appropriate aldehyde and NaCN on 2- $p$ -aminophenylquinoline (this vol., 304) in EtOH and hydrolysis (without isolation) of the nitrile are obtained:  $p$ -2-quinolylanilino-phenyl-, m.p. 178—180° (Et ester, m.p. 173°), - $p$ -tolyl-, m.p. 158—162° (Et ester, m.p. 95°), and - $p$ -isopropylphenyl-, m.p. 102—105°, -acetic acid,  $\alpha$ -( $p$ -2-quinolylanilino)- $\beta$ -phenylpropionic acid, m.p. 120°, and - $\gamma$ -phenyl-n-butyric acid, m.p. 170—190°, all of the type C<sub>6</sub>H<sub>4</sub> $\left\langle \begin{array}{l} \text{CH:CH} \\ \text{N=C}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CHR}\cdot\text{CO}_2\text{H} \end{array} \right.$

XLV. By usual methods the following derivatives of 2-phenyl-4-quinolylaminoacetic acid (A., 1933, 165) are obtained: Pr <sup>$\alpha$</sup> , m.p. 91°; Bu <sup>$\alpha$</sup> , m.p. 74.5°; Bu <sup>$\beta$</sup> , m.p. 105°; isoamyl, m.p. 76° and Ph, m.p. 108°, esters: benzylamide, m.p. 187°;  $p$ -phenetidide, m.p. 127°;  $\alpha$ -pyridylamide, m.p. 233°, and piperidide, m.p. 189—190°.  
J. W. B.

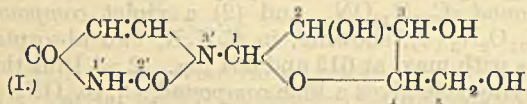
**$\psi$ -Bases. IV. Mechanism of formation of bimolecular ethers from  $\psi$ -bases.** Aromatic nature of heterocyclic compounds. J. G. ASTON and P. A. LASSELLE (J. Amer. Chem. Soc., 1934, 56, 426—433).—The rates of formation of bimol. ethers from 1-methyl- (I) and 1:2-dimethyl-quinolinium hydroxides (from the corresponding iodides and aq. NaOH) are determined at 25° by a conductometric



method (A., 1931, 742); they are proportional to the product of the squares of the concns. of quinolinium and OH ions. Reaction occurs much faster with (I). The formal heat of activation for the reaction with (I) is calc. from measurements at 33.8° to be 10,420 g.-cal. 1:2-Dimethylpyrazolinium and 1:2-dimethylpyridinium hydroxides are strong electrolytes; the conductivity of solutions does not change appreciably at 25°, indicating the absence of ether formation. Decreased conjugation of the ring system favours ether formation. 1:2-Dimethylpyrazolinium iodide appears to be new.

H. B.

**N-Methyluridine and its bearing on the structure of uridine.** P. A. LEVENE and R. S. TIPSON (J. Biol. Chem., 1934, 104, 385—393).—The 1'-position of the uracil residue in uridine (I) is shown to be vacant, so that the ribose residue is attached at the 3'-position.



CPh<sub>3</sub>Cl and (I) in C<sub>5</sub>H<sub>5</sub>N give 5-triphenylmethyluridine, m.p. 200°, [α]<sub>D</sub><sup>25</sup> +9.5° in COMe<sub>2</sub>, +18.8° in MeOH (cf. Bredereck, A., 1933, 149), the 2:3-Ac<sub>2</sub> derivative, a glass, [α]<sub>D</sub><sup>27</sup> +50.9° in MeOH, of which gives with CH<sub>2</sub>N<sub>2</sub> in Et<sub>2</sub>O 2:3-diacetyl-5-triphenylmethyl-N-methyluridine (II), glassy flakes, [α]<sub>D</sub><sup>25</sup> +55.3° in MeOH. Hydrolysis of (II) with Ba(OMe)<sub>2</sub> in MeOH gave N-methyl-5-triphenylmethyluridine, m.p. 173—174°, [α]<sub>D</sub><sup>25</sup> +17.1° in COMe<sub>2</sub>. (II) and 0.5% HCl in MeOH give N-methyluridine, m.p. 108—110°, [α]<sub>D</sub><sup>25</sup> +16.5° in H<sub>2</sub>O, hydrolysed by 10% H<sub>2</sub>SO<sub>4</sub> to l-methyluracil, m.p. 174—175°, identical with a specimen prepared from 6-hydroxy-2-ethylthiol-1-methylpyrimidine (Johnson and Heyl, A., 1907, i, 728).

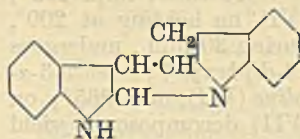
W. S.

**Polymembered cyclic compounds. VIII. cycloDitridecamethylenedi-imine and preparation of hexamethyleneimine.** A. MÜLLER [with E. RÖLZ and M. WIENER] (Ber., 1934, 67, [B], 295—300; cf. A., 1932, 1262).—Eruic acid (improved prep.) is treated with conc. HNO<sub>3</sub> and the mixture of acids is esterified, thereby giving Me brassylate, which is reduced by Na and EtOH to tridecane-α-diol, m.p. 74°, whence α-dibromotridecane (I). Treatment of (I) and p-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>2</sub>·NH<sub>2</sub> with KOH in boiling KOH-EtOH leads to di-p-toluenesulphonyl-cycloditridecamethylenedi-imine (II), m.p. 163°, α-di-p-toluenesulphonamido-n-tridecane (III), m.p. 92° (corr.), and (?) p-toluenesulphonimidocyclotridecamethylene. (II) is hydrolysed by conc. HCl at 155° to cycloditridecamethylenedi-imine, NH<[CH<sub>2</sub>]<sub>13</sub>>NH, b.p. 183—185° (bath)/0.01 mm., m.p. about 52° [hydrochloride; aurichloride; picrate; Bz<sub>2</sub>, m.p. 95° (corr.), and (SO<sub>2</sub>Ph)<sub>2</sub>, dimorphous, m.p. 122.2° (corr.) after softening at about 111° and m.p. about 111° derivatives]. (III) is hydrolysed to α-diamino-n-tridecane (IV), b.p. 172—173°/9 mm., m.p. 51° (corr. vac.) [di-p-toluenesulphonate, m.p. 198° (corr.); aurichloride, decomp. about 150° after softening; platinichloride, decomp. about 225°; picrate, m.p. 145—146°

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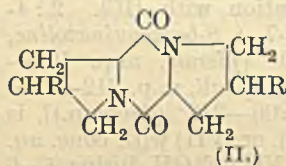
(corr.); Bz<sub>2</sub> derivative, m.p. 124—125° (corr.); hydrochloride, decomp. 321—324°; n-tridecane-α-diphenylthiocarbamide, m.p. 118—119° (corr.)]. (IV) is also obtained from α-phthalimido-n-tridecane, m.p. 102—103° (corr.). H. W.

**Pyrrole-indole group. Series II. XVIII. Polymerisation of indole, and constitution of di-indole.** B. ODDO (Gazzetta, 1933, 63, 898—907).—



A summary of work on polymerides of indoles, with new interpretations of the introduction of Ac and NO groupings. Oddo's formula for di-indole (annexed; cf. A., 1913, i, 755) is preferred to that of Schmitz-Dumont (A., 1933, 959). E. W. W.

**Grignard reaction on l-proline, l-hydroxyproline ester, and diketopiperazines.** J. KAPFHAMMER and A. MATTHES (Z. physiol. Chem., 1934, 223, 43—52).—l-Proline Et ester (I), m.p. 78°, on keeping over H<sub>2</sub>SO<sub>4</sub> in vac. or after 24 hr. at 177°, gives l-proline anhydride (II; R=H), m.p. 146, b.p. 152—153°/0.16 mm., [α]<sub>D</sub><sup>25</sup> -147.2° in H<sub>2</sub>O. With MgPhBr, (I) affords pyrrolidylidiphenylcarbinol, m.p. 83° (hydrochloride, m.p. < 240°; Bz



(II.)

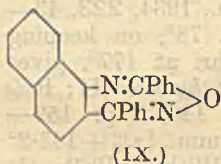
derivative, m.p. 183°), with MgEtBr, pyrrolidylidethylcarbinol isolated as the hydrochloride, m.p. 158°. With MgPhBr, l-proline anhydride affords Ph (N-pyrrolidylidiphenylmethyl)pyrrolidyl ketone (picrate, m.p. 174—175°). l-Hydroxyproline Et ester, b.p. 112—114°/1 mm. [hydrochloride (III), m.p. 147—148°], changes spontaneously into l-hydroxyproline anhydride (II; R=OH), m.p. 245—246° (decomp.), [α]<sub>D</sub><sup>25</sup> -153.4° in H<sub>2</sub>O. With MgPhBr, (III) affords hydroxy-pyrrolidylidiphenylcarbinol, m.p. 187—188°; sarcosine anhydride (IV) yields methylaminoacetophenone (picrate, m.p. 145—146°, hydrochloride) and the sarcosyl derivative (picrate). With MgEtBr, (IV) gives 1:4-dimethyl-2:2:5:5-tetraethylpiperazine (picrate; hydrochloride). J. H. B.

**Complex salts with 2:2'-dipyridyl.**—See this vol., 379.

**Action of benzoyl chloride on α-naphthylamine.**

K. DZIEWOŃSKI and L. STERNBACH (Rocz. Chem., 1933, 13, 704—719).—C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub> (I) and BzCl yield on heating during 3—5 min. at 175—180° with anhyd. ZnCl<sub>2</sub> 1-benzamido-4-benzoylnaphthalene (II), m.p. 178° (2-Bz derivative, m.p. 224—226°), which on hydrolysis gives 4-benzoyl-α-naphthylamine, m.p. 105—106° (picrate, m.p. 142°); this, on diazotising and coupling with β-C<sub>10</sub>H<sub>7</sub>·OH, yields 4-benzoyl-1-naphthylazo-β-naphthol, m.p. 229°, and on coupling with PhN<sub>2</sub>Cl yields 2-benzeneazo-4-benzoyl-α-naphthylamine, m.p. 209—210°, from which 4-benzoylnaphthylene-1:2-diamine (III), m.p. 198°, is prepared. (III) condenses with phenanthraquinone to yield phenanthrobenzoylnaphthazarin, m.p. 252—255°. The double salt, m.p. 310°, of ZnCl<sub>2</sub> and 2:4-diphenyl-7:8-benzo-3-α-naphthylquinazoline 3-chloride (IV) is obtained by heating the original reaction mixture from which (II)

was prepared during 2 hr. at 240°, by heating together (II),  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·NHBz, and ZnCl<sub>2</sub> at 180°, or by heating a mixture of iso-1-benzamido-2-benzoylnaphthalene (V) (prepared as below), m.p. 161—162°, and ZnCl<sub>2</sub> at 180°. The double salt yields with boiling aq.-alcoholic KOH 4-hydroxy-2:4-diphenyl-7:8-benzo-3- $\alpha$ -naphthyl-3:4-dihydroquinazoline (VI), m.p. 184° [hydrochloride, m.p. 209°; 4-Et ether, m.p. 224° (hydrochloride, m.p. 292°); 4-Me ether, m.p. 193°; picrate, m.p. 260—261°]. (VI), on heating at 200°, or on boiling with PhNO<sub>2</sub> during 30 min., undergoes conversion into 2-hydroxy-2:4-diphenyl-7:8-benzo-3- $\alpha$ -naphthyl-3:4-dihydroquinazoline (VII), m.p. 265°; on acid hydrolysis (VI) and (VII) decompose to yield (V) and (I). (V), on heating with aq.-alcoholic KOH during 10 hr. at 170°, yields 2-benzoyl- $\alpha$ -naphthylamine, b.p. 263—265°/14 mm. {picrate, m.p. 200—201°; N-Ac, m.p. 194—195°; N-Bz derivative, m.p. 202° [oxime, m.p. 211° (decomp.)]; oxime (VIII), m.p. 178°}. AcOH solutions of (VIII) yield the substance (IX), m.p. 186—189° (HgCl<sub>2</sub> salt, m.p. 209°), on saturation with HCl. 2:4-Diphenyl-7:8-benzoquinazoline, m.p. 160° [picrate, m.p. 168—170°; HgCl<sub>2</sub> salt, m.p. 212—215° (decomp.)]; ZnCl<sub>2</sub> salt, m.p. 206—212° (decomp.), is prepared by boiling (IV), (VI), or (VII) with conc. aq. NH<sub>3</sub>, or by heating (V) with NH<sub>3</sub>-EtOH during 4—6 hr. at 180°.

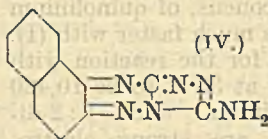


(decomp.); ZnCl<sub>2</sub> salt, m.p. 206—212° (decomp.), is prepared by boiling (IV), (VI), or (VII) with conc. aq. NH<sub>3</sub>, or by heating (V) with NH<sub>3</sub>-EtOH during 4—6 hr. at 180°.

R. T.

**Guanazole.** R. STOLLÉ and W. DIETRICH (J. pr. Chem., 1934, [ii], 139, 193—210).—Guanazole,  $\text{N} \begin{matrix} \text{C}(\text{NH}_2)\text{NH} \\ \text{C}(\text{NH}_2)\text{N} \end{matrix}$ , and tautomeric forms (I) [Ac<sub>2</sub>, not melting at 300°, Bz<sub>2</sub>, sinters 295°, m.p. 300° (decomp.), and monobenzylidene, m.p. 234°, derivatives; dintrate, decomp. 145°] with 1 mol. of C<sub>5</sub>H<sub>11</sub>·O·NO (II) in EtOH gives its 3-NO-derivative, decomp. 172°, but 2 mols. of (II) in HCl-EtOH afford the 3:5-(NO)<sub>2</sub>-derivative, decomp. 187°, reduced (SnCl<sub>2</sub>-HCl) to the hydrochloride, m.p. 217° (decomp.), of 3-amino-5-hydrazino-1:2:4-triazole (III); this with PhCHO gives 5-benzylidenehydrazino-3- $\alpha$ -hydroxybenzylamino-1:2:4-triazole, m.p. 232° (previous sintering), with loss of H<sub>2</sub>O (best at 139°/vac.), to give the 3:5-dibenzylidene derivative, m.p. 232°, of (III). With NaNO<sub>2</sub> at 0° (III), as its hydrochloride, gives 5-azido-3-nitrosoamino-1:2:4-triazole, detonates at 134°, isomerised by 2N-HCl to the 5-azido-3-diazonium chloride, which couples with  $\beta$ -C<sub>10</sub>H<sub>7</sub>·OH to give 5-azido-3-( $\beta$ -hydroxynaphthyl-1-azo)-, m.p. 195° (decomp.), and with NPhMe<sub>2</sub> to give 5-azido-3-p-dimethylaminobenzeneazo-, decomp. 185°, -1:2:4-triazole. Diazotisation of (I) affords a mixture containing the 3-NH<sub>2</sub>-5-diazonium chloride (30%), the 3:5-bisdiazonium chloride (60%), and, by decomp., 3:5-dichloro-1:2:4-triazole, m.p. 148°, and the hydrochloride, m.p. 112°, decomp. 130°, of 5-chloro-3-amino-1:2:4-triazole, since by coupling with PhOH 3:5-di-p-hydroxybenzeneazo-, m.p. 270° (decomp.) [OO-Ac<sub>2</sub>-derivative, m.p. 235° (4-N-Ac-derivative, m.p. 167°)], and 3-amino-5-p-hydroxybenzeneazo-+H<sub>2</sub>O and anhyd., m.p. 260° (decomp.) (hydrochloride+H<sub>2</sub>O, decomp. 240°), -1:2:4-triazole are isolated. With bleaching-powder solution

at 0° (I) affords 3:5-dichloroimino-3:5-dihydro-1:2:4-triazole, detonates at 135°, which when boiled with EtOH- $\beta$ -C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub> gives a dye, m.p. 285° (decomp.), to which structure (IV) is assigned. With PbO in boiling EtOH thiosemicarbazide gives aminoguanazole (monobenzylidene derivative, m.p. 184°), identical with the product of Pellizzari *et al.* (A., 1908, i, 65).



J. W. B.

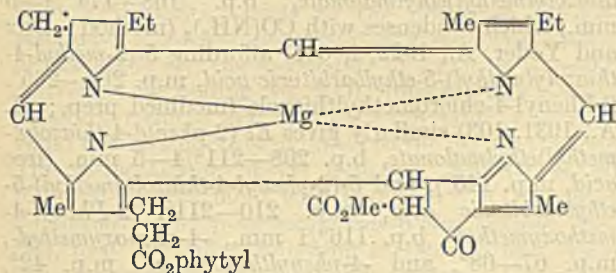
**Condensation products of isatin with pyrroles (pyrrole-blue).** P. PRATESI (Atti R. Accad. Lincei, 1933, [vi], 17, 954—960).—In boiling AcOH solution, isatin gives no blue condensation product with 1-methyl-, 1-ethyl-, 1-phenyl-, 1-acetyl-, 2:5-dimethyl-, or 2:4:5-trimethyl-3-ethyl-pyrrole. 2:3-Dimethylpyrrole gives a blue, cryst. compound, C<sub>14</sub>H<sub>12</sub>ON<sub>2</sub>. 3-Methyl-4-ethylpyrrole yields (1) a blue compound, C<sub>15</sub>H<sub>14</sub>ON<sub>2</sub>, and (2) a violet compound, C<sub>23</sub>H<sub>17</sub>O<sub>2</sub>N<sub>3</sub> (?), showing, in C<sub>5</sub>H<sub>5</sub>N, two absorption bands with max. at 613 and 564  $\mu$ . 2:4-Dimethyl-3-ethylpyrrole gives a blue compound, C<sub>16</sub>H<sub>16</sub>ON<sub>2</sub>.

T. H. P.

**Chlorophyll. XL. Oxoporphyrins: structure of chlorophyll a.** H. FISCHER, J. RIEDMAIER and J. HASENKAMP. **XLI. Conversion of phaeoporphyrin a<sub>5</sub> into phaeoporphyrin a<sub>6</sub> and neophaeoporphyrin a<sub>6</sub>.** H. FISCHER and J. HECKMAIER (Annalen, 1934, 508, 224—249, 250—262).—XL Pyrophaeophorbide a (improved prep. given) is degraded by cold HI-AcOH to (mainly) oxophylloerythrin, C<sub>33</sub>H<sub>32</sub>O<sub>4</sub>N<sub>4</sub> [Me ester, m.p. 275° (dioxime hæmin)], and some phylloerythrin (which is the sole product at 65°). Dihydrophaeophorbide a similarly gives phaeoporphyrin a<sub>5</sub>; a little isophaeoporphyrin a<sub>5</sub> (A., 1933, 959) [now termed oxophaeoporphyrin a<sub>5</sub> (I) is formed when the reaction mixture is kept for several days. The oxime, m.p. 257°, of oxochloroporphyrin Me<sub>3</sub> ester (*loc. cit.*) is readily converted (fusion; heating in C<sub>5</sub>H<sub>5</sub>N) into the oxime of the Me<sub>3</sub> ester of (I). Allomerised (I in AcOH) phaeophorbide a is degraded by HI-AcOH at 65° to neophaeoporphyrin a<sub>6</sub>, phaeoporphyrin a<sub>7</sub>, and rhodoporphyrin (II); in the cold, oxorhodoporphyrin (III), C<sub>32</sub>H<sub>32</sub>O<sub>5</sub>N<sub>4</sub> [Me<sub>3</sub> ester, m.p. 274° (oxime, decomp. 268°)], is also formed (III) is also obtained when oxoneophaeoporphyrin a<sub>6</sub> is kept in 14% HCl for 24 hr.; oxophaeoporphyrin a<sub>5</sub> is probably an intermediate (oxidative fission) product. (III) is reduced (Wolff-Kishner) to (II) and reduced (KOH in a little EtOH) to hydroxyrhodoporphyrin. The products formed by similar degradation of the following compounds are quoted in parentheses: chlorin e (chloroporphyrin e<sub>5</sub> and oxochloroporphyrin e<sub>5</sub>); chlorin e Me<sub>3</sub> ester (chloroporphyrin e<sub>6</sub> and oxochloroporphyrin e<sub>6</sub>); 10-ethoxy methylphaeophorbide (oxophaeoporphyrin a<sub>6</sub>); phaeopurpurins 7 and 18 [an oxoporphyrin spectroscopically identical with (III)]; the former gives a second oxoporphyrin]. The formation of the above oxo-derivatives is considered to involve the following reactions: CH<sub>2</sub>:C<  $\rightarrow$  CH<sub>2</sub>I·CH<  $\rightarrow$  CH<sub>2</sub>I·Cl <  $\rightarrow$  OH·CH<sub>2</sub>:Cl <  $\rightarrow$  OH·CH:C <  $\rightarrow$  CHO·C<; C> is C<sub>1</sub> of the porphin structure.

The presence of CO in (native) methylphaeophorbide

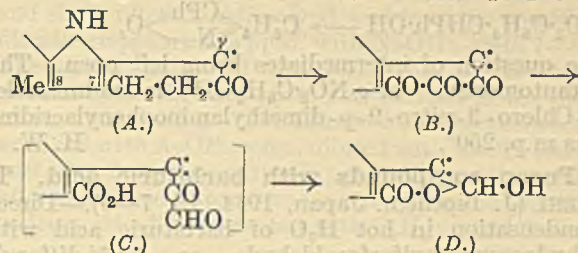
*a* is shown by the prep. of an *oxime* (IV), which is degraded by HI-AcOH at 65° to a small amount of phæoporphyrin *a*<sub>5</sub> *oxime* and hydrolysed (14% HCl) to phæophorbide. Oximation of methylchlorophyllide *a*+*b* in C<sub>5</sub>H<sub>5</sub>N, dilution with Et<sub>2</sub>O, washing with H<sub>2</sub>O and 6% HCl, and subsequent extraction with 14% HCl gives (IV). Structures are suggested for many of the above compounds. Chlorophyll *a* is assigned the following constitution; the position of the CH<sub>2</sub> is uncertain.



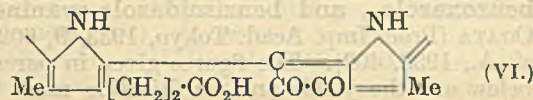
XLI. Phæoporphyrin *a*<sub>5</sub> (Me<sub>2</sub>) ester (I) is oxidised (I, NaOAc, EtOH) to *acetylneophæoporphyrin a*<sub>6</sub> Me<sub>2</sub> ester (II), C<sub>38</sub>H<sub>40</sub>O<sub>7</sub>N<sub>4</sub>, m.p. 305° [Cu salt, m.p. 305° (decomp.); *p*-nitrobenzoate, m.p. 257°; *benzoate*, m.p. 292° (corr.)], which is also prepared from and hydrolysed (cold conc. H<sub>2</sub>SO<sub>4</sub> in N<sub>2</sub>) to *neophæoporphyrin a*<sub>6</sub> [and a little phæoporphyrin *a*<sub>7</sub> (III)]. Hydrolysis (MeOH-KOH in EtOH-C<sub>5</sub>H<sub>5</sub>N) of (II) gives (mainly) *allophæoporphyrin a*<sub>7</sub> (IV). Oxidation (I, Na<sub>2</sub>CO<sub>3</sub>, EtOH) of (I) affords phæoporphyrin *a*<sub>6</sub> Me<sub>2</sub> ester, which is hydrolysed (15% HCl) to *isophæoporphyrin a*<sub>7</sub> (V) and a little (IV). Methylphæophorbide *a*, I, and NaOAc in EtOH give allomerised *acetylphæophorbide a* Me<sub>2</sub> ester, decomp. about 300°, which is degraded (HI-AcOH at 65°) to (II). Prolonged treatment of chloroporphyrin *e*<sub>7</sub> lactone Me<sub>2</sub> ester with cold oleum (30% SO<sub>3</sub>) and subsequent esterification (CH<sub>2</sub>N<sub>2</sub>) affords the Me<sub>3</sub> ester of (IV); the Me<sub>1</sub> ester, I, and NaOAc in EtOH give (after esterification) the Me<sub>3</sub> ester of (III). The Me<sub>3</sub> ester of (V) and oleum afford (III). H. B.

Chlorophyll. XLII. Mesorhodin and its conversion into chlorophyll-porphyrins; oxidation of phyloerythrin. H. FISCHER and J. EBERSBERGER (Annalen, 1934, 509, 19—37).—Mesoporphyrin Me<sub>2</sub> ester (from hæmin) is converted by approx. 10% oleum into *mesorhodin* (I), C<sub>34</sub>H<sub>36</sub>O<sub>3</sub>N<sub>4</sub> [*oxime*; Me ester, m.p. 269° (corr.) (*oxime*)], which is oxidised (KMnO<sub>4</sub>, 10% NaOH, C<sub>5</sub>H<sub>5</sub>N) to chloroporphyrin *e*<sub>5</sub> (II) (18%) [Me<sub>1</sub> ester; Me<sub>2</sub> ester (III), m.p. 288° (corr.) (*Fe* and *Cu* salts), prepared using MeOH-HCl; Me<sub>2</sub> ester, m.p. 286° (*Fe* and *Cu* salts), using CH<sub>2</sub>N<sub>2</sub>]; rhodoporphyrin- $\gamma$ -carboxylic acid (IV) (0.5%), and a crude “diketone” (about 1.5%). (II) and its derivatives are spectroscopically identical with “natural” chloroporphyrin *e*<sub>5</sub> and its derivatives; mixed m.p. show depressions indicating that (I) and (II) are (probably) mixtures of isomerides. (III) is degraded by 30% MeOH-KOH in C<sub>5</sub>H<sub>5</sub>N at 180° to pyrroporphyrin IX, indicating that (I) contains the group (A) and that oxidation to (II) (as D) proceeds through the triketone (B), which undergoes hydrolytic fission to (C) (this is then oxidised to the gly-

oxylic acid which subsequently loses CO<sub>2</sub>). (II) is oxidised (O<sub>2</sub> in dil. HCl) to (IV) and rhodoporphyrin



(V), and reduced (HI-AcOH) to chloroporphyrin *e*<sub>4</sub>. (IV) and boiling HCO<sub>2</sub>H give (V). (II) (as Me<sub>1</sub> ester) is reduced (TiCl<sub>3</sub>, conc. HCl; absence of air) to *hydroxymethylrhodoporphyrinlactone*, C<sub>34</sub>H<sub>36</sub>O<sub>4</sub>N<sub>4</sub>, m.p. 250—256°, also prepared (with m.p. 256°) from chloroporphyrin *e*<sub>5</sub> Me<sub>1</sub> ester (prepared from chlorin *e*). Phæoporphyrin *a*<sub>7</sub> is similarly reduced to chloroporphyrin *e*<sub>7</sub>-lactone. Oxidation (SeO<sub>2</sub>, EtOH) of phyloerythrin gives hydroxyphyloerythrin and *phyloerythrin diketone* (VI) [Me ester, C<sub>34</sub>H<sub>34</sub>O<sub>4</sub>N<sub>4</sub>, m.p. 273° (corr.) (*oxime*, m.p. > 300°)]; (VI) is partly



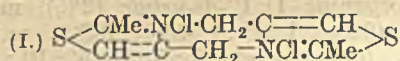
converted by prolonged treatment with 20% HCl in absence and presence of air into (II) and (IV), respectively. H. B.

**Metal complex salts of hæmatoporphyrin.** F. BANDOW (Z. physiol. Chem., 1934, 223, 71—73).—The formation of metal complex compounds of hæmatoporphyrin in the lower fatty acids was examined spectroscopically. Various centres in the porphyrin mol. are affected by the presence of the metal. J. H. B.

**New derivative of chlorophyll with hypnotic action; diethylamine salt of phæophorbide.** M. CUFFARO (Giorn. Chim. Ind. Appl., 1934, 16, 7—9).—The protracted action of HCl on chlorophyll yields phæophorbide, the (NHEt<sub>2</sub>)<sub>2</sub> salt of which swells above 100°, chars at 240°, and shows hypnotic properties. T. H. P.

**Occurrence of chlorophyll derivatives in an oil-shale from the upper Trias.**—See this vol., 387.

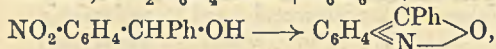
**Polymerisation of 2-methyl-4-chloromethylthiazole.** XII. F. E. HOOPER and T. B. JOHNSON (J. Amer. Chem. Soc., 1934, 56, 470—471).—Thioacetamide and CO(CH<sub>2</sub>Cl)<sub>2</sub> give (cf. A., 1931, 103) 2-methyl-4-chloromethylthiazole, b.p. 65—67°/3 mm., which polymerises slowly at room temp. and more rapidly at 110—115° to the compound (I), not melted at >300°.



H. B.

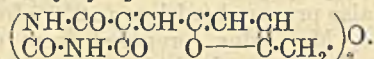
**Formation of C-phenylanthranils and acridones from o-nitrobenzaldehydes and aromatic hydrocarbons.** K. LEHMSTEDT (Ber., 1934, 67, [B], 336—339).—Mainly a reply to Tanasescu (A., 1933, 956). At present, the formation of C-arylanthranils from

*o*-nitrobenzaldehydes is best explained by Kliegl's scheme,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHO} + \text{C}_6\text{H}_6 \rightarrow$



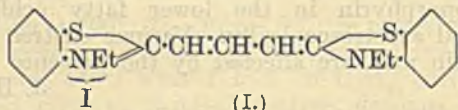
the question of intermediates being left open. The "tautomerism" of *o*- $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$  is inadmissible. 6-Chloro-3-nitro-9-*p*-dimethylaminophenylacridine has m.p. 250°. H. W.

**Furan compounds with barbituric acid.** T. ISEKI (J. Biochem. Japan, 1934, 19, 7—9).—Direct condensation in hot  $\text{H}_2\text{O}$  of barbituric acid with 5-hydroxymethylfurfuraldehyde or 5:5'-di(furylmethyl) ether 2:2'-dialdehyde (cf. A., 1933, 719) affords 5-hydroxymethyl-2-furfurylidenebarbituric acid (I), m.p. 274° (uncorr.), and 5:5'-di(barbiturilydene-methyl)-2:2'-difurfuryl ether



Orally ingested (I) in dogs and rabbits is partly (15—20%) excreted as hydroxymethylfuroic acid (cf. A., 1927, 1107; 1929, 450). F. O. H.

**Cyanine dyes. VI. Benzthiazolo-, thiazolo-, benzoxazolo-, and benzimidazolo-cyanines.** T. OGATA (Proc. Imp. Acad. Tokyo, 1933, 9, 602—605; cf. A., 1933, 402).—The figures given in parentheses below are the yields and sensitisation max. in  $\mu$ , respectively. 2-Methylbenzthiazole ethiodide and  $\text{NPh} \cdot \text{CH} \cdot \text{NPh}$  in piperidine (method A) at 65° (20%) or  $\text{Ac}_2\text{O} \cdot \text{NaOAc}$  (method B, usually with  $\text{KOAc}$ ) at 165° (100%) give 1:1'-diethyltrimethinebenzthiazolocyamine iodide (I), m.p. 269° (decomp.) (590). Similar starting materials give by the method named: 1:5:1':5'-tetramethyltrimethinethiazolo-



(I)

cyanine iodide (B, 125°, 45%), m.p. 268° (decomp.) (590); 1:1'-dimethyltrimethinebenzoxazolocyamine iodide (B, 51%), m.p. 282° (decomp.) (520); 1:1'-diethylpentamethinebenzthiazolocyamine iodide (B, 61%), m.p. 253° (decomp.) (700); 1:1'-di- (A, 5%), m.p. 215° (decomp.) (690), and 1:5:1':5'-tetra-methyl-pentamethinethiazolocyamine iodide (A, 24%), m.p. 226° (690); 1:1'-diethylheptamethinebenzthiazolocyamine iodide (A, 15%), m.p. 240° (800); 1:1'-di-methylheptamethinethiazolocyamine iodide (A, 10%), m.p. 152° (decomp.) (780); 1:5:1':5'-tetramethyl-heptamethinethiazolocyamine iodide (A, 27%), m.p. 174° (decomp.) (780); 1:3:1':3':1'':3'':hexa-methyl-9-benzimidazolyltrimethinebenzimidazolocyamine 1:1''-di-iodide (B, 170°, 5%), m.p. 230° (570). By variations of the  $\text{Et}_3$  orthoformate method were prepared 1:1':1''-triethyl-9-benzthiazolyltrimethine-benzthiazolocyamine 1:1''-di-iodide (2%), m.p. 256° (decomp.) (640), 1:1':1''-tri- (40%), m.p. 250° (decomp.) (640), and 1:5:1':5':1'':5''-hexa-methyl-7-thiazolyltrimethinethiazolocyamine 1:1''-di-iodide (42%), m.p. 283° (decomp.) (640). 2:3-Dimethylbenzimidazole methiodide,  $\text{CCl}_3 \cdot \text{CH}(\text{OH})_2$ , and  $\text{NaOEt}$  in hot  $\text{EtOH}$  give 1:3:1':3'-tetramethyltri-methinebenzimidazolocyamine iodide (13%), m.p. 303° (530). Methods A and B give zero yields when

applied in the cases not specified above. *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$  and  $\text{Ac}_2\text{O}$  at 140° give an 82% yield of 2-methylbenzimidazole, the methiodide of which is obtained in 42% yield by  $\text{MeI}$  and  $\text{MeOH}$  at 110°. R. S. C.

**Cyanine dyes.**—See B., 1934, 268, 314.

**Synthesis of thiazolylbarbituric acids. XIII.**

F. E. HOOPER and T. B. JOHNSON (J. Amer. Chem. Soc., 1934, 56, 484—485).—2-Methyl-4-chloromethyl-thiazole and  $\text{CNaEt}(\text{CO}_2\text{Et})_2$  give *Et* (2-methyl-4-thiazolylmethyl)ethylmalonate, b.p. 168—174°/4—5 mm., which condenses with  $\text{CO}(\text{NH}_2)_2$  (method: Dox and Yoder, A., 1922, i, 681) affording 5-(2-methyl-4-thiazolylmethyl)-5-ethylbarbituric acid, m.p. 264—265°. 2-Phenyl-4-chloromethylthiazole (modified prep.; cf. A., 1931, 103) similarly gives *Et* (2-phenyl-4-thiazolyl-methyl)ethylmalonate, b.p. 208—211°/4—5 mm. (free acid, m.p. 145°), and 5-(2-phenyl-4-thiazolylmethyl)-5-ethylbarbituric acid, m.p. 210—211°. 2-Phenyl-4-methoxymethyl-, b.p. 116°/1 mm., -4-phenoxy-methyl-, m.p. 67—68°, and -4-phenylthiomethyl-, m.p. 42°, -thiazoles have been prepared. H. B.

**Anabasis aphylla alkaloids.** A. P. OREKHOV and S. S. NORKINA (Khim. Farm. Prom., 1933, 109—113).—1-Nitrosoanabasine is reduced with  $\text{Zn}$  and  $\text{AcOH}$  to 1-aminoanabasine. *dl*-Anabasine is prepared by heating anabasine sulphate in closed tubes at 200° for 120 hr. and distilling in vac. CH. ABS.

**Alkaloids of Anabasis aphylla. VII. Amination of anabasine and N-methylanabasine with sodamide.** G. MENSCHIKOV, A. GRIGOROVITCH, and A. OREKHOV (Ber., 1934, 67, [B], 289—292; cf. A., 1932, 952).—Treatment of anabasine with  $\text{NaNH}_2$  in xylene at 150° affords much resin, *r*-anabasine, and *r*-aminoanabasine [2-(2'-amino-3'-pyridyl)piperidine], m.p. 111°. Similar treatment of *N*-methylanabasine yields a substance, b.p. 100—102°/6 mm. (picrate, m.p. 231—232°), 1-methyl-2-(2'-amino-3'-pyridyl)piperidine (I), m.p. 95—95.5° [picrate, m.p. 234—235° (decomp.)], and the non-cryst. (?) 1-methyl-2-(6'-amino-3'-pyridyl)-piperidine (very hygroscopic hydrochloride; picrate, m.p. 220—221°). Diazotisation of (I) in  $\text{HCl}$  (*d* 1.19) leads to 1-methyl-2-(2'-chloro-3'-pyridyl)piperidine, b.p. 145—146°/8 mm., oxidised by aq.  $\text{KMnO}_4$  to 2-chloro-pyridine-3-carboxylic acid, m.p. 192°. H. W.

**Alkaloids of white hellebore. I. Isolation of constituent alkaloids.** K. SAITO, H. SUGINOME, and M. TAKAOKA (Bull. Chem. Soc. Japan, 1934, 9, 15—23).—Separation by  $\text{EtOH}$  of the alkaloids from the roots of *Veratrum album* gives jervine, m.p. 240—241°,  $[\alpha]_D^{25} -177.5^\circ$  in  $\text{EtOH}$  [acetate (+0.5 $\text{H}_2\text{O}$ ), m.p. 234—238°,  $[\alpha]_D^{25} -126.8^\circ$  in  $\text{EtOH}$ ], as the only cryst. product. Hydrolysis with  $\text{HCl}$  of the amorphous base obtained affords tiglic acid or with  $\text{H}_2\text{O}$  under pressure or with  $\text{EtOH} \cdot \text{KOH}$  yields another amorphous base and angelic acid. Separation of the alkaloids by  $\text{HPO}_3$  similarly gives only jervine. F. R. S.

**Alkaloids of Vinca pubescens.** A. OREKHOV, H. GUREVITSCH, and S. S. NORKINA [with N. PREIN] (Arch. Pharm., 1934, 272, 70—74).—*V. pubescens* (I) contains 0.34% of alkaloids, whence with difficulty were separated *vinine* (II),  $\text{C}_{19}\text{H}_{26}\text{O}_4\text{N}_2$ , m.p. 211.5—213°,  $[\alpha]_D^{25} -70.12^\circ$  in dry  $\text{EtOH}$  [hydrochloride, m.p. 212° (decomp.); sulphate, m.p. 229—230° (decomp.);

*platinichloride*, m.p. 226—227° (decomp.), *pubescine*,  $C_{20}H_{26}O_4N_2$ , m.p. 227—228°,  $[\alpha]_D -134.2^\circ$  in dry EtOH, and a small amount of an *alkaloid*, m.p. 194—195°. (I) and (II) depress the blood-pressure. V. *minor* also contains alkaloids. R. S. C.

**Constitution of isochondodendrine. VI. F.** FALTIS and H. DIETERICH (Ber., 1934, 67, [B], 231—238; cf. A., 1932, 1047).—Ozonisation of  $\alpha$ -isochondodendrimethine, m.p. 205° (*loc. cit.*), in dil.  $H_2SO_4$  followed by treatment with spongy Pt and hydrogenation (Pd— $BaSO_4$ ) leads to the non-cryst. 3:4-dimethoxy-2-p-aldehydophenoxy-6- $\beta$ -dimethylaminoethylbenzaldehyde (I), the *methiodide* of which is smoothly converted by boiling 5% KOH into the oily *o*-vinylaldehyde reduced (Pd—C) to the ethylaldehyde which could not be smoothly oxidised to the carboxylic acid. The *methochloride* of (I) with aq.  $KMnO_4$  at 20° followed by treatment with boiling 5% KOH affords 3:4-dimethoxy-2-p-carboxyphenyl-6-vinylbenzoic acid (II), m.p. 192° after softening at 189°, in 64% yield, thus showing that the isochondodendrine (III) mol. is composed of two similar components. (II) is decarboxylated by Cu powder in boiling quinoline and the dimethoxyvinylidiphenyl ether thus produced is directly oxidised by  $KMnO_4$  in  $COMe_2$  at 0° to 3:4-dimethoxy-5-phenoxybenzoic acid (IV), m.p. 161° after softening at 158° [*Me* ester (V), m.p. 69° after softening at 66°]. The constitution of (IV) is established by the synthesis of (V) by the condensation of Me 5-bromoprotocatechuate and KOPh in presence of Cu powder and anhyd.  $Cu(OAc)_2$  at 160—180° followed by hydrolysis. The constitution assigned previously (*loc. cit.*) to (III) is regarded as established, at any rate in so far as the *O*-Me derivative is concerned. H. W.

**Cactus alkaloids. XI. Synthesis of pelletine.** E. SPATH and F. BECKE (Ber., 1934, 67, [B], 266—268; cf. this vol., 87).—2-Hydroxy-3:4-dimethoxyacetophenone is converted by NaOMe and  $CH_2PhCl$  in boiling MeOH into 2-benzyloxy-3:4-dimethoxyacetophenone, b.p. 175—180°(bath)/0.2 mm., m.p. 47—48.5° (vac.), transformed by aminoacetal at 165° into the Schiff's base (I),  $CH_2Ph \cdot O \cdot C_6H_4(OMe)_2 \cdot CMe : N \cdot CH_2 \cdot CH(OEt)_2$ , b.p. 180—200°(bath)/0.02 mm. Treatment of (I) with 73%  $H_2SO_4$  followed by warm  $H_2O$  leads to 8-hydroxy-6:7-dimethoxy-1-methylisoquinoline, m.p. 180—182° (vac.), the *methiodide*, m.p. 188—189.5°, of which is reduced by pptd. Zn and 12% HCl to 8-hydroxy-6:7-dimethoxy-1:2-dimethyl-1:2:3:4-tetrahydroisoquinoline, m.p. 110—112° (vac.), identical with natural pelletine. H. W.

**Composition of strychnine phosphomolybdate.** C. ANTONIANI (Giorn. Chim. Ind. Appl., 1934, 16, 9).—The observation that strychnine and  $NH_4$  phosphomolybdates show different vals. for the ratio  $MoO_3 : P_2O_5$  (A., 1928, 1265) is confirmed and Tetamanzani's contrary statement refuted. T. H. P.

