

# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

FEBRUARY, 1936.

### General, Physical, and Inorganic Chemistry.

**Spectral intensities for hydrogen.** P. RUDNICK (Physical Rev., 1935, [ii], 48, 807—811).—Mathematical. N. M. B.

**Extension of the Paschen series.** B. JOHANSEN (Naturwiss., 1935, 23, 866).—The infra-red spectrum of  $H_2$  has been photographed and the  $\lambda\lambda$  of the 6th—13th members of the Paschen series are determined. A. J. M.

**Fine structure of  $D_a$  with increased resolution.** R. C. WILLIAMS and R. C. GIBBS (Physical Rev., 1935, [ii], 48, 971; cf. A., 1934, 575).—The chief minor component resulting from the coincident transitions  $2p^2P_{1/2}-3s^2S_{1/2}$  and  $2s^2S_{1/2}-3p^2P_{1/2}$  has been resolved. The measured half-intensity breadth of the high-frequency main component is  $0.120\text{ cm.}^{-1}$ , and the average interval between centres of components  $0.134\text{ cm.}^{-1}$ . The deviation from theory may be due to a Stark effect. The val. of  $e/m$  calc. from the measured interval between components of the two isotopes is  $1.7577 \pm 0.0004 \times 10^7$  e.m.u. per g. N. M. B.

**Continuous spectrum of deuterium.** (MLLE.) A. TOURNAIRE and E. VASSY (Compt. rend., 1935, 201, 957—958).—The continuous spectrum of  $D_2$  is slightly more intense than that of  $H_2$  at  $\lambda\lambda < 4000\text{ \AA}$ . H. J. E.

**New investigations of helium and hydrogen lines with crossed electric and magnetic fields.** W. STEUBING (Physikal. Z., 1935, 36, 822—825).—The changes suffered by the Stark effect components of the first secondary series of He which have been magnetically split into duplets, when the strength of the electric field is varied, have been investigated. For  $H_2$  it was shown that the method could be applied in spite of the electrodynamic decomp. of the Balmer lines observed by Wien. Results for  $H_2$  are analogous to those for He. A. J. M.

**Doubly excited states of helium.** T. Y. WU and S. T. MA (Physical Rev., 1935, [ii], 48, 917; cf. *ibid.*, 1934, [ii], 46, 239).—A correction. N. M. B.

**Perturbations in the second positive nitrogen bands.** D. COSTER and F. BRONS (Z. Physik, 1935, 97, 570—572).—Perturbation of the 2nd and 3rd vibration states of the  $^3\pi C$  level of  $N_2$  is characterised by a weakening without displacement of only a few lines, and is not explained by Gero's analysis (A., 1935, 1437). A. B. D. C.

**New afterglow spectrum in nitrogen.** J. KAPLAN (Physical Rev., 1935, [ii], 48, 800—801).—A detailed account of results previously reported (cf. A., 1935, 907). N. M. B.

**Rotational structure of the Schumann-Runge bands of oxygen in the vacuum region.** H. P. KNAUSS and S. S. BALLARD (Physical Rev., 1935, [ii], 48, 796—799).—Data for the absorption bands photographed in the range  $1760-1925\text{ \AA}$ . and rotational analyses are tabulated. An expression for, and table of, band origins are given. The energy of dissociation is  $5.05$  volts. N. M. B.

**Absorption spectra of oxygen at high concentration.** B. J. EISEMAN, jun. (J. Math. Phys. Mass. Inst. Tech., 1935, 14, 260—261).—New data for the ultra-violet triple bands,  $2847-2434\text{ \AA}$ ., using highly purified  $O_2$  at  $440-55\text{ atm.}$ , are given. The bands at  $6280, 5765,$  and  $4775\text{ \AA}$ . at room temp. and  $>440\text{ atm.}$  degrade towards the short  $\lambda$ . The  $4470\text{ \AA}$ . band appeared only at low temp. at const. concn. N. M. B.