**Separation of the opium alkaloids.** S. BUSSE and V. BUSSE (Khim. Farm. Prom., 1933, 127—129).—The combined filtrate after separation of resins from 1 kg. of opium is treated with NaOAc (200 g.) and NaCl (200 g.); the pptd. papaverine is collected, dissolved in aq. AcOH, and the neutralised solution treated with NaOAc (100 g.) and NaCl (100 g.). The

pptd. papaverine is collected and the filtrates are combined. The resin (40—50 g.) is dissolved in AcOH and NaCl, filtered, redissolved, and from the combined filtrates papaverine is pptd. with NaOH; yield 7—9 g. Thebaine is pptd. with aq.  $NH_3$  from the combined filtrates from the first pptn. and purified in the usual way; yield 3—4 g. The filtrate from the thebaine is acidified with AcOH, conc., diluted with EtOH (50%), and after 2 days morphine is pptd. The main portion of the filtrate after removal of thebaine contains codeine, which is extracted with  $C_6H_6$ ; yield 6—8 g.

CH. ABS.

**Oxidation of thebaine with manganic acetate.** F. VIEBÖCK (Ber., 1934, 67, [B], 197—202).—Since crotonic, itaconic, and oleic acids are scarcely attacked by  $Mn(OAc)_3$ , it appears that the double linking must be activated to permit reaction. Treatment of thebaine (I) with  $N-Mn(OAc)_3$  at about 60—70° causes addition of OH and OAc at the double linking 8, 14 with production of the substance (II),  $C_{21}H_{25}O_6N$ , m.p. 198° (Cu block) after softening at 196°. Under the action of 20% HCl, (II) loses OMe and Ac, yielding the compound (III),  $C_{18}H_{21}O_5N$ , m.p. 171° (block) (*chromate*; *oxime*, m.p. 212—215°), and a small amount of oxycodone (IV). Protracted treatment of (I) or (II) with HCl or of (III) with KOH—EtOH yields (IV) almost exclusively. It is suggested that the oxidation of (I) by  $H_2O_2$  to (IV) may proceed through (III). Unexpectedly (III) does not yield reducing substances when acted on by  $Pb(OAc)_4$ . The behaviour of  $Pb(OAc)_4$  towards (I) is similar to that of  $Mn(OAc)_3$ , but the yield is lower and operations are more difficult. Codeine and (IV) appear only to lose the N chain under the action of  $Mn(OAc)_3$ . H. W.

**Specific rotations of alkaloid and alkaloid salt solutions.** R. LILLIG (Pharm. Ztg., 1934, 79, 198—200).—A review. S. C.

**Action of hydrobromic acid on phenylarsinic and *p*-aminophenylarsinic acids.** J. PRAT (Compt. rend., 1934, 198, 583—585).—The action of HBr on  $AsPhO(OH)_2$  takes the following course:

- (1)  $AsPhO_2H_2 + HBr \rightarrow [AsPh(OH)_3]Br$ ;
- (2)  $[AsPh(OH)_3]Br + 3HBr \rightarrow (AsPhBr_3)Br + 3H_2O$ ;
- (3)  $(AsPhBr_3)Br \rightarrow AsPhBr_2 + Br_2$ ;
- (4)  $(AsPhBr_2)Br \rightarrow PhBr + AsBr_3$ .

All these compounds, except  $AsPhBr_4$ , have been isolated. HBr has an analogous action on  $p-NH_2 \cdot C_6H_4 \cdot AsO_3H_2$  with the additional formation of  $2:4-C_6H_3Br_2 \cdot NH_2 \cdot HCl$ . P. G. M.

**Reactions of organo-arsenic, -antimony, -tin, and -lead compounds with mercuric chloride in neutral and alkaline medium.** A. N. NESMEJANOV and K. A. KOZESCHKOV (Ber., 1934, 67, [B], 317—324).—In boiling EtOH,  $HgCl_2$  and  $SnAr_4$  react:  $SnAr_4 + HgCl_2$  (I) =  $SnAr_3Cl$  (II) +  $HgArCl$  (III); (II) + (I) =  $SnAr_2Cl_2$  (IV) + (III); (IV) + (I) =  $SnArCl_3$  (V) + (III); (V) + (I) =  $SnCl_4$  + (III). In the cases of (IV) and (V) reaction is instantaneous and quant.; with  $SnAr_4$  it is markedly slower. With Pb compounds the stage  $PbAr_2Cl_2$  cannot be passed even with excess of  $HgCl_2$  and very protracted heating. With  $SbArHal_2$  and  $SbAr_2Hal$  (VI) reaction occurs as with Sn compounds, being accompanied in the case of (VI) by the oxidation  $(V) + 2(I) = SbAr_2Cl_2Hal + 2HgCl$ . Reaction does not

take place with derivatives of Sb or with compounds of As<sup>III</sup> or As<sup>V</sup>. With HgO in boiling H<sub>2</sub>O-EtOH-NaOH the following changes are typical:  $\text{SnAr}_2\text{O} + \text{HgO} + 2\text{NaOH} = \text{HgAr}_2 + \text{Na}_2\text{SnO}_3 + \text{H}_2\text{O}$ ;  $4\text{SbArO} + 2\text{HgO} = 2\text{HgAr}_2 + 2\text{Sb}_2\text{O}_3$ ;  $2\text{AsPhO} + \text{HgO} = \text{HgPh}_2 + \text{As}_2\text{O}_3$ ;  $2\text{PbAr}_2\text{OH} + \text{HgO} = \text{HgAr}_2 + 2\text{PbAr}_2\text{O} + \text{H}_2\text{O}$ . Reaction generally proceeds as rapidly as that in neutral solution and its rate depends on the solubility of the initial material. The protracted action with  $\text{PbPh}_2\text{Cl}_2$  is accompanied by production of  $\text{PbO}_2$  and  $\text{HgPh}\cdot\text{OH}$ . With  $\text{SbArO}$  and  $\text{SbAr}_2\text{OH}$  the normal process is accompanied by oxidations. Compounds of Sb<sup>V</sup> are stable towards HgO.  $\text{AsPhO}$  reacts normally to the extent of 25–30%, the remainder is oxidised to  $\text{AsPhO}_3\text{H}_2$ ; oxidation occurs exclusively with  $(\text{AsPh}_2)_2\text{O}$ . The de-alkylating power of  $\text{HgAr}\cdot\text{OH}$  in contrast with  $\text{HgArCl}$  is shown by the reactions  $\text{HgPh}\cdot\text{OH} + \text{SbPhO} + \text{NaOH} = \text{HgPh}_2 + \text{NaSbO}_2 + \text{H}_2\text{O}$ ;  $(\text{VII}) + \text{AsPhO} + 2\text{NaOH} = \text{HgPh}_2 + \text{Na}_2\text{HASO}_3 + \text{H}_2\text{O}$ ;  $\text{SnPh}_n\text{Hal}_{4-n} + n\text{HgPhHal} + 6\text{NaOH} = n\text{HgPh}_2 + \text{Na}_2\text{SnO}_3 + 4\text{NaHal} + 3\text{H}_2\text{O}$ . The possibility of thus preparing compounds  $\text{HgAr}'\text{Ar}''$  is discussed. The interactions of (I) with arylboric acids, arylsulphonic acids, and arylido-compounds are analogous and individual instances of the above general reaction. H. W.

**Organic compounds of selenium. IV. Confirmation of structure of 4:4'-dihydroxy-3:3'-dicarbomethoxydiphenyl selenide dichloride.** R. E. NELSON and R. G. BAKER (J. Amer. Chem. Soc., 1934, 56, 467).—The dichloride (I) (A., 1933, 407) is reduced (Zn) to the selenide (II) (*loc. cit.*), which is then hydrolysed to 4:4'-dihydroxy-3:3'-dicarbomethoxydiphenyl selenide (III) (Morgan and Burstall, A., 1929, 202). Esterification (MeOH) of (III) gives (II), reconverted into (I) through the dibromide and dihydroxide. (III) and Br in  $\text{CHCl}_3$  give 3:5-dibromosalicylic acid. H. B.

**Selenonaphthen.** G. KOMPPA and G. A. NYMAN (J. pr. Chem., 1934, [ii], 139, 229–236).—3-Hydroxy-selenonaphthen (Lesser *et al.*, A., 1912, i, 642) (*picrate*, m.p. 120°; *semicarbazone*, m.p. 245°) is reduced (58% yield) by 4% Na-Hg in boiling 50% EtOH to selenonaphthen (I), b.p. 238.5–240°/775 mm., m.p. 50–51° (*picrate*, m.p. 156–157°; *stypnate*, m.p. 146–147°). With Br in  $\text{CHCl}_3$  (I) gives its 3-Br-derivative, b.p. 286–289°/768 mm. (*picrate*, m.p. 128–129°), and, with excess of Br-H<sub>2</sub>O, its 2:3-Br<sub>2</sub>-derivative, m.p. 129–130°. Passage of Cl<sub>2</sub> into a  $\text{CCl}_4$  solution of (I) gives a (? 2:3:4-)Cl<sub>3</sub>-derivative, b.p. 143°/8 mm. (*picrate*, m.p. 135–136°). With  $\text{Ac}_2\text{O}$ -fuming  $\text{HNO}_3$  at 0° (I) gives its 3-NO<sub>2</sub>-derivative, m.p. 97°, and with  $\text{AcCl-AlCl}_3$  in  $\text{CS}_2$  at 0° is obtained 3-selenonaphthenyl Me ketone, m.p. 91–93° [*semicarbazone*, m.p. 254–256° (uncorr.)], converted by NaOBr in  $\text{C}_6\text{H}_6$  into selenonaphthen-3-carboxylic acid, m.p. 270–280° (decomp.). When condensed with benzoic acid in  $\text{AcOH-H}_2\text{SO}_4$  (I) affords diphenyl-3-selenonaphthenylacetic acid, m.p. 254–255°. All m.p. are corr. J. W. B.

**Action of vanadium oxytrichloride on various organic compounds.** R. E. NELSON and A. H. McFADDEN (Proc. Indiana Acad. Sci., 1933, 42, 119–122).— $\text{VOCl}_3$  and  $\text{NH}_2\text{Ph}$  give  $\text{VO}(\text{NHP})_3$  and a

compound, containing C, H, and N, m.p. 236°.  $\text{PhCHO}$  and  $\text{VOCl}_3$  afford  $(\text{C}_6\text{H}_4\cdot\text{CHO})_2\text{VCl}_3$ .

CH. ABS.

**Physico-chemical studies on proteins. VIII. Rotatory dispersion of three gliadin preparations peptised by different solutions.** H. O. WILES and R. A. GORTNER (Cereal Chem., 1934, 11, 36–48).—Gliadin prepared by three different methods (cf. A., 1933, 730) was peptised by 10% and 70% EtOH, distilled H<sub>2</sub>O, *N*-KI, and *N*-KBr, and  $[\alpha]$  of the resulting sols determined at five different vals. of  $\lambda$ . The differences in the rotatory dispersions of the three protein preps. are > the experimental errors (*E*). *N*-KCl, *N*-NaCl, *N*-LiCl, and *N*-K<sub>2</sub>SO<sub>4</sub> did not peptise enough gliadin to yield a readable  $\alpha$ . The peptising agent appears to have no effect on the rotatory dispersion; if a Hofmeister series exists, its effect is > that of *E*. E. A. F.

**Analyses of azoproteins: casein, gelatin, and zein coupled with arsanilic acid.** W. C. BOYD and S. B. HOOKER (J. Biol. Chem., 1934, 104, 329–337).—Determinations of As:N support but do not confirm Pauly's theory (A., 1904, i, 1068; 1915, i, 725) that proteins couple with diazo-compounds in virtue only of their tyrosine and histidine residues, each of which attaches two R-N:N groups. Unlike azo-dyes, azoproteins yield all their N to the Kjeldahl treatment. W. S.

**Determination of the membrane potentials of protein solutions and the valency of protein ions.** G. S. ADAIR and M. E. ADAIR (Biochem. J., 1934, 28, 199–221).—When solutions of hæmoglobin of sheep or ox, serum-albumin (I), acid hæmatin, kathæmoglobin, and edestin (II) are equilibrated at 0° with dialysates of well-defined [H<sup>+</sup>] with  $p_H$  vals. ranging from 2.0 to 7.8, and salt concns. from 0.005 to 0.16M, the observed membrane potential *E* is approx. proportional to the concn. *C* of protein (III) expressed in g. per 100 ml. solvent, when *E* is < 2.0 mv. From a full theoretical discussion, it appears that the mean valency  $n_p$  of the protein ions may be calc. by the formula  $n_p = 0.00425MJ(E/C)_0$  [ $M$  = mol. wt. of protein,  $J$  = sum of concns. of ions in dialysate  $\times$  squares of valencies,  $(E/C)_0$  is the limiting val. of the ratio for  $C=0$ ]. In the case of (II) and Congo-red, this formula is consistent with other observations, whilst in the case of (I) the results can be reconciled with the investigations of the distribution of ions on the assumption that the protein exists as a zwitterion and that some of the positive charges are neutralised by phosphate ions. W. O. K.

**Action of papain on ovalbumin.**—See this vol., 450.

**Methods of organic chemical analysis by [catalytic] hydrogenation and oxidation.** H. TER MEULEN (Rec. trav. chim., 1934, 53, 118–125).—Use in analysis by catalytic methods (*e.g.*, for As or Hg) of the van den Berg (this vol., 162) in place of the Fletcher furnace simplifies procedure in many cases. Even heating of the whole or part of a tube is secured by use of Al blocks bored centrally to carry the tube and heated by a Bunsen burner. In the determination of O by hydrogenation the use of Ni spirals in place of asbestos is recommended with

difficultly reduced compounds (e.g., cholesterol). The slow reduction of NiO is obviated by use of (less of) the highly active Ni-ThO<sub>2</sub> (10 : 1). The Ni spirals retain S but not halogens, which must be absorbed in Ag<sub>2</sub>SO<sub>4</sub> if present. Ni-ThO<sub>2</sub> is the best catalyst for determination of N, except in oils, where pure Ni is best. For S Pt spirals are used as catalyst, and if N is also present ZnSO<sub>4</sub> + NaOAc as absorbent for the H<sub>2</sub>S to avoid errors due to (CN)<sub>2</sub>; if the sample carbonises badly it is mixed with Pt-black. In the determination of C and H by combustion with O<sub>2</sub> and MnO<sub>2</sub> a Pt spiral is recommended to volatilise the substance completely before it reaches the MnO<sub>2</sub>. In the determination of S by Heslinger's method SO<sub>3</sub> fog is passed through aq. NH<sub>3</sub>; although the fog persists it is then an (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> fog, and the alkali used can be determined by titration. H. A. P.

**Schöbel's heating mortar for Pregl carbon-hydrogen determinations.** H. LIEB (Mikrochem., 1934, 14, 263—264).—An all-glass cymene boiler is described. J. S. A.

**Attempt to apply a new principle to organic micro-analysis.** K. SCHWARZ (Mikrochem., 1934, 14, 271—279).—The attempt is made to apply measurement of the vol. change on combustion in O<sub>2</sub>, and the vol. and pressure at which the H<sub>2</sub>O vapour formed reaches saturation, to C, H, O, and N determinations using min. quantities of material. J. S. A.

**Semi-micro-Kjeldahl methods.** J. A. SCARROW and C. F. H. ALLEN (Canad. J. Res., 1934, 10, 73—76).—For certain substances which give low results by the ordinary method a preliminary reduction with P and HI is recommended. A. G.

**Determination of nitrogen in organic substances.** N. POPOV (Khim. Farm. Prom., 1933, 218—220).—Anderson and Jensen's method (A., 1931, 638) is slightly modified. CH. ABS.

**Detection of nitrogen, phosphorus, sulphur, and halogens in organic compounds by means of sodium peroxide.** O. HÖGL (Mitt. Lebensmitt. Hyg., 1933, 24, 164—170; Chem. Zentr., 1933, ii, 1225—1226).—5—10 mg. of the substance (I) are placed in a depression in Na<sub>2</sub>O<sub>2</sub> contained in a Ni spoon, which is then inverted over a red-hot Ni crucible so that (I) is covered by Na<sub>2</sub>O<sub>2</sub>. After heating to bright redness and cooling, the melt is treated with 6—8 c.c. of H<sub>2</sub>O, and the Na<sub>2</sub>O<sub>2</sub> destroyed by heating. P, S, N, and the halogens are then confirmed as usual. Volatile substances, e.g., CHCl<sub>3</sub> and CS<sub>2</sub>, can be tested with certainty in this way. L. S. T.

**Determination of halogens in organic substances.** K. REVVA (Khim. Farm. Prom., 1933, 147—148).—The sample is treated with H<sub>2</sub>SO<sub>4</sub> and air is passed through the boiling liquid for 1 hr., the halogen being collected in dil. aq. NaOH and determined by Fresenius' method. CH. ABS.

**Determination of iodine in organic compounds.** J. L. GOLDBERG (Mikrochem., 1934, 14, 161—166).—Combustion is effected by Pregl's method, and I' absorbed in Na<sub>2</sub>CO<sub>3</sub>, without NaHSO<sub>3</sub>. I' is oxidised by Br-H<sub>2</sub>O to IO<sub>3</sub>', which is determined iodometrically. The acidity requires control; excess of Br is removed by PhOH. J. S. A.

**Micro-determination of phosphorus in organic material.** A. VILA (Compt. rend., 1934, 198, 657—659).—0.2—2 mg. P is determined in 0.5 hr. by measuring the vol. of the NH<sub>4</sub> phosphomolybdate ppt. formed. In the absence of Si and As, the error is 2—5%. J. L. D.

**Micro-method of determining methoxyl and ethoxyl groups.** H. R. NANJI (Analyst, 1934, 59, 96—98; cf. A., 1932, 928).—A modification of Pregl's micro-Zeisel apparatus is used. The substance is boiled with HI and PhOH in CO<sub>2</sub>, and the alkyl iodide absorbed in Br-H<sub>2</sub>O. The HIO<sub>3</sub> formed is determined as usual. E. C. S.

**Fractional separation of unsaturated hydrocarbons.** F. N. VORONOV (Sintet. Kautschuk, 1932, 1, 7—13; Chem. Zentr., 1933, ii, 2483).—Components of a complex hydrocarbon mixture are adsorbed on active C in the reverse order to their volatility. The process is followed with an interferometer. Desorption follows in the reverse order, and may be applied in separating the mixture. H. J. E.

**Determination of chloroform.** M. SCHTSCHIGOL (Khim. Farm. Prom., 1933, 150—151).—10 drops of CHCl<sub>3</sub> in 5 c.c. of PhMe are treated for 2 hr. with 0.5N-EtOH-KOH; after dilution and acidification with HNO<sub>3</sub> the Cl' is determined by Volhard's method. CH. ABS.

**Titration of betaine.**—See this vol., 338.

**Determination of nitrotoluene.** K. LESNOCENKO (Chem. Obzor, 1932, 7, 246—248, 265—268; Chem. Zentr., 1933, ii, 2710).—The HNO<sub>3</sub> used to convert C<sub>7</sub>H<sub>7</sub>·NO<sub>2</sub> into C<sub>7</sub>H<sub>6</sub>(NO<sub>2</sub>)<sub>2</sub>, using as nitrating mixture 35% H<sub>2</sub>SO<sub>4</sub>, 15% HNO<sub>3</sub>, and 50% H<sub>2</sub>O, is measured with a nitrometer. C<sub>7</sub>H<sub>6</sub>(NO<sub>2</sub>)<sub>2</sub> and C<sub>7</sub>H<sub>5</sub>(NO<sub>2</sub>)<sub>2</sub> are without influence. H. J. E.

**Detection and determination of small quantities of cholesterol and other sterols.** A. WASITZKY (Mikrochem., 1934, 14, 289—310).—A review.

**2 : 4-Dinitrophenylhydrazine as a quantitative reagent for carbonyl compounds. I. Benzaldehyde.** R. E. HOUGHTON (Amer. J. Pharm., 1934, 106, 62—64).—2 : 4-Dinitrophenylhydrazine in dil. H<sub>2</sub>SO<sub>4</sub> is added to a solution of PhCHO in aq. EtOH. A. E. O.

**Microchemical and microscopical identification of santonin.** M. WAGENAAR (Pharm. Weekblad, 1934, 71, 260—264).—Santonin (I) forms characteristic, oblong crystals when pptd. from solution in H<sub>2</sub>SO<sub>4</sub>, glycerol (II), or especially C<sub>5</sub>H<sub>5</sub>N. Dichroic crystals are obtained with I-KI solution. The most characteristic microchemical reactions are the violet coloration with H<sub>2</sub>SO<sub>4</sub> and a trace of Fe<sup>III</sup> salt and the rose coloration when a solution of (I) in (II) is treated with freshly-ignited CaO. S. C.

**Use of silicotungstic acid for the detection and determination of novocaine.** G. VALETTE (Bull. Sci. pharmacol., 1933, 40, 28—33; Chem. Zentr., 1933, ii, 2300).—Pptn. of 12W<sub>3</sub>SiO<sub>3</sub>·2H<sub>2</sub>O·2C<sub>13</sub>H<sub>20</sub>O<sub>2</sub>N<sub>2</sub>·3H<sub>2</sub>O (anhyd. from hot solution) in characteristic crystals is optimal at room temp. in 0.5N-HCl. The novocaine content of a solution is given (±1%) by : 0.1916(p+0.000033V),

where  $p$  is the residue on ignition of the ppt. and  $V$  is the vol. of solution and wash- $H_2O$ . A. A. E.

**Determination of nicotine.** A critical investigation. P. KOENIG and W. DÖRR (Z. Unters. Lebensm., 1934, 67, 113—144).—The physiological, colorimetric, and nephelometric methods are not accurate. Of the volumetric methods only Kissling's (A., 1916, ii, 587) is reasonably accurate. Pptn. with silicotungstic acid gives accurate results if certain specified precautions are taken, the most important of which is the maintenance of a particular [HCl]. Pfyl and Schmitt's method (B., 1927, 955), depending on pptn. of nicotine (I) with picric acid, is recommended when many routine determinations are to be made. Minor improvements are suggested. The more important of these are: by gradual addition of (II) in feebly acid solution a more easily filterable ppt. is formed; by cooling in ice a further 0.5 mg. of (I) per 200 c.c. of solution can be separated; addition of PhMe is necessary only when large quantities of (I) are present. The eosin titration can be dispensed with. E. C. S.

**Determination of nicotine.** M. G. RUITKOV (Khim. Farm. Prom., 1933, 140—142).—The sample dissolved in 50 c.c. is distilled with steam and 2 g. of fresh MgO into dil. HCl. An aliquot of the distillate is treated with 1.5 c.c. of HCl and 3 c.c. of 12%

$H_8Si(W_2O_7)_6 \cdot 22H_2O$ . The ppt. is formed in 3 min. at 85° and is ready for filtration after 2 hr. CH. ABS.

**Dimethylaminobenzaldehyde test for atropine.** A. A. O'KELLY and C. F. POE (J. Lab. Clin. Med., 1933, 18, 1235—1241).—Compounds which mask or interfere with the test are listed. CH. ABS.

**Determination of quinine.**—See this vol., 346.

**Otto test for strychnine.** C. F. POE and J. BAILEY (J. Lab. Clin. Med., 1933, 19, 40—46).—Compounds which mask or interfere with the test are listed. CH. ABS.

**Determination of alkaloids.** Y. FIALKOV and S. BABICH (Khim. Farm. Prom., 1933, 148—149).—2 c.c. are dispersed with 70 c.c. of  $CHCl_3$  and 5 g. anhyd.  $Na_2SO_4$ ; aq.  $NH_3$  is then added, the mixture shaken, the  $CHCl_3$  filtered and evaporated, and the residue dissolved in 0.02N-acid, the excess of which is titrated with 0.02N-NaOH. CH. ABS.

**Homoneurine derivatives of the cinchona alkaloids as reagents for iodide ions.**—See this vol., 380.

**Determination of nitrogen in sericin.** C. BARONI (Boll. Uff. R. Staz. sperim. Seta, 1933, 28—29; Chem. Zentr., 1933, ii, 2478).—The N determination of sericin in the high-temp.  $H_2O$  extract of silk gives the same results as an indirect determination. H. J. E.

## Biochemistry.

**Determination of hæmoglobin.** H. SCHULTEN (Münch. med. Woch., 1933, 80, 1017—1019; Chem. Zentr., 1933, ii, 1226). L. S. T.

**Food and hæmoglobin regeneration. III. Eggs compared with whole wheat, prepared bran, oatmeal, ox-liver, and -muscle.** M. S. ROSE, E. McC. VAHLTEICH, and G. MACLEOD (J. Biol. Chem., 1934, 104, 217—229).—For hæmoglobin regeneration (I) of 10—11 g. in 6 weeks from 4 to 6 g. per 100 c.c. of rat blood, < 0.25 mg. Fe, and 0.05 mg. Cu per day are required; on these levels only whole wheat, oatmeal, and prepared bran are effective. In egg-yolk (II) the first limiting factor is Cu. In liver and, in a smaller degree, in (II) another factor is the form of combination of Fe; for equiv. (I), twice as much Fe in the form of liver as of whole wheat is necessary. H. G. R.

**Red blood-cell count and hæmoglobin in the adolescent male.** S. M. GOLDHAMER and A. I. FRITZELL (J. Lab. Clin. Med., 1933, 19, 172—177).—The blood of boys (12—17 years) contains 3.28—5.8 (average 4.718)  $\times 10^6$  erythrocytes per cu. mm. The hæmoglobin (I) content is 9.80—13.58 (average 11.55) g. per 100 c.c. The average (I) coeff. is 12.35 g. per 100 c.c. and colour index 0.87. CH. ABS.

**Factors causing variation in the hæmoglobin level with age in the first year of life.** H. M. M. MACKAY (Arch. Dis. Child., 1933, 8, 251—264).—Hæmoglobin (I) varies inversely with birth-wt. (II)

during the first week of life, *i.e.*, it varies inversely with maturity at birth, the post-natal fall in (I) commencing normally *in utero*. This fall, which may amount to 50%, is more rapid in infants of low (II). The breakdown products are in part stored, and increase the Fe content of the liver. After 2—3 months, cell regeneration occurs to a degree and for a period determined by the reserve stores and Fe content of the diet, and complete only on a sufficient supply of Fe.

NUTR. ABS. (b)

**Relation of hæmoglobin to bilirubin and hæmatin in normal and diseased men.** I. DUESBERG (Arch. exp. Path. Pharm., 1934, 174, 305—327).—Hæmoglobin (I) and hæmatin (II) were injected into the veins, transudates, and exudates of normal and diseased men and the contents of (I), (II), and bilirubin (III) in the serum and fluids were determined after 1—24 hr. The results indicate that the formations of (II) and (III) are two distinct routes of (I) decomp. and that (I), whether in the blood-stream or not, may quantitatively yield (III). In disease, (I) yields (II), but the formation of (III) from (II) does not occur. The mechanism of the decomp. of (I) is discussed. F. O. H.

**Chemical composition of Herzog's "hæmatoprostheticin."** F. HAUROWITZ (Z. physiol. Chem., 1934, 223, 74—75; cf. A., 1933, 1180).—The composition of "hæmatoprostheticin" corresponds with that of a half anhydride of oxyhæmin (cf. Hamsik, A. 1927, 1100). J. H. B.



**Hæmin prepared with the help of formic acid.** J. BRÜCKNER (Biochem. Z., 1934, 268, 181—186; cf. Partos, A., 1920, i, 773).—Heat-coagulated horse-blood or horse-oxyhæmoglobin on rapid extraction with cold MeOH or EtOH containing 3—4% HCO<sub>2</sub>H yields a solution which deposits cryst. hæmin formate (I), C<sub>35</sub>H<sub>33</sub>O<sub>6</sub>N<sub>4</sub>Fe, 2EtOH (yield 1.3 g. per 1000 c.c. blood). (I), which is purified by dissolution in C<sub>5</sub>H<sub>5</sub>N—CHCl<sub>3</sub> and addition of HCO<sub>2</sub>H in EtOH, is not esterified.

W. McC.

**Hæmoerythrin from *Sipunculus*.** J. ROCHE (Bull. Soc. Chim. biol., 1933, 15, 1415—1435).—Cryst. hæmoerythrin (I) is obtained from the colomic fluid of *Sipunculus* by repeated dissolution in aq. NaCl and dialysis. The absorption spectrum (II) of methæmoerythrin is unchanged on treatment with CO; the large band at 3500 Å. observed by Florkin for (I) (A., 1933, 81) was not seen. (I) has a solubility min. (III) at  $p_H$  5.7 and a min. of cataphoresis at  $p_H$  5.8. From the titration curve (I) behaves as a univalent base of  $p_K$  2.9 and a multivalent acid of  $p_K$  6.6, 8.0, and 10.5 approx. Keeping (I) for 2—20 min. at  $p_H$  1.8 and 16° reduces the solubility and shifts (III) to lower  $p_H$ . The val. of  $p_H$  4.8 of Florkin (*loc. cit.*) for the (III) obtained in AcOH—NaOAc buffers is explained by denaturation. A protein-free compound containing Fe, hæmoferin (IV), is separated from (I) by pptn. with COMe<sub>2</sub> and dissolution in HCl and COMe<sub>2</sub> and purified by means of EtOH and C<sub>5</sub>H<sub>5</sub>N. (IV) gives pyrrole reactions; its ultra-violet (II) is similar to that of (I) and is unchanged in acid solution.

H. D.

**Combination of carbon monoxide with hæmocyanin.** R. W. ROOT (J. Biol. Chem., 1934, 104, 239—244).—The affinity of CO for *Limulus* hæmocyanin is about 1/20 that of O<sub>2</sub>, and the compound formed is less stable. As in oxyhæmocyanin, 1 mol. CO corresponds with 2 atoms Cu.

H. G. R.

**Fibrinogen formation in the animal body.** E. HORI (Sei-i-kwai Med. J., 1932, 51, No. 8, 97—111).—Venous blood contains more fibrinogen (I) than arterial blood. In the rabbit (I) is formed chiefly from the leucocytes by the liver.

CH. ABS.

**Origin of the plasma-proteins.** H. A. REIMANN, G. MEDES, and L. C. FISHER (J. Clin. Invest., 1933, 12, 968).—Leucocytes (I) disintegrated by freezing with liquid air contained proteins with the salting-out characteristics of fibrinogen (II), globulin (III), and albumin (IV). Destruction of (I) *in vivo* in rabbits by C<sub>6</sub>H<sub>6</sub> injections led to marked increase of plasma- (III) and -(II), generally at the expense of the -(IV). The marked leucopenia produced by X-rays caused little change in the plasma-proteins apart from some increase in (II). (III) and (II) may in part be derived from the decomp. of (I) in the circulation or hæmatopoietic system.

NUTR. ABS. (b)

**Micro-determination of blood-plasma-proteins.** G. MEDES (Amer. J. Clin. Path., 1933, 3, 439—442).—The method consists in fractional pptn. with anhyd. Na<sub>2</sub>SO<sub>4</sub>, pptn. of protein in the various filtrates with CCl<sub>3</sub>·CO<sub>2</sub>H, dissolution of the ppts. in NaOH, and determination of N in aliquot parts of the solutions.

CH. ABS.

**Condition of hydration of serum-protein.** M. SIGNON (Z. ges. exp. Med., 1933, 89, 211—214; Chem. Zentr., 1933, ii, 2157).—A new expression is based on the viscosity and albumin : globulin content of serum; a nomogram is given.

A. A. E.

**Specific gravity of synthetic solutions of serum-albumin and -globulin.** R. L. NUGENT and L. W. TOWLE (J. Biol. Chem., 1934, 104, 395—398).—The *d* of a protein solution plotted against the protein concn. gives a straight line which is identical for both ox serum-albumin and -globulin.

H. D.

**Effect of deamination on the combination curves of serum-albumin and -globulin.** E. B. R. PRIDEAUX and D. E. WOODS (Proc. Roy. Soc., 1933, B, 114, 110—123).—Ox-serum-albumin and -globulin were deaminated using HNO<sub>2</sub>. The products contained no free NH<sub>2</sub>-N, and some slight introduction of NO-groups had occurred. Their isoelectric points were at  $p_H$  4.0±0.1 and 4.3±0.2, respectively. They were capable of combination with acid, and combined with more alkali than the original proteins, suggesting combination at peptide linkings. On allowing for hydrolysis, the max. difference between the alkali or acid taken up by 1 g. of natural and deaminated protein was approx. equiv. to the ε-NH<sub>2</sub> of lysine, which is lost on deamination. The effect of CH<sub>2</sub>O on the titrations of natural and deaminated serum-albumin favoured the "zwitterion" theory of combination; the titration of the deaminated protein was complete at  $p_H$  8.5, consistent with absence of ε-NH<sub>2</sub> of lysine.

**Effect of ultra-violet radiation and heat on protein solutions of low concentrations.** M. SPIEGEL-ADOLF (Biochem. J., 1934, 28, 372—379).—Electrolyte-free serum-albumin and -pseudoglobulin (0.2—0.002%) are almost completely pptd. by heat or by ultra-violet irradiation, but in the latter case the filtrate contains a substance (I), probably proteose in nature, which coagulates colloidal Au. When a conc. solution of (I) is added to normal spinal fluid the mixture gives a Au sol reaction similar to that obtained in general paralysis. The filtrates obtained from protein solutions (0.2—0.5%) containing acid or alkali, after irradiation, neutralisation, and heat-coagulation, do not show a positive reaction with colloidal Au.

W. O. K.

**Basic amino-acids of serum-proteins. II. Effect of heating to 58°.** R. J. BLOCK. III. **Chemical relationship between serum-proteins of various origins.** R. J. BLOCK, D. C. DARROW, and M. K. CARY (J. Biol. Chem., 1934, 104, 343—346, 347—350).—II. The amount and the basic NH<sub>2</sub>-acid composition of the protein fraction pptd. from cattle-serum by half saturation with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> are the same in serum unheated, and heated at 58° for 3 hr. Albumins obtained from cattle-serum by means of aq. (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> yield more lysine than the globulins.

III. Determination of albumin, globulin, and basic NH<sub>2</sub>-acid (I) content of various samples of mammalian serum indicates that although the total amount of protein and the albumin content may vary widely, the (I) content of the protein is const. both in abs. and relative amount. Serum-protein,

like the keratins, might therefore be classified according to the mol. ratio of  $\text{NH}_2$ -acids it yields on hydrolysis. Probably the proteins obtained from blood-serum are not of const. (I) composition, but are artefacts produced by reagents employed in their prep.

A. L.

**Zeiss interferometer and Hirsch's interferometric method.** C. O. GUILLAUMIN (Bull. Soc. Chim. biol., 1933, 15, 1392—1414).—The use of the Zeiss interferometer, with special reference to Hirsch's method of determining the changes in the molar concn. of sera produced by gland extracts, is described. The most trustworthy results are obtained by direct comparison of pathological and normal sera. The methods of correction of Durupt and Schlesinger (A., 1933, 1331) are criticised.

H. D.

**Changes in blood-glutathione at high altitudes.** G. DELRUE and A. VISCHER (Compt. rend. Soc. Biol., 1933, 113, 942—944).—The glutathione content (I) of the blood increases at high altitude (3400 m.) (in three cases from 17 to 50 mg. per 100 c.c.). The relative increase in (I) is  $>$  that in red blood-cells.

NUTR. ABS. (m)

**Depressor substance of blood.** C. H. FISKE (Proc. Nat. Acad. Sci., 1934, 20, 25—27).—Blood is deproteinised at  $0^\circ$  with  $\text{CCl}_3\text{-CO}_2\text{H}$  and the filtrate neutralised with saturated aq. NaOH. The Hg salt of the active principle is then pptd. by  $\text{Hg(OAc)}_2$  and decomposed with  $\text{H}_2\text{S}$ ; the Ag salt is next pptd. by  $5N\text{-AgNO}_3$  and decomposed with  $\text{H}_2\text{S}$  (repeated twice), and finally the acid Ca salt is pptd. by  $\text{CaCl}_2$  and EtOH. By this method 6.45 mg. (as P) of the acid Ca salt of adenosine triphosphate were isolated from 100 c.c. of blood. The acid Ag salt has the composition  $\text{C}_{10}\text{H}_{13}\text{O}_{13}\text{N}_5\text{P}_3\text{Ag}_3$ . All operations must be carried out at a low temp. to minimise deamination of the adenine to hypoxanthine. The depressor principle of blood (adenylic acid) is present exclusively as adenosine triphosphate.

P. G. M.

**Acetylcholine in ox-blood.** K. GOLLWITZER-MEIER (Arch. exp. Path. Pharm., 1934, 174, 456—467).—No acetylcholine-like substance (I) occurs in fresh blood (II) or in normal or deproteinised plasma, but is found in deproteinised extracts of fresh (II) (0.01—0.07 mg. per litre) and in lysed (II) (0.005—0.013 mg. per litre) when the (II) is previously treated with eserine or kept for 1—2 hr. Hence (I) originates in the red corpuscles, where it is either preformed and bound, or arises by a reaction of the (II) constituents.

F. O. H.

**Determination of non-protein-nitrogen with special reference to the Koch-McMeekin method.** C. A. DALY (J. Lab. Clin. Med., 1933, 18, 1279—1285).—A slight modification for blood of the Koch-McMeekin method is described. The chief differences from Folin's original method (I) are the use of  $\text{H}_2\text{O}_2$  previously added to the  $\text{H}_2\text{SO}_4$  for digestion of the protein-free filtrate and the addition of gum ghatti and Na citrate to the slightly modified Nessler solution. The results agree with those obtained by (I).

NUTR. ABS. (m)

**Titrimetric micro-determination of non-protein-nitrogen of blood without distillation.**

F. RAPPAPORT (Klin. Woch., 1933, 12, 1184—1185).—Blood (0.1—0.2 c.c.) is deproteinised, the filtrate is ashed with phosphomolybdic acid or a  $\text{Ti(SO}_4)_2\text{-H}_2\text{SO}_4$  reagent, the free acid is neutralised, and after addition of buffered aq. NaOBr, KI, and HCl, titration with 0.01N- $\text{Na}_2\text{S}_2\text{O}_3$  follows. Excellent agreement with distillation methods is found. NUTR. ABS. (m)

**Deproteinisation with cadmium hydroxide and blood-sugar.** C. DUMAZERT (Compt. rend. Soc. Biol., 1933, 113, 1061—1062).— $\text{Cd(OH)}_2$  is recommended as a protein precipitant in determining the true (*i.e.*, fermentable) sugar in blood. The ratio of free sugar in the cells to that in the whole blood is with normal subjects about 8, with diabetics, a little  $>$  6.

NUTR. ABS. (m)

**Distribution of sugar between plasma and corpuscles in animal and human blood.** A. ANDREEN-SVEDBERG (Skand. Arch. Physiol., 1933, 66, 113—190).—Vals. for the corpuscle: plasma (I) distribution of true sugar are given for the blood of seventeen different vertebrates. With the exception of the goose-fish, human blood (II) shows the highest ratio. In (II), in hyperglycæmia (III), or when large quantities of glucose have been added to the blood *in vitro*, the (I) ratio rises, but in fish, dogs, and rabbits, under similar conditions, it falls. An increase is observed in rabbit's and dog's blood in (III). These results support the theory that sugar is adsorbed at the surface of animal blood corpuscles, but in man is probably partly adsorbed, partly dissolved in the  $\text{H}_2\text{O}$  of the corpuscles, and to some extent chemically bound to the lipins of the cell wall.

NUTR. ABS. (m)

**Determination of animal lipins and their components.** H. PATZSCH (Pharm. Zentr., 1934, 75, 98—102, 116—120).—A summary of suitable known methods for determination (in blood and serum) of cholesterol, cholesteryl esters, lecithin, choline, lipin-P, and fat.

P. G. M.

**Precipitation of albumins and lipins from serum by neutral salts as function of  $p_{\text{H}}$ .** G. SANDOR, A. E. BONNEFOI, and P. GORET (Bull. Soc. Chim. biol., 1933, 15, 1472—1482).—Machebœuf's method of pptn. (A., 1931, 1447) is approx. quant. between  $p_{\text{H}}$  3.34 and 2.30 for the horse and sheep. Albumin (I) left at  $p_{\text{H}}$  3 for 1 hr. is not denatured. The pptn. of (I) from conc.  $(\text{NH}_4)_2\text{SO}_4$  solutions shows a max. at  $p_{\text{H}}$  6.55 and a min. at 4.8. The ppt. formed at  $p_{\text{H}}$  6.55 redissolves on further acidification. The presence of a protein of isoelectric point 6.55 in serum is suggested.

H. D.

**Lipin- and inorganic phosphorus in the blood after irradiation with artificial sunlight.** H. STEMENS and G. C. HERINGA (Nederland. Tijdschr. Geneesk., 1933, 77, 1635).—Irradiation of the skin of young men, with few exceptions, did not affect the lipin-P of the blood, but inorg. P increased slightly.

NUTR. ABS. (b)

**Absorption of ether by serum.** F. SEELICH (Biochem. Z., 1934, 268, 34—45; cf. A., 1932, 1053).—Aq. solutions of Na oleate (I) and Na glycocholate (II) resemble serum in taking up  $\text{Et}_2\text{O}$  on shaking. The amount taken up is const. for given quantity

(III) of substance and concn. (IV) of solution, and is dependent for (II) on (III) and (IV), but for (I) on (III) only. The  $\text{Et}_2\text{O}$  no. (V) (amount of  $\text{Et}_2\text{O}$  taken up by 1 c.c. of solution or serum) of solutions of (I) and (II) of unknown (IV) may be used for deducing (IV). The decrease in (V) produced by heating for 10 min. at  $> 50^\circ$  can be partly counteracted by  $\text{CO}_2$  treatment. There appears to be a relation between (V) and hæmolytic complement action. W. McC.

**Variations in blood-cholesterol due to sunlight.** S. MALCZYNSKI (Compt. rend. Soc. Biol., 1933, 113, 1300—1302).—Exposure of the shaved backs of two dogs for 20—30 min. to summer sunlight daily for 9 days caused an immediate rise in blood-cholesterol from 167 to  $> 200$  mg. per 100 c.c. after the first exposure; for 3 weeks after the ninth exposure the level was high (180 mg.), but fluctuating, and thereafter fell to pre-exposure level. NUTR. ABS. (b)

**Determination of the iodine value of unsaturated fatty acids in blood.** W. BRANDT, K. HINSBERG, and G. HOLLAND (Z. ges. exp. Med., 1933, 90, 216—224).—Extraction with  $\text{EtOH}$ -light petroleum (9:1) is best. All types of saponification lower the I val.; the use of  $\text{NaOEt}$  is most advantageous. Rupp's modification of Winkler's method yields figures nearest the theoretical vals.; other methods give low vals. for blood and tissues. NUTR. ABS. (m)

**Hydrogen-ion concentration in blood of healthy and sick horses.** A. MEYER (Arch. wiss. pr. Tierheilk., 1933, 66, 512—520).—The  $p_{\text{H}}$  of normal horse blood was 7.38—7.54 (average 7.46). Vals. are given for cases with various diseases. The variations were not sp. for the type of disease. NUTR. ABS. (b)

**Potassium of serum.** H. WAELSCH and S. KITTEL (Kolloid-Z., 1934, 66, 200—205).—Experiments in Fürth's high-tension apparatus (A., 1925, ii, 1057) show that K in serum migrates to the anode even at  $p_{\text{H}}$  4, at which the albumin migrates to the cathode. Combination of K with serum-albumin is excluded under these conditions. E. S. H. NUTR. ABS. (m)

**Bound calcium of blood-serum.** F. ROSENTHAL (Klin. Woch., 1933, 12, 1140—1141).—The hypothesis underlying Berency and Hermann's method of determining protein-bound Ca is untenable. When aq.  $\text{CaCl}_2$  is added to serum, part (5—50%) of the added Ca is pptd. with the protein. NUTR. ABS. (m)

**Blood-phosphate during work.** H. GÜNTHER (Z. ges. exp. Med., 1933, 90, 479—488).—A small rise in serum- $\text{PO}_4'''$  occurs, due to concn. The chief cause of the increased val. for whole blood- $\text{PO}_4'''$  during work is a relative increase in the proportion of red cells. NUTR. ABS. (b)

**Total and ultrafilterable calcium and the acid-soluble phosphate content of the blood-serum of children.** M. S. NEEDELS and C. M. MARBERG (J. Lab. Clin. Med., 1933, 18, 1227—1234).—Serum-Ca, total and diffusible, is slightly lower in the spring than in autumn in children on standard diet, but there is little or no seasonal variation in children

receiving, in addition, orange and lemon juice daily. Serum-inorg. P shows no seasonal variation in either case, but is lower in older children. No correlation can be found between total Ca, ultrafilterable, Ca or inorg. P of the blood-serum and the incidence of dental caries. NUTR. ABS. (m)

**Thiocyanogen metabolism I. Thiocyanogen content of blood.** B. STUBER and K. LANG (Deut. Arch. klin. Med., 1933, 175, 564—567).—The normal SCN content of blood, determined as  $\text{Cu C}_5\text{H}_5\text{N}$  thiocyanate, is 0.1—0.2 mg. per c.c. It is greatly reduced in thyroid disease, but not in renal insufficiency. NUTR. ABS. (m)

**Level, distribution, and physico-chemical state of bromine in blood in normal subjects and conditions other than mental disease.** C. O. GUILLAUMIN and B. MEREJKOWSKY (Compt. rend. Soc. Biol., 1933, 113, 1428—1430).—The average ratio of Br in blood-corpuses to that in the plasma is 0.36. The Br content of the blood is 2—20 mg. per litre (average 10). Apparently 63—88% of the Br in blood resists ultra-filtration and is therefore present either as an adsorption complex or in org. combination. NUTR. ABS. (m)

**Blood-chlorine in the normal dog.** V. ROBIN, A. BRION, and R. MONPERT (Compt. rend. Soc. Biol., 1933, 113, 1174—1176).—The Cl content of the serum (I) of normal dogs fed on a normal diet is 0.320—0.350 g. per 100 c.c. and 0.200—0.220 g. for whole blood (II). The ratio of Cl in (II) to that in (I) is 0.65—0.70. NUTR. ABS. (m)

**Penetration of erythrocytes by anions.** M. MAIZELS (Biochem. J., 1934, 28, 337—350).—Erythrocytes (I) were exposed to a solution containing  $\text{Cl}'$  and a second anion (II), the amount of (II) entering (I) being usually found indirectly on the assumption (experimentally verified) that in 5 min. the sum of all the anions entering (I) = amount of  $\text{Cl}'$  entering (I) suspended in aq.  $\text{KCl}$  at the same  $p_{\text{H}}$ . The order of permeation of inorg. ions into (I) is  $\text{CNS}' > \text{I}' > \text{NO}_3', \text{Cl}' > \text{SO}_4'' > \text{PO}_4'''$  (a lyotropic series), the permeation rate (III) of (II) relative to  $\text{Cl}'$  increasing with  $[\text{H}']$ . Anions of lower fatty acids permeate more readily than  $\text{Cl}'$  at low  $p_{\text{H}}$ , but the presence of additional polar group(s) (IV) decreases (III), especially if  $\alpha$  to  $\text{CO}_2\text{H}$ . In the aromatic series, (IV) enhances (III).  $\text{C}_2\text{O}_4''$  permeates more rapidly than  $\text{Cl}'$  or any other anion at low  $p_{\text{H}}$ . Substances permeating rapidly are usually poorly dissociated, have a relatively high  $\text{Et}_2\text{O}$ - $\text{H}_2\text{O}$  partition coeff., and are capillary-active. The problem of the nature of the membrane of (I) is discussed in the light of these results. A. E. O.

**Passage of chlorine from erythrocytes to plasma under influence of sodium citrate.** S. RASZEJA and A. SLAVINSKI (Bull. Soc. Chim. biol., 1933, 15, 1569—1571).—Addition of Na citrate to horse blood fails to alter the plasma or erythrocyte  $[\text{Cl}']$ . H. D.

**Influence of trisodium citrate on migration of chlorine between corpuscles and plasma of human blood.** C. O. GUILLAUMIN (Bull. Soc. Chim. biol., 1933, 15, 1572—1574).—The criticisms of Raszeja and

Slavinski (see preceding abstract) against the author's work (A., 1930, 944) are rebutted. H. D.

**Retardation of blood-coagulation by trisodium citrate.** M. LARGET, J. P. LAMARE, R. C. WEYL, and R. LECOQ (Bull. Sci. pharmacol., 1933, 40, 408—416; Chem. Zentr., 1933, ii, 2284).—Of the substances which retard blood-coagulation *in vitro*, only Na<sub>3</sub> citrate is suitable for use *in vivo* (8—16 g. in 4% solution orally). A. A. E.

**Temporary inhibition of coagulation in the blood of insects.** W. E. SHULL and P. L. RICE (J. Econ. Entom., 1933, 26, 1083—1089).—Exposure to AcOH vapour inhibits the coagulation of the blood of cockroaches, the intensity of the action varying with temp. and period of exposure. A. G. P.

**Antigens.** J. G. FITZGERALD (Trans. Roy. Soc. Canada, 1933, [iii], 27, V, 1—9).—A lecture. F. O. H.

**Nature of antibodies.** J. MARRACK (Nature, 1934, 133, 292—293).—Tetrazotised benzidine coupled with R salt and with the proteins of an agglutinating serum gives a deep red compound (I), but the agglutinin is not wholly destroyed. If the agglutinins (II) of the serum are proteins (I) should be adsorbed specifically by homologous bacteria, but actually the protein dyes thus formed are adsorbed non-specifically. When dil. solutions are used, however, a marked quant. difference can be observed between the degree of adsorption by homologous and heterologous bacteria. This sp. adsorption of the dye from the homologous coloured agglutinin agrees with the view that (II) are proteins. Other alternatives are mentioned. L. S. T.

**Application of f.-p. measurements to the dilution of antitoxic globulin.** E. M. TAYLOR and P. J. MOLONEY (Trans. Roy. Soc. Canada, 1933, [iii], 27, V, 193—196).—The f.p. of 0.4—1.0% aq. NaCl is lowered proportionately by the addition (10—20%) of pseudoglobulin (I) from the serum (II) of immunised animals and also by the further addition (0.3%) of "tricrosol" (III). With (I) the effect is due to the vol. of H<sub>2</sub>O it occupies, and is slightly more marked with KCNS than with NaCl. Addition of approx. 0.7% of NaCl to 18—20% aq. (I) containing 0.38% of (III) yields a solution isotonic with the average human (II) (f.p. —0.55°). F. O. H.

**Carrier-function of serum-proteins and its significance in serological reactions.** E. KYLIN (Arch. exp. Path. Pharm., 1934, 174, 483—489).—Cataphoresis of serum with a positive serological reaction (I) (e.g., Wassermann, Kahn) yields pure albumin (II), a mixture of (II) and globulin (III), a protein-free fluid, and (III). The (III)-containing fractions, but not the protein-free serum nor (II), give a positive (I), and hence (III) appears to be the carrier on which the factors responsible for (I) are adsorbed. F. O. H.

**Organ-specificity of a hæmoglobin-precipitating antiserum.** K. YORIMITSU (Tôhoku J. Exp. Med., 1933, 22, 1—6). CH. ABS.

**Immunological study of native, denatured, and reversed serum-albumin.** B. F. MILLER (J. Exp. Med., 1933, 58, 625—633).—Native and reversed

horse serum-albumin are indistinguishable by the precipitin reaction. CH. ABS.

**Phenylcarbimide derivatives and their immunological properties.** III.—See this vol., 405.

**Organ-specificity.** T. ISHIKAWA and H. YAMAMOTO (Tôhoku J. Exp. Med., 1933, 21, 524—531).—The lens (I), vitreous humour (II) and cornea of fish (I) and (II) of fowl, and the naked nuclei of fowl red cells contain a common antigenic factor. The nuclei of the hepatic cells, freed from protoplasm by peptic digestion, are organ-sp. CH. ABS.

**Post-mortem glycogenolysis in human infant and foetus.** W. HERTZ (Z. Kinderheilk., 1933, 55, 410—420).—The rate of glycogenolysis, determined under strictly sterile conditions in buffered media, is very rapid in the livers of 15-week-old foetuses (I) but less rapid in the livers of older (I) and of new-born infants which have not breathed; the small liver glycogen content of young (I) is thus explained. NUTR. ABS. (m)

**Phosphoric esters in normal and malignant tissue.** E. L. OUTHOUSE (Trans. Roy. Soc. Canada, 1933, [iii], 27, V, 123—133).—The tissue (I) is extracted with 4% aq. CCl<sub>3</sub>·CO<sub>2</sub>H and the extract is fractionated by means of the Ba, Hg<sup>II</sup>, and bicine salts. Normal avian muscle (II) yields hexose mono- (but not di-)phosphate and adenylic acid, the carbohydrate residue from light (II) containing 75% and from dark (II) 66% of aldose. Data are given for the partition of P in human and bovine tumour. Fibrous (I) has a low content of acid-sol. P. Malignant (I) contains an org. phosphate, the Pb and Ba salts of which are sol. in EtOH and Et<sub>2</sub>O, which appears to be absent from muscle. F. O. H.

**Glycerophosphoric acid. II. Glycerophosphoric acid of the naturally-occurring phosphatides.** J. J. RAE (Biochem. J., 1934, 28, 151—156).—Brain-lecithin and -kephalin and Ca phosphatide contain mainly the α-form, egg-lecithin the β-form, whereas liver-lecithin contains about equal amounts of the two forms. H. G. R.

**Constitution of ovomucin.** T. ISEKI (J. Biochem. Japan, 1934, 19, 1—5).—Ovomucin (cf. A., 1927, 372) was digested with trypsin, the digest pptd. with HgCl<sub>2</sub>, and the resulting filtrate freed from Hg and pptd. with basic Pb acetate. The material regenerated from this ppt. on pptn. from conc. aq. solution by EtOH afforded a substance (22.5% yield) with 5.35% N, free from NH<sub>2</sub>-acids, giving a marked biuret reaction, and containing 49.43% of glucosamine. F. O. H.

**Paraffin in the egg of *Bombyx mori*.** D. ONGARO (Annali Chim. Appl., 1933, 23, 567—572).—The unsaponifiable portion of the Et<sub>2</sub>O extract of silk-worms' eggs contains a saturated hydrocarbon, C<sub>28</sub>H<sub>58</sub>, m.p. 62°, similar to that obtained from the chrysalis, and a sterol. T. H. P.

**Sterols of molluscs.**—See this vol., 404.

**Pigments of animal fats.** L. ZECHMEISTER and P. TUZSON (Ber., 1934, 67, [B], 154—155).—The isolation of a mixture of α- and β-carotene from the kidney-fat of an aged cow is described. H. W.

**Reducing substance found in chromophilic adenomas and in the normal anterior pituitary.** T. J. PUTNAM and H. B. WILCOX (Amer. J. Path., 1933, 9, 649—650).—The substance reduces methylene-blue, but does not reduce Benedict's solution or give other common tests for sugar. CH. ABS.

**Thyroglobulin. III. Thyroglobulin content of the thyroid gland.** B. O. BARNES and M. JONES (Amer. J. Physiol., 1933, 105, 556—558).—Of the I in thyroids from pigs and dogs >95% is present as thyroglobulin. The % remains the same irrespective of the total I content. NUTR. ABS. (m)

**Iron content of thyroid gland.**—See this vol., 382.

**Composition of pig's thymus.** E. KATAOKA (J. Biochem. Japan, 1934, 19, 21—24).—The fresh glands (64.1% H<sub>2</sub>O) contain 9.3% of fat, a constituent of which is  $\alpha$ -palmitodistearin. Hydrolysis of the fat-free dry substance yields alanine (1.19%), valine (0.81%), leucine (3.24%), isoleucine (1.28%), proline (0.84%), glutamic+aspartic acid (2.8%), lysine (1.58%), arginine (2.0%), and histidine (0.21%).

F. O. H.

**Composition of the pancreas.** E. KATAOKA (J. Biochem. Japan, 1934, 19, 25—32).—The following data are given for ox- and pig-glands, respectively: H<sub>2</sub>O, 69.0—74.2, 68.5—69.5%; fat, 9.5—14.2 (partly  $\beta$ -stearodipalmitin), 10.6—11.3% (partly  $\beta$ -laurodistearin). Hydrolysis of the fat-free dried tissue yields mainly lysine (2.89—3.56, 3.01—3.94%), arginine (2.45—2.60, 2.33—2.54%), leucine (5.44, 5.34%), and glutamic acid (1.93, 1.23%).

F. O. H.

**Histamine in canine gastric tissues.** G. GAVIN, E. W. MCHENRY, and M. J. WILSON (J. Physiol., 1933, 79, 234—238).—The mucous membrane of the dog's stomach contains relatively large amounts of histamine (I), the gastric muscle much less. The fundic mucosa (II) contains about 80% of the (I) contained in the stomach. Extracts of dog's (II) and pyloric tissue (III) have secretagogue powers, which are lost after incubation of the solutions with histaminase. (II) contains more secretagogue material than the (III). NUTR. ABS. (b)

**Distribution and origin of sulphur in wool. I. Methionine.** J. BARRITT (Biochem. J., 1934, 28, 1—5).—The methionine content of the degreased wools from a no. of breeds of sheep, determined by Bernstein's method (A., 1932, 1149), was 0.44—0.67% of the dry wt. and represented 2.4—4.8% of the total S.

H. D.

**Phenomena occurring in solutions of collagen at the limits of action of acids and neutral salts.** L. GUYON (Compt. rend., 1934, 198, 975—977).—Solutions of the collagen from the tendons of the tails of rats form a homogeneous gel when dialysed against 0.01% AcOH. NaCl inhibits gel formation. With 0.1% NaCl and 0.001% AcOH, spherules (A) and birefringent fibres are formed. With 0.1% NaCl in 0.0001% AcOH or 0.03% NaCl in H<sub>2</sub>O, only (A) are obtained. R. S. C.

**Basic amino-acids of keratins.** R. J. BLOCK (J. Biol. Chem., 1934, 104, 339—341).—The mol. ratios of histidine, lysine, and arginine present in human

finger-nails and cattle horn are 1 : 5 : 15 and 1 : 5 : 13, respectively, indicating that these tissues have a composition resembling that of keratinoid tissue. These vals. do not agree with those of Abderhalden and Heyns (A., 1932, 637). A. L.

**Nucleotide component of mammalian cardiac muscle. I. Composition and chemical properties of the nucleotide.** F. BEATTIE, T. H. MILROY, and R. W. M. STRAIN. II. Biological and co-enzyme properties of the cardiac dinucleotide. R. W. M. STRAIN (Biochem. J., 1934, 28, 84—90; 90—93).—The chemical composition and behaviour on hydrolysis at 100° with *N*-HCl show that the nucleotide of cardiac (I) differs from that of voluntary (II) muscle in being more closely allied to a dinucleotide composed of 1 mol. each of adenosine-di- and -tri-phosphoric acids. Approx. 60% of its total P is labile. The only distinctive difference in the pharmacological action of the two nucleotides is obtained with intestinal musculature, when (I) lowers the tone without a subsequent rise, whilst (II) has the double action. (I) has a more powerful co-enzyme action in reactivating inactive extracts of both voluntary and cardiac muscle. P. W. C.

**Crystalline myoglobin. II. Sedimentation constant and mol. wt. III. Light absorption by oxy-, carbon monoxide-, meta-, and reduced myoglobin. IV. Myoglobin in equilibrium with oxygen and carbon monoxide. V. Fixation of oxygen by myoglobin.** H. THEORELL (Biochem. Z., 1934, 268, 46—54, 55—63, 64—72, 73—82; cf. A., 1932, 1054).—II. Myoglobin (I) from expressed muscle juice of horse, ox, or cat has sedimentation const. (II)  $2 \times 10^{-13}$ . The mol. wt. of (I) from horse muscle is 34,800 but aq. extracts of horse heart contain in addition a (I) having (II) =  $4 \times 10^{-13}$  and probable mol. wt. 68,000. Within the  $p_H$  range 6.0—13 (I) is stable. It is probably the low mol. wt. of (I) which enables it to diffuse so readily in the kidney.

III. The light absorption curves of these forms of myoglobin are plotted and the max. and min. recorded. The curve for metamyoglobin yields vals. which vary with [H<sup>+</sup>] ( $p_H$  6.2, 7, and 8 chosen).

IV. Vals for the tensions (III) at 20° and 37° and  $p_H$  7.4—6.0 (as well as in absence of salts and in presence of phosphate buffer) of O<sub>2</sub> and CO in (I) solutions are given. The order of magnitude of (III) differs greatly from that of the corresponding vals. for haemoglobin (IV), although as regards effect of temp. and [H<sup>+</sup>] (effect insignificant) the pigments behave similarly.

V. The strictly hyperbolic O<sub>2</sub> dissociation curve (V) of (I) solutions shows that, at  $p_H$  7.4, the affinity of (I) for O<sub>2</sub> is six times  $p_H$  that of (IV). (V) is little affected by [H<sup>+</sup>] and affected by temp. changes < the corresponding (IV) curve. (I) acts physiologically as an O<sub>2</sub> reservoir. At 37° (I) solutions are half-saturated with CO when its pressure is 0.2 mm.

W. McC.

**Extractives of muscle. XXXVIII. Dromæus sp.** N. TOLKATSHEVSKAYA (Z. physiol. Chem., 1934, 223, 57—60; cf. A., 1929, 1479).—The flesh of an exotic bird, *Dromæus sp.*, contains anserine,

methylguanidine, creatinine, xanthine, carnitine (?), and choline (?). Carnosine is absent. J. H. B.

**Ratio of calcium to phosphorus content of fish.**

A. DE CLERCQ (Natuurwetensch. Tijds., 1934, 15, 229—236).—The P:Ca ratio is remarkably high in fish (0.29—1.58). In herrings the ratio increased from 0.28 to 0.78 from Nov. to Jan. S. C.

**Colour reactions of the aqueous solution of the cocoon layer.** H. KANEKO (Bull. Sericult. Japan, 1932, 4, No. 3, 10—12).—A flavone-like compound, glycine,  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ ,  $(\text{NH}_4)_2\text{CO}_3$ , and a small quantity of aspartic acid are probably present. CH. ABS.

**Aqueous solution of domestic cocoons. XI. Nitrogen distribution of sericin-A and -B. XII. Solubility of sericin.** H. KANEKO (J. Agric. Chem. Soc. Japan, 1933, 9, 45—49, 301—311).—XI. Sericin-A is rich in arginine. High arginine content of the aq. solution indicates good reelability. Sericin-A and -B contain, respectively, tyrosine 2.62, 5.53; glycine 6.18, 4.89 (fibroin 33.5)%.

XII. Sericin is more sol. in aq. solutions of Na salts of org. acids than in those of salts of inorg. acids. Sericin-A is least sol. in HCl at  $p_{\text{H}}$  4.5 and -B at  $p_{\text{H}}$  4.7; for  $\text{H}_2\text{SO}_4$ , 4.4, 4.6. CH. ABS.

**Toad poisons. VI. Ch'an su, the dried venom of the Chinese toad, and the secretion of the tropical toad, *Bufo marinus*.**—See this vol., 412.

**Electrical phenomena of the cornea. I.**

**Potential differences against electrolytes. II. Potential of the cornea.** K. HAYASHI (J. Biochem. Japan, 1934, 19, 145—163, 165—172).—I. No significant p.d. exists between the posterior and anterior chambers of the eye (ox). That between the vitreous humour and an aq. electrolyte (I) in contact with the outside of the cornea depends on the character of (I),  $\text{CuCl}_2$ ,  $\text{AlCl}_3$ ,  $\text{H}^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{Fe}(\text{CN})_6^{3-}$  yielding small or negative vals. and  $\text{KSCN}$ ,  $\text{KNO}_3$ ,  $\text{KBr}$ , and  $\text{NaOH}$  yielding high positive vals.

II. The p.d. between two different concns. of (I) in contact with the two sides of the cornea (fresh or formolised) was determined for various (I).

F. O. H.

**Calcium content of the aqueous and vitreous humours and serum.** P. W. SALT (J. Biol. Chem., 1934, 104, 275—280).—The Ca content of the aq. and vitreous humours (I) and serum (II) of young calves is 5.82, 8.34, and 11.54 mg. per 100 g., whilst for aged cattle the vals. are 4.60, 6.75, and 9.69, respectively. The Ca content of (I) is directly dependent on the Ca of (II). H. G. R.

**Porphyryn content of human amniotic fluid.**

R. FIKENTSCHER (Arch. Gynäk., 1933, 154, 129—146).—The coproporphyrin content of human amniotic fluid rises from zero in the first few weeks to a max. about the middle of pregnancy, falling to zero again in the last month. Uroporphyrin is absent.

NUTR. ABS. (m)

**Chemical origin of the biliary elements.**

G. RANZOLI (Boll. Chim. Farm., 1934, 73, 41—46).—A review.

R. N. C.

**Isolation of bilirubin.**

C. E. MAY, R. MARTINDALE, and W. F. BOYD (J. Biol. Chem., 1934, 104, 255—257).—Bilirubin (I) is pptd. from dil. aq. solu-

tion with  $\text{BaCl}_2$  and  $\text{Na}_2\text{HPO}_4$  or  $\text{Na}_3\text{PO}_4$ . With diazo-chlorides (I) gives stable coloured products, whereas biliverdin does not react. H. G. R.

**Effect of diet on hydrogen-ion concentration of bile.** H. BRONNER (Klin. Woch., 1933, 12, 1562—1563).—Cholecystectomised patients were fed alternately on vegetarian (I) and meat (II) diet and the  $p_{\text{H}}$  was determined electrometrically in the bile collected by drainage of the bile duct. In cases with no liver damage the  $p_{\text{H}}$  was approx. 7.5 on (I) and 6.5 on (II). In cases with liver disease, bile was acid even with (I). NUTR. ABS. (b)

**Complete absorption of chlorine from the gall-bladder of the dog.** E. CHABROL, R. CHARONNAT, M. MAXIMIN, and J. COTTET (Compt. rend. Soc. Biol., 1933, 113, 1347—1348).—In fasting dogs in which the cystic duct had been ligated, the bile from the gall-bladder was much more conc. than the hepatic bile and contained practically no Cl. The urea content was unchanged. NUTR. ABS. (b)

**Gastric secretion.** T. TEORELL (Skand. Arch. Physiol., 1933, 66, 225—317).—In decrebrated cats which had previously been starved for 24 hr., secretion of gastric juice (I) was induced by slow and continuous intravenous infusion of histamine. The flow of (I) continued even when the blood-pressure was very low, and was unaffected by complete denervation of the stomach (II). Long-continued gastric secretion tended to cause acute gastric ulceration. An "alkaline tide" in the blood as the result of secretion of HCl into the (II) is doubtful. The regulation of the acidity of the (I) depends neither on dilution of the gastric contents nor on neutralisation by alkaline juices from the duodenum. The diminution of gastric acidity is due to diffusion of  $\text{H}^+$  into the (II) mucosa, and so into the blood, and to the passage of anions from the blood into the (II) contents. NUTR. ABS. (b)

**$p_{\text{H}}$  of the arterial blood during gastric secretion.** C. E. BRUNTON (J. Physiol., 1933, 79, 4—5p).—Gastric secretion excited by meat extracts caused no change in the  $p_{\text{H}}$  of human blood. NUTR. ABS. (b)

**Mode of action of secretagogues (liver extract) in promoting gastric secretion.** M. S. KIM and A. C. IVY (Amer. J. Physiol., 1933, 105, 220—240).—Liver and meat extracts, either with or without vasopressor (I) substances, had approx. the same secretagogue (II) action after direct application to dogs, but when given by mouth (Pavlov pouch dogs) or into the intestine, the (I) extracts were more effective than the (I)-free. Both types of extract excited gastric secretion on intravenous injection, but the (I)-free was less effective. (II) action in the stomach did not, but in the intestine did, depend on absorption of the extract. NUTR. ABS. (b)

**Proteins as stimulants for the secretion of pepsin.** E. R. B. SMITH and G. R. COWGILL (Amer. J. Physiol., 1933, 105, 697—705).—When two basal rations of a commercial dog food and nine artificial diets, in which the protein varied, were fed to Pavlov-pouch dogs, vol. and rate of secretion of gastric juice varied widely, but free and total acidity and total Cl were const. NUTR. ABS. (b)

**Secretory activity of the gastric mucosa in the region of the lesser curvature.** A. ALLEY (Trans. Roy. Soc. Canada, 1933, [iii], 27, V, 71—78).—Following ingestion of meat, milk, or bread by dogs, the vol., pepsin content, and acidity of the secretion from the mucosa of the lesser curvature region of the stomach are > those of the greater curvature region. F. O. H.

**Changes in acid secretion by the stomach at high altitudes.** G. DELRUE and J. P. BOUCKAERT (Compt. rend. Soc. Biol., 1933, 113, 940—942).—At high altitudes (3400 m.) the acidity of gastric secretion in dogs with gastric fistulae was reduced—from  $p_H$  1.02 to 3.6, in one case—during the first 4 days. Acclimatisation and exercise increased the acidity.

NUTR. ABS. (b)

**Acidity of the stomach contents of premature infants.** S. SEYFFARTH (Jahrb. Kinderheilk., 1933, 140, 164—179).—Gastric acidity (I) in 50 premature infants after the ingestion of breast milk was low for the first two months of life, increased to the fourth month, and then fell to the limits found in full-time infants of the same age. (I) was max. about 2 hr. after a feed. In 16 infants the  $p_H$  after 1 hr. was > 3.7, and of the infants over 4 weeks the  $p_H$  was < 3.7 in all cases in 2 hr. When the  $p_H$  was < 4.0, only a slight growth of *B. coli* could be got from the gastric contents. No const. correlation was found between (I) and parenteral infection, dyspepsia, or type of faecal flora.

NUTR. ABS. (b)

**Gastric digestion of fresh and ripe cheese.** F. RAMOND, G. GUITTONNEAU, E. NICHOLAS, and M. BÉJAMBES (Compt. rend. Soc. Biol., 1933, 113, 1023—1025).—Gastric analyses were conducted on man, using Camembert (I), Gruyère (II), and white cheese (III). Practically all the HCl secreted was bound by (I) and (II). The results were confirmed *in vitro*. (I) and (II) therefore contain larger proportions of degraded proteins than (III).

NUTR. ABS. (b)

**Acid-combining power of gastric juice and its significance for the regulation of gastric acidity.** H. SCHWARZ and M. TAUBENHAUS (Z. ges. exp. Med., 1933, 89, 506—528).—Marked acid-combining power (I) was shown by anacid juices, particularly unfiltered specimens, but not by acid juices. Max. (I) was obtained when the final  $p_H$  was 2.4—1.6; thereafter no more acid was bound. The Cl<sup>-</sup> behaved as if the juice were a solution of inorg. salts. There was no significant correlation between (I) and N content. Mucus had a definite (I), but did not account for nearly all.

NUTR. ABS. (b)

**Buffering action and protective power of gastric mucus.** B. GROÁK (Z. ges. exp. Med., 1933, 89, 86—96).—Electrometric titration of the gastric juice, with and without contained mucus, from patients with gastritis showed that the mucus had no buffering action, except above  $p_H$  2.5.

NUTR. ABS. (b)

**Thiocyanic acid in gastric juice.** H. R. KANITZ (Arch. Verdauungs-Krankh., 1933, 54, 42—52).—In Pavlov pouch dogs, HCNS secretion, unlike that of HCl, is not sustained at a uniform level, but falls gradually. The concn. of CNS<sup>-</sup> varied from 0.2 to 2.3 mg. per 100 c.c. of juice.

NUTR. ABS. (b)

**Enzymic activity of dogs' intestinal juice and its relation to intestinal digestion.** F. A. CAJORI (Amer. J. Physiol., 1933, 104, 659—668).—The enzymic activity (I) of the intestinal juices from Thiry loops in the jejunum and ileum showed wide variations, even in samples from the same loop, which could not be correlated with physiological conditions, but were related to the quantity of juice secreted. (I) of juice from jejunal loops was > that from the low ileal loops. Histamine subcutaneously increased the vol. of secretion and decreased enzyme concn. No correlation was found between (I) and food intake, any difference being related to the quantity of juice secreted. Peptone, starch, sucrose, and lactose, inserted into jejunal loops, were readily absorbed, whilst ovalbumin, inulin, raffinose, and glucosureide were recovered unchanged. The absorption rate of peptone, sucrose, and lactose was > would have been predicted on the basis of the (I) of the juice, whilst that of starch was commensurate with the amylase content.

NUTR. ABS. (b)

**Relation between nutrition and lactation.** V. ZAGAMI (Atti R. Accad. Lincei, 1933, [vi], 17, 973—979).—Further experiments on rats (A., 1933, 743) on various diets emphasise the close connexion between nutrition and lactation. Under some conditions lactation may be affected while all other functions, including reproduction, remain normal. T. H. P.

**Absence of a second phase in milk secretion.** S. FILIPOVIC (Milch. Zentr., 1934, 63, 1—4, 17—20, 29—33).—The work of Isaachsen is refuted.

E. B. H.

**Nutritional deficiencies of cow's milk and various milk preparations.** E. GLANZMANN (Z. Vitaminforsch., 1934, 3, 2—27).—Young rats fed for a year solely on full-cream milk or milk powder showed subnormal growth, atrophy of the sexual glands, sterility, and lactational deficiency; rickets did not occur. When glass cages were used, there occurred an alimentary anaemia which was cured by administration of Fe+Cu, but not by either alone. A supplement of 0.05% Mn to the diet removed the lactation deficiency, whilst addition of black bread restored growth, fertility, and lactation. A diet of sweetened (but not of unsweetened) condensed milk caused pellagra, which was cured by feeding coagulated ovalbumin. Separated milk powder was still more inadequate, glucose or sucrose being necessary to correct the deficiency of fat. Buttermilk powder produced a protein intoxication which ultimately proved fatal.

F. O. H.

**Effect of milk products on  $p_H$  of intestinal contents of domestic fowl.** D. W. ASHCRAFT (Poultry Sci., 1933, 12, 292—298).—Rations containing milk products [20% and 40% buttermilk (I), 28% dried whey (II), 40% dried skim milk (III), and 20% lactose (IV)] as compared with a ration containing 20% meat scrap increased the  $p_H$  of the duodenal contents from 5.96 to 6.23—6.5, and that of the ileal contents from 7.13 to 7.16—7.68. The  $p_H$  of the caecal contents, however, fell from 7.06 to 5.1—6.7, and that of the contents of the large intestine from 7.26 to 7.04—6.28; 20% (IV) was the most effective agent, followed in order by (III), (II), and (I). The effect produced

was not proportional to the (IV) content of the ration.

NUTR. ABS. (b)

**Rôle of the mineral salts of milk in nutrition.**

O. B. WANSCHENK and E. J. DOLAN (Med. J. Rec., 1933, 138, 172—173).—Protein-Ca, extracted from sour whey, obtained in the manufacture of cream cheese, should be added to sweet whey from renneting in order to restore its mineral balance. The product is of high nutritive val. either in the liquid or the dried state.

NUTR. ABS. (m)

**Iodine content of milk. I. Effect of desiccation and storage.** Z. M. HANFORD, G. C. SUPPLEE, and R. E. REMINGTON. **II. Variation in the mixed milk of herds.** R. E. REMINGTON and G. C. SUPPLEE (J. Dairy Sci., 1934, 17, 15—18, 19—28).—I. The I content of milk dried either by the roller process or by slow evaporation after addition of NaOH was 60—80% of the initial val. Drying (by either process) of milk to which free I had been added resulted in the retention of approx. 83% of the total initial I. Changes in acidity within the range suitable for roller-drying did not influence the amount of I retained. No loss of I from dried milk occurred during storage for 7 months.

II. The average I content of 117 samples of milk from various sources was  $572 \pm 16$  pts. per  $10^{12}$ . Variations due to locality and season are recorded.

A. G. P.

**Crystalline globulin from the albumin fraction of cow's milk.** A. H. PALMER (J. Biol. Chem., 1934, 104, 359—372).—After removal of the caseinogen, the whey is conc. by freezing and the globulin fraction removed by pptn. with  $\text{Na}_2\text{SO}_4$  (18 g. per 100 c.c.). The filtrate at  $30^\circ$  again treated with an equal amount of  $\text{Na}_2\text{SO}_4$  gives a ppt. which, when dissolved in  $\text{H}_2\text{O}$  and dialysed at  $p_{\text{H}}$  5.2, yields a cryst. protein (I). Since this is insol. in salt-free  $\text{H}_2\text{O}$  between  $p_{\text{H}}$  4.5 and 5.5, it is considered to be a globulin. Solubilities of (I) in salt solutions are recorded. The distribution gives vals. similar to those for lactalbumin.

A. L.

**Pus in milk.** F. WIEDMANN (Z. Unters. Lebensm., 1934, 67, 174—178).—In certain cases, e.g., advanced mastitis, the Tromsdorff (T) sediment consists largely of casein (I) and its vol. is therefore no indication of the pus content of the milk. (I) is removed by digestion for 5 min. with pepsin and HCl, the sediment centrifuged again in the T tube, and its vol. measured. Normal milks having T vals. (T.V.) between 0.1 and 0.6 have Wiedmann vals. (W.V.) between 0.05 and 0.3. Milk from a cow suffering from advanced mastitis had a T.V. of 300—400, a W.V. of 5—7. Pasteurisation increases the T.V. from a mean of 0.3 to a mean of 1.0, the W.V. remaining unaltered.

E. C. S.

**Albuminuria in the normal male rat.** M. E. BELL (J. Physiol., 1933, 79, 191—193).—A protein, coagulable by heat, was found in the urine of normal adult male rats, in a concn. of 0.5—0.8 g. per litre. The protein was not identified, and was not present in the urine of female rats on the same régime.

NUTR. ABS. (b)

**Determination of urobilin in urine by Terwen's method.** (MLLE.) CHRISTOPHE (J. Pharm. Chim., 1934, [viii], 19, 105—111).—Details are given for

determining urobilin ( $> 1$  mg. per litre) in urine within  $\pm 5\%$ , with special directions for urine containing albuminoids and indole. The presence of novocaine invalidates the method.

R. S. C.

**Detection and determination of the bile acids in urine.** G. RANZOLI (Boll. Chim. Farm., 1934, 73, 81—83).—A review of the surface tension methods. A 5-c.c. microburette, with a tap calibrated to deliver 5 c.c. of distilled  $\text{H}_2\text{O}$  in 100 drops at  $15^\circ$ , is recommended as a substitute for the Duclaux drop-counter.

R. N. C.

**Rennin content of infants' urine.** G. SERÉNYI and L. VESZELSZKY (Orvosi Hetilap, 1933, 77, 757—759).—Urine (I) of infants contains no rennin (II) when they are fed with human milk. If about half of the necessary milk is replaced by other food, (II) appears in the (I). This also occurs, independently of the food ingested, in toxicosis.

NUTR. ABS. (m)

**Iodometric determination of cystine in urine.** R. W. VIRTUE and H. B. LEWIS (J. Biol. Chem., 1934, 104, 415—421).—The method of Okuda (A., 1929, 730) requires, as optimal conditions for reaction, low temp., 2% HCl, and only a min. excess of I. In applying the method to determinations in urine the latter is decolorised with norit. Satisfactory recovery vals. for added cystine were obtained.

H. D.

**Excretion of ammonia and neutrality regulation.** A. P. BRIGGS (J. Biol. Chem., 1934, 104, 231—238).—Administration of KCl causes the urine to become more alkaline, because of excretion (I) of more fixed base (II) than mineral acid (III), with diminished (I) of  $\text{NH}_3$ .  $\text{Na}_2\text{SO}_4$  causes (I) of more (III) than (II) with an increased (I) of  $\text{NH}_3$ . It is suggested that the mechanism of (I) of  $\text{NH}_3$  is not controlled by acid-base changes in the tissues.

H. G. R.

**Fixation of, and chemical and optical methods of staining, urinary sediments. Permanent preparations.** P. SCHUGT (Pharm. Ztg., 1934, 79, 228—231).—The choice of a fixative and the techniques involved in chemical and optical methods of staining urinary sediments are discussed.

P. G. M.

**Sugar tolerance in experimental acidosis and the effect of insulin and vitamin-B.** S. TATSUZAWA (Sci-i-kwai Med. J., 1932, 51, No. 8, 1—16).

CH. ABS.

**Production of acidosis and alkalosis by salts and diet.** H. DENNIG, H. J. GOTTSCHALK, and L. TEUTSCHER (Arch. exp. Path. Pharm., 1934, 174, 468—475).—Diets yielding an acidic or basic ash produce in man a slight acidosis (I) or alkalosis (II), respectively. Soya-bean meal produces a fairly marked (II), but in all cases relatively small amounts of acid- or base-forming salts influence the result.  $\text{NH}_4\text{Cl}$  and Na citrate have an influence on (I) and (II)  $>$  those of  $\text{CaCl}_2$  and  $\text{NaHCO}_3$ , respectively.

F. O. H.

**Sulphur content of hair and nails in abnormal states. Therapeutic value of hydrolysed wool.** I. Hair. H. BROWN and J. V. KLAUDER (Arch. Dermatol. Syph., 1933, 27, 584—604).—Hair normally contains 4.6—5.1 (average 4.86)% S. In alopecia areata it contains 4.38%, and after hydrolysed wool



therapy 5.5%. Loss of hair is not necessarily associated with low S. The metabolism of S (cystine) is not exclusively concerned in hair loss. Dietary deficiency as a cause of hair loss is more apparent in laboratory animals than in man. CH. ABS.

**Calcium and inorganic phosphorus in the blood in arthritis with ankylosis.** J. MORELLE (Rev. belge Sci. méd., 1933, 5, 417—425).—In arthritis deformans, rhizomelic spondylitis, and vertebral rheumatism, serum-Ca (I) usually exceeds 11 mg. per 100 c.c. Plasma-phosphate is within normal limits and does not vary inversely with (I).

NUTR. ABS. (m)

**Plasma-proteins, -calcium, and -cholesterol in beriberi.** G. V. VILLELA (Compt. rend. Soc. Biol., 1933, 113, 1277—1279).—In five cases of wet beriberi the serum-albumin rose with the disappearance of œdema, whilst the serum-globulin was unchanged. Ca and cholesterol were normal in seven cases.

NUTR. ABS. (b)

**Soil and mineral supplements in the treatment of bush sickness.** T. RIGG and H. O. ASKEW (Empire J. Exp. Agric., 1934, 2, 1—8).—Sheep in bush-sick areas were maintained in perfect health by drenching with a suspension of a soil containing 6% of  $Fe_2O_3$  sol. in  $H_2C_2O_4$ . Except in one instance drenching with  $Fe^{III} NH_4$  citrate prevented sickness, but the wts. of sheep varied considerably under experiment. Suspensions of limonite were ineffective. A. G. P.

**Experimental production of cancer by dust obtained from tarred roads.** J. A. CAMPBELL (Lancet, 1934, 226, 233—234).—Road dust containing approx. 2% of tar causes cancer of the skin in mice with metastases sometimes in the lungs.

L. S. T.

**Prevention of mineral oil and tar dermatitis and cancer.** C. C. TWORT and J. M. TWORT (Lancet, 1934, 226, 286—287).—Textile grades of mineral oil are, on the whole, the most carcinogenic. Internal-combustion lubricating oils are of relatively low carcinogenic power (I), and "spirits," whilst capable of causing dermatitis, had no (I). In crude oils, (I) varies markedly with the geographical source, and, in general, is less the more fully hydrogenated is the oil. Treatment with  $H_2SO_4$  or  $SO_2$ , or, in general, any process which tends to hydrogenate or saturate the oils decreases (I). Refractivity is closely related to (I), and in most cases its determination can replace animal tests. Where exposure to carcinogenic oils is unavoidable, protection of exposed surfaces by lanolin and olive oil is effective. L. S. T.