**Influence of foreign gases on the higher principal series lines of sodium.** C. FUCHTBAUER and P. SCHULZ (Z. Physik, 1935, 97, 699—707).—Ne, A, and  $N_2$  produced dissymmetry towards the red at the end of the series. A. B. D. C.

**Arc spectrum of alkali metals with high vapour density.** A. CARRELLI and M. BATTISTA (Nuovo Cim., 1934, [ii], 11, 685—689; Chem. Zentr., 1935, i, 2776).—The intensity of forbidden lines and of the continuum is explained by the formation of quasi-mols., the effect increasing with the polarisability of the atoms from Na to Cs. J. S. A.

**Absorption spectra of sulphur vapour.** L. D'OR (Compt. rend., 1935, 201, 1026—1028).—Changes in the absorption spectrum of S vapour with concn. and temp. indicate four species as well as S atoms. The band system between  $3600$  and  $4200\text{ \AA}$ . is due to  $S_4$  or  $S_3$ , and not  $S_8$  or  $S_2$ . The validity of Preuner's conclusions is questioned (A., 1912, ii, 1145). T. G. P.

**Predissociation in the sulphur bands.** B. ROSEN, M. DÉSIRANT, and J. DUCHESNE (Physical Rev., 1935, [ii], 48, 916).—The feature of predissociation is that the emission band system stops abruptly at  $v'=8$  and the last observed band (8,0) is shorter than the others. Spectroscopic examination showed abrupt termination of the rotational structure in the  $v'=8$  and  $v'=7$  progressions and in the (8,0) band. It is concluded that there is a predissociation in the  $v'=7$  level, and the derived heat of dissociation is  $4.41 \pm 0.02$  e.v. N. M. B.

**Spectrum of Se II.** D. C. MARTIN (Physical Rev., 1935, [ii], 48, 938—944).— $\lambda$  measurements were made in the region  $500-2600\text{ \AA}$ . of the spectrum

excited by a hollow-cathode discharge in He. Identifications and  $J$  vals. of new terms are given, and data and classifications of all known Se II lines are tabulated.

N. M. B.

**Anomalous dispersion of silver vapour.** L. ALEGRETTI (Nuovo Cim., 1934, [ii], 11, 717—722; Chem. Zentr., 1935, i, 2776).—The intensity ratio of the first doublet of the Ag principal series was measured by means of anomalous dispersion. J. S. A.

**Spark spectrum of cadmium.** R. RICARD and A. SAUNIER (Compt. rend., 1935, 201, 1115—1116).—Lines of Cd III and Cd IV at  $\lambda\lambda$  3400—5000 Å. were measured. H. J. E.

**Absorption spectrum of the iodine molecule in the vacuum ultra-violet.** H. CORDES (Z. Physik, 1935, 97, 603—624). A. B. D. C.

**Arc spectrum of cerium.** K. HASPAS (Z. Physik, 1935, 96, 410—430).—430 lines are arranged in terms, the lowest being a  $^2D$  term. The first and second ionisation potentials are 6.9 and 14.8 volts, respectively. A. B. D. C.

**Spectrum of polonium.** B. KARLIK and H. PETERSSON (Sitzungsber. Akad. Wiss. Wien, IIA, 1934, 143, 379—383; Chem. Zentr., 1935, i, 2496).—2 (or 3 ?) strong Po lines are recorded from a Po deposit on Pt, enclosed in a heated SiO<sub>2</sub> tube and excited with radiation of short  $\lambda$ . J. S. A.

**Ultra-violet spectrum of radium emanation.** H. PETERSSON (Sitzungsber. Akad. Wiss. Wien, IIA, 1934, 143, 303—311; Chem. Zentr., 1935, i, 2647).— $\lambda\lambda$  and intensities are recorded for 169 lines, not due to other elements, between 3700 and 2280 Å. The lines found do not correspond with those reported by previous workers. J. S. A.

**Energy transfer in collisions of excited thallium atoms with gas molecules.** N. PRILESHAEVA (Acta Physicochim. U.R.S.S., 1935, 2, 647—664).—Results on the quenching of the Tl fluorescence line 5351 Å. by various gases, previously published (A., 1934, 340), are discussed theoretically. F. L. U.