**Serum-calcium, -potassium, and -inorganic phosphate in cancer. Effect of X-ray irradiation.** H. JACKSON, jun., and F. H. L. TAYLOR (Amer. J. Cancer, 1933, 19, 379—388).—Blood-Ca was normal in 52% and low in 48% of cases. Low vals. appear to result from disturbed nutrition associated with advanced carcinoma. Vals. for K and inorg.  $PO_4$  were normal. After X-ray therapy K, Ca, P, Ca : P, and K : P were unaltered. CH. ABS.

**Possibility of glycolysable haptene in tumour.** W. R. FRANKS (Trans. Roy. Soc. Canada, 1933, [iii],

27, V, 135—140).—Attempts to demonstrate the presence of a glycolysable haptene in mouse tumour or Rous sarcoma failed. F. O. H.

**Cataract as a result of dietary deficiency in larval *Amblystoma tigrinum*.** E. M. PATCH (Science, 1934, 79, 57—58).—In larvæ of the tiger salamander fed on highly-purified milk powder-casein diets the lenses of the eyes turn milky-white, and pass through stages like those of senile cataract of the cortical type. The disease is due to inadequacy of the basic milk diet, and is not prevented by an increase in vitamin-A or  $-B_2$ . L. S. T.

**Blood- and skin-cholesterol in dermatoses with atypical keratosis.** T. CHORAZAK (J. Physiol. Path. gén., 1933, 31, 408—413).—In psoriasis, eczema, lupus, etc. administration of Ca, As, or fat or ultra-violet irradiation causes increase in skin- (I) and blood- (II) -cholesterol. No direct relationship between (I) and (II) can be traced, but there is a well-defined relation between (II) and Ca content.

NUTR. ABS. (m)

**Abnormalities of calcium deposition in diabetes mellitus.** H. F. ROOT, P. WHITE, and A. MARBLE (Arch. Int. Med., 1934, 53, 46—53).—Diabetes may be accompanied by osteomalacia and by abnormal Ca deposits in the body. Adequate Ca intake is essential. W. O. K.

**Availability of fructose in normal and diabetic animals.** M. ABE (J. Biochem. Japan, 1934, 19, 69—110).—With normal dogs the min. amount of fructose (I) necessary to cause fructosuria (II) is < that of glucose (III) necessary to cause glycosuria; the degree of hyperglycæmia (IV) is also lower with (I) than with (III). Hence the renal threshold (V) for (I) is low compared with that for (III). With diabetic dogs, (V) is increased, and the degree of (II) and (IV) indicates that the diabetic organism utilises (I) more readily than (III). F. O. H.

**Choline and liver-fat in diabetic dogs.** C. H. BEST, G. C. FERGUSON, and J. M. HERSHEY (J. Physiol., 1933, 79, 94—102).—In depancreatized dogs on a lean beef diet plus vitamins, the symptoms associated with accumulation of liver-fat (I) and degeneration of liver cells, were prevented by giving choline. The decrease in (I) which also occurred was sometimes accompanied by increased sugar excretion. NUTR. ABS. (b)

**Liver and the respiratory metabolism of pancreatic diabetes.** G. C. RING and C. W. HAMPEL (Amer. J. Physiol., 1933, 105, 306—310).—The raised metabolism (I) of the depancreatized cat persists after the formation of an Eck fistula or the removal of 50—70% of the liver tissue. It seems unlikely, therefore, that processes occurring in the liver are responsible for the high (I), and the results support the previous conclusion that protein catabolism is not alone responsible. NUTR. ABS. (b)

**Protein metabolism in pancreatic diabetes.** G. C. RING and C. W. HAMPEL (Amer. J. Physiol., 1933, 105, 300—305).—Following pancreatectomy, with insulin administration, in most cases the post-absorptive urinary N excretion (I) of cats was increased, although the metabolism (II) was normal; withdrawal of insulin produced the usual rise of (II),

but no significant increase of (I). The raised (II) of the diabetic cat is not completely explained by the sp. dynamic action of protein. NUTR. ABS. (b)

**Hyperglycæmia, glycosuria, and the respiratory quotients following insulinisation of non-diabetics.** W. D. PAUL, B. B. CLARK, and C. MARTIN (Amer. J. Physiol., 1933, 105, Proc. 79).—Non-diabetic individuals on mixed diet tolerate insulin (I) up to 75 units daily, without hypoglycæmia. On discontinuing (I), glucose-tolerance curves of a mild diabetic type are obtained, together with lowered R.Q. Return to the normal state is progressive over several days. NUTR. ABS. (m)

**"Fatty diarrhoea," with special reference to nitrogen metabolism.** A. G. ANDERSON and A. LYALL (Quart. J. Med., 1933, 2, 339—351).—Although both types of fatty diarrhoea showed a grossly negative total N balance, only in the type with a pancreatic lesion was there high N excretion by the bowel. NUTR. ABS. (b)

**Chemical composition of exudates.** J. S. HEPBURN and H. B. FEGLEY (Amer. J. Pharm., 1934, 106, 16—17).—A pleural exudate and a peritoneal exudate (I) contained, respectively, total solids 5.96, 5.64; moisture 94.04, 94.36; ash 0.40, 0.48; fat 0.72, 0.83; total N 0.03, 0.20. Neither contained blood; (I) contained amylase but not esterase. W. O. K.

**Reduced glutathione content of organs in artificially-produced fever [in dogs].** L. BINET and G. WELLER (Compt. rend. Soc. Biol., 1933, 113, 124; Chem. Zentr., 1933, ii, 1200).—Intravenous injection of  $\text{ONa}\cdot\text{C}_6\text{H}_5(\text{NO}_2)_2$  in dogs produces a rise in temp. to 44°. The SH-glutathione content of the liver is markedly increased, whilst those of the spleen and lungs are decreased. L. S. T.

**Blood-sugar in scarlet fever, measles, and varicella.** L. MANZONI (Riv. clin. pediatr., 1932, No. 12).—Blood-sugar rises during the febrile stage of scarlet fever and measles. No change was found in varicella. CH. ABS.

**Diazo-urine. III. Composition of urine in scarlet fever. IV. Composition of urine in measles.** S. NAKAYAMA (J. Biochem. Japan, 1934, 19, 33—38, 39—43; cf. A., 1927, 170).—III. 9.7 litres of diazo-urine (I) from scarlet-fever patients yielded 7.18 g. of antoxyproteic acid (II) (A., 1906, i, 122), 1.07 g. of oxyproteic acid (III), 0.02 g. of histidine (IV), 0.08 g. of arginine (V), 0.25 g. of lysine (VI), and  $(\text{NH}_2)_1$ -acids equiv. to 0.56 g. of N.

IV. 6.8 litres of (I) from measles patients yielded 6.5 g. (as Ba salt) of (II), 4.5 g. (as Ba salt) of (III), 0.08 g. (as picrolonate) of (IV), 0.32 g. (as picrate) of (V), and 0.55 g. (as picrate) of (VI). F. O. H.

**Goitre and drinking water in Switzerland.** T. VON FELLEBERG (Mitt. Lebensmitt. Hyg., 1933, 24, 123—142; Chem. Zentr., 1933, ii, 1201).—No relation between the frequency of goitre (I) and the I content or the inorg. constituents could be established for the 57 principal tap  $\text{H}_2\text{O}$  (II), which were poor in I (0.2 to  $1.8 \times 10^{-8}$  g. per litre). In general, but not invariably, (I) increases with an increase in wt. of dried residue from (II), and especially with hardness. It

decreases with the age of the geological formation from which the  $\text{H}_2\text{O}$  is drawn. Since the places supplied with lake  $\text{H}_2\text{O}$ , in spite of the softness of the  $\text{H}_2\text{O}$ , are not free from (I), it appears that factors other than hardness which partly decrease with age of the rocks are responsible for (I). An Fe-containing (II) lost most of its I in the removal of Fe by de-aeration. L. S. T.

**Lactic acid metabolism in disturbed thyroid function. I. Variations in blood-lactic acid after injection of lactate. II. Lactic acid and gas metabolism during muscular work. III. Lactic acid metabolism in the liver after injection of lactate.** K. KATO (Tôhoku J. Exp. Med., 1933, 21, 238—256, 257—279, 280—297).—I. Oxidation and resynthesis of intravenously injected Na lactate are disturbed in hyperthyroid and thyroidectomised rabbits, and in exophthalmic goitre.

II. Increase in blood-lactic acid and  $\text{O}_2$  consumption caused by muscular contraction in hyperthyroid is  $>$  in normal animals. Resynthesis of lactic acid (I) is delayed. The effect of exercise in thyroidectomised rabbits is normal.

III. (I) is resynthesised to glycogen during its passage through the liver. Normal (I) vals. are: arterial  $>$  portal  $>$  hepatic venous; hyperthyroid vals. are: venous  $>$  portal  $>$  arterial, glycogen being mobilised more rapidly than it is synthesised. CH. ABS.

**Blood-catalase in heart disease. I.** J. C. HEALY and H. BAKER (J. Lab. Clin. Med., 1933, 19, 133—141).—Blood-catalase is increased in rheumatic heart disease and scarlatinal endocarditis, and normal in cases of scarlet fever and diphtheria which show no heart damage. CH. ABS.

**Quantity of the glomerular filtrate. II. Cardiac insufficiency and hypertension.** F. NAKAZAWA, J. IZUMI, and I. SEKI (Tôhoku J. Exp. Med., 1933, 22, 159—166).—In cardiac decompensation and in hypertension with kidney disease the quantity of glomerular filtrate and creatinine excretion decrease. CH. ABS.

**Possibility of a pressor principle in the blood in hypertension.** A. H. ELLIOT and F. R. NUZUM (J. Lab. Clin. Med., 1933, 18, 1255—1260).—Intravenous injection of large amounts of fresh citrated blood from normal persons into rabbits usually produces a transitory rise in blood-pressure followed by a prolonged fall. Injection of blood from patients with hypertension produces a higher initial rise. Injection of EtOH, Et<sub>2</sub>O, and  $\text{H}_2\text{O}$ -sol. fractions of blood cause a transitory fall. CH. ABS.

**Blood-sugar in experimental hypertension.** E. NETER (Klin. Woch., 1933, 12, 1317—1318).—Since section of the aortic nerves and the nerves of the carotid sinus of rabbits and dogs has usually no effect on the blood-sugar, the view that the rise of blood-pressure in these circumstances is due to adrenalinæmia is not supported. NUTR. ABS. (m)

**Colloid-osmotic pressure of the blood in normal and pathological conditions. VIII. Hunger.** J. HATAFUKU and F. NAKAZAWA (Tôhoku J. Exp. Med., 1933, 21, 226—237).—Blood-protein (I) in fasting dogs is increased, but the colloid-osmotic pres-

sure (II) per unit protein first decreases and then increases. In hyperthyroid dogs (I) increases and (II) decreases, hunger producing an increase in both factors.

CH. ABS.

**Hunger hypoglycæmia in infants. III. Blood-sugar following administration of acid or alkali during fasting.** H. SCHÖNFELD (Jahrb. Kinderheilk., 1933, 140, 215—218).—Administration of 0.1N-HCl or -NaHCO<sub>3</sub> during a hunger period of 4 or 16 hr. decreases the fall in the fasting blood-sugar level. The cause may be reduced glycolysis in the tissues.

NUTR. ABS. (m)

**Disturbances of metabolism in acute under-nutrition in infants. III. Creatine excretion and basal metabolism. IV. Creatine excretion and specific dynamic action.** L. GAROT (Rev. franç. Pédiat., 1933, 9, 273—312, 313—333).—III. Determinations of the basal metabolic rate (I) in healthy infants and those in the first stage of hypothyrepsia yield vals. (47.8—57.6; average 51.0 g.-cal. per kg. actual wt. per 24 hr.) very similar to those obtained by Benedict and Talbot. In those infants in the second stage of hypothyrepsia the vals. of group A with a normal excretion of total creatinine compounds are high, whilst in group B with reduced excretion of creatinine the (I) is reduced. In group B there is a qual. as well as a quant. disturbance (II) of metabolism, whereas in group A the increase in (I) per kg. body-wt. is due to loss of "inactive" tissue and not to any change in the metabolic processes. The use of wt. loss as a criterion of hypothyrepsia is valueless, since it is no indication of the nature of (II).

IV. In healthy infants receiving buttermilk containing 5% of maltose the sp. dynamic action (III) is 20% of the basal metabolism, lasting for 3 hr. after the ingestion of the feed. In hypothyrepsia of the second stage (III) is increased (25.2—30.7%) in group A. In group B (III) is markedly reduced (6.7%).

NUTR. ABS. (m)

**Colloid-osmotic pressure of the blood in normal and pathological conditions. VIII. Experimental ileus.** J. IZUMI (Tohoku J. Exp. Med., 1933, 22, 149—158).—In rabbits the serum-protein increases, but the colloid-osmotic pressure per unit protein decreases.

CH. ABS.

**Effect of obstruction of the bile-duct on the bilirubin content of serum and on the number of erythrocytes.** A. VISCHER (Biochem. Z., 1934, 268, 116—120).—In rabbits the very low (< 0.1 mg. per 100 c.c.) bilirubin content of the blood-serum increases greatly (> 10-fold in 24 hr.) when the duct is obstructed.

W. McC.

**Liver insufficiency and amino-acid metabolism.** K. HOESCH and C. STEVERT (Klin. Woch., 1933, 12, 1357—1358).—The intravenous injection of 1.0 g. of glycine followed by the determination of free and combined NH<sub>2</sub>-N and blood-urea is a suitable test of liver function. In liver injury the primary rise of free NH<sub>2</sub>-N is prolonged, and the subsequent rise of combined NH<sub>2</sub>-N and blood-urea delayed.

NUTR. ABS. (b)

**Galactose in physiological and pathological conditions. V. Significance of galactose and glucose in the blood after ingestion of galactose**

**for the diagnosis of liver function.** H. KOSTERLITZ (Z. ges. exp. Med., 1933, 90, 465—478).—After ingestion of 40 g. of galactose (I) by healthy subjects the blood-(I) rose to about 40 mg. per 100 c.c. (max. 63) in 1 hr., falling to nil at 2 hr.; blood-glucose (II) rose by 40 mg. per 100 c.c. In icterus simplex the (I) rose to 150 mg., whilst the rise in (II) was normal or less. In diabetes mellitus the rise of (I) was normal, that of (II) excessive. In hepatic diseases the (I) curve was abnormal only when there was cellular damage. In Graves' disease the curve may be normal or of the hepatic or diabetic types. Ordinarily examination of the urine for (I) after ingestion of (I) suffices as a test, but a blood curve gives more information.

NUTR. ABS. (b)

**Diagnostic value of serum-protein changes in kala-azar.** M. R. G. MUDALUJAR, S. K. SUNDARAM, and A. S. RAMACHANDRAN (Indian J. Med. Res., 1933, 21, 361—378).—Serum-globulin increases, -albumin decreases, and -eu-: -total globulin increases. Determinations of serum-protein and -albumin: -globulin are valuable, but not diagnostic.

CH. ABS.

**Lipolytic activity of rat lepromas during treatment with various antileprotics.** G. EMERSON, H. H. ANDERSON, and C. D. LEAKE (Proc. Soc. Exp. Biol. Med., 1933, 31, 18—20).—The low lipase content of rat lepromas and of other tissues of infected rats is probably due to the invasion of normal tissue by *Mycobacterium lepræ muris*. The lipolytic activity of lepromas was unchanged by treatment with various antileprotics.

CH. ABS.

**Derivatives of 8-aminoquinoline as anti-malarials. III.**—See this vol., 417.

**Mechanism of Henry's reaction [for paludism].** V. CHORNE and R. GILLIER (Ann. Inst. Pasteur, 1934, 52, 193—216).—This reaction depends on the state of non-equilibrium between dissolved substances (slightly sol. in distilled H<sub>2</sub>O) and the mol. concn. of the serum. Dialysis increases the ability to undergo flocculation, whilst addition of salts diminishes it. In paludism globulins and the Et<sub>2</sub>O-sol. substances of the serum are increased, and negative sera become "positive" on addition of globulin, lecithin, cholesterol, or uric acid. No sp. antibody is involved and melanin serves merely as a suitable indicator.

P. G. M.

**Osteitis deformans.** H. D. KAY, S. L. SIMPSON, and G. RIDDOCH (Arch. Int. Med., 1934, 53, 208—248).—During osteitis deformans the contents of fat and org. matter of the bones increase, whilst the ash content decreases. The % Ca and Mg are < normal. Whilst the serum-Ca and -P are approx. normal, the serum-phosphatase is markedly increased. A retention of Ca, Mg, and P in the body, but a loss of S, occur.

F. O. H.

**Blood in normal pregnancy. II. Hæmoglobin, hæmatocrit, and erythrocyte determinations.** W. J. DIECKMANN and C. R. WEGNER (Arch. Int. Med., 1934, 53, 188—207).—During pregnancy in women, the hæmoglobin (I) per kg. body-wt. slightly increases, but the (I) per 100 c.c. of blood decreases by a max. of 15% (26th to 35th week); at 2 and 8 weeks *post partum*, it is 17 and 14%, respectively, < normal. Similar changes occur in the

hæmatocrit val. (II) and the erythrocyte count. Although (I) and (II) experience a relative decrease, there is an abs. increase in both owing to the large increase in plasma vol. Thus the total amount of (I) shows an average increase of 13% and of (II) 20%.

F. O. H.

**Choline in the human uterus in pregnancy and non-pregnancy; relations between the choline content of the human uterus and uterine contraction.** L. CATTANEO (Atti R. Accad. Lincei, 1933, [vi], 17, 968—973).—The results of previous workers and those now given indicate that choline cannot be regarded as a normal constituent of either the pregnant or the non-pregnant uterus, and that the hypothesis that choline is the hormone of uterine peristalsis is without foundation.

T. H. P.

**Sexual hormone in women with gynæcological diseases, particularly menstrual disturbance.** R. BOMPIANI (Rass. Clin. Terap. Sci. aff., 1933, 31, 149—158; Chem. Zentr., 1933, ii, 2155).—Zondek and Aschheim's reaction 3 is almost exclusively confined to pregnancy. Reaction 1 is frequently given by women with carcinoma of the genital organs, after surgical and X-ray castration, after the natural menopause, and in anomalous menstrual function.

A. A. E.

**Carbohydrate metabolism in pruritus and chronic urticarias.** J. G. PRIETO and M. G. REY (Arch. med. cirurg. espec., 1932, 35, No. 52).—Hypoglycæmia was found in 10 of 16 cases.

CH. ABS.

**Investigation of scalding.** S. NICOLAU and P. POINLOUX (Ann. Inst. Pasteur, 1934, 52, 217—240).—In the blood of rabbits which have been scalded an increase in the no. of mononuclear and primordial cells can be observed, together with a slight increase in Türk cells and the appearance of some Rieder cells. A toxin appears in the blood which, on intraperitoneal injection in mice, causes death; it is also present in the liver. The blood exhibits a definite flocculation phenomenon.

P. G. M.

**Silicic acid content of the lungs of quartz workers in Styria.** H. LIEB and E. SCHADENDORFF (Arch. Gewerbepath. Gewerbehyg., 1933, 4, 576—579; Chem. Zentr., 1933, ii, 2701).—SiO<sub>2</sub> constituted 0.3—1.46% of the dry residue or 4.6—22.8% of the ignited residue from the lung, the normal vals. being 0.08—0.21% and 1.28—4.0%, respectively.

H. J. E.

**Effect of splenectomy on blood-calcium and -potassium.** L. BOUISSET and G. DUCLOS (Compt. rend. Soc. Biol., 1933, 113, 1358—1360).—The alkali reserve (I) and the total and plasma-Ca of the blood of dogs fall slightly after splenectomy, the vals. returning to normal after about 45 days. No regular variations occur in the K content of whole blood or plasma. The changes occurring in (I) and Ca may be associated with the hypertrophy of Aselli's pancreas and the hæmal glands associated with the digestive tract.

NUTE. ABS. (m)

**Cerebrospinal fluid-sugar and -chlorides in neurosyphilis.** G. BREWER (Amer. J. Syphilis, 1933, 17, 382—386).—The normal ratio cerebrospinal fluid: blood-sugar is 0.647, and of Cl' 1.48. The Cl' ratio is significantly decreased in neurosyphilis only in severe meningeal irritation or damage; in general

paresis the average ratio is 1.36. The sugar ratio (in paresis 0.519) tends to decrease with increasing meningeal damage.

CH. ABS.

**Relation of amino-acid-nitrogen to the Wassermann reaction.** G. BREWER (Amer. J. Syphilis, 1933, 17, 221—227).—In neurosyphilis the blood: cerebrospinal fluid-NH<sub>2</sub>-acid-N was 0.261 (0.171—0.335); normal vals. were 0.260 (0.163—0.431). NH<sub>2</sub>-acid-N is apparently not related to the Wassermann reaction.

CH. ABS.

**Vitiation of the Wassermann reaction and other reactions by tannic acid from cork stoppers of sample tubes.** F. PLAUT (Münch. med. Woch., 78, 1125—1126; Chem. Zentr., 1933, ii, 2693).—Interference with the Wassermann reaction and protein and colloid reactions of blood and cerebrospinal fluid may occur. The use of rubber stoppers is recommended.

H. J. E.

**Cork and complement binding.** W. RIMPAU and G. SCHNEIDER (Zentr. Bakt. Par., 1932, I, 124, 568—571; Chem. Zentr., 1933, ii, 2694).—Plaut's results (see above) were not confirmed.

H. J. E.

**Cork and complement binding.** F. PLAUT (Zentr. Bakt., Par., 1932, I, 126, 135—137; Chem. Zentr., 1933, ii, 2694).—A reply to Rimpau. Tannic acid solutions and aq. extract from cork are shown to hinder hæmolysis in the complement-binding reaction.

H. J. E.

**Mapharsen (*m*-amino-*p*-hydroxyphenylarsine oxide) as an antisyphilitic agent.** A. L. TATUM and G. A. COOPER (J. Pharm. Exp. Ther., 1934, 50, 198—215).—The max. tolerated and min. lethal doses, and therapeutic index of mapharsen (I), for rats, rabbits, cats, and dogs, were const., whereas those of mixtures such as the arsphenamines (II) varied considerably. Slow oxidation of (I) reduced the toxicity, whilst those of (II) were increased. In experimental syphilis in rabbits, (I) had a curative action in 1/30 the amount of neoarsphenamine required. The single sterilising dose of (I) was 6 mg. per kg.

R. N. C.

**Glucose-tolerance curves in pulmonary tuberculosis.** D. W. KRAMER (J. Lab. Clin. Med., 1933, 18, 1212—1220).—Tolerance for glucose is increased. High or diabetic types of curve were found in 17%, low curves in 24%, and normal curves in 59% of the 100 patients examined.

CH. ABS.

**Serum-proteins in pulmonary tuberculosis.** I. SATO (Tôhoku J. Exp. Med., 1933, 22, 116—125).—The globulin: albumin ratio increases.

CH. ABS.

**Vitamin therapy in pulmonary tuberculosis. III. Effect of viosterol on absorption, retention, and excretion of calcium.** P. D. CRIMI, J. W. STRAYER, H. L. WATSON, and G. HEIMANN (Amer. Rev. Tuberc., 1933, 28, 202—216).—During early administration, in man, urinary Ca (I) and faecal Ca (II) decrease; on continued administration serum-Ca and (I) increase, whilst (II) decreases.

CH. ABS.

**Auto-antibodies in tuberculosis.** O. FISCHER (Z. Tuberk., 1933, 68, 5—6).—Certain tuberculous sera gave a positive complement fixation reaction with EtOH lung extracts. The reaction may be due to the presence of lung-lipin antibodies in the sera or to serum lability.

CH. ABS.

**R and S types of tubercle bacilli in pulmonary tuberculosis.** G. B. REED, C. E. RICE, and J. H. ORR (Trans. Roy. Soc. Canada, 1933, [iii], 27, V, 225—227).—The ratio of the complement fixation with *S* and *R* tubercle bacilli antigens ("S/R index") (cf. following abstract) is high in active tuberculosis in man, but low in chronic or improving cases. F. O. H.

**Complement-fixing antibodies in rabbits immunised with *S* and *R* tubercle bacilli.** G. B. REED, C. E. RICE, and B. G. GARDINER (Trans. Roy. Soc. Canada, 1933, [iii], 27, V, 219—224).—The serum of rabbits treated with heat-killed *S* bacilli gives approx. twice as much complement fixation (I) with *S* antigens (II) as with *R* (II). Parallel experiments with *R* organisms, however, yield the same degree of (I) with both *S* and *R* (II). Hence the *S* type contains two (II), one *S*-sp. which reacts only with *S* antibodies (III), and another which reacts equally with *S* and *R* (III), whilst the *R* form contains the species- but not the *S*-sp. (II). F. O. H.

**Blood-sugar in typhoid.** E. V. KASSATKIN (Wien. Arch. inn. Med., 1933, 24, 85—100).—Hypoglycæmia is common in typhoid, occurring usually after the fifteenth day, and resulting from exhaustion of glycogen reserves by starvation. A high-carbohydrate diet is therefore important.

NUTR. ABS. (m)

**Chemical processes in embryonic induction.** M. W. WOERDEMAN (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 842—849).—Introduction of suitable agents (rat and human cancer tissue, human muscle, gelatin gels containing glycogen) into the blastocœle of axolotl gastrulæ results in the formation of a secondary neural plate, in a thickening of the ectoderm, etc. Induction by localised rise of temp. occurred in only a few instances. Whilst effective inductors are generally associated with a high glycogen content or with marked glycolysis, the phenomenon probably depends on a localised change of the metabolism of the ectodermal cells (cf. A., 1933, 630, 855, 1074). F. O. H.

**Metabolism in the sea-urchin embryo.** P. E. LINDAHL (Naturwiss., 1934, 22, 105).—An inhibitory action of Li on respiration may be observed 3 hr. after fertilisation of eggs of the sea-urchin. This effect, which also occurs in yeast, is counteracted by K.

R. K. C.

**Urochrome and the part played by lyochromes in cellular respiration.** T. WAGNER-JAUREGG and H. WOLLSCHITT (Naturwiss., 1934, 22, 107; cf. Stern and Greville, A., 1933, 1324).—Urine contains very small amounts of a lumiflavin. Urochrome is not a flavin. Lactoflavin does not convert hæmoglobin into methæmoglobin: the effect observed by Stern and Greville is due to impurities or to flavin and an activator.

R. K. C.

**Tissue respiration and the indophenol-oxidase reaction of serous membranes.** K. KIYOHARA and S. KAGIYAMA (J. Biochem. Japan, 1934, 19, 59—68).—The O<sub>2</sub> consumption of various tissues (omentum, mediastinum, pericardium, mesentery, pleura, and peritoneum) of the dog and rabbit is approx. proportional to the no. of oxidase granules present.

F. O. H.

**Variations in oxidation and reduction activities of tissues with sex. V. Influence of the organs of reproduction.** S. KAGIYAMA (J. Biochem. Japan, 1934, 19, 45—58).—With embryonic, young, or adult rabbits, the oxidation and reduction activities of the tissues of the male are respectively > and < those of the female. Castration and transplanting experiments indicate that these differences are correlated with the sexual organs (cf. A., 1933, 527).

F. O. H.

**Diurnal cycle in the liver of the white rat. II. Food, a factor in its determination.** G. M. HIGGINS, J. BERKSON, and E. FLOCK (Amer. J. Physiol., 1933, 105, 177—186).—There is a diurnal cycle in the glycogen, protein, and H<sub>2</sub>O contents, and the total wt. of the liver of the white rat. The position of the two peaks in the curve is determined by the time of food intake.

NUTR. ABS. (m)

**Effects of chlorophyll in the diet of the albino rat.** F. R. EDWARDS and K. T. HOLLEY (Georgia Agric. Exp. Sta. Bull., 1932, No. 173, 1—11).—Addition of chlorophyll (I) to Sherman's diet *B* for rats produced no significant difference in body-wt. increases, although a slight lowering of the food requirement per unit gain in wt. was apparent. The major part of the ingested (I) was eliminated in the faeces as phaeophytin.

A. G. P.

**Digestibility of Steffen sugar-beet slices by fowls.** E. MANGOLD and H. BRÜGGEMANN (Arch. Geflügelk., 1933, 7, 161—170).—When 20, 25, or 40% of the total ration is replaced by the slices (I), their digestibility is < that of the normal ration. N-free extractives, which total 77% of the dry matter and include 35% sugar, give only 54% digestibility. Good results with (I) must be due to a "dietetic" effect.

NUTR. ABS. (m)

**Food value of seeds of *Vicia faba*, L. V.** ZAGAMI (Atti R. Accad. Lincei, 1933, [vi], 18, 327—329).—For growing rats these seeds are an incomplete food, being deficient in salts and in vitamin-A and -D; vitamin-B and -E are present in suitable proportions.

T. H. P.

**Biological value of proteins of peas. I. P.** TSCHUKITSCHEV and M. N. TSCHUKITSCHEV (Biochem. Z., 1934, 268, 83—92).—The proteins (I) of peas are as satisfactory for maintaining life and growth in rats as is caseinogen. The contradictory results of Osborne *et al.* (A., 1912, ii, 1190) and McCollum may be due to differences in methods of prep. and physical properties of (I).

W. McC.

**Soya-bean milk and chicken protein.** J. S. HEPBURN, K. S. SOHN, and L. P. DEVLIN (J. Franklin Inst., 1934, 217, 213—221).—Soya-bean milk (I) contains protein 3.5%, carbohydrate 0.61, fat 2.35, Ca 0.034, and P<sub>2</sub>O<sub>5</sub> 0.091 [cow's milk (II) 3—4, 4.6—5.0, 3—6, 0.120, 0.23]. (I) curdles at a lower c<sub>H</sub> than (II) and cannot replace (II) in a basal diet so efficiently, although no avitaminosis occurs. Chicken protein is a less efficient protein than caseinogen in the diet of young rats.

P. G. M.

**Relationship of the metabolic nitrogen of the faeces to body-weight and to food intake for rats.** B. H. SCHNEIDER (Biochem. J., 1934, 28, 360—

364).—The metabolic N (I) in the faeces of rats depends partly on the food intake and partly on the body-wt., but for intakes of food above a certain min. val. the ratio of (I) to the intake of dry food assumes a practically const. level. W. O. K.

**Validity of the Terroine-Sorg-Matter law on endogenous protein metabolism in cold-blooded animals.** R. BONNET (Arch. internat. Physiol., 1933, 37, 104—120).—The ratio (I) N output : respiratory exchange per kg. body-wt. per hr. is const. between 0° and 30° for turtles and frogs. The metabolism of the tortoise per kg. body-wt. at any temp. is > that of the frog. (I) approaches more closely, in the tortoise, than in the frog, to that of the homeotherms (II). Reptiles are intermediate, physiologically and biochemically, between poikilotherms and (II). NUTR. ABS. (m)

**Chemical separation of urine and faeces in birds and its use in determining the digestibility of proteins.** H. STOTZ (Arch. Tierernähr. Tierzucht, 1933, 9, 426—437).—A method for the separate analysis of faecal and urinary N in birds is based on the oxidation of uric acid from the urine by HNO<sub>3</sub>, and is utilised in determining the digestibility of cereal proteins by hens. The digestibility of crude protein in wheat (I), barley (II), oats, and rye (III), and that of the crude fibre of (II) and (III), was higher for summer than for winter varieties. In (I) the fibre of winter varieties had much the higher digestibility. A. G. P.

**Digestibility of nutrients in commonly used feeding-stuffs by hens, with special reference to protein as examined by a new method.** H. PETERS (Arch. Tierernähr. Tierzucht, 1933, 9, 438—469).—Digestibility trials with a no. of cereals and fish meal are recorded. Vals. obtained for crude protein digestibility by Stotz's method (preceding abstract) differ in some cases from those usually accepted. A. G. P.

**Fate of *dl*-methionine, glycine, *d*-glutamic acid, and *l*-pyrrolidonecarboxylic acid in the dog.** J. A. STEKOL and C. L. A. SCHMIDT (Univ. California Pub. Physiol., 1933, 8, 31—42).—In dogs receiving a const. diet, methionine caused an increased excretion of urea (I), SO<sub>4</sub>'', and creatinine (II). Both *d*- and *l*-forms were metabolised. Glycine caused an increased excretion of (I), (II), and sometimes SO<sub>4</sub>''. *d*-Glutamic acid caused an increased excretion of (I) and SO<sub>4</sub>''. Pyrrolidonecarboxylic acid had no effect on the urinary excretion beyond a decrease in the output of SO<sub>4</sub>''. It probably combined with SO<sub>4</sub>'' and was excreted in the bile. NUTR. ABS. (b)

**Formation of sulphate from cysteine and methionine by tissues *in vitro*.** N. W. PIRIE (Biochem. J., 1934, 28, 305—312).—Slices of rat liver (I) and kidney (II) (cf. A., 1933, 856) when shaken in 95% O<sub>2</sub> with a solution of cysteine (III) in NaHCO<sub>3</sub>-Ringer solution oxidise (III) to SO<sub>4</sub>'' (IV) at a rate comparable with that calc. from feeding tests with the intact animal (cf. A., 1932, 646). Cystine is oxidised only after reduction to (III), and glutathione (V) only after hydrolysis. (II) has a much greater power of oxidising (V) than (I), and its peptide-splitting enzymes make (III) available more rapidly than it can

be oxidised. Methionine (VI) is oxidised to (IV) at approx. the same rate by both (I) and (II), but much more slowly than (III), and there is little quant. relation between *in vitro* and *in vivo* rates of oxidation of (VI). Ethylcysteine is very slowly oxidised at relatively high concn. and ergothioneine and thiocarbamide not at all, nor do these last act as catalysts in the oxidation of other S compounds. Blood, testis, spleen, heart, and lung are inactive. A mechanism for the oxidation of (III) and (VI) is proposed. A modification in the technique of colorimetric micro-sulphate determination is described (cf. A., 1931, 1177).

A. E. O.

**Increase of liver-proteins by mixed diet containing a natural mixture of amino-acids.** C. GAUTIER (Bull. Soc. Chim. biol., 1933, 15, 1563—1565).—On a diet containing a natural mixture of NH<sub>2</sub>-acids and glucose the frog's liver increases in wt. by 2—4 times and the liver-proteins by 90—125%.

H. D.

**Tryptophan metabolism. IV. Influence of optical activity on the utilisation of tryptophan for growth and for kynurenic acid production.** C. P. BERG (J. Biol. Chem., 1934, 104, 373—384).—*d*- and *l*-Tryptophan (I) and acetyl-*l*-tryptophan are equally effective in promoting the growth of the rat, whilst acetyl-*d*-tryptophan is not utilised in this way. Of these substances only *l*-(I) leads to kynurenic acid excretion, acetylation reducing its convertibility very considerably. A. L.

**Effect of oral administration of creatinine on blood and urine.** J. D. S. CAMERON (Quart. J. Exp. Physiol., 1933, 23, 351—366).—On an "ordinary diet" with an average of 95 g. of protein per day the blood-creatinine (I) level was const. (1.35—1.55 mg. per 100 c.c.) with an average urinary output of 1.48 g. On a protein-free diet, the (I) was 1.15—1.55 mg. per 100 c.c. and the urinary creatinine (II) 1—1.3 g. per day. The ingestion of pure creatinine (III) was followed by a sharp rise in the (I) and (II) curves with a slow fall to normal level. The whole of the administered (III) was found in the urine within 24 hr. Raised (I) concn. alone does not cause "uræmic" symptoms. NUTR. ABS. (b)

**Nitrogen balance.** H. PÉNAU and J. GAUDUCHON (Bull. Soc. Chim. biol., 1933, 15, 1483—1497).—Intake of N in man is determined on a dried, powdered, aliquot portion of the total daily ingesta. The Dumas technique gave results > a no. of others.

H. D.

**Purine metabolism. I. Exogenous. II. Endogenous.** K. TOMITA (Sei-i-kwai Med. J., 1932, 51, No. 5, 95—136; No. 6, 37—118).—I. Feeding purine (I) to guinea-pigs does not increase uric acid excretion, although total N is proportionally increased. The average uricolytic index of the normal guinea-pig is 98.8 and the (I) coeff. 309. The end-product of (I) metabolism is allantoin (II).

II. The end-product, chiefly (II), is low in summer and high in winter. Partial removal of the liver or blockage of the reticulo-endothelial system diminishes (I) metabolism. CH. ABS.

**Purine metabolism.** J. PAROULEK (Acta med. Scand., 1933, 80, 127—135).—The peripheral tissues

in man did not absorb uric acid injected into the portal and/or peripheral veins.

NUTR. ABS. (b)

#### Real value of endogenous purine metabolism.

E. F. TERROINE and G. MOUROT (Compt. rend., 1934, 198, 772—774).—Purine metabolism accounts for only 16—23% of the purine compounds and 2% of the total N excreted by rats subjected to protein starvation.

R. S. C.

**Lipin metabolism. I. Hypercholesterolaemia in omnivora and herbivora caused by parenteral dosage with colloidal cholesterol and lecithin. I. REMESOV and N. TAVASTYERNA. II. Blood-sugar curves in carnivora and herbivora during experimental lipaemia. III. Changes in lipin metabolism caused by adrenaline, insulin, and some alkaloids. I. REMESOV and D. MATROSSOVITSCH. IV. Relation between cholesterol and carbohydrate metabolism in herbivora and omnivora. I. REMESOV and O. SEPALOVA. V. Blood-lipase in carnivora and herbivora during experimentally-produced lipaemia. I. REMESOV and N. TAVASTYERNA. VI. Influence of cholesterol on pepsin secretion. I. REMESOV and D. MATROSSOVITSCH (Z. ges. exp. Med., 76, 419—462; 77, 67—86, 87—98, 100—119; 1933, 87, 613—622, 623—624; Chem. Zentr., 1933, ii, 2695—2696).—I. Colloidal cholesterol (I) causes hypercholesterolaemia (II) in rabbits, (I) being absorbed in the lungs. Parenterally administered lecithin causes lecithinaemia in herbivora and carnivora; simultaneous (II) occurs in herbivora.**

III. Intravenous adrenaline injection causes hyperglycaemia (III) and a fall in blood-(I). A change from carbohydrate to lipin is indicated. Injection of nicotine, adonidin, and strophanthin causes similar results. Hypoglycaemia after insulin injection occurs with diminution of the blood-sugar, showing a change from lipin to carbohydrate.

IV. Intravenous injection of (I) sol with glucose and fructose solution causes strong (III) and a simultaneous fall in (I) in herbivora and omnivora. In the latter, glucose also causes (II).

V. *In vitro* and *in vivo* (I) sol hinders the action of blood-lipase (IV) in carnivora and herbivora, owing to adsorption. Reactivation of the adsorbate is caused by Mn or Ni sols. Bi sol is feebly active, Au, Pt, Fe, and Ag sols and KCNS are inactive, whilst Se and Cu have the opposite action. Lecithin inactivates (IV) *in vivo* in carnivora. Adrenaline and nicotine also inactivate (IV). Insulin strengthens the lipase action and produces hypocholesterolaemia and hypoglycaemia.

VI. (I) dissolved in oil inactivates, and in the colloidal state activates, the action of pepsin in dogs.

H. J. E.

#### Degradation of cholesterol by the animal organism. III. Excreted degradation products.

K. BOSSERT, I. H. PAGE, and W. MENSCHICK (Biochem. Z., 1934, 268, 93—103; cf. A., 1933, 857).—The faeces of rabbits and cats to which cholesterol (I) has been fed contain increased amounts of unsaponifiable matter (II) which has low m.p. and is not pptd. by digitonin. (II), which is dextrorotatory, and gives modified colour reactions of sterols, closely resembles

material extracted from hay. Although a good part of the degraded (I) is not found in (II), the increased excretion of (II) may account for part of the degradation.

W. McC.

**Fat metabolism. J. B. BROWN (Ohio J. Sci., 1933, 33, 359—371).—A review. Fatty acids of high mol. wt. undergo the same reactions as fats.**

CH. ABS.

**Fat metabolism. II. P. E. VERKADE and J. VAN DER LEE (Biochem. J., 1934, 28, 31—40; cf. A., 1933, 417).—Administration of triundecoin, trinonoin, tridecoic, or trilaurin together with adequate carbohydrate to healthy individuals gave quantities of undecanedioic, azelaic, sebacic, and dodecanedioic acids decreasing in this order. Tristridecoic gave no diacid in the urine. Thus there is no contrast in the behaviour of triglycerides of acids containing odd and even nos. of C atoms. H. D.**

**Fat metabolism. III. P. E. VERKADE and J. VAN DER LEE (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 876—887; cf. A., 1933, 417, 742).—Ingestion of the glycerides of the fatty acids, tri-octoin to trilaurin, is followed by excretion of dicarboxylic acids ("diaciduria"), especially with triundecoin and tridecoic (I); tristridecoic is not diacidogenic. No significant  $\omega$ -oxidation occurs with either "diafat" (mainly tridecoic acid or its triglyceride) or "intarvin" (A., 1930, 1206). Ingestion of the oil (II) from the seeds of *Ulmus campestris* [which contains approx. 50% of (I)], but not of coconut oil [containing mainly low fatty acids (B., 1928, 23)], produces diaciduria [mainly sebacic acid with (II)].**

F. O. H.

**Effects of high-fat diets on respiratory metabolism and ketosis. E. E. HAWLEY, C. W. JOHNSON, and J. R. MURLIN (Amer. J. Physiol., 1933, 105, Proc. 46—47).—In man and the pig R.Q. vals. too low to be accounted for by the formation of sugar from protein (max. depression of R.Q. 0.025) or glycerol (max. depression 0.003) or by the ketosis (I) produced (max. depression 0.005) occur. Using butter-fat (II), the combined effect of these factors would not account for a R.Q. < 0.69. Possible explanations of low R.Q. vals. are given and attention is directed to the sp. dynamic action of (II), to the absence of any relationship between R.Q. and (I), and to the influence of cold in producing a low R.Q.**

NUTR. ABS. (m)

**Relationship between carbohydrate and fat metabolism. H. FESTEN (Diss., Utrecht, 1933, 160 pp.).—Micro-chemical methods are given for the determination of fats (I) (fatty acids), cholesterol (II), and phosphatides (III) in 0.2—0.4 c.c. of blood. To determine the (II) content, the light petroleum extract is evaporated to dryness and saponified so as to prevent a brown discoloration in the Liebermann-Burchard test. (III) are pptd. from the EtOH-Et<sub>2</sub>O extract with COMe<sub>2</sub> and MgCl<sub>2</sub>, and H<sub>3</sub>PO<sub>4</sub> is determined in the ppt. by Tisdall's method. In normal dogs fasted for 14 hr. (I) varies between 381 and 1089, (II) between 128 and 180, and (III) between 313 and 350 mg. per 100 c.c. blood. Vals. are similar in the same animal on different days. After injection of insulin (IV) no significant change occurs in the fat**

or lipin content. After a meal of 100 c.c. olive oil, there is a rise in (I), which reaches its highest val. after 5—6 hr. After 9 hr. it falls to the initial val. or below. (II) increases and then decreases, the lowest val. corresponding with the highest for (I). A regular increase follows. After removing the pancreas, tolerance for fat is considerably diminished; it increases after (IV). NUTR. ABS. (m)

**Biochemistry and physiology of glycuronic acid.** IV. (a) Occurrence of conjugated glycuronic acids in the animal body. (b) Conjugation of *d*- and *l*-borneol. J. PRYDE and R. T. WILLIAMS. V. Site and mechanism of the formation of conjugated glycuronic acid. A. HEMINGWAY, J. PRYDE, and R. T. WILLIAMS (Biochem. J., 1934, 28, 131—135, 136—142).—IV. The normal occurrence of glycuronic acid (I) in the urine and blood of various animals is examined and a preferential conjugation of (I) *in vivo* with *d*- rather than *l*-borneol is demonstrated.

V. A technique for perfusing liver, spleen, and hind limbs in combination with the kidney is described. The main, if not the only, site of conjugation of (I) is in the liver. The process of conjugation is abolished by CN'. The hypothesis that the production of a glucoside is an intermediate stage in glycuronide formation is not supported. P. W. C.

**Carbohydrate metabolism.** J. R. MURLIN (Ohio J. Sci., 1933, 33, 335—358).—A review. Fats were converted into carbohydrates in the germinating bean and in persons having a high fat tolerance. CH. ABS.

**Carbohydrate metabolism of the warm-blooded organism in muscular activity.** E. JOKL (Pflüger's Archiv, 1933, 232, 687—702; Chem. Zentr., 1933, ii, 1290).—After running for several hr. the muscle- and liver-lactic acid (I) of rats has fallen, whilst the blood-(I) has risen; muscle- and liver-glycogen have fallen, whilst blood-sugar (II) remains const. Exhausting exercise causes a further fall in muscle- and liver-(I) and, with almost complete disappearance of the glycogen store in the muscle and liver, of (II) also. In exercise, muscle- and liver-hexose monophosphoric acid decreases, whilst phosphagen increases. A. A. E.

**Factors determining the glucose-tolerance curve.** S. SOSKIN and D. ALLWEISS (Amer. J. Physiol., 1933, 105, Proc. 89).—Sugar-tolerance tests on (a) hepatectomised dogs receiving a const. intravenous injection of glucose (I) sufficient to keep the blood-sugar level (II) const., and (b) depancreatized dogs receiving a const. intravenous injection of insulin (III) or (III) and (I) sufficient to maintain a const. (II), yield results indicating that (a) the liver plays the major rôle in determining the normal (I) tolerance curve (IV), (b) no (III) secretion, beyond that necessary to maintain a const. (II), need be predated to account for (IV). NUTR. ABS. (m)

**Abnormal sugar tolerance curves.** L. POLLAK (Wien. med. Woch., 1933, 83, 1245—1247, 1290—1292).—The alimentary rise in blood-sugar depends on the permeability of the liver to sugar (I), the rate of assimilation by peripheral organs, and the rate

of liberation of (I) by the liver. These processes cannot be separated by glucose-tolerance tests, but may be by using galactose (II). In that case blood-glucose is derived from the liver; the (II) curve measures the rate of removal of (I). NUTR. ABS. (m)

**Oxidation of glucose after fasting.** W. H. CHAMBERS and M. DANN (Amer. J. Physiol., 1933, 105, Proc. 18).—The efficacy of various foods in restoring the normal carbohydrate metabolism of the dog after a 3 weeks' fast has been studied. Improvement in the ability to oxidise carbohydrate was determined by the rise in R.Q. during the second, third, and fourth hr. following a test meal of glucose given 18—24 hr. after the food studied. The height of the R.Q. increases with the size of the carbohydrate mol. fed, *i.e.*, from monosaccharide to starch. 50 g. of wheat flour are more effective than 6 units of insulin per kg. The effects obtained are not in proportion to the vitamin-B content of the foods. NUTR. ABS. (m)

**Absorption of glucose by chronic loops of colon.** G. E. BURGET, P. H. MOORE, and R. W. LLOYD (Amer. J. Physiol., 1933, 105, 187—190).—Sugar was absorbed more rapidly from 20% than from 5 or 10% solutions, and the rate of absorption tended to increase with time. NUTR. ABS. (b)

**Absorption of glucose by closed loops of colon.** G. E. BURGET, P. MOORE, and R. W. LLOYD (Amer. J. Physiol., 1933, 105, Proc. 15).—Isotonic solutions of glucose (5%) were absorbed at a rate which increased directly with time, by a closed loop of colon; 0.7 g. of glucose was absorbed from 10 c.c. of a 20% solution per hr. The absorption is slower than for loops of small intestine. NUTR. ABS. (b)

**Serum- and muscle-phosphate changes following glucose injection.** H. POLLACK (Amer. J. Physiol., 1933, 105, Proc. 79—80).—The changes in serum-PO<sub>4</sub> during continuous injection of glucose are described for normal, adrenalectomised, dehepatized, and demuscled animals and for perfused preps. with and without insulin. NUTR. ABS. (m)

**Regulation of blood-sugar after administration of carbohydrate.** J. MELKA (Z. ges. exp. Med., 1933, 90, 22—27).—Gargling (I) with 10—20% aq. glucose (II) causes a rise of blood-sugar in only a few subjects, but in all, after 30 min., there is a fall which does not occur when the oral mucosa are anaesthetised with 5% cocaine. Ingestion of (II) after (I) causes less marked hyperglycæmia than usual both in diabetic and non-diabetic patients. The presence of (II) in the mouth produces a reflex increase in the secretion of insulin by way of the nerves of taste and the vagus. NUTR. ABS. (m)

**Conversion of glycerol into glucose by the animal organism.** F. H. LASHMET and L. H. NEWBURGH (J. Clin. Invest., 1933, 12, 968).—< 30% of glycerol, and hence only 2—3% (not 10%) of fat, is converted into glucose. NUTR. ABS. (m)

**Relation between blood-lactic acid and sugars or sugar-forming substances.** T. KOIKE (J. Biochem. Japan, 1934, 19, 111—143).—Intraperitoneal injection of glucose (I), fructose (II), mannose (III), maltose (IV), and galactose (V), but not of



lactose, arabinose, or xylose, produces in rabbits an increase in the blood-lactic acid (VI). The hyperglycaemia due to (IV) or (V) is more prolonged than that due to (I), (II), or (III). A blood-sugar (VII) level of approx. 0.20% is attained before (VI) appreciably increases; the max. of the two curves, however, occur practically simultaneously. With sorbose and glycerol, (VI) increases even when (VII) is < 0.20%, and attains higher levels than with the hexoses. With adrenaline, (VII) reaches its max. before (VI), the ratio (VI)/(VII) being < those with the sugars. Injection of Na lactate increases (VII) but does not significantly influence (VI). The mechanism of these changes is discussed. F. O. H.

**Carbohydrate metabolism of the liver. I. Glycogen and other carbohydrates in decapitate cats.** C. TSAI (Chinese J. Physiol., 1933, 7, 215—227).—Ether anaesthesia and decapitation cause a reduction in glycogen (I) and other polysaccharides in the liver (II) and a rise in (II)- and blood-sugar. With initial low (I) content, sugar in the circulation is > can be accounted for by loss from (II), and the regeneration of (I) is more rapid. H. G. R.

**Assimilation of sugar in Eck-fistula dogs. Glycosuria after administration of sugar per os or intravenously.** S. LIVIERATO, M. VAGLIANO, and A. DERVENAGA (Compt. rend. Soc. Biol., 1933, 113, 1393—1395).—Ingestion of 100 g. of glucose causes more marked hyperglycaemia (I) in Eck-fistula than in normal dogs. Lactose (70 g.) and fructose (20 g.) cause only very slight (I) and are removed in the urine. NUTR. ABS. (m)

**Assimilation of sugar in Eck-fistula dogs. Blood-sugar after administration of sugar per os.** S. LIVIERATO, M. VAGLIANO, and A. DERVENAGA (Compt. rend. Soc. Biol., 1933, 113, 1396—1398).—Glucose, either per os or intravenously, is not excreted in the urine of normal (I) or Eck-fistula (II) dogs. Lactose and fructose are excreted particularly in (II), in which also the glycogen content of the liver is < in (I). The liver of the dog retains more lactose and fructose than all the other tissues combined. NUTR. ABS. (m)

**Effect of injection of glucose on blood-sugar of normal and vagotomised pigeons.** E. MORACCI (Riv. Patol. sper., 1933, 10, 443—458).—Vagotomy (I) increases and prolongs the hyperglycaemia (II) which follows intramuscular injection (III) of glucose. When the interval between (I) and (III) is increased from 1—2 to 3—5 days, (II) is more marked, and serious general disturbance, ending in death, results. The prolonged inanition (due to the inability of the vagotomised pigeon to take food) is not responsible for these results, which are probably due to an impairment in the glycogenic function of the liver. NUTR. ABS. (m)

**Carbohydrate metabolism and specific dynamic action in partly hypophysectomised dogs.** A. G. EATON and R. G. DAGGS (Amer. J. Physiol., 1933, 105, Proc. 29).—Partly hypophysectomised dogs show a decreased glucose tolerance. Post-insulin hypoglycaemia is more prolonged in these than in normal dogs. NUTR. ABS. (m)

**Ovarian cycle and carbohydrate metabolism.** J. BLÖCH and A. BERGEL (Wien. Arch. inn. Med., 1933, 24, 29—51).—Blood-sugar in many women rises immediately preceding and during the first days of menstruation. This may be correlated with thyroid activity. NUTR. ABS. (m)

**Renal excretion of sucrose when injected intravenously in man.** N. M. KEITH, M. H. POWER, and R. D. PETERSON (Amer. J. Physiol., 1933, 105, Proc. 60—61).—After intravenous injection of 5 g. of sucrose in the adult, recovery of sugar in the urine was quant., 40% of the dose appearing in 1 hr. and 19% in the second hr. NUTR. ABS. (b)

**Metabolism of galactose. II. Behaviour of the rat towards galactose.** V. J. HARDING, G. A. GRANT, and D. GLAISTER (Biochem. J., 1934, 28, 257—263; cf. A., 1933, 307).—Galactose (I) fed to rats [1.2 g. of (I) per kg. body-wt.] disappears from the intestine almost completely within 1, and from the tissues within 3, hr. Excretion of (I) into the urine is proportionately much > in man. Muscle- and liver-glycogen formed after ingestion of (I) give only glucose on hydrolysis. No evidence of the conversion of (I) into any other reducing carbohydrate was obtained. A. E. O.

**Inositol metabolism in mammalian heart.** L. B. WINTER (Biochem. J., 1934, 28, 6—10).—Inositol (I) is determined by disintegrating the tissue with 10% KOH, clearing with Pb(OAc)<sub>2</sub>, pptn. of (I) with EtOH-Ba(OH)<sub>2</sub>, and weighing the recryst. (I) after decomp. of the Ba ppt. The method has an average error of 13%; 73% of added (I) is recovered. The (I) obtained from the heart increases with the length of treatment with KOH, and in hearts kept in N<sub>2</sub> for 90 min. at 37° was > in those immediately treated. Mincing and incubating the tissue in HPO<sub>4</sub>'' buffer increase the yield of (I). H. D.

**Wool growth in sheep as affected by the carbohydrate content of the diet.** A. H. H. FRASER and J. E. NICHOLS (Empire J. Exp. Agric., 1934, 2, 9—19).—Addition of maize starch to a maintenance ration resulted in an increase in body-wt. and gross fleece-wt. The latter was reflected in the wt. of clean wool, and was due to increased fibre thickness, a slight increase in fibre length, and possibly to a larger proportion of follicles actively elaborating fibres. A. G. P.

**Wood digestion by insect larvæ.** K. MANSOUR and J. J. MANSOUR-BEK (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 795—799).—Wood-eating larvæ are not dependent on micro-organisms for the digestion of wood. Larvæ of *Xystrocera globosa* obtain their carbohydrates from the sugar and starch in the wood, whilst *Macrotoma palmata* obtain them from the decomp. of cellulose by intestinal enzymes. The latter species can live on woods poor in sugar and starch. J. W. S.

**Chemistry of active heart-muscle.** B. WEICKER (Arch. exp. Path. Pharm., 1934, 174, 383—404).—The active surviving cold- (frog) or warm-blooded heart (I) (rabbit, cat) under aerobic conditions shows a slight rise in phosphagen (II) and a fall in lactic acid (III), whilst the adenylypyro- (IV) and hexose-phos-

phoric acids (V) remain approx. const.; under anaërobic conditions (II) and (IV) are decreased and (III) is increased. Poisoning of (I) aëroically with  $\text{CH}_3\text{I}\cdot\text{CO}_2\text{H}$  slightly lowers the  $\text{O}_2$  consumption (VI), (III) and (IV) decreasing, and the total acid-sol.  $\text{PO}_4$  increasing. Lack of  $\text{O}_2$  increases the production of (V). The fall in free adenylic acid (VII) is parallel with that in work efficiency (VIII) and with the compensatory rise in (III). Perfusion with media containing (VII) increases (VI) and (VIII) in the hypodynamic, but not in the fully active, heart.

F. O. H.

**Changes in composition of muscle, blood, and liver of the dog after muscular work.** T. CAHN and J. HOUGET (Compt. rend. Soc. Biol., 1933, 113, 1132—1133).—Prolonged exercise does not alter the  $\text{H}_2\text{O}$  or P content of muscle (I). Glycogen is greatly reduced in both (I) and liver. Lactic acid (II) is also reduced in (I), and since there is only a small increase in blood and liver, most of the (II) formed appears to be oxidised.

NUTR. ABS. (m)

**Relation between the electrical stimulation of muscle and the creatinephosphoric acid decomposition.** Y. RENQVIST and C. E. RAIHA (Skand. Arch. Physiol., 1933, 66, 78—91; Chem. Zentr., 1933, ii, 2419).—The effect of electrical stimulation of muscle is attributed to the decomp. of creatinephosphoric acid.

H. J. E.

**Muscle-calcium during calcium-free perfusion.** G. TAUBMANN (Arch. exp. Path. Pharm., 1934, 174, 476—482).—Perfusion (I) of the frog's gastrocnemius (II) with Ca-free Ringer's solution (III) does not produce a permanent loss of total or ultrafilterable Ca from the muscle. Ca is removed by (III) and the excitability of (II) decreases, but cessation of (I) is followed by a replacement of the Ca from the bone, and the response to stimulation returns to normal.

F. O. H.

**Methods of determining the degree of calcium deficiency of sheep.** A. H. H. FRASER, W. GODDEN, and D. W. AUCHINACHIE (Biochem. J., 1934, 28, 157—161).—The arrest of growth on a Ca-deficient ration is due to a decreased consumption and insufficient utilisation of food. Serum-Ca is lower, but returns to normal with supplements of cod-liver oil (I) and chalk, their effects being additive. The effect of (I) in retaining a normal serum-Ca is > its effect in increasing Ca retention or rate of growth.

H. G. R.

**Serum-calcium and -magnesium level in the ovarian cycle of the laying hen.** E. CHARLES and L. HOGGEN (Quart. J. Exp. Physiol., 1933, 23, 343—349).—In sexually immature White Leghorn pullets the serum-Ca averages 11.4 mg. and the Mg 2.4 mg. per 100 c.c. In the interval between oviposition and the next ovulation Ca varies from 14.7 to 19.6 mg. (average about 17) and Mg from 1.9 to 2.9 mg. In hens having an egg in the oviduct (I) with no shell formed, the Ca varies from 12.9 to 19.4 mg. In hens where the egg is in the shell gland and the shell in different stages of deposition the Ca varies from 10.4 to 28.5 mg. During shell secretion (II) Mg vals. appear to be > when no egg is present in (I) or when shell formation is complete. Possibly the presence of the egg in (I) stimulates

the mobilisation of Ca in the tissues during (II), producing a transitory rise in blood-Ca.

NUTR. ABS. (m)

**Simultaneous administration [to rats] of lime and phosphoric acid with a colloidal lime-phosphoric acid-protein preparation.** M. GÜRSCHING (Münch. med. Woch., 1933, 80, 1143—1144; Chem. Zentr., 1933, ii, 1204).—The Ca and P metabolism of rats treated with a colloidal Ca phosphate-milk protein prep. has been investigated. Ca and P retention and bone formation are better than when Ca and P are added as ordinary  $\text{Ca}_3(\text{PO}_4)_2$ .

L. S. T.

**Feeding lucerne and timothy hays to dairy cows.** Milk-production values and calcium and phosphorus utilisation of the hays after balancing the protein in the ration. C. W. HOLDAWAY, W. B. ELLET, J. F. EAHEART, and H. G. CUNNINGHAM, jun. (Virginia [Blacksburg] Agric. Exp. Sta. Tech. Bull., 1932, No. 45, 27 pp.).—A lucerne-grain ration (I) proved superior to a timothy-grain ration (II) in point of yields of milk and butter-fat and the net food energy required per kg. of milk and fat. Differences in the protein digestion coeffs. of the two rations and in the actual protein consumption were small, but the Ca contents diverged considerably (Ca : P = 2.1 : 1 and 1.06 : 1, respectively). The Ca balance of the cows was positive in nearly all cases, but the body-gain in Ca of cows receiving (I) was > that of those receiving (II). These differences became more marked as the lactation period advanced. During the fourth to ninth months of lactation the P retention with (I) was much > during the first to fourth months.

A. G. P.

**Phosphorus requirement of dairy cattle when lucerne furnishes the principal source of protein.** C. F. HUFFMAN, C. W. DUNCAN, C. S. ROBINSON, and L. W. LAMB (Michigan Agric. Exp. Sta. Tech. Bull., 1933, No. 134, 1—75).—Heifers receiving a low-P ration of lucerne-maize silage-maize supplemented with bone meal required 10—12 g. of P daily for growth and maintenance. The demand for milk production averaged 0.5—0.7 g. of P per lb. of milk. The P requirement for growth is not directly proportional to body-wt., but depends also on the rate of growth. The most pronounced symptom of P deficiency was anorexia usually preceded by a lowered org. P content of the blood.

A. G. P.

**Effect of decalcium phosphate, without vitamin-D, in the nutrition of chicks.** G. M. HIGGINS and C. SHEARD (Anat. Rec., 1933, 56, 395—408).— $\text{Ca}_2\text{H}_2(\text{PO}_4)_2$ , in absence of vitamin-D, does not maintain growing chicks or protect against results of disturbed Ca metabolism.

CH. ABS.

**Copper in Chinese food materials.** W. H. ADOLPH and T. P. CHOU (Chinese J. Physiol., 1933, 7, 185—188).—The Cu content of forty Chinese food materials corresponds closely with that of similar American products.

H. G. R.

**Influence of alkalinity on the respiratory level of *Telphusa* and the crayfish.** A. RAFFY (Compt. rend., 1934, 198, 680—681).—*T. fluviatilis* progressively lowers its  $\text{O}_2$  consumption as the salinity of its environment varies from that of fresh  $\text{H}_2\text{O}$  (I) to that of sea- $\text{H}_2\text{O}$  (II). Its respiratory level is regained in (I)

after immersion in (II). The crayfish is not so adaptable. J. L. D.

**Effect of pyocyanine on the respiration of normal tissues and tumours.** E. A. H. FRIEDHEIM (Biochem. J., 1934, 28, 173—179).—The increase due to pyocyanine (I) in respiration (II) of tissues with aerobic glycolysis is dependent on the presence of glucose. With  $\text{CO}_3$ "-Ringer, (II) of rat kidney is not affected by (I), but there is a considerable increase with  $\text{PO}_4$ "-Ringer, the  $\text{PO}_4$ " fundamentally altering the oxidation mechanism of the cell. (I) is less toxic than methylene-blue. H. G. R.

**Effect of guanidine derivatives on tissue respiration.** C. BANU and N. GAVRILESCU (Biochem. J., 1934, 28, 270—272).—Guanidine (I) and methylguanidine (II), in 0.05% concn., depress the  $\text{O}_2$  uptake of isolated tissues (brain, liver, muscle) and of rat's brain *in vivo*. The general toxic effect of (I) leading to tetanic symptoms is ascribed in part to depression of tissue metabolism, particularly of the brain. No direct antagonistic action between parathyrin and (I) or (II) was observed. A. E. O.

**Natural reversible oxidation-reduction systems as accessory catalysts in respiration: juglon and Lawson.** E. A. H. FRIEDHEIM (Biochem. J., 1934, 28, 180—188).—Lawson (I) (the colouring matter in the leaves of the henna plant) in the oxidised form, and juglon (II) (the colouring matter in the husks of walnuts) in the reduced form, act as true intracellular reversible oxidation-reduction systems. The potentials in the semi-reduced condition at  $p_{\text{H}} 7.0$  are: (I)  $-0.139$ , (II)  $+0.033$ . Whereas both (I) and (II) increase the respiration of erythrocytes, only (II) oxidises hæmoglobin to methæmoglobin. H. G. R.

**Tissue metabolism. III. Effect of oxidised 1:2:5:6-dibenzanthracene.** E. BOYLAND and M. E. BOYLAND (Biochem. J., 1934, 28, 244—256).—A  $\text{H}_2\text{O}$ -sol. oxidation product of 1:2:5:6-dibenzanthracene (A., 1932, 1156) has similar inhibitory effects on oxidation and glycolysis in both normal and malignant rat tissues. A. E. O.

**Effect of carbohydrate content on cardiac muscle. I. Agents directly affecting sugar metabolism. II. Cardiacs.** F. LASCH and K. TRIGER (Z. ges. exp. Med., 1932, 85, 390—399; 1933, 88, 588—592; Chem. Zentr., 1933, ii, 1211, 1212).—I. The effect of insulin (I), glucose, and phloridzin on the total carbohydrate content (II) of cardiac muscle in comparison with that of the liver has been investigated for rats and guinea-pigs in short- and long-period experiments. (II) is affected to only a limited extent. (I) reduces (II) in short-period experiments with guinea-pigs, and in long- but not in short-period experiments with rats. Glucose does not increase in rats, but in one short-period experiment with guinea-pigs an increase was observed.

II. In rats neither caffeine nor hexeton alters the (II) of cardiac muscle or the liver, but in guinea-pigs strophanthin raises (II) in both cases. L. S. T.

**Peptone hyperglycæmia in animals deprived of suprarenals or suprarenal medulla.** T. KAIWA (Tôhoku J. Exp. Med., 1933, 21, 1—12).—Bilateral adrenalectomy in rabbits and removal of the supra-

renal medulla in dogs, 3—6 weeks previous to intravenous injection of peptone (I) (0.1—0.3 g. per kg. in 0.9% aq. NaCl), results in a decrease and an increase, respectively, in the usual vals. for (I) hyperglycæmia (II). When adrenaline hydrochloride (III) is given subcutaneously to adrenalectomised rabbits immediately after administration of (I) the (II) produced is < with (III) alone, but similar to that with (I) alone, whilst the length of the (II) period and the time of greatest intensity coincide with those obtained with (III) alone. NUTR. ABS. (m)

**Effect of spices on the movements of the intestinal villi and the absorption of glucose.** E. DE KOKAS and G. DE LUDANY (Orvosi Hetilap, 1933, 77, 638—639).—Spices (cloves, garlic, onions, pepper, paprika) in low concn. stimulate the movements of the intestinal villi. Absorption of glucose in the small intestine was accelerated by spices; the most effective were those which had the greatest stimulating effect on the movements of the villi. NUTR. ABS. (b)

**Diffusion of alcohol in the organism. Bound water.** M. NICLOUX (Compt. rend., 1934, 198, 983—985).—The ratio 0.85—0.90 for the EtOH content of the tissues of gudgeon in equilibrium with dil. EtOH is explained by the assumption that some of the  $\text{H}_2\text{O}$  in the tissues is bound by the proteins, and then does not dissolve EtOH. The quantity thus bound is much < that usually known as "bound," is very sensitive to electrolytes, and is reduced to 0 by death or destruction of the tissues. R. S. C.

**Configuration and anæsthetic activity of aromatic alcohols.** P. K. KNOEVEL and G. A. ALLES (Proc. Soc. Exp. Biol. Med., 1930, 30, 1076—1077).—Increase in length of the straight C chain and/or transformation into *sec.*- or *tert.*-alcohol increased the anæsthetic activity. CH. ABS.

**[Physiological effect] of acetophenone and certain derivatives.** G. FLORENCE (Bull. Sci. pharmacol., 1933, 40, 325—336; Chem. Zentr., 1933, ii, 2123—2124).—The solubility in  $\text{H}_2\text{O}$ , distribution between olive oil and  $\text{H}_2\text{O}$ , and physiological effects have been determined. The following are new: 3:4-dichloroacetophenone, m.p.  $74^\circ$ ; m-, m.p.  $146^\circ$ , and p-, m.p.  $148^\circ$ , -ureidoacetophenone; acetophenone-m-, m.p.  $187^\circ$ , and p-, m.p.  $201^\circ$ , -ureide. p-Methylacetophenone is more active than acetophenone, but further substitution by Me diminishes the activity. Substitution by Et or halogen destroys the narcotic power. Certain halogen derivatives are toxic. None of the N-derivatives is active. A. A. E.

**Adrenaline secretion and blood-sugar in dogs after chloralose.** H. SATO and F. OHMI (Tôhoku J. Exp. Med., 1933, 21, 433—443).—Chloralose causes hypoglycæmia and decreased adrenaline secretion, but does not increase blood-pressure. CH. ABS.

**[Physiological] action of isomerides of amyl nitrite.** B. E. READ, K. Y. YU, and T. M. PENG (Chinese J. Physiol., 1933, 7, 253—268).—By intravenous injection the order of potency is *iso*- (I), *n*- (II), *sec*- (III), and *tert*- (IV); by inhalation the order is (III), (IV), (II), (I). (III) and (IV) are least toxic in producing vaso-constriction and (IV) is the best for therapeutic purposes. H. G. R.

**Combination of avertin with magnesium chloride.** W. KEIL (Arch. exp. Path. Pharm., 1934, 174, 490—492).—Subcutaneous injection of sublethal doses of  $MgCl_2$  into rats lowers both the min. lethal dose and the min. narcotic dose (by as much as approx. 45%) of subsequently administered avertin. F. O. H.

**Assay of analgesics.** F. HILDEBRANDT (Arch. exp. Path. Pharm., 1934, 174, 405—415).—The method depends on the reaction of guinea-pigs to the application of heat to the skin. Opium derivatives have an analgesic power much > that of acetylsalicylic acid, quinine, atophan, etc. F. O. H.

**Effect of methylprotocatechualbarbituric [5-4'-hydroxy-3'-methoxybenzylidenebarbituric] acid in rabbits.** E. KATASKA (J. Biochem. Japan, 1934, 19, 11—13).—Vanillin with barbituric acid in hot  $H_2O$  yields 5-4'-hydroxy-3'-methoxybenzylidenebarbituric acid (I). Following ingestion (2—3 g. daily) of (I) by rabbits, vanillic acid appears in the urine to the same extent as after ingestion of the equiv. amount of vanillin. F. O. H.

**Central blood-sugar regulation. I. Effect of pyramidone on blood-sugar. II. Veronal or luminal. III. Small quantities of pyramidone. IV. Magnesium salts.** F. HÖGLER (Z. ges. exp. Med., 1932, 84, 14—23, 29—49, 50—61, 62—73; cf. A., 1933, 411).—I. Pyramidone (I) hyperglycaemia is prevented or diminished by veronal (II) and luminal (III), arrested by ergosterol, and increased by atropine, Ca salts, and parathormone. (I) hypothermy is unaffected.

II. Blood-sugar is practically unaffected by (II) and (III), but adrenaline hyperglycaemia is increased. Ergotamine (in doses otherwise inactive) with (II) causes hypo- and atropine (IV) hyper-glycaemia. Hypoglycaemia following small (not large) doses of insulin (V) is increased and extended by both hypnotics.

III. Small doses of (I) cause hypoglycaemia and hyperthermy.

IV. Mg hyperglycaemia is restrained by ergotamine, but scarcely affected by (II), (III), (IV), or (V). Ca interrupts Mg narcosis and hyperglycaemia; parathormone retards it. A. A. E.

**Relation between constitution and chemical or pharmacological properties. I. Reactions between nitrogenous compounds and phenols.** R. LABES (Arch. exp. Path. Pharm., 1934, 174, 255—285).—The pptn. reactions of various phenols ( $PhOH$ ,  $p-C_6H_4Cl-OH$ , 2 : 4 : 6- $C_6H_2Cl_3-OH$ , resorcinol) with cyclic N compounds (quinoline, antipyrine, pyramidone, and  $C_5H_5N$ ) are correlated with their solubility products and with the limiting mol. solubility of the complex produced. F. O. H.

**Chemical constitution and physiological action. Comparative effects of benzyl- $\beta$ -phenylethyl- and di-( $\beta$ -phenylethyl)-amines and some of their derivatives.** A. M. HJORT (J. Pharm. Exp. Ther., 1934, 50, 131—150).—Benzyl- $\beta$ -phenylethylamine (I), di-( $\beta$ -phenylethyl)amine (II), and many of their derivatives containing one or more OH, OMe, or  $CH_2O_2$  groups in either ring, were examined and compared with one another and with adrenaline (III) and other

$\beta$ -phenylethylamine (IV) derivatives. The toxicities of (I) and (II) were lowered by the introduction of substituent groups, whilst the tone-depressant effects on isolated intestinal muscle were increased, the extent of the increase or decrease varying with the no., nature, and positions of the substituent groups. None of the (I) or (II) derivatives exhibited any tone-depressant effect comparable with that of (III), although comparable with other (IV) derivatives. Most of the (I) and (II) derivatives lowered the blood-pressure, a few producing a slight initial rise. The effects on the melanophores, pulse, and respiration varied.

R. N. C.

**Synthesis of substances similar to papaverine.**—See this vol., 403.

**Toxicity of nitriles of  $\alpha$ -amino-acids.** C. SAN-NIÉ (Bull. Soc. Chim. biol., 1933, 15, 1436—1461).—In the fatty acid series lengthening the chain or the introduction of Ph at the extremity decreases the toxicity. Straight-chain compounds are less toxic than their isomerides. A MeO group in the  $C_6H_5$  nucleus or a double linking in the aliphatic group increases the toxicity. The amounts of HCN liberated from the alkaline solutions of the  $NH_2$ -nitriles on exposure to air are not large enough to be toxic.

H. D.

**Action of tetramethylammonium and tetraethylammonium iodides on the vessels of the posterior limbs of the frog.** G. COLANTUONI (Arch. Farm. sperim., 1934, 57, 36—43).—Introduction of  $NMe_4I$  (I) into the vessels of the posterior limbs of the frog produced a slight vaso-dilatation (II), followed by an intense vaso-constriction (III). Increasing the concn. of (I) produced an increased (III) without (II). With solutions of  $NEt_4I$  equimol. to those of (I), (II) lasted longer, whilst (III) was less intense than for (I). R. N. C.

**Chemotherapy of derivatives of harmine and harmaline. II.** C. E. COULTHARD (Biochem J., 1934, 28, 264—267; cf. A., 1933, 859).—The amœbicidal val. of *O-n*-nonylharmol (the most lethal of 14 *O*-alkylharmols tested) is much < that of emetine (I) under optimal conditions for (I), but is comparable with that of (I) at  $p_H$  6.2 or 6.3, the probable *in vivo*  $p_H$  in amœbic dysentery. A. E. O.

**Enhanced action of morphine in experimental nephrosis after oral ingestion of magnesium sulphate.** A. D. HIRSCHFELDER (Proc. Soc. Exp. Biol. Med., 1933, 30, 1057—1058). CH. ABS.

**Effect of morphine on the adrenaline output, blood-sugar, and blood-pressure in dogs.** H. SATO and F. OHMI (Tôhoku J. Exp. Med., 1933, 21, 411—432).—Subcutaneous injection of morphine into dogs (10—40 mg. per kg.) causes a 5—25-fold increase in adrenaline secretion and somewhat retarded hyperglycaemia. Blood-pressure is not regularly affected. CH. ABS.

**Physiological action of nucleic acids and their derivatives.** O. FLÖSSNER (Arch. exp. Path. Pharm., 1934, 174, 245—254).—The following compounds, prepared from both yeast- and thymus-nucleic acids, were investigated: adenylic, guanylic, and inosic acid (I), adenosine (II), guanosine, inosine, xanthine,

adenine, hypoxanthine, guanine, pancreatic nucleic acid, "vicin" (2:5-diamino-4:6-dihydroxypyrimidine glucoside), and 4:5-diamino-2:6-dihydroxypyrimidine. All [especially (II)] lower the blood-pressure and [especially (I)] retard the heart, whilst some increase and others decrease the strength of the heart-beat. With the intestine and uterus, tonus-increasing and -decreasing actions, respectively, generally occur.

F. O. H.

**Comparative effects of various diuretics in dogs, with special reference to the excretion of urine, chloride, and urea.** M. N. FULTON, H. A. VAN AUKEN, R. J. PARSONS, and L. F. DAVENPORT (J. Pharm. Exp. Ther., 1934, 50, 223—239).—The greatest increase in both vol. of urine excreted and urinary Cl' was produced by salyrgan (I) both with and without NH<sub>4</sub>Cl, the others, in diminishing order of potency, being novasurol (II), NH<sub>4</sub>Cl (III), digitan (IV), urea (V), theophylline-C<sub>2</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> (VI), theocin (VII), caffeine, and theobromine-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>Na. Increase in urinary Cl' was given by (I), (II), (III), (V), (VI), and (VII). Blood-Cl' remained const. except in cases of excessive Cl' excretion. The effects of the diuretics on urea excretion were not consistent. Blood-urea generally fell during the periods of action of the drugs, but except in cases of small urine vols. the blood-urea clearance was unaffected. Pituitrin inhibited the increased excretion of urine after (II), but not the Cl' excretion.

R. N. C.

**Influence of panax ginseng on serum-calcium and -potassium. II. Effects of convulsants.** K. IN (J. Chosen Med. Assoc., 1933, 23, 725—732).—Injection into normal rabbits of camphor, picrotoxin, caffeine, or strychnine increases serum-Ca. If the rabbit has been fed with ginseng the effect is greater.

CH. ABS.

**Toxic constituent of *Ryania acuminata*.** S. NAKARAI and T. SANS (Arch. Pharm., 1934, 272, 1—4).—Injection of ryanin (I), m.p. < 100°, extracted from the root of *R. acuminata*, into frogs (0.00001 g./10 g.), mice (0.000005 g./10 g.), rabbits (0.00025 g./kg.), cats, and dogs (min. lethal dose in parentheses) has no influence on the heart and blood, but acts first as a stimulant and then as a paralytic poison to the respiratory system, death being due to suffocation. Death is delayed when (I) is injected into a narcotised (CCl<sub>3</sub>·CHO) animal.

J. W. B.

**Tests of the potency of digitalis preparations on man.** E. EDENS (Klin. Woch., 1933, 12, 1012—1015; Chem. Zentr., 1933, ii, 2701).—The quantity of the digitalis prep. necessary to give the same effect as a definite quantity of strophanthin must be measured.

H. J. E.

**Chemico-therapeutic interference phenomena.** A. HASSKÓ (Z. ges. exp. Med., 1933, 87, 567—577; Chem. Zentr., 1933, ii, 1209—1210).—Of the nine CHPh<sub>3</sub> dyes investigated, only brilliant-green (I) gives a therapeutic interference phenomenon (III) in rats after a period of 1 hr. The trypanflavine (II) test shows that fuchsin, parafuchsin, and (I) after 1 hr. hinder the union between (II) and the trypanosome cell. (III) depends on a process of saturation of the parasite protoplasm probably through a change in the physico-chemical cell-structure.

L. S. T.

**Toxicity of fish-liver oils and fish oils, and the antitoxic effect of yeast.** I. YAMAMOTO (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1—2).—The retardation of the growth of rats fed on a basal diet to which 10—15% of liver or fish oils are added as the sole source of fat, together with a quantity of oryzanin solution, can be alleviated by addition of yeast. Substitution of butter or olive oil gives better growth. Skate-liver oil, which is more potent in vitamin-A (I) than cod-liver oil, is less toxic. The toxicity of an oil is not reduced by removal of (I), and is associated with the fatty acids.

P. G. M.

**Spectroscopic investigation of the action of poisons in the blood.** C. L. CARBONESCHI (Semana méd., 1933, II, 1187—1196).—Absorption spectra of blood treated with CO, N<sub>2</sub>O, C<sub>2</sub>H<sub>2</sub>, H<sub>2</sub>S, PhNO<sub>2</sub>, and F compounds are recorded. Spectroscopic characteristics of methæmoglobin, hæmatin, hæmochromogen, and hæmatoporphyrin are discussed.

CH. ABS.

**Arsine poisoning: blood changes in experimental animals.** F. FRETWURST, S. HORWITZ, and R. ROSENBAUM (Z. klin. Med., 1933, 123, 703—730; Chem. Zentr., 1933, ii, 1212).—In cats poisoned by AsH<sub>3</sub>, a strictly regular dependence of morphological structural changes of the red and white constituents of blood on the poisoning action was not observed. The characteristic symptoms of the acute AsH<sub>3</sub> poisoning are mainly hæmolysis with the appearance of methæmoglobin and incidental hæmatin in the blood, the separation of oxyhæmoglobin, and different degrees of leucocytosis. The principal attendant phenomena are the appearance of erythrocytes (III) in the urine and an increase in the residual-N content of the blood. The AsH<sub>3</sub> is mainly taken up by (III), the As content of the plasma increasing with the degree of hæmolysis.

L. S. T.

**Adsorption, distribution, and excretion of injectable bismuth preparations.** M. R. THOMPSON, C. I. ICHNIOWSKI, and B. S. ROBERTS (Amer. J. Syphilis, 1933, 17, 205—220).

CH. ABS.

**Deposition of lead in the kidney.** F. RAUH (Arch. exp. Path. Pharm., 1934, 174, 352—356).—Oral administration of Pb salts to guinea-pigs is followed by Pb deposition (I) in the intercalary region and ascending tube of Henle's loop (II), but seldom in the cortical region. Subcutaneous administration produces (I) in the vessels and capillary endothelium, the descending tube of (II) being practically free from Pb.

F. O. H.

**Detection and determination of radium in living persons. IV. Retention of soluble radium salts administered intravenously.** H. SCHLUNDT and J. T. NERANCY (Amer. J. Roentgenol., 1933, 30, 515—522).—In psychiatric patients receiving RaCl<sub>2</sub> intravenously, 4.3% was retained 6 months after treatment and 1.9% 6 months later. Precautions in making the necessary  $\gamma$ -ray measurements are described.

CH. ABS.

**Distribution and excretion of thorium after injection of Thorotrast.** T. LEIPERT (Wien. klin. Woch., 1933, 46, 994—996; Chem. Zentr., 1933, ii, 2023).—Th is found principally in the spleen and

liver; smaller amounts are present in the lungs and the red marrow.

A. A. E.

**Toxicity of sodium chromate and dichromate.** A. RABBENO (Boll. Soc. Eustach., 1933, 31, 57—58; Chem. Zentr., 1933, ii, 2023).—On intravenous injection into rabbits  $\text{Na}_2\text{Cr}_2\text{O}_7$  is twice as toxic as  $\text{Na}_2\text{CrO}_4$ .

A. A. E.

**Formation of methæmoglobin by sodium chromate and dichromate *in vivo*.** A. RABBENO (Boll. Soc. Eustach., 1933, 31, 59—62; Chem. Zentr., 1933, ii, 2023—2024).—< 70% conversion was observed; > 70% is fatal.

A. A. E.

**Formation of methæmoglobin by sodium and potassium dichromate.** M. MATTUCCI (Boll. Soc. Eustach., 1933, 31, 121—128; Chem. Zentr., 1933, ii, 2141).—The change takes place in very dil. solution; the effects of time and  $[\text{CrO}_4^{2-}]$  are recorded.

A. A. E.

**Iodine distribution after injection of Abrodil.** II. J. OLIVET (Klin. Woch., 10, 2396—2397; Chem. Zentr., 1933, ii, 2700).—Intravenous injection of 20—40 g. of Abrodil results in a uniform I distribution in the organs in 0.25—1.5 hr.

H. J. E.

**Mechanism of absorption of sodium fluoride by roaches.** G. L. HOCKENYOS (J. Econ. Entom., 1933, 26, 1162—1169).—Although a lethal dose of NaF may be absorbed by roaches through the body integument, the rate of absorption is too low to be an effective factor in control measures. When the antennæ and tarsi are coated with NaF dust, sufficient may be taken in through the mouth to cause death.