**Anomalous diffraction gratings.** R. W. WOOD (Physical Rev., 1935, [ii], 48, 928—936).—A Cr-plated echelette grating of 7200 lines per in. on Cu, and one of 15,000 lines on Al film on glass, showed narrow bright and dark bands in the continuous spectrum of a white source. The variation of the bands with incidence angle is studied, and the bands, unexplained by classical theory, are attributed to a type of destructive interference along the plane of the grating. N. M. B.

**Initiation of electrical discharges by field emission.** J. W. FLOWERS (Physical Rev., 1935, [ii], 48, 954—959).—The initiation of highly over-voltage discharges in effectively ion-free gases by short-duration voltage impulses is independent of the gas between the electrodes, and of the pressure over the range 1 atm.—vac. spark stage. Oscillograms for discharges in asymmetrical fields are given and discussed. N. M. B.

**Interpretation of the fine structure coefficient,  $\alpha$ .** S. A. DE MAYOLO (Compt. rend., 1935, 201, 1097—1099). H. J. E.

**Behaviour of certain diatomic molecules in stellar atmospheres.** E. BODSON and F. E. NISOLI (Bull. Acad. roy. Belg., 1935, [v], 21, 922—926).—Russell's theory is applied to the stellar spectra of the oxides and hydrides of B, Al, Ca, and Mg in the dwarf and giant stars, and temp.—abundance curves are given and discussed in relation to influence of dissociation and ionisation. N. M. B.

**Red-shift from nebulae.** F. ZWICKY (Physical Rev., 1935, [ii], 48, 802—806).—Mathematical. The expansion of the universe, the red-shift of light through intergalactic space, and the width of spectral lines from distant nebulae are examined. N. M. B.

**Artificial crystal lattice for interference with optical light.** W. KRAMER (Physikal. Z., 1935, 36, 841—843).—A method for obtaining interference diagrams of a similar nature to X-ray interference patterns, with ordinary light, is described. The process depends on the use of stationary waves produced by a method similar to that employed in the Lippmann process for colour photography. A. J. M.

**X-Ray determinations with the diamond.** M. RENNINGER (Physikal. Z., 1935, 36, 834—837).—Intensity determinations of the reflexions from the (222) plane have been made using Cu  $K\alpha$  rays. The structure factor,  $F_{222}$ , lies between 2.1 and 2.6. A. J. M.

**K X-ray absorption of light elements.** E. DERSHEM (Physical Rev., 1934, [ii], 45, 768).—Absorption of the  $L\alpha_{12}$  lines of Cu, Ni, and Fe in CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, and Ne have been measured. L. S. T.

**K-Absorption of X-rays at the K-edges.** H. NITKA (Naturwiss., 1935, 23, 866).—The determination of the absorption of X-rays by intensity measurements gives uncertain results for the heavier elements, but if the change of intensity coeff. on crossing an edge is considered, the effect of scattering is considerably reduced. There is a linear dependence of at. K-absorption at the K-edge on the  $\lambda$  of the edge. A. J. M.

**Change in relative intensity of the satellites of  $L\alpha$  in the atomic number range 47—52.** F. R. HIRSH, jun., and F. K. RICHTMYER (Physical Rev., 1934, [ii], 45, 754). L. S. T.

**Measurements of small light intensities with counter tubes. II.** K. H. KREUCHEN (Z. Physik, 1935, 97, 625—632; cf. A., 1935, 800).—Photo-electric sensitivity is given for Zn, Cd, and Cu in the region 400—185 m $\mu$ , both as solid and as deposited cathodes. A. B. D. C.

**Neon lamps in counter circuits. I. Limits of region of photo-electric sensitivity.** G. VALLE and B. ROSSI (Nuovo Cim., 1934, [ii], 11, 708—716; Chem. Zentr., 1935, i, 2778).—The dependence of photo-electric sensitivity on  $\lambda$  has been investigated. The upper limit gives a max. rate of potential increase between two impulses. J. S. A.