A. G. P.

**Blood-calcium after the administration of sodium oxalate to normal and thyro-parathyroidectomised cats.** W. SALANT, W. M. PARKINS, and L. E. SHEPPARD (J. Lab. Clin. Med., 1933, 19, 142—152).—Fall in serum-Ca of normal cats after injection of  $\text{Na}_2\text{C}_2\text{O}_4$  is due to injury of the parathyroid gland. Decrease in serum-Ca caused by intravenous injection of 30—40 mg. per kg. after thyro-parathyroidectomy is 0.25 as great as that produced by injection of the same amounts into normal cats. The reduction produced by injection of large amounts is < 0.5 as great.

CH. ABS.

**Effects of feeding sodium bicarbonate or lactic acid on the sex ratio in rats.** F. E. D'AMOUR (Science, 1934, 79, 61—62).—Rats bred on stock diet to which was added  $\text{NaHCO}_3$  or lactic acid showed no variation in the sex ratio due to feeding with acid or base.

L. S. T.

**Variations in mineral composition of blood due to irradiation by sunlight.** S. MALCZYNSKI (Compt. rend. Soc. Biol., 1933, 113, 1297—1300).—Irradiation with summer sunlight does not appreciably affect the P or Na content of the blood of dogs, but causes immediate increase (I) in the Ca content. (I) persists for several weeks, but the accompanying increase in the K content soon disappears.

NUTR. ABS. (m)

**Spectral erythemic reaction of the untanned human skin to ultra-violet radiation.** W. W. COBLENTZ and R. STAIR (Bur. Stand. J. Res., 1934,

12, 13—14).—Data for the erythemic response of skin are revised and extended.

A. G.

**Effect of X-rays on substances of biological importance.** J. P. BECKER and S. FREYTAG (Pflüger's Archiv, 1932, 231, 26—32; Chem. Zentr., 1933, ii, 2278).—The fluorescence power of ovalbumin, a mixture of various  $\text{NH}_2$ -acids, and histidine (I) was increased. The effect on the absorption spectrum of (I) is similar to that caused by ultra-violet irradiation, a physiologically active substance being produced.

A. A. E.

**Vital oxidation of succinic acid in air and in pure oxygen with change in  $p_{\text{H}}$ .** J. LEHMANN (Skand. Arch. Physiol., 1933, 65, 291—303; Chem. Zentr., 1933, ii, 1195).—The oxidation of succinic acid with succinodihydrogenase from horse muscle in air and in  $\text{O}_2$  has been studied at different  $p_{\text{H}}$  vals. At  $p_{\text{H}}$  7.4 approx.  $\text{O}_2$  consumption is independent of the partial pressure; at  $p_{\text{H}}$  > 7.4 it is smaller, and at  $p_{\text{H}}$  < 7.4 greater, in  $\text{O}_2$  than in air.

L. S. T.

**Xanthine-oxidase. XI. Xanthine-oxidase and lactoflavin.** D. E. GREEN and M. DIXON (Biochem. J., 1934, 28, 237—243).—Rate of  $\text{O}_2$  uptake (I), and the ratio of (I) and rate of reduction of methylene-blue (II) by milk xanthine-oxidase (III) are both unaffected by lactoflavin (IV). (II) is reduced by (III) anaerobically 64 times as fast as (IV), which cannot be a catalytic flavin (cf. this vol., 109).  $\text{O}_2$  probably reacts directly with the activated substrate.

A. E. O.

**Alcohol dehydrogenase from yeast. II.** D. MÜLLER (Biochem. Z., 1934, 268, 152—157; cf. A., 1933, 982).—At  $p_{\text{H}}$  6.3 the activity (I) of the dehydrogenase (II) is reduced by 50% on heating to 58°. (I) is optimal between  $p_{\text{H}}$  7.5 and 10, decreases slowly between 7.5 and 3.5, and reaches a min. between 10 and 11. KCN has little effect on (I), which is reduced only 50% even by 0.1N solution. The reduction of methylene-blue in presence of extract containing (II) is accelerated by many org. compounds (mono- and poly-hydric alcohols, aldehydes, ketones, pentoses, hexoses, neutral salts of acids), but no succino-, triose-, or xanthine-(II) is present.

W. McC.

**Quinones as enzyme models. XII. Metal salts as activators.** B. KISCH and K. SCHUWERTH (Biochem. Z., 1934, 268, 158—163; cf. A., 1933, 979).—Low concns. (0.001—0.0000005M) of  $\text{AlCl}_3$ ,  $\text{TiCl}_3$ ,  $\text{FeCl}_3$ ,  $\text{CoSO}_4$ ,  $\text{NiSO}_4$ ,  $\text{HgCl}_2$ ,  $\text{CuSO}_4$ ,  $\text{AgNO}_3$ ,  $\text{AuCl}_3$ ,  $\text{PtCl}_4$ , and especially  $\text{CdCl}_2$  activate the oxidative deamination of glycine in presence of hydroxyquinol, resorcinol, adrenaline, pyrocatechol, and gallic acid. The degree of activation varies with the salt used, its concn.,  $[\text{H}^+]$ , the catalyst, and the buffer used.

W. McC.

**Formation of urea from uramido-acids, hydroxintoxins, and proteins by the action of enzymes (reductases) in neutral solution.** M. WADA (Proc. Imp. Acad. Tokyo, 1934, 10, 17—20; cf. A., 1933, 1063).—Urea (I) is formed in small yield when citrulline, prollysine, carbamyl-leucine (II), carbamylphenyl-alanine (III), ovalbumin, gelatin, and various hydroxintoxins are incubated, in neutral solution at 65°, with fresh milk (IV), blood-serum, or liver or pancreas extracts. The last-named all contain small amounts

of (I), not increased by heating at 100°. 80% yields of (I) from (II) and (III) are obtained in presence of  $\text{CH}_2\text{O}$  at 35°, using a filtrate (conc. by evaporation) from (IV) treated with citric acid. The (I)-producing activity runs parallel with reducing power. A. E. O.

**Nature of lysozyme action.** K. MEYER, R. THOMPSON, J. W. PALMER, and D. KHORAZO (Science, 1934, 79, 61).—Lysozyme (I) appears to be an enzyme or enzyme mixture which splits off reducing sugar from certain mucoids and from the polysaccharides derived from them. The occurrence of (I) in tears, nasal, bronchial, and gastro-intestinal mucus, egg-white, and semen can thus be understood, the bacteriolytic action being incidental. L. S. T.

**Enzymic amylolysis. III. Crystalline hexaose from starch.** E. WALDSCHMIDT-LEITZ and M. REICHEL (Z. physiol. Chem., 1934, 223, 76—80; cf. A., 1932, 304).—From the products of pancreatic hydrolysis of erythroamylose, there was isolated in 7—11% yield a cryst. *hexaose*, m.p. 258—263° (decomp.),  $[\alpha]_D^{20} +183^\circ$ . It is hydrolysed by  $\alpha$ -amylase to  $\alpha$ -maltose, and by  $\beta$ -amylase to  $\beta$ -maltose, but not by maltase. J. H. B.

**Inactivation of animal amylase by plant paralyzers and the presence of inactivating substances in solutions of animal amylase.** T. CHRZASZCZ and J. JANICKI (Biochem. J., 1934, 28, 296—304).—Plant sistoamylase (A., 1933, 749, 980, 1080, 1343) inhibits the action of animal amylase (I) of saliva and pancreas, dried preps. being more active than undried. Animal sistoamylases (II) occur together with (I) in nature, inactivating  $\frac{2}{3}$  and  $\frac{1}{3}$  of salivary and pancreatic (I), respectively. Sistoamylase-amylase systems can be reactivated by addition of eleuto-substances, notably peptone, which are regarded as causing elution of (I) from the adsorbing (II). C. G. A.

**Biological significance of enzymic activation.** E. WALDSCHMIDT-LEITZ (Böhm. Bierbrauer, 1933, 60, 299—302, 317—319; Chem. Zentr., 1933, ii, 2683).—Enzyme activity depends on the presence of activators (or inhibitors). Amylokinase, occurring in malt, is an activator for  $\alpha$ - and  $\beta$ -amylase. H. J. E.

**Activity of technical invertase preparations.** R. WEIDENHAGEN (Chem.-Ztg., 1934, 58, 185—187).—The enzyme val. of a prep. is defined as the time in min. taken by 1 g. of the prep. to effect 50% inversion of 2.375 g. of sucrose at  $p_H$  4.62 and 30° in a total vol. of 50 c.c. P. G. M.

**Glyoxalase. I. Manometric method for the study of glyoxalase.** M. E. PLATT and E. F. SCHROEDER (J. Biol. Chem., 1934, 104, 281—297).—The manometric method (A., 1932, 1287) is suitable for determination of glyoxalase (I) activity. With low concn. of glutathione (II) and AcCHO (III), the rate (IV) of enzyme reaction is directly proportional to the amount of (I) present. With high concn. of (II), (IV) is independent of (I) and proportional to (III). In pure solution (II) and (III) react and reach equilibrium; it is suggested that this complex forms the enzymic substrate.  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$  inhibits  $\text{COME}_2$ -yeast (I) by destroying (II), (I) not being affected. H. G. R.

**Glyoxalase activity of tissues.** M. JOWETT and J. H. QUASTEL (Biochem. J., 1934, 28, 162—172).—The glyoxalase activity of tissue slices is proportional to the surface area and is inhibited by  $\text{O}_2$ . AcCHO and glucose probably compete as substrates. H. G. R.

**Conversion of glyceraldehydophosphoric acid into methylglyoxal and lactic acid.** M. KOBEL and H. COLLATZ (Biochem. Z., 1934, 268, 202—204).—Under the conditions most favourable for the production from hexose diphosphate of AcCHO yeast produces only traces of it from glyceraldehydophosphoric acid (I), lactic acid being almost quantitatively formed. During fermentation of sugars, AcCHO is thus a primary product, and is not derived from (I). W. McC.

**Influence of arsenate and arsenite on the enzymic breakdown of phosphoric acid esters.** L. B. PETT and A. M. WYNNE (Biochem. J., 1934, 28, 365—371).—Of the phosphatase systems of *Cl. acetobutylicum*, *P. jensenii* (I), *B. subtilis*, *B. lactis aërogenes*, yeast, takadiastase, pig kidney, and ox erythrocytes, the only one in which the action on Na glycerophosphate was accelerated by  $\text{AsO}_4'''$  (II) and  $\text{AsO}_3'''$  (III) is that of (I). With hexose diphosphate as substrate, (II) and (III) sometimes, but not always, increase the rate of liberation of inorg. P, but in this case the effect on the glycolytic enzyme is a complicating factor. F', which up to 0.01M does not inhibit the phosphatase action of (I), reduces the accelerating effect of (II). W. O. K.

**Urinary phosphatases.** A. DMOCHOWSKI (Compt. rend. Soc. Biol., 1933, 113, 956—957).—The activity of hexosediphosphatase (optimum  $p_H$  4.8—5.8) found in normal urine has been studied, using substrates of (1) Na glycerophosphate, (2) the Na salt of yeast-nucleic acid, (3) thymus-nucleic acid, and (4)  $\text{Na}_4\text{P}_2\text{O}_7$ , the P being determined by the method of Lohmann and Jendrassik. Large variations occur in normal and pathological urines of the same sp. gr., as well as in the same sample over several hr. Dialysis and dilution of the urine greatly increase the activity of the enzyme, whilst pptn. of the urinary  $\text{PO}_4'''$  with Mg decreases it. Nucleophosphatase shows little activity either in normal or pathological urines, whilst pyrophosphatase, which has an optimum  $p_H$  of 5.5, is completely inactivated at  $p_H$  9. NUTR. ABS. (b)

**Serum-lipases.** N. FIESSINGER, M. ALBEAUX-FERNET, and A. GAJDOS (Ann. Méd., 1933, 34, 101—135).—Decrease of total serum-lipases occurs in cases of rapid emaciation. Increase of quinine-resistant lipase frequently occurs in hepatic disorders, and increased atoxyl-resistant lipase in pancreatic disorders. These changes are not, however, characteristic of the respective disorders, and are influenced by the thyroid and probably by other internal secretory glands. NUTR. ABS. (b)

**Relative concentration of esterase and lipase in adipose tissue.** J. S. HEPBURN and H. M. MOORE (Amer. J. Pharm., 1934, 106, 14—15).—In adipose tissue both esterase (I) and lipase (II) are present, (I) being predominant in goose, lamb, and man and (II) in chicken and turkey. W. O. K.

**Determination of pancreatic lipase.** E. WALDSCHMIDT-LEITZ and R. JUNOWICZ (Biochem. Z., 1934, 268, 178—180).—Steudel's criticisms (A., 1933, 981) of the method of Willstätter *et al.* (A., 1923, i, 403) are unfounded, since his curves show wt. of gland instead of wt. of lipase. W. McC.

**Lipase and esterase action of pancreatic juice.** H. P. WOLFEKAMP and K. GRIFFIOEN (Z. physiol. Chem., 1934, 223, 36—42).—In pancreas there appear to be at least two esterases, (I) and (II), hydrolysing tributyrin and EtOAc, respectively. Heating at 67° destroys (II) more rapidly than (I). The rates of inactivation at  $p_H$  9.92 are about equal; at  $p_H$  3.3 (II), but not (I), is inactivated in 1 hr. J. H. B.

**Intracellular enzymes of tissues and glands.**  
**IV. Pancreatic lyo- and desmo-lipases.** E. BAMANN and P. LAEVERENZ (Z. physiol. Chem., 1934, 223, 1—20; cf. this vol., 108).—In extraction of COMe<sub>2</sub>-dried preps. of pancreas with aq. glycerol (I), the yield of lyo-enzyme varies with the H<sub>2</sub>O present, being max. with 50% (I). With 100% (I) the yield is only 2—3%. From fresh minced tissue 100% (I) extracts only 1.5% of the total lipase; the effect of H<sub>2</sub>O is much less. The yield is increased when autolysed tissue or the dried prep. from it is used. Extracts with high (I) content show the greatest activatability (II). The (II) of dried is > that of minced tissue. Autolysed preps. give solutions of low (II). Differences in the colloidal carrier are the cause of the variations in (II). J. H. B.

**Absorption of enzymes on protein. II. Inhibition and activation of pancreatic enzymes.** H. DYCKERHOFF, H. MIEHLER, and V. TADSEN (Biochem. Z., 1934, 268, 17—33; cf. A., 1933, 535).—Pig pancreas contains substances (I), some sol. in solvents usually employed for extracting the enzymes (II), which inhibit the action of lipase, amylase, and trypsin (III). (I) are only partly or not at all removed during the process used for determination of (II). Another inhibitor (IV) for (III) accompanies it. (IV) is inactivated by enterokinase (V). (III) hydrolyses proteins even in the absence of (V). W. McC.

**Proteolytic enzyme in cucumber (*Cucumis sativus*).** R. N. CHOPRA and A. C. ROY (Indian J. Med. Res., 1933, 21, 17—23).—Cucumber juice contains an ereptic enzyme (I), capable of hydrolysing Witte's peptone and caseinogen, forming tryptophan, but without action on fibrin. (I), which also liquefies gelatin and clots milk, acts best at  $p_H$  5.4—6.2. The endocarp has a higher concn. of (I) than the mesocarp and the juice of mature fruit shows a higher activity than that of immature or ripe fruit. Activation by HCN is not sp. NUTR. ABS. (m)

**Ultracentrifugal study of the action of papain on ovalbumin.** T. SVEDBERG and I. B. ERIKSSON (J. Amer. Chem. Soc., 1934, 56, 409—412; cf. A., 1933, 427).—The action of papain (I) activated by HCN on ovalbumin (II) gives three types of degradation products: (a) non-centrifugable material (probably containing lower polypeptides and NH<sub>2</sub>-acids), (b) a centrifugable substance [sedimentation const. (III) about  $0.6 \times 10^{-13}$ ] with a mol. wt. of the same order as that of the protamines, and (c) a substance [(III)

about  $2.7 \times 10^{-13}$ ] having the same mol. wt. as (II) but a highly unsymmetrical mol. (which probably arises by the weakening of some of the linkings in the original mol.). (II) is unaffected by inactivated (I). H. B.

**Action of oxidising and reducing agents on papain. II. Effect of light, organo-arsenicals, and ascorbic acid.** T. BERSIN (Z. physiol. Chem., 1933, 222, 177—186; cf. A., 1933, 1203).—Ultra-violet light activates oxidised papain (I) by reduction of ·S·S· to ·SH. *p*-Aminophenylarsine oxide similarly activates by reduction, but *p*-acetamido- and *p*-amino-phenylarsinic acid oxidise ·SH, and hence inactivate the enzyme. Ascorbic acid, which is unable to reduce ·S·S· to ·SH, does not activate (I). J. H. B.

**Chemical nature of rennin.** H. TAUBER and I. S. KLEINER (J. Biol. Chem., 1934, 104, 259—266).—Rennin (I) is completely digested by pepsin (II) and trypsin, but not by erepsin, and may be easily separated from (II) by this method. Absorption on cryst. edestin indicates that, in the case of (I), no exchange of carrier is taking place. H. G. R.

**Activation of pro-rennin.** R. EGE and E. LUNDSTEEN (Biochem. Z., 1934, 268, 164—173; cf. A., 1933, 1081).—Aq. extracts (I) of calf's stomach contain only small amounts (5—10% of total enzyme) of active rennin. Activation (II) is induced by acid reaction beginning at  $p_H < 5$ ; hence at the optimal  $p_H$  (5—6) no (II) takes place. The rate of (II) increases rapidly (from 30 min. at 3.4 to 1.5 min. at 3) as the  $p_H$  decreases. Spontaneous (II) occurs even at  $p_H$  about 7 when (I) are kept, probably as a result of bacterial proteolysis. Pancreatin produces similar (II). W. McC.

**Trypsin. I. Chemical nature. II. Effect of trypsin on caseinogen.** I. S. KLEINER and H. TAUBER (J. Biol. Chem., 1934, 104, 267—270, 271—274).—I. By complete autolysis of pancreatic tissue for 18 months, a protein-free trypsin (I) prep. has been obtained.

II. (I) will coagulate milk at low concn. only, otherwise the casein stage is passed without formation of Ca caseinate, and no clot can be obtained with rennin (II). The velocity of coagulation is proportional to [H<sup>+</sup>] for (I), (II), and pepsin. H. G. R.

**Dilatometric studies in the proteoclastic degradation of proteins. I. Tryptic hydrolysis.** M. SREENIVASAYA, B. N. SASTRI, and H. B. SREERANGACHER (Biochem. J., 1934, 28, 351—355).—During the tryptic digestion of solutions of caseinogen (I) and of gelatin (II), the ratio of the change in vol. measured by the two-bulbed dilatometer (A., 1932, 880) to the NH<sub>2</sub> groups set free varies during the early stages, but is const. after 30 or 40 min., when the dilatometric depression per millimol. of NH<sub>2</sub>-N set free is for (I) 10.8 cu. mm. and for (II) 8.7 cu. mm. W. O. K.

**Specificity of dipeptidase and aminopoly-peptidase.** W. GRASSMANN and H. BAYERLE (Biochem. Z., 1934, 268, 214—219).—Dipeptides (I) obtained from asparagine (II) and aspartic acid (III) by introducing natural NH<sub>2</sub>-acid radicals into their NH<sub>2</sub> groups are hydrolysed by dipeptidase (IV), but are



not attacked by aminopolypeptidase (V) from yeast or intestine. Diglycylasparagine is attacked by (V), but not by (IV). Erepsin, obtained from intestine by the method of Waldschmidt-Leitz and Schäffner (A., 1926, 323), behaves as a mixture of (IV) and (V). (I) from (III) are more resistant to hydrolysis than are (I) from (II). Asparagyl-*l*-tyrosine, asparagylglycine, and *d*-leucyl-*l*-asparagine are not hydrolysed by (IV). W. McC.

**Effect of preservatives on enzyme action.** T. SABALITSCHKA (Z. Unters. Lebensm., 1934, 67, 203—204).—A criticism of Kluge (this vol., 108). Pancreatic trypsin is not inhibited by esters of  $p$ -OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H. Infusions of coffee and 1% NaCl both inhibit peptic digestion *in vitro*, but have no deleterious effect on digestion *in vivo*. E. C. S.

**Effect of preservatives on avitaminotic animals.** H. CREMER (Z. Unters. Lebensm., 1934, 67, 205; cf. this vol., 108).—The esters of  $p$ -OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H have no deleterious effect on either normal or scorbutic animals. E. C. S.

[Effect of preservatives on enzyme action etc.] H. KLUGE (Z. Unters. Lebensm., 1934, 67, 205—206).—A reply (cf. preceding abstracts). E. C. S.

**Phase changes in enzyme systems: azotase activity in relation to  $p_H$ .** D. BURK and H. LINEWEAVER (J. Physical Chem., 1934, 38, 35—46).—Azotase activity in *Azotobacter* varies abruptly with  $p_H$ , and a characteristic zero limit at  $p_H$  5.97 is approached reversibly and practically perpendicularly. By applying the phase rule, it may be regarded as a two-component heterogeneous system with three phases in equilibrium at the crit.  $p_H$ : H<sub>2</sub>O, active non-aq. (basic) (I), and inactive non-aq. (acidic) (II). (I) exists above the crit.  $p_H$  and (II) below. Slight phase non-homogeneity may occur between  $p_H$  5.97 and 6.37. The conditions are similar to those which obtain in the dissociation of a hydrated salt. Phase-rule applications to micro-heterogeneous systems, surfaces, and problems of general enzyme reaction velocity and stability are considered. M. S. B.

**Arginase. I. Relation between activity of enzyme and concentration of hydrogen ions.** A. HUNTER and J. A. MORRELL. **II. Influence of hydrogen-ion concentration on the stability of the enzyme.** A. HUNTER and J. A. DAUPHINEE (Quart. J. Exp. Physiol., 1933, 23, 89—117, 119—126).—I. The activity of arginase determined by a two-stage method described is unsymmetrically arranged about an optimum  $p_H$  (I) of 9.8 with a second less marked optimum (II) between 7 and 8. (II) persists in arginase complexes extracted from fresh liver and left for 3 or 4 weeks, whilst (I) becomes less evident. These results may be explained by assuming the existence of two arginases or, better, by supposing that ionisation of the protein complex associated with the enzyme occurs. The activity curve of arginase thus becomes the alkali titration curve of the enzyme-protein ion.

II. As regards its stability at various [H<sup>+</sup>] in the absence of its substrate arginase is not destroyed at  $p_H$  6.6—7.8, but on either side of this zone it undergoes

progressive destruction. Below 4 and above 12, it is completely inactivated at 37° in 10 min.

NUTR. ABS. (m)

**Uricase. VII. Soluble uricase.** R. TRUSZKOWSKI (Biochem. J., 1934, 28, 62—67).—Ro's conclusion (A., 1932, 428) that uricase (I) is indissociable from traces of alkali-sol. protein (II) and his method of prep. of sol. (I) have been confirmed. The activity varies in proportion to the (II) in the solution. The non-extractability of (I) is due to the presence of lipins, and after their removal (I) may be extracted with dil. aq. Na<sub>2</sub>CO<sub>3</sub>. H. G. R.

**Isolation of heteroxanthine [7-methylxanthine] from yeast.** P. W. WIARDI and B. C. P. JANSEN (Rec. trav. chim., 1934, 53, 205—208).—The yeast is extracted with HCl at  $p_H$  4.5 and the extract stirred with fuller's earth, which is then separated and extracted with iced aq. Ba(OH)<sub>2</sub>. This extract is acidified to  $p_H$  4.8, pptd. with Na silicotungstate, and the ppt. decomposed with Ba(OH)<sub>2</sub>. Acidification of the resulting solution to  $p_H$  2 and pptn. with AgNO<sub>3</sub> gives 7-methylxanthine. H. A. P.

**Acid production in autolysis of yeast.** H. HAEHN and H. LEOPOLD (Z. Unters. Lebensm., 1934, 67, 50—58).—Between 30° and 55° the total acid production in alkaline media is > that in acid media, but the NH<sub>2</sub>-acid production is less, owing to decamination. In normal yeast autolysates at these temp. the acids produced inhibit the growth of putrefactive bacteria. E. C. S.

**Inhibition of fermentation in maceration extract by oxygen in presence of a positive oxidoreduction system.** F. LIPMANN (Biochem. Z., 1934, 268, 205—213; cf. A., 1933, 1202).—Fermentation (I) in Lebedev's maceration extract (II) is inhibited by amounts of I which are more than equiv. to the SH content. (I) of (II), which is not sensitive to the action of O<sub>2</sub>, is inhibited by O<sub>2</sub> in presence of dichlorophenol-indophenol. Vals. for the oxidoreduction potential are given, and the effect on them of addition of traces of thionine and naphtholsulphonate-indophenol (III) is measured. When (III) and O<sub>2</sub> are present (I) ceases, but not because of resynthesis. W. McC.

**Bios from lecithin.** E. JANSSENS (Arch. internat. Physiol., 1933, 37, 70—86).—The presence of "bios" in choline-free lecithin from egg yolk was demonstrated by fermentation experiments, using the method of Wildiers. An attempt was made to separate the "bios" from the lecithin complex, but the substance appeared to be present as a salt or soap of the lipophosphoric acid, which could not be separated from other similar compounds occurring in egg yolk.

NUTR. ABS. (b)

**Influence of dyes on the functions of cells and organs. V. Poisoning of zymase and its specific groups.** F. AXMACHER and G. OPETZ (Arch. exp. Path. Pharm., 1934, 174, 427—439).—Benzidine diazo-compounds which inhibit glucose fermentation (I) by isolated zymase (II) (cf. A., 1933, 531) also inhibit the decarboxylation of AcCO<sub>2</sub>H to MeCHO. Of various arylsulphonic acids, only SO<sub>3</sub>H·C<sub>6</sub>H<sub>4</sub>·NH·NH<sub>2</sub> and sulphosalicylic acid inhibit (I); other ·CO-reagents (NHPh·NH<sub>2</sub>, NH<sub>2</sub>OH, and

$\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$  in 0.008M solution) act similarly on (II), but to only a slight extent on the living cell. Experiments on (I) by (II) preps. after reacting with  $(\text{PhN}_2)_2\text{SO}_4$ ,  $\text{Ac}_2\text{O}$ ,  $\text{Bz}_2\text{O}$ ,  $\text{BzCl}$ ,  $\text{C}_{10}\text{H}_7 \cdot \text{SO}_2\text{Cl}$ ,  $p\text{-C}_6\text{H}_4\text{Me} \cdot \text{SO}_2\text{Cl}$ , or  $\text{CH}_2\text{N}_2$  yielded no conclusive results.

F. O. H.

**Biological action of ultra-short electromagnetic waves. I. Alcoholic fermentation of sucrose solutions by brewer's yeast in a Lakhovsky oscillatory circuit.** F. PIRRONE (L'Ind. Chimica, 1934, 9, 16—21).—Exposure to an oscillatory circuit of wave-length 188.5 cm. for 1—2 days raises the vol. of  $\text{CO}_2$  produced to 101—105% of that obtained with the control, and after 6—7 days to 127%.

H. F. G.

**Biological action of ultra-short electromagnetic waves. II. Alcoholic fermentation of sucrose solutions by beer yeast exposed to electromagnetic waves of  $\lambda=1.7$  metre.** F. PIRRONE (L'Ind. Chimica, 1934, 9, 167—173).—Aq. suspensions of the yeast were exposed, and for the subsequent fermentations of 10% sucrose solutions, 10% of yeast was used. Although weaker and somewhat variable, the action of Lakhovsky oscillating circuits is analogous to that of wireless transmitters capable of emitting waves of  $\lambda=1.7$  m. For exposures of 10—40 min. if continuous, or up to 90 min. if broken, these waves enhance the rate of fermentation and cell-multiplication, but the effects diminish with more prolonged exposures.

T. H. P.

**Micro-calorimeter for measurement of the heat output of mould cultures.** H. TAMIYA and A. YAMAMOTO (Acta Phytochim., 1933, 7, 245—263).—The mould is grown in an air-tight culture bomb which serves as calorimeter. The respiratory exchange is determined by measuring the vol. change of the gas mixture (originally 85%  $\text{O}_2$ , 15%  $\text{N}_2$ ) in the bomb and the  $\text{CO}_2$  evolved.

J. H. B.

**Germination [of fungus spores].** R. G. TOMKINS (Trans. Brit. Mycol. Soc., 1932, 17, 147—149).—The latent period of germination is slightly prolonged in presence of narcotics and certain acids, and markedly prolonged in presence of  $\text{MeCHO}$ ,  $\text{HCN}$ ,  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ , and heavy-metal salts.

CH. ABS.

**Phoma species.** M. GRIMES, M. O'CONNOR, and H. A. CUMMINS (Trans. Brit. Mycol. Soc., 1932, 17, 97—111).—*P. hibernica* (described) grows well on nutrient lactose agar at  $p_{\text{H}}$  7.0 or 3.5. Litmus milk becomes slightly alkaline (6 days) and gelatin is slightly liquefied (3 weeks). No diastatic action on starch in various cultures was observed, and no gas is produced from glucose, lactose, mannitol, dextrin, or glycerol.

CH. ABS.

**Nitrogen assimilation by *Aspergillus niger*.** H. HÄRDTL (Biochem. Z., 1934, 268, 104—115).—The rate and extent of N assimilation by *A. niger* vary with the kind (org. and inorg.) and amount of N source, and also with the amount of C source (sugar). After the first few days increase in the abs. amount of N assimilated is accompanied by decrease (I) in the % N content. (I) runs parallel with increase in amount of N and C source supplied. The N of the medium is never completely consumed. Sugar serves to intensify

respiration as well as growth, and is extensively utilised. Production of citric acid continues throughout the period of growth when the N supply is small, but occurs only during early stages when it is large.

W. McC.

**Acids produced from sugar by a *Penicillium* parasitic on *Aspergillus niger*.** J. L. YVILL (Biochem. J., 1934, 28, 222—227).—When grown on a sucrose medium containing chalk, *Penicillium* "R.B." (I), a mould parasitic on *A. niger*, produces Ca citrate and a small quantity of Ca oxalate as well as the Ca salt of an insol. acid,  $\text{C}_{18}\text{H}_{20}\text{O}_7$ , probably glauconic acid I (Wijkman, A., 1931, 523). This acid is also formed in an acid medium, but no citrate or oxalate is then produced. When grown on a glucose or fructose medium, (I) produces the insol. acid. Citric acid is also formed when chalk is present.

W. O. K.

**Biochemistry of micro-organisms. XXXVI. Metabolic products of *Penicillium Charlesii*.** G. SMITH, P. W. CLUTTERBUCK, W. N. HAWORTH, H. RAISTRICK, G. SMITH, and M. STACEY (Biochem. J., 1934, 28, 94—110).—A new mould species, *P. Charlesii*, G. Smith, isolated from Italian maize, when grown at 24° on a Czapek-Dox or Raulin-Thom medium containing glucose as the sole carbohydrate gave the following products: a *polygalactose*,  $[\alpha]_{5700} -84^\circ$  in  $\text{H}_2\text{O}$ ; a *polymannose*,  $[\alpha]_{5790} +63^\circ$  in  $\text{H}_2\text{O}$ ; *carolic acid*,  $\text{C}_9\text{H}_{10}\text{O}_4$ , m.p. 132°,  $[\alpha]_{5461} +84^\circ$  in  $\text{H}_2\text{O}$ , monobasic; *carolinic acid*,  $\text{C}_9\text{H}_{10}\text{O}_6$ , m.p. 123°,  $[\alpha]_{5461} +60^\circ$  in  $\text{H}_2\text{O}$ , dibasic; *carlic acid*,  $\text{C}_{10}\text{H}_{10}\text{O}_6$ , m.p. 176°,  $[\alpha]_{5461} -160^\circ$  in  $\text{H}_2\text{O}$ , dibasic; *carlosic acid*,  $\text{C}_{10}\text{H}_{12}\text{O}_6$ , m.p. 181°,  $[\alpha]_{5461} -160^\circ$  in  $\text{H}_2\text{O}$ , dibasic; *ramigenic acid*,  $\text{C}_{16}\text{H}_{20}\text{O}_6$ , m.p. 171°,  $[\alpha]_{5461} +28^\circ$  in EtOH, lactic acid; *verticillic acid*,  $\text{C}_{26}\text{H}_{32}\text{O}_{12}$ , m.p. 171°,  $[\alpha]_{5461} -53^\circ$  in EtOH, lactic acid. The acids were isolated from the metabolism solution by taking advantage of their differing solubilities and precipitability by various metallic salts. The variety of products obtained from the metabolism solutions of moulds isolated from spoiled Italian and American maize suggests a possible connexion with human pellagra.

P. W. C.

**Cytochrome and the supposed direct spectroscopic observation of oxidase.** D. KEILIN (Nature, 1934, 133, 290—291; cf. this vol., 109).—Further spectroscopic observations on bacteria are recorded. All the absorption bands of h amatin (I) compounds seen by direct spectroscopic observation of the cells of different organisms belong either to free (I) or to the different components of cytochrome. None can be ascribed to the oxidase or the  $\text{O}_2$ -transporting enzyme.

L. S. T.

**Spectroscopic detection of the oxygen-carrying enzyme in *Azotobacter*.** E. NEGELEIN and W. GERISCHER (Biochem. Z., 1934, 268, 1—7; cf. preceding abstract).

W. McC.

**Significance of cytochrome in the physiology of cell respiration.** K. SHIBATA and H. TAMIYA (Acta Phytochim., 1933, 7, 191—231).—In the oxygenation (I) of cytochrome (II), the  $\text{O}_2$  mol. probably forms a complex with several (II) mols., and CO combines only with a certain fraction of the (II) mols., thus hindering (I). The formula relating CO inhibition to

the ratio of concns. of  $O_2$  and CO derived on this basis agrees with the results of Meyerhof and Schulz (A., 1932, 1067) for the respiration of *Azotobacter chroococcum*. The spectroscopic properties and genetic relationships of the (II) components are considered. Warburg's respiratory enzyme is probably component  $\alpha$  of (II). The function of (II) as  $O_2$  carrier is not regarded as depending on valency change of the Fe atom. J. H. B.

**Cytochrome spectrum of various micro-organisms.** H. TAMAYA and S. YAMAGUTCHI (Acta Phytochim., 1933, 7, 233—244).—The type of cytochrome spectrum given by various bacteria and yeasts is systematically described. J. H. B.

**[Bacterial] nitrogen assimilation.** A. ISAKOVA (Bull. Acad. Sci. U.R.S.S., 1933, 1493—1504).—Both *Azotobacter Winelandii* and *A. chroococcum* assimilate  $NH_3$  in presence of glucose, mannitol, NaOAc, or NaOBz, the mechanism of the action being the same in the two cases, although the action is more rapid with the former organism. The bacteria were grown in neutral or faintly alkaline media, which exclude autolysis, and the assimilation of the  $NH_3$  must be regarded as a function of the vital activity of the organisms. The experiments with NaOBz show that the  $NH_3$  may be assimilated as deaminated  $NH_2$  groups and as  $N_2$ . Deamination occurs also with  $NH_2$ -acids, but to a smaller extent than was observed by Kostytschev and Brilliant (A., 1923, i, 659). Experiment shows that development of  $NH_3$  is possible under approx. natural conditions, the rapidity of the process and the amount of  $NH_3$  formed depending largely on the nature of the substance supplying the energy. This observation has a bearing on the rapid accumulation by higher plants of  $N_2$  assimilated by azotobacteria. T. H. P.

**Rhizobium species in relation to nodule formation on the roots of Florida legumes.** W. R. CARROLL (Soil Sci., 1934, 37, 117—135).—Modifications of cultural methods are described and cross-inoculation data for a no. of species are recorded and discussed. A. G. P.

**Physiology of the acetic acid bacteria. I. Gluconic acid fermentation.** K. TANAKA (Acta Phytochim., 1933, 7, 265—297).—The  $O_2$  uptake by *Bacterium aceti* shows a much greater increase than the  $CO_2$  output on addition of glucose (I), owing to the formation of gluconic acid (II). The increased  $CO_2$  production is due to alcoholic fermentation, since it is repressed by  $CH_2I \cdot CO_2Na$ . The absence of the fermentation EtOH, normally oxidised to AcOH, causes a slight decrease in  $O_2$  consumed. The aerobic oxidation of (I) is independent of (I) concn., but sensitive to  $p_H$  (optimum 5—6). The production of (II) is greater when the bacteria have been grown in absence of (I) than when cultivated on media containing (I). Mannose, galactose, and maltose, but not fructose, sucrose, and lactose, can serve as substrates. (I) is oxidised more rapidly than EtOH when both are present. Methylene-blue,  $O_2$ , and benzoquinone (III) act as H acceptors, the activity increasing in that order. The (I) fermentation in presence of  $O_2$  is inhibited by KCN, CO, and PhMe, but in presence of (III), not by KCN, indicating that cytochrome (IV) probably takes part

in the fermentation as  $O_2$  carrier, but since fermentation of (I) is less sensitive to inhibitors than that of AcOH, part of the  $O_2$  may react without intervention of (IV). J. H. B.

**Metabolism of propionic acid bacteria. I. Degradation of phosphoric esters by *Propionibacterium Jensenii* (van Niel).** L. B. PERR and A. M. WYNNE (Trans. Roy. Soc. Canada, 1933, [iii], 27, V, 119—122).—AcCHO is formed by the action of the dried organism on 1% aq. Mg hexose phosphate at  $p_H$  6.1 or Na  $\beta$ -glycerophosphate at  $p_H$  7.0; with the latter glyceraldehyde (or dihydroxyacetone) is probably also formed. F. O. H.

**Chemistry of *Lactobacillus acidophilus*. II. Composition of neutral fat.** J. A. CROWDER and R. J. ANDERSON (J. Biol. Chem., 1934, 104, 399—406; cf. A., 1932, 1066).—The neutral fats in the EtOH-Et<sub>2</sub>O extract of *L. acidophilus* contain glycerides of lauric, myristic, palmitic, stearic, and oleic acids. The unsaponifiable matter contains cholesterol. A phosphate is pptd. from the extract with  $COMe_2$ . H. D.

**Enzymic formation of hydrogen sulphide by certain heterotrophic bacteria. II.** H. L. A. TARR (Biochem. J., 1934, 28, 192—198).—Extraction of  $COMe_2$ -dried *P. vulgaris* cells with  $PO_4'''$  buffer yields 2—3% of the enzyme (I) which produces  $H_2S$  from org. S compounds. In the intact cells (I) requires the presence of an  $NH_2$  group before it can become active. The activity is nil at  $p_H$  5.5, max. at  $p_H$  7.8—9.0, and 20% at  $p_H$  12. The optimum temp. is 40° and aerobic conditions are most favourable. H. G. R.

**Factors preventing the synthesis of a bacterial pigment.** A. GROOTEN and N. BEZSSONOV (Compt. rend., 1934, 198, 987—989).—The development of colour in *Bacillus balticus* at  $p_H$  7 and 20° is prevented by nineteen substances containing an OH (a *tert.* group being most effective), enolisable CO, or C·O·C group. The final  $p_H$ , which normally rises to 8.4 in a week, is then 6.2—8.0. Substances with  $k$  4—10 are generally more effective than those with low  $k$ , and a lowering of the temp. increases the effect. R. S. C.

**Influence of salt on diffusion from bacterial cells.** C. E. A. WINSLOW and H. H. WALKER (Proc. Soc. Exp. Biol. Med., 1933, 30, 1033—1035).—NaCl at low concn. (0.05—0.08M) increases viability of *Es. coli* and the diffusion of  $NH_3$  outwards through the cell wall; higher concns. ( $> 2M$ ) have an opposite and toxic effect. CH. ABS.

**Influence of cations on aerobic sporogenesis in a liquid medium.** F. W. FABIAN and C. S. BRYAN (J. Bact., 1933, 26, 543—547).—Chlorides of Na, Li,  $NH_4$ , and K, and also Na lactate stimulated spore production in *B. cereus*, *B. subtilis*, *B. mesentericus*, and *B. megatherium*. Chlorides of a no. of bi- and ter-valent metals were without effect. Slightly acid media appeared to favour spore formation, although in the range  $p_H$  5.0—7.5 the influence of reaction was very small. A. G. P.

**Tropical soil microbiology. I. Evolution of carbon dioxide from the soil and the bacterial growth curve.** A. S. CORBET (Soil Sci., 1934, 37,

109—115).—Evolution of  $\text{CO}_2$  from soil under laboratory conditions and at const. temp. is represented by the equation  $y = Ft^m$  ( $y$  = total yield of  $\text{CO}_2$  after time  $t$ ,  $m$  is a const. expressing the retardation of  $\text{CO}_2$  production due to laboratory conditions, and  $F$  is a const. representing  $\text{CO}_2$  produced during the initial unit of time in the experiment). Vals. for  $F$  and  $m$  are determined for a no. of soils. Curves showing daily yield of  $\text{CO}_2$  with advancing time correspond with the phase of decrease of bacterial growth. During this phase only a portion of the total organisms present are concerned in the production of  $\text{CO}_2$ . A. G. P.

**Poisonous principles of so-called Bongkrek poisoning of Java.** A. G. VAN VEEN and W. K. MERTENS (Rec. trav. chim., 1934, 53, 257—266).—The yellow cryst. substance, m.p. 171—172° (decomp.) (cf. A., 1933, 1206), formed alone by cultivation of the appropriate bacteria in glycerol-peptone media is accompanied in most other media (e.g., glycerol-agar or stearic acid-agar) by a colourless amorphous substance, which is N-free, has acidic properties ( $\text{H}_2\text{O}$ -sol. Na salt), and when injected intraperitoneally is toxic to rats in doses of  $< 0.1$  mg. The isolation of the latter is described. It is separated from accompanying fatty acids only with difficulty, and when pure is very sensitive to heat and oxidation. H. A. P.

**Poisons and disease and some experiments with the toxin of the *Bacillus tetani*.** J. J. ABEL (Science, 1934, 79, 63—70, 121—129).—An address. L. S. T.

**Lysis of tubercle bacilli *in vitro*.** H. J. CORPER (Amer. Rev. Tuberc., 1933, 28, 138—143).—Loss of acid-fastness in tissues sterilised with  $\text{H}_2\text{SO}_4$  is due to acid retained by the tissues, and not to the action of autolytic enzymes. CH. ABS.

**Detoxifying effect of ox bile on diphtheria toxin.** M. D. SMITH and P. J. MOLONEY (Trans. Roy. Soc. Canada, 1933, [iii], 27, V, 183—186).—Diphtheria toxin is detoxified by ox bile (I) when fresh, but not when heated at 100° for 20 min. Extraction of (I) by  $\text{Et}_2\text{O}$  at  $p_{\text{H}}$  2.0 yields a heat-stable detoxifying agent (II). The residue on neutralisation and addition of  $\text{AcOH}$  to  $p_{\text{H}}$  3.6 gives a ppt. which contains a heat-labile detoxifying agent (III). Whilst neither (II) nor (III) alone is significantly effective, (II)+(III) detoxify equally as well as (I). F. O. H.

**Enzymic capabilities and anaerobic growth of paratyphoid-*B* bacillus.** K. AARON (Biochem. Z., 1934, 268, 121—151).—Many org. compounds (I) (alcohols, acids, carbohydrates,  $\text{NH}_2$ -acids, peptides, and other N compounds) are dehydrogenated by the bacillus (II), including some (e.g.,  $\text{HCO}_2\text{H}$ ,  $\text{EtCO}_2\text{H}$ ) which cannot serve as C source (III) for its growth. Conversely, some (I) (e.g., *l*-tartaric acid, rhamnose) are not dehydrogenated, but can serve as sole (III) during aerobic growth. In presence of Na lactate and (II),  $\text{NaNO}_3$ , Na fumarate, Na *l*- and *i*-malate, Na aspartate, and asparagine (but not Na *l*- and *d*-tartrate, Na mesotartrate, and Na citrate) act as H acceptors. For the anaerobic growth of (II) in presence of Na lactate and  $\text{NO}_3^-$ , leucine, serine, aspartic acid, asparagine, glutamic acid, lysine, arginine, phenylalanine, tryptophan, histidine, proline, and glycyl-

glycine, but not  $\text{NH}_4\text{Cl}$ , glycine, alanine, urea, and uric acid, act as N sources. When glucose is the C source, glycine also serves as N source. When serine is the N source, the presence of  $\text{NaNO}_3$  is unnecessary. Strains of (II) which grow feebly anaerobically with  $\text{NH}_4\text{Cl}$  as N source can, however, be propagated. In presence of Na aspartate and  $\text{NaNO}_3$ , acetates, succinates, fumarates, *i*- and *l*-malates, *l*-tartrates, citrates, and glycerol (but not  $\text{EtOH}$ ) serve as C sources for the anaerobic growth of (II).  $\text{AcCO}_2\text{H}$  maintains anaerobic growth even in the absence of a H acceptor when the N source is serine, Na glutamate, histidine, proline, or  $\text{NH}_4\text{Cl}$ . W. McC.

**Biochemical and serological properties of *B. typhi flavum*.** J. SEYDEL (Ann. Inst. Pasteur, 1934, 52, 179—192).—*B. typhi flavum* (I) exhibits several points of difference from Eberth's bacillus (liquefaction of gelatin, production of  $\text{H}_2\text{S}$ , etc.). Serologically at least three groups can be distinguished, and the *flavum* strains are agglutinated more often by anti-typhoid and paratyphoid sera (80%) than by antisera to (I) (55%). P. G. M.

**Soluble specific substance of *Pneumococcus*.** I. Acetylpolysaccharide of *Pneumococcus* type I. O. T. AVERY and W. F. GOEBEL (J. Exp. Med., 1933, 58, 731—755).—In the isolation of the acetylpolysaccharide (I), excess of alkali is avoided. (I) contains 4.85% N, of which 45% is liberated in the  $\text{NH}_2$  form with  $\text{HNO}_2$  in the cold. Hydrolysis affords a polysaccharide identical with that hitherto termed the sol. sp. substance. Immunological reactions are described. CH. ABS.

**Antigenic structure of *Vibrio cholerae*.** III. Specific carbohydrates. R. W. LINTON and D. L. SHRIVASTAVA. IV. Carbohydrates in rice-water faeces. R. W. LINTON, D. L. SHRIVASTAVA, and B. N. MITRA (Indian J. Med. Res., 1933, 21, 379—384, 385—388).—III. On hydrolysis, 5 strains (from patients) yielded galactose (I) and 5 (from  $\text{H}_2\text{O}$ ) yielded arabinose (II).

IV. Polysaccharides afforded on hydrolysis probably (I) and (II). CH. ABS.

**Ramon flocculation reaction and fixed amounts of antigen or antiserum.** W. TIMMERMAN (Ann. Inst. Pasteur, 1934, 52, 146—154).—The different results obtained by taking either a fixed amount of diphtheria toxin or a fixed amount of antiserum are due entirely to the varying vols. of saline added to give a const. total vol. P. G. M.

**Effect of resection of the stomach on the bacteriology and chemistry of the small intestine and its clinical significance.** E. HERTEL and F. SARTORIUS (Arch. klin. Chirurg., 1933, 176, 197—235).—Experiments on dogs with intestinal fistulae (duodenum or lower ileum) showed that after gastric resection (Billroth I and II) the organisms of the upper and middle portions of the small intestine tended to increase in no. and to resemble those of the large intestine: differences between the two operations were principally apparent at the duodenal fistula. There was also an increase in the indole of the intestinal contents, and of urinary indican, particularly after a meat diet; indole was diminished after whey and milk,

especially sour milk. Resection produces abnormal fermentation and foulness in the upper parts of the gut.

NUTR. ABS. (b)

**Method of counting bacteria in milk.** W. M. BOGDANOFF (Lait, 1934, 14, 37—48).—The milk of suitable dilution is mixed in a known proportion with a standard suspension of stained *Schizosaccharomyces pombe* (I), and is then stained in the usual manner. On several "fields" the bacteria and the (I) are separately counted, and from the known count of the latter and the proportion of mixing of the two liquids the bacterial count may be calc.

E. B. H.

**Bacteriostatic action of gentian-violet and its dependence on the oxidation-reduction potential.** M. A. INGRAHAM (J. Bact., 1933, 26, 573—598).—Bacteriostasis caused by gentian-violet is closely related to its controlling effect on the oxidation-reduction potential of the medium. It affects the cultures only in the lag phase.

A. G. P.

**Influence of colloidal lecithin on microbial cytolysis by bacteriophage.** B. S. LEVIN and I. LOMINSKI (Compt. rend., 1934, 198, 989—991).—The cytolytic action of antistaphylococcal bacteriophage (I) is partly or completely inhibited by colloidal lecithin. This may account for the greater effect of (I) *in vitro* than *in vivo*.

R. C. S.

**Internal secretion of the parotid gland.** L. TAKÁCS (Orvosi Hetilap, 1933, 77, 659—661).—Fresh, minced parotid gland is extracted with EtOH and Et<sub>2</sub>O and the residue taken up in 0.4% HCl. After neutralising and concn., a yellow substance is obtained, insol. in EtOH, Et<sub>2</sub>O, C<sub>6</sub>H<sub>6</sub>, PhMe, readily sol. in H<sub>2</sub>O or dil. acids and alkalis. Injected into rabbits starved for 24 hr., material from 0.5—5.0 g. of fresh gland causes hypoglycæmia within 1—3 hr. Blood-sugar is lowered by 30—70% and remains low for > 24 hr. despite continued abundant feeding. Hypoglycæmic symptoms are not observed although vals. of 30 mg. per 100 c.c. are recorded.

NUTR. ABS. (m)

**Effect of injection of spleen extract on sugar-tolerance test in the normal and splenectomised dog.** F. RATHERY and I. COSMULESCO (Compt. rend. Soc. Biol., 1933, 113, 1115—1118).—Intravenous injection (I) of spleen extracts considerably diminishes the hyperglycæmia which normally follows (I) of glucose and causes the "bound" blood-sugar to fall slightly. With splenectomised dogs there are similar but less intense effects.

NUTR. ABS. (m)

**Influence of spleen extract on blood-sugar and experimental hyperglycæmia in dogs depancreatized before or after splenectomy.** F. RATHERY and I. COSMULESCO (Compt. rend. Soc. Biol., 1933, 113, 1430—1433).—Spleen extract, intravenously injected into the depancreatized dog, has the same slightly hypoglycæmic effect (free sugar) as in normal and splenectomised dogs. When the dog is both depancreatized and splenectomised, the effect is greatly intensified.

NUTR. ABS. (m)

**Liver-glycogen and splenectomy.** F. RATHERY, P. M. DE TRAVERSE, and (MLLE.) PATIN (Compt. rend.

Soc. Biol., 1933, 113, 1433—1435).—Splenectomy sometimes affects liver-glycogen in the dog.

NUTR. ABS. (m)

**Glycolytic hormone of the spleen.** N. FIESINGER and R. CATTAN (J. Physiol. Path. gén., 1933, 31, 380—399).—In the dog and rabbit, splenectomy and injection of extracts of spleen (I) indicate that (I) produce a hormone (not insulin) which causes hypoglycæmia.

NUTR. ABS. (m)

**Glycolytic hormone of the spleen. II. Application to human pathology.** N. FIESINGER, S. GOTHÉ, and H. R. OLIVIER (J. Physiol. Path. gén., 1933, 31, 759—765).—Intravenous injection of 2 c.c. of deproteinised splenic extract produces an inconst. fall in blood-sugar in normal and diseased subjects. Splenic feeding in diabetic patients gives no const. results.

NUTR. ABS. (m)

**Influence of the parathyroid on the metabolism of creatine and phosphoric acid.** C. G. IMRIE and C. N. JENKINSON (J. Physiol., 1933, 79, 218—225).—The creatine phosphate of the muscles (I) of thyroparathyroidectomised cats is < normal, and its rate (II) of resynthesis after stimulation of the (I) is reduced. After the administration of parathormone (II) is normal.

NUTR. ABS. (m)

**Influence of desiccated thyroid gland, thyroxine, and inorganic iodine on the storage of glycogen in the liver of the albino rat.** H. C. COGGESHALL and J. A. GREENE (Amer. J. Physiol., 1933, 105, 103—109).—Liver-glycogen (I) is reduced following administration of desiccated thyroid gland (II) and thyroxine (III), but remains practically unaltered after KI. The reduction after (II) or (III) is not proportional to the dose, although the effect is in general greater with greater doses. When given in doses of equiv. I content, (III) lowers (I) more than does (II), except in myxœdema, when both are equally effective.

NUTR. ABS. (m)

**Absorption of thyroxine from the gastrointestinal tract, with special reference to the effect of alkali.** W. O. THOMPSON, P. K. THOMPSON, S. G. TAYLOR, and L. F. N. DICKIE (J. Clin. Invest., 1933, 12, 990).—Pure thyroxine given orally or intraduodenally has little effect on the B.M.R.; as Na salt given orally it has about  $\frac{1}{4}$  the effect when given intravenously. When given in solution with excess NaOH (*i.e.*, as Na<sub>2</sub> salt) oral administration has almost as great an effect as intravenous.

NUTR. ABS. (m)

**Calorigenic action of thyroglobulin and its constituents.** J. LERMAN and W. T. SALTER (J. Clin. Invest., 1933, 12, 973—974).—In patients with myxœdema treated with thyroglobulin (I) obtained from hyperplastic or colloid glands the calorigenic response is proportional to the total I content. Since di-iodotyrosine (II) peptone obtained by peptic digestion of (I) is inactive in cases where thyroxine peptone obtained in this way is active in proportion to its I content, it follows that no calorigenic activity is lost in the isolation of (I) from whole thyroid gland and that (II) loses its activity in the first stage of proteolytic digestion of (I).

NUTR. ABS. (m)

**Peculiarity of thyroid extracts in exophthalmic goitre with respect to the increase in oxygen**

consumption. I. Increased oxygen consumption in rabbits following the injection of thyroid extracts from cases of exophthalmic goitre, [commercial] thyroid preparations, and extracts of normal glands. II. Variations in the oxygen consumption of rabbits after injection of splenic extracts, spleen preparations, and solutions of potassium iodide. K. SAITO (*Tôhoku J. Exp. Med.*, 1933, 22, 85—104, 105—115). CH. ABS.

Alteration of muscle metabolism in relation to the increase of muscular work by the adrenal cortex hormone. K. LANG (*Naturwiss.*, 1934, 22, 91).—After treatment with cortin, isolated frog's muscle develops tensions approx. 30% > normal, and its phosphagen content increases. W. O. K.

Effect of insulin and adrenaline on the amino-acid content of the blood of adrenalectomised rabbits. B. L. DAVIS, jun., and W. VAN WINKLE, jun. (*J. Biol. Chem.*, 1934, 104, 207—215).—A lowering (I) of the blood-NH<sub>2</sub>-acid of adrenalectomised rabbits is caused by adrenaline (II), but not by insulin (III). It is concluded that the (I) observed in normal animals following injection of (III) is caused by an increased secretion of (II). H. G. R.

Adrenaline liberation during insulin hypoglycæmia. T. J. YEN, T. AOMURA, and T. INABA (*Tôhoku J. Exp. Med.*, 1933, 21, 542—555).—Intravenous injection of insulin into dogs (0.25—10 units per kg.) increases the secretion of adrenaline. Blood-pressure falls somewhat, body temp. rises, and respiratory rate increases. CH. ABS.

Effect of insulin in accelerating the discharge of adrenaline. H. SATO, F. OHMI, and S. KANO-WOKA (*Tôhoku J. Exp. Med.*, 1933, 22, 53—64). CH. ABS.

Effect of adrenaline and insulin on the lactic acid metabolism in the liver. K. KATO and K. KIMURA (*Tôhoku J. Exp. Med.*, 1933, 21, 298—313).—Adrenaline increases the formation of lactic acid (I) in muscle and in organs drained by the portal vein, arterial and portal blood-(I) being correspondingly increased. Mobilisation of liver-glycogen and the attendant liberation of (I) exhibit an even greater acceleration. Splanchnicotomy decreases this effect. Insulin (II) increases hepatic venous blood-(I), but does not greatly affect arterial or portal blood-(I). (II) hypoglycæmia depends largely on the transformation of glucose into (I), and mobilisation of glycogen causes a further increase in venous blood-(I). Splanchnicotomy has no effect. CH. ABS.

[Precipitation of insulin.] V. D. YANKOVSKI and S. S. BRYUKHONENKO (*Bull. Nauch. Issledov. Khim.-Farm. Inst.*, 1931, 223—228).—Insulin is completely pptd. from aq.-EtOH, but not from EtOH, solution by Benzoechtrosa 2BL. The red double compound with NH<sub>3</sub> can be used for its colorimetric determination. CH. ABS.

Sugar in blood and subcutaneous lymph following insulin administration. J. W. HEIM and B. N. BERG (*Amer. J. Physiol.*, 1933, 105, 674—677).—In dogs the lymph-sugar (I) is usually > or = the sugar in arterial plasma; it is never significantly lower. Injection of insulin causes a fall in plasma- and (I), the vals. remaining very close together. The diffusion of

sugar from blood to lymph is similar in the normal and diabetic dog. NUTR. ABS. (m)

Insulin and sugar tolerance in thin people. H. BLOTNER (*Arch. Int. Med.*, 1934, 53, 153—158).—Administration of insulin (small doses during several weeks) to certain thin normal persons results in a temporary decrease of sugar tolerance, evidenced by glycosuria with or without an abnormally high blood-sugar curve after a glucose test-meal. W. O. K.

Significance of the action of insulin on the respiratory quotient of the diabetic heart. E. W. H. CRUICKSHANK (*J. Physiol.*, 1933, 79, 2—4P).—Addition of insulin to the perfusing blood of the isolated heart is followed by a rise in the R.Q. to 1, an increase in the rate of disappearance of blood-sugar, and a slight increase in O<sub>2</sub> consumption, whilst the glycogen content of the heart remains high. These results support the view that a failure in the oxidation of carbohydrate is the primary defect in pancreatic diabetes. NUTR. ABS. (m)

Effect of insulin on the serum-inorganic phosphate in normal and adrenalectomised dogs. R. ELLSWORTH and A. WEINSTEIN (*Bull. Johns Hopkins Hosp.*, 1933, 53, 21—30).—The fall in serum-inorg. PO<sub>4</sub>''' in a given interval after insulin injection is approx. the same in completely adrenalectomised dogs maintained on cortical extract, as in normal dogs. After the fall in PO<sub>4</sub>''' there is a rise to a level > the control val. NUTR. ABS. (m)

Effect of previous hypophysectomy on the diabetes resulting from pancreatectomy. J. F. REGAN and B. O. BARNES (*Amer. J. Physiol.*, 1933, 105, Proc. 83).—In two hypophysectomised dogs subsequent pancreatectomy did not produce the usual hyperglycæmia. In another which survived for 5 weeks there was no glycosuria, blood-sugar was about normal, and a small dose of insulin produced convulsions. NUTR. ABS. (m)

Influence of insulin-free pancreatic extract on the gaseous exchange of the white rat. C. J. CARR, J. E. SCHMIDT, and W. HARNE (*J. Pharm. Exp. Ther.*, 1934, 50, 151—156).—Insulin-free pancreatic extracts, injected subcutaneously into the fasting rat, increased R.Q. without significantly affecting O<sub>2</sub> consumption (I). Mixtures of the extract and adrenaline produced a slight increase in R.Q., but the extract did not antagonise the increased (I) produced by adrenaline. Intravenous injection of the extract in rabbits showed marked hypoglycæmic effects. R. N. C.

Effect of the pituitary hypolipæmic substance on man. W. RAAB (*Z. ges. exp. Med.*, 1933, 89, 588—615; *Chem. Zentr.*, 1933, ii, 2263—2264).—The effects of various pituitary preps. on the blood-fat after administration of arachis oil have been studied. The factor responsible, lipotrin, is not identical with any previously described pituitary hormone. A. A. E.

Relation of the posterior pituitary hormone to carbohydrate metabolism in man. S. THAD-DEA (*Z. klin. Med.*, 1933, 125, 175—194; *Chem. Zentr.*, 1933, ii, 2415).—After subcutaneous injection of orasthin the blood-sugar is unchanged, but it increases after subcutaneous tonephin injection, and then falls. This is a result of increased insulin secretion, and con-

sequently does not occur in diabetes mellitus. In exophthalmic goitre and severe liver parenchyma disease no rise in the blood-sugar occurs. Toneyphin will prevent insulin hypoglycæmia in healthy subjects, but not in cases of exophthalmic goitre and liver diseases.

H. J. E.

**Effect of Loeb's anterior pituitary extract on the basal metabolism of dogs.** J. G. BUENO and B. O. BARNES (Amer. J. Physiol., 1933, 105, Proc. 15).—In normal dogs daily injections of the extract cause a rise in basal metabolism which reaches a peak of about 30% above normal on the fourth or fifth day. Other changes observed include increased respiration and heart rate, thirst, and polyuria. All the symptoms disappear about 5 days after the last injection. None of these changes occurs in the thyroidectomised dog.

NUTR. ABS. (m)

**Preparation, identification, and assay of prolactin—a hormone of the anterior pituitary.** O. RIDDLE, R. W. BATES, and S. W. DYKSHORN (Amer. J. Physiol., 1933, 105, 191—216).—A hormone ("prolactin") is prepared from the anterior lobe of the pituitary by methods described. It is obtained free from the gonadotropic and thyrotropic substances and probably also from growth-promoting activity. It excites lactation in a mature non-lactating mammary gland and also leads to sp. enlargement and activity of the crop gland of pigeons, a fact made use of in the assay. It has not been detected in tissues other than the pituitary.

NUTR. ABS. (m)

**Pituitary substance giving increased gonadotropic effects when combined with prolan.** H. M. EVANS, M. E. SIMPSON, and P. R. AUSTIN (J. Exp. Med., 1933, 58, 545—559).—The synergic factor itself possesses slight gonadotropic activity. The substance is unaffected by digestion with trypsin, or with trypsin followed by short digestion with erepsin, but is inactivated by pepsin.

CH. ABS.

**Gonad-stimulating hormones. II. Influence of length of period of administration of certain extracts.** C. F. FLUHMAN (Proc. Soc. Exp. Biol. Med., 1933, 30, 1014—1016).

CH. ABS.

**Influence of the gonads on protein metabolism. IV. Effect of ovariectomy and of injections of gonadal and anterior pituitary extracts on urinary creatinine in female rabbits.** I. SCHRIER and H. ZWARENSTEIN (Biochem. J., 1934, 28, 356—359).—In ovariectomised (I) adult rabbits (II) the excretion of creatinine (III), const. for 5 months, had slightly increased 9 months after the operation. Administration of extracts of ovaries or testicles causes a larger fall in the high (III) of (I) than in the (III) of normal (II), whilst extracts of the anterior lobe of the pituitary increase the output of (III) in normal (II), but have little effect on (I) (II).

W. O. K.

(A) Biological characteristics of ovary-stimulating extracts made from blood of pregnant women. (B) Induction of ovarian growth with an extract made from blood of pregnant women. C. F. FLUHMAN (Proc. Soc. Exp. Biol. Med., 1932, 29, 1193—1195; 1933, 30, 149—150).

CH. ABS.

**Recognition and comparison of prolan and prolan-like substances.** H. M. EVANS, M. E.

SIMPSON, and P. R. AUSTIN (J. Exp. Med., 1933, 58, 561—574).—The gonadotropic hormone of the blood of the pregnant mare is conc. by adsorption on active  $Al(OH)_3$  followed by elution. Biological effects of its injection are described.

CH. ABS.

**Preparation of prolan, theelin, and theelol from the same urine.** P. A. KATZMANN and E. A. DOISY (Proc. Soc. Exp. Biol. Med., 1933, 30, 1196—1197).—Prolan is adsorbed on BzOH. The filtrate, acidified with HCl, is kept for a few days and the supernatant liquid is extracted (continuously) with BuOH. The residue on evaporation of the BuOH is extracted with  $C_6H_6$ , which is removed by distillation. The residue from 100 gals. of urine is dissolved in 1500 c.c. of 80% EtOH containing 150 c.c. of conc. HCl; after boiling for 4 hr. the EtOH is distilled off and solid NaOH is added in excess (phenolphthalein). The solution is extracted with BuOH- $C_6H_6$  (50%), and the process continued as from stage 3 of Doisy and Thayer's method (A., 1931, 879). Theelol (yield 2—5 mg. per gallon of urine) is purified as the Na salt.

CH. ABS.

**League of Nations; Committee of Hygiene. International standard for oestrogenic hormone.** C. LORMAND (Bull. Soc. Chim. biol., 1933, 15, 1566—1568).—The unit of oestrogenic activity is defined as that contained in  $10^{-7}$  g. of ketohydroxyoestrin.

H. D.

**Oestrogenic activity of condensed-ring compounds in relation to other biological activities.** J. W. COOK, E. C. DODDS, C. L. HEWETT, and W. LAWSON (Proc. Roy. Soc., 1934, B, 114, 272—286).—Condensation of the appropriate Mg alkyl halide with 1:2:5:6-dibenzanthraquinone affords 9:10-dihydroxy-9:10-diethyl-9:10-dihydro-1:2:5:6-dibenzanthracene (I), m.p. 248—250°, and its homologues, -9:10-di-n-propyl- (II), m.p. 245—247° [stereoisomeric (?), m.p. 192—195° (III)], -9:10-di-n-amyl- (IV), m.p. 178—179°, and -9:10-di-n-hexyl- (V), m.p. 164—165°. Phenanthraquinone and 1:2-benzanthraquinone with  $MgBu^eBr$  similarly yield 9:10-dihydroxy-9:10-di-n-butyl-9:10-dihydrophenanthrene, m.p. 134—134.5°, and -9:10-dihydro-1:2-benzanthracene, m.p. 126°. Et 2:4-diketo-1:2:3:4:9:10:11:12-octahydrophenanthrene-1-carboxylic acid, m.p. 133—134°, is obtained from Et  $\Delta^1$ -dihydro-1-naphthoate and  $CH_2AcCO_2Et$ . Oestrogenic activity (VI) is shown by (I), (II), [40,000 rat units per g., max. of this series], (III) [20,000 rat units per g.], their  $Bu^e_2$  analogue (A., 1931, 612), and, to a smaller extent, by 1-keto-1:2:3:4-tetrahydrophenanthrene, neoergosterol, calciferol, ergosterol, 5:6-cyclopenteno-1:2-benzanthracene, 1:2-benzpyrene, and 1:9-dimethylphenanthrene. A large no. of inactive polycyclic compounds include (IV), (V), the  $Me_2$  analogue (*loc. cit.*), fluorene, chrysene, retene, 1:2-benz-, and 1:2:5:6-dibenzanthracene, and 1:2-cyclopentenophenanthrene. The (VI) of varied mol. types is discussed, in relation to their carcinogenic or antirachitic activities.

A. C.

**Sex change in plumage of Brown Leghorn capons following injection of certain oestrogen-producing compounds.** J. W. COOK, E. C. DODDS, and A. W. GREENWOOD (Proc. Roy. Soc., 1934, B, 114, 286—290).—Injection of 1-keto-1:2:3:4-tetra-

hydrophenanthrene or 9:10-dihydroxy-9:10-di-*n*-butyl-9:10-dihydro-1:2:5:6-dibenzanthracene causes the appearance of female characteristics in the plumage of Brown Leghorn capons. No acceleration in comb growth is observed. A. C.

**Progesterin in placental extract.** A. A. ADLER, P. DE FREMERY, and M. TAUSK (Nature, 1934, 133, 293).—The presence of progesterin has been demonstrated in human and animal (cow) placenta.

L. S. T.

**Assay of vitamin-A.** J. B. ORR and M. B. RICHARDS (Nature, 1934, 133, 255).—In a series of assays by the curative method of the vitamin-A content (I) of fish oils and dried milk, it was found that in most cases the wt. curve did not give a trustworthy indication of the state of depletion of the vitamin-A (II) reserve of an animal, and that an increase in wt. after administration of a supplement could not always be ascribed to its (I). Further, when (II) is the only known factor absent from the diet there is no cessation of growth (increase in size). (II) cannot be considered more essential for growth *per se* than any other of the many factors responsible for an increase in wt. The characteristic loss in wt., termed "cessation of growth," is apparently due to pathological conditions (III) arising from the (II) deficiency, and the diversity of (III) which may arise during the preliminary depletion period makes it impossible to secure uniformity at the beginning of a test period. This makes the curative method of (II) assay of doubtful val.

L. S. T.

**Spectrophotometric method for the assay of carotene and vitamin-A in butter.** A. E. GILLAM (Biochem. J., 1934, 28, 79—83).—The average ratio of carotene (I) to xanthophyll (II) in butter, from determinations on 70 samples, is 14:1 by wt. and the (I) content can be calc. with sufficient accuracy by assuming that 94% of the light absorption of the unsaponifiable fraction at 455—460  $m\mu$  is due to (I). In this way, the removal of (II) before determination of (I) is avoided and the author's method (A., 1933, 848) is shortened, permitting its use for routine purposes.

P. W. C.

**Chemical evaluation of the vitamins.** A. L. BACHARACH and E. L. SMITH (Analyst, 1934, 59, 70—81).—A review. E. C. S.

**Determination of vitamin-A.** N. EVERS (Analyst, 1934, 59, 82—85).—48 samples of cod-liver oil gave a mean "true blue val." calc. from the intensity of absorption at 328  $m\mu$  2.17 times the actual mean blue val. of the oils. The determination of the blue val. of ordinary commercial oils is adequate to express the approx. vitamin-A content. E. C. S.

**Relationship between the Carr-Price value and the 328  $m\mu$  absorption coefficient of preparations containing vitamin-A.** S. K. CREWS and S. J. COX (Analyst, 1934, 59, 85—90).—The blue val. of liver-oil (I) when determined on the unsaponifiable fraction is usually > when determined on the oil itself, but in neither case is the vitamin-A content (II) so determined as great as (II) calc. from the absorption at 328  $m\mu$  (the *E* val.). The inhibiting substances present in (I) cause a depression of the blue val. > any in-

crease due to chromogenic substances other than vitamin-A. The apparatus and technique employed in the determination of the *E* val. are described. Vitamin-A has a max. absorption between 325 and 330  $m\mu$ , carotene at 450  $m\mu$  approx., and vitamin-D between 265 and 270  $m\mu$ . The colour given with  $SbCl_3$  by (I) is pure blue or violet-blue, by concentrates of (I), greenish-blue. E. C. S.

**Chemical tests for vitamins.** L. J. HARRIS (Analyst, 1934, 59, 93—95).—For accurate determination of the vitamin-A content of a foodstuff by the  $SbCl_3$  method it is essential to saponify first and make the test on the unsaponifiable fraction. The blue val. is then determined by the tintometer. Semi-chemical tests for vitamin- $B_1$ , and a modification of Tillmans' method (cf. A., 1933, 433) for -C, are described. E. C. S.

**Carotene. VII. Physical properties of carotenes from different plant sources.** J. H. C. SMITH and H. W. MILNER (J. Biol. Chem., 1934, 104, 437—447; cf. A., 1933, 1151).—The m.p. of different samples of carrot-root carotene (I) are plotted against their  $[\alpha]$ , giving a typical two-component m.-p. curve. Mixed m.p. of  $\alpha$ - (II) and  $\beta$ -carotene (III) lie on the curve. The inactive carotenes from sunflower, chard, and cauliflower leaves have approx. identical m.p. and solubilities; the solubilities of mixtures of leaf carotene and (I) lie between those of the pure components. The ultra-violet absorption (IV) max. of (II) are 4472 and 4755  $\text{\AA}$ ., and of (III) are 4529 and 4796  $\text{\AA}$ .. The (IV) curves of mixtures of (II) and (III) shift quantitatively towards the violet as their  $[\alpha]$  increases.

H. D.

**Physical and chemical properties of bioosterin (vitamin-A) and its physiological significance.** V, VI, and VII. Z. NAKAMIJA (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 3—5).—V. Fractional distillation in vac. of methylperhydrobioosterin from cod-liver oil yielded a hydrocarbon (b.p. 50—90°) and a no. of fractions containing OMC (b.p. 90—193°), indicating the presence of OH in the original bioosterin.

VI. Nonacosane and a liquid hydrocarbon were obtained from perhydrobioosterin.

VII. 90% of bioosterin condensed with maleic anhydride in 20 hr. at 140°, whilst 15—20% condensed with citraconic anhydride at room temp. in 1 month (35% of the vitamin-A fraction of "Ischinagi" oil condensed in 8 days). The non-condensing fraction gave a *hydrochloride*, m.p. 131—132° (Cl 32.4%), and a *bromide*, darkens above 170° (Br 62.5%). Bioosterin-maleic acid may be acetylated and hydrogenated; ozonisation yields geronic and succinic acids.

P. G. M.

**Carotene-vitamin-A in man.** W. VON DRIGALSKI (Z. Vitaminforsch., 1934, 3, 37—74).—The liver (I), whether normal or diseased, is the main storehouse of vitamin-A-carotene (II). Following saturation of (I) with (II), (II) passes into the blood, the highest level attained being 0.00027%; such a condition is due to excess ingestion of (II) and is not pathological. The blood-(II) varies considerably. Small amounts of (II) are found in transudates, more in exudates, but none in sweat, bile, semen, cerebrospinal fluid, faeces, or urine. Destruction (by oxidation) of (II) probably



occurs in (I). The protection of epithelial tissue by (II) is emphasised.

F. O. H.

**Vitamin-A and carotene. XI. Distribution of vitamin-A in the organs of the normal and hypervitaminotic rat.** A. W. DAVIES and T. MOORE (Biochem. J., 1934, 28, 288—295).—The vitamin-A (I) content of the organs of rats receiving differing amounts of (I) and of carotene (II) was determined. Kidneys (III) and lungs (IV) contained small amounts even when the liver (V) content was low. Administration of large but non-toxic doses of (I) to adult rats caused extremely high concn. in (V), that in (IV) being increased to about the normal (V) level, whilst the (III) level remained low. Distribution of (I) in young rats given toxic doses of (I), causing emaciation, hæmorrhagic rhinitis, lung and bone lesions, was similar to that in rats given non-toxic doses, except that the concn. in (IV) was even higher. It was impossible to produce hypervitaminosis-A by feeding (II), rats receiving 8 mg. per day growing normally; storage of (I) in (V) was moderately high and in (III) and (IV) very low.

C. G. A.

**Growth investigations with carotenoids.** H. VON EULER, P. KARRER, and A. ZUBRYS (Helv. Chim. Acta, 1934, 17, 24—29).—PBr<sub>3</sub> added to a dry C<sub>6</sub>H<sub>6</sub> solution of zeaxanthine (I) and xanthophyll (II) causes partial replacement of OH by Br and partial elimination of HBr from the product. Extraction with 90% MeOH of the ligroin extract of the residue from the washed C<sub>6</sub>H<sub>6</sub> solution removes unchanged (I) and (II), giving products (P<sub>I</sub> and P<sub>II</sub>) containing 2—5% Br, the absorption spectra of which differ but slightly from those of (I) and (II). Daily doses of P<sub>I</sub> (40 × 10<sup>-6</sup> g.) or P<sub>II</sub> (10 × 10<sup>-6</sup> g.) caused wt.-increase of 1.4 g. and 0.8 g. per day, respectively, in rats. Growth promotion by α- and β-carotene is greatly dependent on the composition of the basic diet, the min. daily doses being 5 and 2.5 × 10<sup>-6</sup> g., respectively. Ca(OH)<sub>2</sub> adsorption of purest vitamin-A preps. gives a main β-fraction (growth increase 0.7 g. per day for a dose 0.3 × 10<sup>-6</sup> g.) and a small α-fraction, *hepaxanthine* (absorption spectrum with SbCl<sub>3</sub> gives max. at 580 mμ), which is much less active (dose 3 × 10<sup>-6</sup> g. per day).

J. W. B.

**Vitamin-A content of pasteurised milk and native [Puerto Rican] cheese.** D. H. COOK and J. H. AXTMAYER (Puerto Rica J. Pub. Health, 1933, 9, 90—92).—Vals. for pasteurised milk and whole milk cheese are, respectively, 2 units per c.c. and 20 units per g.

CH. ABS.

**Fat metabolism in vitamin-A deficiency: blood-serum-esterase.** H. N. GREEN (Biochem. J., 1934, 28, 16—24).—Esterase activity (I) was determined by titration of the acid liberated from esters by incubation with the serum. (I) decreases in vitamin-A (II) deficiency and infection in rats and dogs, increases with excess of (II) in the diet, and is unaffected by vitamin-B deficiency.

H. D.

**Fat metabolism in vitamin-A deficiency: utilisation of fat and desaturation of fat in the liver.** H. N. GREEN (Biochem. J., 1934, 28, 25—30).—Large quantities of fat can be absorbed by vitamin-A (I) deficient rats. The lowering of the % of fat in

the liver and the raising of its I val. by (I)-deficiency are similar to the effects of inanition and infection.

H. D.

**Vitamin content of fish fat. II. Antirachitic value of the fat of the Japanese sardine and cat-fish.** S. N. MATZKO (Z. Unters. Lebensm., 1934, 67, 172—174; cf. A., 1932, 887).—The vitamin-D content of the fat of the Japanese sardine is < 10 units per g., that of the visceral fat of the cat-fish 50—65 units per g.

E. C. S.

**Vitamin-D activity of butter. II. Complex nature of the antirachitic action of butter. III. Nature of the labile factor in butter antirachitic for the rat. Antirachitic potency of lard, olive oil, egg oil, and the fatty acids of butters and lard.** S. K. KON and R. G. BOORH (Biochem. J., 1934, 28, 111—120, 121—130).—II. At least two factors antirachitic to the rat are present in butter, one which is not recoverable in the non-saponifiable residue, and the other (vitamin-D) which is resistant to saponification. By exposure to summer conditions or by feeding to cows irradiated yeast or cod-liver oil, the concn. of the stable, but not of the labile, factor is greatly increased. Direct irradiation of the butter also leads to the formation of the stable factor only. > 75% of the potency of autumn and winter butters is either destroyed or diverted to another fraction on prep. of the non-saponifiable residue. Attempts to separate the two factors by Zucker's method were unsuccessful.

III. A sample of home-rendered lard had almost the same antirachitic activity (I) for rats as winter and autumn butter, and an American sample was as active as summer butter. The (I) of lard is impaired by saponification. Fatty acids prepared from various butters possessed a slight but definite (I) which was not due to incomplete removal of non-saponifiable residue (II). Butter incorporated in the diet had a lower (I) than when fed separately. Autumn butter loses a large part of its (I) on saponification, but its (I) is almost completely recovered when the administration of (II) is accompanied by feeding the fatty acid fraction (III). Loss of (I) on saponification may be explained in terms of loss of a new labile factor but is more simply accounted for in terms of loss of the antirachitic effect on the rat of (III). The bearing of these results on the interpretation of the vals. usually obtained in feeding experiments is discussed.

P. W. C.

**Occurrence of antirachitic vitamin in green plants.** O. RYGH (Nature, 1934, 133, 255).—Meadow hay from Oslo gave an extract possessing the same antirachitic effect as a high-quality cod-liver oil. Vitamin-D in this extract has the same characteristics as have been described (A., 1933, 1089) for that in butter.

L. S. T.

**Influence of fat-soluble vitamin on the amounts of cholesterol substances in the bile in rabbits.** S. KUSAKA (Japan. J. Gastroenterol., 1933, 5, 31—35).—Excess of cholesterol is excreted by the liver.

CH. ABS.

**Products of ultra-violet irradiation of ergosterol.** A. V. TRUFANOV (Khim. Farm. Prom., 1933,

196—203).—The products were tested for vitamin efficiency on rats. CH. ABS.

**Enrichment of vitamin-D in yeast by ultra-violet irradiation.** S. N. MATZKO (Arch. Tierernähr. Tierzucht, 1933, 9, 623—636).—The vitamin-D content of baker's yeast may be raised to 5000—10,000 units per g. by irradiation. When prepared in presence of atm. O<sub>2</sub> and CO<sub>2</sub>, the material has no toxic action if administered in customary amounts. The vitamin potency remained unchanged during storage for 2 months, but weakened somewhat after 4 months.

A. G. P.

**Calcium compound in serum following overdosage with parathyroid hormone or ergosterol.** N. B. TAYLOR, C. B. WELD, and J. F. SYKES (Trans. Roy. Soc. Canada, 1933, [iii], 27, V, 247—252).—When normal blood or Ca-free saline is transfused into hypercalcaemic dogs, the high serum-Ca (I) is maintained. This is probably due to the rapid transference of Ca from the tissue-fluids to the blood. Similarly, when part of the blood of parathyroidectomised dogs is replaced by that from parathyroid-treated dogs, (I) immediately increases, the same effect being obtained by the infusion of an equiv. amount of Ca as Ca gluconate. Hence the parathyroid gland does not appear to control the formation of a non-diffusible Ca compound (cf. A., 1925, i, 857). The anomaly of a high kidney threshold for Ca is explained by re-absorption in the tubules.

F. O. H.

**Effect of activated ergosterol administration on the cerebrospinal fluid-calcium.** C. R. K. JOHNSTON and E. J. KING (Trans. Roy. Soc. Canada, 1933, [iii], 27, V, 87—89).—Oral administration of large doses of activated ergosterol to dogs is followed by a rapid rise in the serum-Ca, which reaches a max. after 48—60 hr., when the cerebrospinal fluid-Ca commences to increase. Both levels gradually decrease during the third to fifth day, and secondary rises occur from the fifth to eighth day, after which the levels very slowly return to normal. The theory that vitamin-D acts through the parathyroid hormone is supported.

F. O. H.

**Hypervitaminosis in the chicken. Mobilisation of calcium by irradiated ergosterol.** G. E. HALL and E. J. KING (Trans. Roy. Soc. Canada, 1933, [iii], 27, V, 149—158).—Oral administration of large amounts of irradiated ergosterol produces a loss in body-wt. and an increase in serum-Ca, whilst calcification occurs in the stomach wall and kidney. Addition of 10% of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> to the diet considerably enhances the above Ca changes, whilst the imperfect bone calcification due to hypervitaminosis-D is reduced. The mechanism of the changes in bone-Ca is discussed.

F. O. H.

**Fat-soluble vitamins: their relation to growth and resistance to disease.** R. SUTHERLAND (Diss., Aberdeen, 1933).—School-children given daily doses of radiostoleum (vitamin-A and -D) for 6 months showed a slight superiority, regarded as statistically significant, in height, and possibly also in wt. and nutritive condition, over controls, but no decreased susceptibility to infection or increased resistance to established disease.

NUTR. ABS. (b)

**Mortality among tropical fish.** J. I. SPIRA (Science, 1934, 79, 140—141).—High infant and adult mortality among tropical fish is prevented by the addition of viosterol to a diet of desiccated shrimp, beetle, and ground fresh liver. Deeper pigmentation, increased activity, and recovered rigidity of deformed vertebræ also result.

L. S. T.

**Recent developments of sterol chemistry in relation to biological problems.** J. PRYDE (Nature, 1934, 133, 237—239).—A review.

L. S. T.

**Lipins and vitamins-B. I. Rôle of vitamins-B in utilisation of lipins by the organism.** R. LECOQ. II. Influence of constitution of lipins on progress of avitaminosis in pigeon. General need of vitamins-B in utilisation of lipins. R. LECOQ and J. SAVARE. III. Are alcohol-water-soluble vitamins-B equally lipin-soluble? J. SAVARE (Bull. Soc. Chim. biol., 1933, 15, 1498—1507, 1508—1516, 1517—1519).—I. Pigeons fed on a vitamin-B-deficient diet (I) containing muscle powder lived longer than those fed on a similar diet containing muscle peptones. High doses of lipins failed to prevent the onset of polyneuritis, which was, however, cured rapidly by the administration of yeast.

II. Pigeons on (I) containing muscle peptones live longer when fed with difficultly digestible lipins than when fed with easily digestible ones.

III. Olive oil left in contact with a yeast extract for 10 days was not antineuritically active.

H. D.

**Physiology of vitamins. XXIII. Effect of lack of the vitamin-B complex on the secretion of gastric juice in dogs with gastric pouches.** G. R. COWGILL and A. GILMAN (Arch. Int. Med., 1934, 53, 58—70).—The gastric activity, as evidenced by response to histamine injection, of three dogs with Pavlov pouches was decreased when the diet was deficient in vitamin-B, but a dog with a Heidenhain pouch (vagus innervation interrupted) was not thus affected by lack of vitamin-B. The factor involved is probably B<sub>1</sub> and not B<sub>2</sub>.

W. O. K.

**Growth-vitamin-B in egg-yolk.** C. SZYMANSKA (Bull. Soc. Amis Sci. Poznań, 1932, B, Ci. math. nat. No. 5, 15—37; Chem. Zentr., 1933, ii, 2287).—H<sub>2</sub>O extracts 40% of the vitamin-B from defatted, dry egg yolk, but the residue is inactive; on reunion of extract and residue the original activity is attained. The vitamin is considered to be compound in nature.

A. A. E.

**Physiology of vitamins. XXII. Effect of experimentally-induced hyperthyroidism on the vitamin-B requirement of pigeons.** G. R. COWGILL and M. L. PALMIERI (Amer. J. Physiol., 1933, 105, 146—150).—After hyperthyroidism had been induced in pigeons by the administration of desiccated thyroid, the min. dose of a vitamin B<sub>1</sub> concentrate needed to maintain wt. and prevent anorexia was much increased. The relative increase varied widely in individual birds. The vitamin-B<sub>1</sub> requirement is probably related to the caloric intake.

NUTR. ABS. (b)

**Vitamin-B<sub>1</sub> and the conception of a beri-beri quotient (Q<sub>b</sub>).** G. AMANTEA (Atti R. Accad. Lincei, 1933, [vi], 18, 317—323).—The beri-beri quotient is

defined as the ratio of the total consumption to the initial wt. of the animal, and is given by  $Q_b = (\text{rice retained} + \text{body-wt. lost}) / \text{initial wt.}$  Although  $Q_b$  may vary between 0.7 and about 1 for different pigeons, yet, under similar experimental conditions, it is sufficiently const. for one and the same animal to serve as an index in quant. experiments on vitamin- $B_1$ .

T. H. P.

**Extractability of vitamin- $B_2$  from yeast by acetone-water and methyl alcohol-water mixtures.** P. L. DAY [with W. J. DARBY] (J. Amer. Chem. Soc., 1934, 56, 452—454).—Vitamin- $B_2$  (I) is not extracted from dry baker's yeast by 80 and 99.5%  $\text{COMe}_2$  or abs. MeOH; 60%  $\text{COMe}_2$  and 60% MeOH extract about 50% and 80% MeOH removes about 20% of (I). All % are by wt. Yeast extracts which do not promote growth do not prevent the onset of cataract, keratitis, and conjunctivitis. H. B.

**Vitamin- $B_2$ .** B. C. GUHA and P. N. CHAKRAVORTY (Indian J. Med. Res., 1933, 21, 211—219).—Extracts of ox- and buffalo-kidney and of fowl-liver were good sources of vitamin- $B_2$  (I), and "Hilsha" fish was a poor source. Extracts of liver were most potent if made at  $p_H$  5. (I) in the ox-kidney extract was largely destroyed by heating at 100° for 15 min. at  $p_H$  10.5. NUTR. ABS. (b)

**Vitamin- $B_2$ .** P. GYÖRGY, R. KUHN, and T. WAGNER-JAUREGG (Klin. Woch., 1933, 12, 1241—1245).—Lactoflavin (I) and ovoflavin may be identical with one constituent of vitamin- $B_2$  (II), and vitamin- $B_4$  (Reader) a second constituent. Warburg and Christian's oxidation enzyme from yeast, in which "yeast flavin" is united with a polysaccharide, was rich in (II) even after the enzyme was destroyed by boiling. The flavin group, after irradiation, was sol. in  $\text{CHCl}_3$  and showed a composition and absorption spectrum similar to that of pure (I) but no (II) activity. The (II) activity of (I) and of boiled food extracts was also destroyed by irradiation with visible light, filtered from ultra-violet rays. The relation of (II)-deficiency to pellagra, anaemia, and sprue is discussed. Treatment of a condition resembling sprue in older infants with (II) (as cooked meat extract or yeast extract) and Fe was successful. NUTR. ABS. (b)

**Behaviour on oxidation-reduction and a colour reaction of lactoflavin (vitamin- $B_2$ ).** R. KUHN and T. WAGNER-JAUREGG (Ber., 1934, 67, [B], 361—363).—Reduction of lactoflavin (I) by Zn, Sn, or Na-Hg, in 10% HCl does not immediately yield the leuco-compound, an intense red, comparatively stable intermediate product being formed. Analogy with pycocyanine indicates this to be due to a radical-like  $\text{H}_2$ -compound. The biological importance of the behaviour of (I) on oxidation-reduction is discussed; in addition, its vitamin properties are determined by peculiar constitutive features, notably the sugar-like side-chain  $[\text{CH}\cdot\text{OH}]_3\cdot\text{CH}_2\text{OH}$ . H. W.

**a. Distribution of vitamin- $B_2$  in the animal body. b. Preparation of vitamin- $B_2$  concentrates.** P. GYÖRGY, R. KUHN, and T. WAGNER-JAUREGG (Z. physiol. Chem., 1934, 223, 21—27, 27—35).—a. Various tissues showed vitamin- $B_2$  activity decreasing in the order: ox-heart, calf's heart, fowl's

leg, veal, beef, fowl's breast. Ox-spleen has a high, carcinomatous tissue a low, activity. Boiled juices have 50—80% of the activity of the tissue, but the wt. curve of the test animal rapidly flattens owing to the absence of a  $\text{H}_2\text{O}$ -insol. accessory factor R.

b. Vitamin- $B_2$  is conc. by pptn. methods or by adsorption on fuller's earth in  $N$ -acid solution and elution of the adsorbate with dil.  $\text{C}_5\text{H}_5\text{N}$  (cf. A., 1933, 1090). J. H. B.

**Relative vitamin- $B_2$  content of lactose feed (dried whey) and dried skim-milk.** V. HEIMAN and L. C. NORRIS (Poultry Sci., 1933, 12, 332).—Growth tests on White Leghorn chicks showed that lactose (I) feed contained 50% more vitamin- $B_2$  (II) than dried skim-milk (III). Cheese that had been made from the same milk sample also contained but little (II). When fed in limiting amounts (2.5%), better hatching took place with the (I) feed than with (III), but with 5% of either no difference was detected. (I) feed could be used as a source of (II) in practical chicken rearing. NUTR. ABS. (b)

**Relation of vitamin- $B_2$  complex to hatchability and nutritive value of eggs.** R. M. BETHKE, P. R. RECORD, and D. C. KENNARD (Poultry Sci., 1933, 12, 332—333).—The vitamin- $B_2$  (I) complex had a beneficial effect on hatchability (II). The (I) potency of eggs from differently fed hens varied, but could be correlated with the (II) of the eggs. NUTR. ABS. (b)

**Vitamin- $B$  and vitamin- $C$  content of egg-plants and pumpkins.** P. JURIST and A. CHANUTIN (Problems of Nutrition [U.S.S.R.], 1933, 2, No. 4, 12—14).—The two vegetables were nearly equal in vitamin- $C$  content, about 15 g. daily of the fresh substance protecting guinea-pigs from scurvy. As a source of vitamin- $B_1$ , 30 g. of fresh egg-plant (I) protected pigeons from polyneuritis, but wt. was lost. 7—8 g. of (I) (dry wt.) equalled in vitamin val. 0.5 g. of dried brewer's yeast. The vitamin- $B_1$  content of pumpkins was similar to that of (I). NUTR. ABS. (b)

**Behaviour of vitamin- $C$  (ascorbic acid) and other reductones towards cathepsin and other enzymes.** H. VON EULER, P. KARRER, and F. ZEHENDER (Helv. Chim. Acta, 1934, 17, 157—162).—The activating power of vitamin- $C$  (I) for proteases of the cathepsin type (II) (A., 1933, 873) is effective in  $\text{H}_2$ , is increased by  $\text{Fe}^{++}$ ,  $\text{Fe}^{+++}$ , and  $\text{Ca}^{++}$ , but inhibited by  $\text{Cu}^{++}$ , but the smaller activating power of reductone and reductic acid is slightly decreased by Fe and Ca. Hexose diphosphate also activates (II), but dehydro-ascorbic acid neither activates nor inhibits. (I) inhibits wheat-amylase and catalase, but has no action on guanase. Possible mechanisms for the action of (I) are discussed. J. W. B.

**Separation of cysteine from ascorbic acid by mercuric acetate.** A. EMMERIE (Biochem. J., 1934, 28, 268—269).—Cysteine, a source of error in the determination of ascorbic acid by 2 : 6-dichlorophenol-indophenol indicator, is quantitatively pptd. by  $\text{Hg}(\text{OAc})_2$ . Ergothioneine is also pptd. A. E. O.

**Vitamin- $C$  in the ovary and the corpus luteum.** A. GIROUD, C. P. LEBLOND, and M. GIROUX (Compt. rend., 1934, 198, 850—851).—The presence of

vitamin-C (I) in the interstitial tissue of the male genital organs (rodents) and in the corpus luteum is demonstrated by its reduction of  $\text{AgNO}_3$ . By this test (I) is proved to be absent from the follicles and the oocytes of the normal animal. (I) is completely absent in avitaminosis. J. W. B.

**Vitamin-C in the chick embryo.** S. N. RAY (Biochem. J., 1934, 28, 189—191).—There is no vitamin-C (I) in the fresh egg, but after 4 days' incubation considerable amounts of reducing substance are formed. Injection of (I) into the egg does not affect the growth rate of the embryo.

H. G. R.

**Distribution of a reducing substance (vitamin-C) in the tissues of fluorine-fed cows.** P. H. PHILLIPS and F. T. STARE (J. Biol. Chem., 1934, 104, 351—358).—Vitamin-C (I) as determined by the method of Bessey and King (A., 1934, 227) is widely distributed in the various organs and tissues of the dairy cow. The content is low in striated and heart muscle, but high in the suprarenal cortex (II) and the anterior lobe of the pituitary (III). After ingestion of 0.088% F with the grain mixture an increase in (I) content was observed in the kidney, liver, (II), and (III). In chronic F toxicosis, total cellular respiration in (II) is lowered as indicated by  $\text{O}_2$  uptake determinations, and the anaërobic phase, as indicated by the effect of  $\text{CN}'$ , is increased considerably. A. L.

**Alleged vitamin-C of Rygh.** B. SPUR (Z. Vitaminforsch., 1934, 3, 27—37).—Methylhornarotine does not replace vitamin-C (lemon-juice) in the diet of guinea-pigs (A., 1932, 1294). F. O. H.

**Antiscorbutic value of black-currents preserved in sugar.** G. P. SCHELESNY and E. S. KANEVSKA (Problems of Nutrition [U.S.S.R.], 1933, 2, No. 4, 21—23).—Black-currant jam was devoid of vitamin-C, but black-currents preserved raw in sugar for 9 months apparently contained it.

NUTR. ABS. (b)

**Fresh and pickled cucumbers as antiscorbutic vitamin carriers.** N. JARUSOVA (Problems of Nutrition [U.S.S.R.], 1933, 2, No. 4, 25—28).—About 12 g. of fresh cucumber daily provided the min. prophylactic dose of vitamin-C for a guinea-pig. Pickled cucumbers were devoid of the vitamin.

NUTR. ABS. (b)

**Antiscorbutic factor.** W. M. CAHILL (Bull. Soc. Chim. biol., 1933, 15, 1462—1471).—Unfermented grape juice, kept for 6 months with  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H}$  and Et glycol bromoacetate as preservative, when treated by the method of Szent-Györgyi (A., 1929, 98) gives an acid similar to ascorbic acid but lacking antiscorbutic activity (I). 5-Ketogluconic acid has no (I).

H. D.

**Determination of the antiscorbutic potency of vegetable products, chiefly berries, grown in Norrland.** G. F. GÖTHLIN (Acta med. Scand., 1933, Suppl. 53, 1—120).—The berries (tested on guinea-pigs on the Sherman diet) gave the following vals. calc. as min. daily protective ration for a human adult of 60 kg.: fresh black-currents 30—40 g., fresh cloudberries 60—85 g., cloudberry beverage (stored 7 months) 85—120 c.c., cultivated raspberries 100—140

g. Blueberries, arctic raspberries, and red whortleberries were less potent. NUTR. ABS. (b)

**Titration of vitamin-C in citrus juices.** A. H. BENNETT (Analyst, 1934, 59, 91—93; cf. A., 1933, 1090).—The method of prep. of the indicator solution used in Tillmans' method (cf. A., 1933, 433) is described. The vitamin-C (I) content of lemon juices (II) can vary by 100%. (II) pasteurised and preserved in a vac. lost only 20% of its (I) in 35 days, whilst pasteurised (II) exposed to air (in a tube stoppered with cotton wool) lost 100% in 12 days. Preserved with  $\text{SO}_2$ , 30% was lost after 56 days, 40% after 110 days in a vac., 100% after 26 days when exposed to air. E. C. S.

**Experimental scurvy. XVI. Purine metabolism of guinea-pigs fed on a vitamin-C-free diet.** K. TOMITA (Sei-i-kwai Med. J., 1932, No. 7, 1—12).—Urinary total N, purine bases, uric acid (I), and allantoin decrease during the course of scurvy, but [except (I)] increase at the terminal state. Urea is parallel with total N, but  $\text{NH}_3$  increases with the progress of the disease. CH. ABS.

**Vitamin-E. I. Chemical and physiological properties.** H. S. OLCOTT and H. A. MATTILL (J. Biol. Chem., 1934, 104, 423—435).— $5\frac{1}{2}$  times the min. dose of vitamin-E (I) required to produce fertility (II) in rats is insufficient to preserve (II) for more than a second gestation. The paralysis of the suckling young of (I)-deficient mothers is uninfluenced by administration of (I). A (I)-active concentrate, b.p. 200—233°, from the unsaponifiable lipins of lettuce was obtained, similar in properties to that of Evans and Burr (Mem. Univ. Calif., 1927, 8) from wheat-germ oil (III). The Evans-Burr prep. of (I) from (III) is modified by vac.-distillation of the MeOH extract of the unsaponifiable residue from which the sterols have been removed. The product so obtained is further conc. by freezing out impurities from  $\text{CO}_2$ , and still further by adsorption on  $\text{Al}_2\text{O}_3$ . Br and  $\text{KMnO}_4$  destroy, whilst acetylation, benzoylation,  $\text{AgNO}_3$ , and  $\text{H}_2$  do not influence, the activity of (I). In a rancid food mixture (I) is stable for 4 weeks. From comparison of the effects of hebin (IV) and (I) on immature female rats, it is concluded that (I) and (IV) play entirely different rôles in the physiology of reproduction. H. D.

**Chlorophyll content as an index of the productive capacity of selfed lines of maize and their hybrids.** H. W. SPRAGUE and N. CURTIS (J. Amer. Soc. Agron., 1933, 25, 709—724).—The chlorophyll (I) and carotene contents of leaves of maize were highest in the uppermost and least in the lowest leaves. The gradient was regular and vals. for middle leaves were fairly representative of the whole plant. Xanthophyll vals. were very erratic. Correlation between mean (I) contents, genetic factors, and productivity are examined. A. G. P.

**Oxidation potential and protein change in the leaf.** K. MOTHES (Flora, Karsten Festschr., 1933, 58—98).—High  $\text{O}_2$  tension stabilises the protein, protects it from decomp., and furthers its synthesis. Low  $\text{O}_2$  tension renders the protein subject to the attack of leaf proteinases. CH. ABS.

**Formation of protein in plants.** O. LOEW (Angew. Bot., 1933, 15, 518—539).—The synthesis of protein from asparagine with the intermediate formation of the di-aldehyde of aspartic acid is discussed.

A. G. P.

**Formation of alkaloids in the plant.** T. WEEVERS (Chem. Weekblad, 1934, 31, 19—24).—Pictet's theory that alkaloids are built up from the degradation products of proteins, particularly proline, tyrosine, and tryptophan (cf. A., 1905, i, 541; 1907, i, 954), is extended and discussed from a physiological-phytochemical point of view. Experiments on *Ricinus* plants and seeds are described.

S. C.

**Transformation of nicotine in the ripening of tobacco seeds.** G. ILJIN (Biochem. Z., 1934, 268, 253—259).—Nicotine is formed in the early ripening processes of the seeds, the amount then rapidly diminishing during the regeneration of reserve protein.

P. W. C.

**Method of formation of grains of wheat-flour in the grasses, and the production therein of hydroxyflavones and anthocyanins.** J. CHAZE (Compt. rend., 1934, 198, 840—842).—Mainly botanical. Hydroxyflavone derivatives are first formed in the vacuoles and may become converted into anthocyanins during maturation.

J. W. B.

**Effect of yeast extract on the growth of plants.** A. I. VIRTANEN and S. VON HAUSEN (Nature, 1934, 133, 383; cf. A., 1933, 1093, 1342).—The factor which stimulates blooming of the pea is sol. in Et<sub>2</sub>O, and is equally effective in sterile H<sub>2</sub>O cultures and in the usual pot cultures with quartz sand.

L. S. T.

**Effect of female sex hormones on plant growth.** M. M. JANOT (Compt. rend., 1934, 198, 1175—1178).—The growth of hyacinths and lilies is increased by watering with saturated aq. solutions of equilin, equilenin, folliculin (I), and dihydrofolliculin. Similar results are obtained by using a solution containing 4 mg. per litre, but trihydroxycestrin is toxic under these conditions. (I) is the least effective of the compounds used.

P. G. M.

**Influence of boron and of other complementary elements on the growth of flax.** M. J. SCHKOLNIK (Bull. Acad. Sci. U.R.S.S., 1933, 7, 1163—1188).—Normal growth was obtained in nutrient solutions containing, in addition to the usual salts, 0.5 mg. B, 1.5 mg. Mn, 0.5 mg. Al, 0.125 mg. Cu, and 0.25 mg. I per litre of distilled H<sub>2</sub>O (I); previous attempts at cultivating flax in solutions of salts in (I) failed owing to the absence of the above elements. Of these, B is the most important, development of the root system failing in its absence; concns. of > 0.5 mg. B per 100 c.c. are toxic. Al, Mn, Cu, and I are of only secondary importance.

R. T.

**Influence of the temperature of germination on the chemical composition of cereal seedlings.** E. GÄUMANN (Z. Bot., 1932, 25, 385—361; Bied. Zentr., 1933, A, 4, 199—200).—Increasing germination temp. (I) is associated with rising fresh wt. and declining dry matter content in seedlings. The total carbohydrate in seedlings is unaffected by (I) between 3° and 15° but varies irregularly with temp. above this. Differences in glucose, sucrose, and amylose con-

tents with varying (I) are traced. The crude fat and total N increase with rising (I). The mobilisation and transport of N and the proportions of NH<sub>2</sub>-, amide-, protein-, and humin-N show little variation, but polypeptide- and residual N are definitely related to the (I). Increasing (I) results in lower proportions of K and P but not of Ca in the plants. Low (I) followed by slow seedling growth induces the formation of much cell-wall material containing relatively higher proportions of cellulose, lignin, and cutin and less xylan than when (I) is high and subsequent growth rapid. The latter conditions favour the dissolution of the cell wall by enzymes of *Fusarium*.

A. G. P.

**Degradation of amino-acids in flowers.** W. GRASSMANN and H. BAYERLE (Biochem. Z., 1934, 268, 220—228).—Some pulped flowers or extracts (I) (e.g., from *Rosaceæ*) partly decompose NH<sub>2</sub>-acids although no decarboxylation occurs and primary amines are not produced. NH<sub>3</sub> is the only recognisable reaction product. No decomp. occurs anaerobically. For each mol. of NH<sub>3</sub> produced almost 0.5 mol. of O<sub>2</sub> is consumed. The extent of deamination is < one tenth of that produced by kidney. Thermostable catalysts are involved. There is no appreciable difference in the rate of decomp. of optical antipodes. Peptides (glycyl-alanine, -leucine, and -asparagine, diglycyl-asparagine) are deaminated 2—3 times as rapidly by (I) as are corresponding mixtures of the appropriate NH<sub>2</sub>-acids.

W. McC.

**Acidity of epidermal cells and stomata in *Rumex acetosa* in light and in darkness.** J. PEKAREK (Planta [Z. wiss. Biol.], 1933, 21, 419—446).—Both stomatal and surrounding epidermal cell saps have  $p_H$  approx. 6.0 in daylight. In darkness there is a change of  $p_H$  of stomatal cells towards the acid region and in epidermal cells towards the alkaline side.

A. G. P.

**Relationships between geo-electric effects and geotropism.** H. U. AMLONG (Planta [Z. wiss. Biol.], 1933, 21, 211—250).—Geotropic effects are examined in relation to the p.d. induced by differences in electrolyte concn. of the cell sap and that of external liquids with which the tissues are in contact. "Electrotropic" effects produced by roots and shoots of seedlings when placed in an electrostatic field are recorded.

A. G. P.

**Action of salts in water cultures [of plants].** K. SCHMALFUSS (Flora, Karsten Festschr., 1933, 197—210).—The effects of various mineral deficiencies on the growth of *Callisia repens* in H<sub>2</sub>O have been studied. Fe chlorosis is favoured by the presence of easily sol. phosphates, alkaline reaction, and excess of Ca<sup>++</sup>.

CH. ABS.

**Rôle of mineral and organic matter in plant life. II. Mineral and organic metabolism in leaves and shelled seed of *Aesculus hippocastanum* during growth.** N. T. DELEANO and C. BORDEIANU (Beitr. Biol. Pflanzen, 1932, 20, 179—197; Bied. Zentr., 1933, A, 4, 205).—By means of the "biometric" method, three phases of leaf development are differentiated. In the initial "development" stage the dry wt. per leaf increases steadily, remaining unaltered during the second period of "protoplasmic constancy," and declining in the final

stage of "negative translocation." The length of each stage is sp. for each species of plant and for each plant organ. The depletion of mineral and org. constituents from old leaves may be as high as 50% of the max. content, and is unrelated to the elimination of H<sub>2</sub>O, which begins at an earlier stage when the cell walls are still semipermeable. A. G. P.

**Cellulose and xylan. Constitution and relation between the material, form, and function [of the plant membrane].** M. LÜDTKE (Biochem. Z., 1934, 268, 372—393).—The relationship between the cellulose (I) and xylan (II) constituents of plant membranes and the change of the membrane due to various factors within and without the plant are investigated. The isolated parenchymatous cells (III) of bamboo canes and beechwood contain more (II) than the fibrous cells, the relationship appearing to be a general one. The acid val. of (III) and the loss on fractionation with NaOH are > for fibrous cells. The residue after removal of material sol. in 0.2% NaOH does not appear to be a chemical individual. The view that (I) and (II) are combined as an ester is negated. P. W. C.

**Starch formation in the leaves of sugar cane.** W. M. COBLEIGH and V. J. KONINGSBERGER (Arch. Suikerind. Ned.-Indic, 1932, 1325—1340; Bied. Zentr., 1933, A, 4, 221—222).—Starch (I) formed during normal CO<sub>2</sub> assimilation occurs only in the bundle sheaths (II). In darkness leaves placed in solutions of maltose, sucrose, glucose, or fructose produce (I) mainly in the palisade cells of the parenchyma. Such (I) is partly translocated to (II) on exposure of leaves to sunlight in a CO<sub>2</sub>-free atm. Leaves placed in sugar solutions in daylight but in the absence of CO<sub>2</sub> accumulated (I) in (II). A. G. P.

**Regularities in the carbohydrate composition of barley grain.** L. R. BISHOP and D. MARX (J. Inst. Brew., 1934, 40, 62—74).—A regular relation is found between amounts of pentosan (Kröber) (I), "insol. carbohydrate" (II), and extract (III), respectively, and total carbohydrate (IV) of Plumage-Archer barley, all quantities being calc. as g. per 1000 corns. Similar regularities hold for other barley varieties, although abs. amounts may differ. With increase in (IV), (I), (II), and (III) also increase regularly, the last the most rapidly. For 2-rowed barleys (III) is higher, (I) and (II) are regularly lower, than with 6-rowed, for any given val. of (IV). There is a definite arrangement of carbohydrate, typical of each barley variety, during development and at maturity. The regularities observed are analogous to those previously described for barley proteins. The curve relating reserve protein (hordein) with total protein is of the same form as that for (III) and (IV), and similarly with the curves for non-reserves in each case plotted against total protein or carbohydrate. During malting, decomp. of protein leads ultimately to formation of asparagine, whilst decomp. of carbohydrates leads to production of sucrose. I. A. P.

**Physiology of the cold-resistance of winter cereals.** E. CONSTANTINESCU (Planta [Z. wiss. Biol.], 1933, 21, 304—323).—In plants maintained at const. temp. the total dry matter, sugar content, and osmotic pressure of the cell sap in the first three leaves

remain const. Transition from a high to a low temp. induces an increase in osmotic pressure, a small increase in sugar, and a slight increase in dry matter. Differences in the case of varieties of varying hardiness are small. A. G. P.

**Seasonal variations in the sulphur content of pastures.** ANON. (Sci. Rep. Govt. Agric. Chem., Coimbatore, 1932—1933, 25).—There is a seasonal variation in the S content (I) which rises as a rule to a max. during the dry season and falls to a min. in the wet. (I), which was always very low, showed a parallelism with the Ca content. NUTR. ABS. (m)

**Beginning of hydrolysis of agar-agar.** A. KORENTZVIT (Khim. Farm. Prom., 1933, 153).—The process is followed colorimetrically on addition of EtOH-I. CH. ABS.

**Comparison of plant and animal chitin.** L. ZECHMEISTER and G. TÓTH (Z. physiol. Chem., 1934, 223, 53—56).—From *Boletus edulis* chitin, octa-acetylchitobiose, and undeca-acetylchitotriose were obtained, identical with the products from crab chitin. J. H. B.

**Scillin of *Scilla maritima* and the fructoside of *S. nutans*.** H. COLIN and A. CHAUDUN (Bull. Soc. Chim. biol., 1933, 15, 1520—1526).—A fructoside,  $[\alpha]_{5461} -32^\circ$ , is prepared from *S. maritima* by clearing the EtOH extract with H<sub>2</sub>WO<sub>4</sub> and pptn. with Ba(OH)<sub>2</sub> and EtOH; another,  $[\alpha]_{5461} -51.4^\circ$ , prepared from *S. nutans* by clearing with Pb(OAc)<sub>2</sub> and pptn., appears to yield a mixture containing 97% of fructose and 3% of glucose on hydrolysis. H. D.

**Ovary liquid of the corn cockle (*Agrostemma githago*, L.) and its relation to the seminal tegument.** M. MOLLIARD and R. ECHEVIN (Compt. rend., 1934, 198, 780—783).—When kept in EtOH the fluid (100 c.c.) (I) expressed from the capsules of *A. githago* deposits a H<sub>2</sub>O-sol. gum,  $[\alpha]_D +149^\circ$  (0.472 g. after desiccation), hydrolysed by 2% H<sub>2</sub>SO<sub>4</sub> at 120° to a reducing sugar giving an osazone resembling galactosazone; the sol. matter (4 g.; ash 0.166 g.) consists of glucose (2.043 g.), fructose (1.668 g.), and sucrose (II) (0.438 g.). As the capsules develop, the total sugars, and especially (II), diminish (7.104—2.458 g. per 100 c.c.), (II) being absent when (I), originally colourless, has become brown. J. W. B.

**Constituents of hornbeam bark.** O. BRUNNER and G. WIEDEMANN (Monatsh., 1934, 63, 368—373).—In agreement with Zellner *et al.* (A., 1926, 983) the ligroin extract of the nonaponifiable fraction of an EtOH extract of the bark of *Carpinus betulus*, L., affords ceryl alcohol, a phytosterol, m.p. 136° (Ac derivative, m.p. 122°), shown by Windaus' bromination method to be a sitosterol containing no stigmasterol, and betulin. J. W. B.

**Chemical composition of "St. John's root" [*Berberis laurina*, Billb. (Thunb.)].** O. DE A. COSTA and R. D. DA SILVA (Rev. Soc. Brasil. Quím., 1933, 4, 199—201).—The root contains hydrastine (I) as well as berberine (II); the analysis by the Dragendorff-Schlagdenhauffen method is detailed. Besides its use in the dye industry, the root might be used as a commercial source of (II), and possibly as a sub-

stitute for *Hydrastis canadensis*, on account of its content of (I). E. L.

**Fatty oil of seeds of *Cydonia vulgaris*.** A. STEGER and J. VAN LOON (Rec. trav. chim., 1934, 53, 24—27).—The fatty acids (94.2%) comprise saturated acids (8.6%), oleic (42.5%), linoleic (39.2%), and linolenic acid (3.9%). A trace of OH-acid may be present but there is no evidence of the existence of the acid  $C_{17}H_{32}(OH)CO_2H$  of Herrmann (A., 1899, i, 822). H. A. P.

**Fatty oil of seeds of *Cassia occidentalis*.** L. A. STEGER and J. VAN LOON (Rec. trav. chim., 1934, 53, 28—30).—The oil contains unsaponifiable matter 7.4%, saturated acids 19.7%, oleic 30.7%, linoleic 31.4%, and linolenic acids 6.3%. H. A. P.

**Fatty oil of millet (*Panicum miliaceum*).** A. STEGER and J. VAN LOON (Rec. trav. chim., 1934, 53, 41—44).—The oil contains 3.3% of unsaponifiable matter and 88.7% of fatty acids comprising saturated acids 10.7%, oleic 23.9%, linoleic 46.9%, and linolenic acid 7.2%. A small amount of OH-acid is probably present, but no evidence of the existence of "Hirseölsäure" is found. H. A. P.

**Coffee oil.** A. HEIDUSCHKA and R. KUHN (J. pr. Chem., 1934, [ii], 139, 269—276).—The ligroin-extracted fat (I) of unroasted coffee beans contains 96.95% of total fatty acids (Hehner), analysis of which (full details) gives the following composition of (I): linoleic 37.60%, oleic 20.20% (total liquid fatty acids, 59.59%), palmitic 23.60%, carnaubic 14.25%, stearic 1.05%, and *n*-decoic 0.35% (total solid fatty acids 40.47%). J. W. B.

**Dark-coloured duramen of ebony.** K. GRIFFIOEN (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 897—988).—A large part of the colouring matter of ebony woods consists of ulmic acids. C. W. G.

**Tomato pigments. Pigment in American red and purple tomatoes (*Lycopersicum esculentum*).** M. B. MATLACK and C. E. SANDO (J. Biol. Chem., 1934, 104, 407—414).—The pigment from American-grown tomatoes is identical with the lycopene obtained from an Italian variety. H. D.

**Plant pigments. LV. Presence of  $\alpha$ - and  $\beta$ -carotene in various natural products.** P. KARRER and W. SCHLIENTZ. LVI. **Autumn colours of leaves.** P. KARRER and O. WALKER (Helv. Chim. Acta, 1934, 17, 7—8, 43—54).—LV. Differential chromatic absorption of the carotene from spinach, paprika, nettle, and corpus luteum confirms the conclusion of Kuhn *et al.* (A., 1931, 1421) that it is almost pure  $\beta$ -carotene, only traces of the  $\alpha$ -form being detected spectroscopically.

LVI. The methods of differential chromatic absorption, extraction with 90% MeOH and ligroin, and pptn. of the carotenoids with I (and regeneration with  $Na_2S_2O_3$ ) are applied to the examination of the pigments present in green and yellow leaves of *Aesculus hippocastanum*, *Acer pseudoplatanus*, *Ginkgo biloba*, and *Ulmus campestris*. The unhydrolysed pigment extract is pptd. with I and pptd. carotenoids are regenerated with  $Na_2S_2O_3$ : free phytoanthin (I) is removed from the extract with MeOH and the ligroin-sol. pigments are hydrolysed with NaOMe or

NaOH-MeOH. The resulting pigments remain almost exclusively in the ligroin layer, thus disproving the hypothesis that the production of autumn tints is due to increased esterification of the xanthophyll (II). Whilst both carotene (III) [as isocarotene (IV) after regeneration from the I-compound] and (II) can be isolated from the green autumnal leaves, the yellow leaves give only spectroscopic traces of (IV), and a little (II) mixed with some violaxanthin. The "autumn (II)" can be extracted from ligroin solution by large vols. of 90% MeOH, and *vice versa*. Thus during autumn necrosis the (III) and (I) decrease, the former more rapidly, due to oxidative destruction, "autumn (II)" containing the oxidation products, but intermediate compounds could not be isolated.

J. W. B.

**Enzymic clarification of fruit juices and sweet wines. I. Changes in fruit juices during spontaneous clarification and on treatment with filtration enzymes. II. Determination of pectolase action of filtration enzymes.** A. MEHLITZ and M. SCHEUER (Biochem. Z., 1934, 268, 345—354, 355—363).—I. Enzymic clarification of fruit juices consists of the complete hydrolysis of pectins.

II. Pectolysis in pectin solutions can be followed with a fair degree of accuracy in terms of changes of viscosity and the liberation of CHO groups by I titration. Determination of residual pectin by pectase coagulation gives inaccurate, but by the Ca pectate method accurate, results. The action of pectolase may also be followed polarimetrically. P. W. C.

**Chemistry of the brown algæ. I. M. HEILBRON, R. F. PHIPERS, and H. R. WRIGHT (Nature, 1934, 133, 419).—Fucosterol,  $C_{29}H_{48}O$  or  $C_{30}H_{50}O$ , m.p. 124° (acetate, m.p. 119°; propionate, m.p. 104°), isolated from *Fucus vesiculosus* and from *Pelvetia canaliculata*, contains two double linkings. L. S. T.**

**Choline in marine algæ. A. ZELLER (Biochem. Z., 1934, 268, 187—188).—The micro-chemical detection of choline in some marine algæ is reported.**

W. McC.

**Determination of chlorophyll. N. T. DELEANO and J. DICK (Biochem. Z., 1934, 268, 317—321).—The method depends on the separation of chlorophyll from the EtOH extract by means of  $CHCl_3$ , with determination of the nuclear Mg as  $MgNH_4AsO_4 \cdot 6H_2O$ , from which the chlorophyll content is calc. P. W. C.**

**Micro-analytical tobacco determinations. V. Determination of ammonia. J. BODNÁR, V. L. NAGY, and L. BARTA (Biochem. Z., 1934, 268, 174—177; cf. A., 1931, 132).— $NH_3$  is determined in a HCl extract of 0.25 g. of finely powdered tobacco after pptn. of nicotine with silicotungstic acid, by subjecting the filtrate to steam-distillation in presence of MgO, using excess of 0.01N-HCl for trapping the  $NH_3$  and back-titrating with 0.01N-NaOH. W. McC.**

**Mineral composition of plantains of varying degrees of keeping quality. ANON. (Sci. Rep. Govt. Agric. Chem., Coimbatore, 1932—1933, 21—22).—In the better keeping varieties of plantain the mineral ash (especially K) content is > that in poorer keeping qualities. Plantains manured with ashes give fruit which keeps better and tastes sweeter.**

NUTR. ABS. (m)

Analyses of the ash of bean seed and of leaves of different varieties of vines: potassium compounds in the respective ashes. A. TEGOROULOS (Z. Pflanz. Düng., 1934, A, 33, 95—98).—Ash of vine leaves contains K in H<sub>2</sub>O-sol., HCl-sol., and HCl-insol. (probably silicate) forms. The last named is absent from bean ash. A double salt similar to that produced by heating K<sub>2</sub>CO<sub>3</sub> with Ca phosphate may exist in plants. A. G. P.

Nitrate content of grasses and legumes. G. DE VITO (Italia Agricola, 1932, 69, 1028—1029; Bied. Zentr., 1933, A, 4, 203).—Analyses of various species of grasses and legumes in different stages of growth show that the relatively high NO<sub>3</sub>' contents of young plants decline rapidly with advancing growth. A. G. P.

Determination of phosphorus fractions of plants. M. JAVILLIER and Y. COLIN (Bull. Soc. Chim. biol., 1933, 15, 1552—1562).—The proportions of the total P in the lipin, nucleotide, and phytin fractions of wheat germ were 9, 28, and 42% and in lentil powder 12, 11, and 51%, respectively. H. D.

Use of cresol-blue in systematic mycology. R. KÜHNER (Compt. rend., 1934, 198, 843—846).—The colour reactions of cresol-blue with various species of agaric and boletus are described. J. W. B.

Aldehydes as cytological fixatives. C. ZIRKLE (Protoplasma, 1933, 20, 169—179).—The use is described of a no. of the simpler aliphatic aldehydes in conjunction with AcOH, HCO<sub>2</sub>H, Cu propionate, lactate, dichromate, Müller's fixative, etc. for the fixation of root tips of *Zea mais*. A. G. P.

Effect of mosaic disease on certain metabolic products in the tobacco plant. H. CORDINGLEY, J. GRAINGER, W. H. PEARSALL, and A. WRIGHT (Ann. Appl. Biol., 1934, 21, 78—89).—Diseased leaves contained more N and less carbohydrate than healthy ones, differences being more marked during photosynthesis. The decrease in carbohydrate during storage of leaves in the dark falls mainly on insol. carbohydrates in healthy leaves and on disaccharides in diseased leaves. In the latter protein breakdown is retarded and insol. substances are less readily hydrolysed. A. G. P.

Possible chemical nature of tobacco mosaic virus. E. BARTON-WRIGHT and A. M. MCBAIN (Nature, 1934, 133, 260).—A reply to criticism (this vol., 337). L. S. T.

Physiology of potato leaf roll. I. Respiration of healthy and leaf-roll-infected potatoes. T. WHITEHEAD (Ann. Appl. Biol., 1934, 21, 48—77).—Except for a short period at the end of the dormant period until the first unfolding of leaves infected plants had the higher respiratory rate. The latter is related to the amount of available respirable substrate present, and thus only indirectly to the effect of the virus. A. G. P.

Plant tumours and polyploidy produced by bacteria and other agents. D. KOSTOFF and J. KENDALL (Arch. Mikrobiol., 1933, 4, 487—508).—Tumours produced by *B. tumefaciens* are similar in

structure to those formed by injection of various chemicals into the internodal cavities of *Ricinus*. The action of chemicals in producing tumours is paralleled by their ability to cause pptn. in tissue extracts. A. G. P.

Effect of various elements on bacterial tumours of *Pelargonium*. A. GOSSET, J. MAGROU, and A. TCHAKIRIAN (Compt. rend., 1934, 198, 1097—1100).—Inoculation with *B. tumefaciens* gives rise to a uniform production of tumours in *P. zonale*. Introduction of compounds of Ge, Ce, Mo, Sn, Zr, and Al into the tumour tissue produces rapid and permanent necrosis without, in suitable doses, any harmful effect on the plant. P. G. M.

Chlorophyll-containing parasites. J. RICHTER (Pharm. Zentr., 1934, 75, 157—163, 176—179).—The development and morphological relationships of the parasite, particularly the mistletoe and those of the genera *Cuscuta* and *Orobranche*, to their particular hosts are discussed. E. H. S.

Photometer. A. H. SANFORD, C. SHEARD, and A. E. OSTERBERG (Amer. J. Clin. Path., 1933, 3, 405—420).—A new type of apparatus and its use in determining blood-haemoglobin, -glucose, and -creatinine are described. CH. ABS.

Photo-electric colorimeter.—See this vol., 383.

Horizontal micro-burette.—See this vol., 384.

Rapid dialysis. I. A. NELSON and I. H. NELSON (Amer. J. Clin. Path., 1933, 3, 447—453).—Two types of apparatus, applicable to blood, are described. CH. ABS.

Incineration of small laboratory animals for bismuth determinations. C. DESGREZ, M. GLAUME, and R. WOLFF (Bull. Soc. Chim. biol., 1933, 15, 1527—1534).—The method of incineration of Desgrez and Meunier (A., 1920, ii, 554) is applied to whole guinea-pigs. H. D.

Detection of elements in tissues. VII. Determination of gold in tissues by spectrum analysis, with histochemical comparisons. W. GERLACH, K. RUTHARDT, and L. PRÜSENER (Beitr. pathol. Anat., 1933, 91, 617—642).—For the detection and determination of traces of heavy metals and for diagnostic purposes, the spectrographic method is unsurpassed. In the determination of Au in animal organs the method is more trustworthy than histochemical methods. NUTR. ABS. (m)

Micro-determination of bromine in blood and organs. A. SALVATORI (Atti R. Accad. Lincei, 1933, [vi], 18, 324—326).—Pincussen and Roman's method (A., 1929, 713) is untrustworthy. T. H. P.

Margosches' quick iodine value method. H. MOHLER and H. BENZ (Mitt. Lebensm. Hyg., 1933, 24, 277—280).—25 c.c. of 0.2N-I in EtOH are mixed with 0.2—0.4 g. of fat dissolved in 10 c.c. of EtOH; 200 c.c. of H<sub>2</sub>O are added, with shaking, and the closed flask is kept for 5 min. Without addition of KI the liquid is titrated, with starch as indicator. This method gives the same results as are obtained by the Hanus method. NUTR. ABS. (m)