**Foreign ionisation and decrease of discharge potential in gases.** W. ROGOWSKI and A. WALLRAFF (Z. Physik, 1935, 97, 758—764). A. B. D. C.

**Rôle of space charge in the study of the Townsend ionisation coefficients and the mechanism**

of static spark breakdown. R. N. VARNEY, H. J. WHITE, L. B. LOEB, and D. Q. POSIN (Physical Rev., 1935, [ii], 48, 818—822).—The mechanism of spark breakdown is investigated by a study of the deviations of the pre-spark current from the simple electron ionisation law, on the basis of distortion of the field of the spark gap by space charge. N. M. B.

Electron affinity of iodine from space-charge effects. G. GLOCKLER and M. CALVIN (J. Chem. Physics, 1935, 3, 771—777; cf. A., 1934, 1054).—The electron affinity  $\Delta E_0$  of I atoms, determined directly by measuring the equilibrium of reaction  $I^- \rightarrow I + E^- - \Delta E_0$  at the surface of a hot W filament, was 74.6 kg.-cal., in good agreement with available data. The concn. of the several ions of different masses ( $I^-$  and  $E^-$ ) was calc. from their effect on space charge. I has no effect on the thermionic emission of W. N. M. B.

Charging potential and secondary emission of bodies irradiated with electrons. M. KNOLL (Physikal. Z., 1935, 36, 861—869).—The charging potential of a homogeneous metallic plate in a high vac. is discontinuous with respect to the velocity of the primary electrons over the range 0—5000 volts. For C, however, the charging potential  $\propto$  velocity of primary electrons. This behaviour is connected with the variation of emission of secondary electrons. A. J. M.

Energy distribution of electrons in the photo-electric effect. E. RUDBERG (Physical Rev., 1935, [ii], 48, 811—817).—Available expressions for the distribution of electron levels and the transition probabilities from these levels, characterising the photo-electric emission from a metal, are examined, and equations for the energy distribution are derived in each case. Results are compared with data for Mo (cf. Roehr, A., 1934, 130), and Mitchell's theory is supported (cf. *ibid.*, 1290). N. M. B.

Photo-ionisation in gases. R. N. VARNEY and L. B. LOEB (Physical Rev., 1935, [ii], 48, 822—824).—When the radiation emitted from a H discharge tube passed through a fluorite window into a balanced space-charge positive ion detector containing gas at 0.02 mm., it was proved that the ionisation, for discharge tube pressures  $>$  5 mm., was of electrostatic origin, and not caused by radiation. This may explain Lenard's observations on the ionisation of gases. For a given gas at each end of a tube, photo-ionisation of A and of Xe by its own radiation was found, but this disappeared when a fluorite window was inserted; no ionisation of  $N_2$  or air by its own radiation was observed with or without the window. Results indicate that in pure, clean, dry gases photo-ionisation by radiation of energy appreciably  $<$  the ionisation potential of the gas is improbable. N. M. B.

Surface ionisation of potassium on tungsten. A. L. REIMANN (Physical Rev., 1934, [ii], 45, 898).—The results of Copley and Phipps (cf. A., 1935, 1303) are discussed. L. S. T.

Surface ionisation of potassium on tungsten. M. J. COPLEY and T. E. PHIPPS (Physical Rev., 1935, [ii], 48, 960—968).—Work previously reported (cf.

A., 1935, 1303) is continued under improved conditions, and observations of degree of ionisation are made up to 2800° abs. The calc. work function for W is  $4.51 \pm 0.01$  volts. Difference between experiment and theory in the log ion-atom ratio- $1/T$  graph indicates a temp. coeff.  $\alpha$  of the work function; the calc. val. of  $\alpha$  is  $5.6 \times 10^{-5}$  volt per degree. N. M. B.

Monatomic films of alkali metals on platinum. H. MAYER (Physikal. Z., 1935, 36, 845—848).—The prep. of monat. films of alkali metals on Pt by means of at. rays is described. The thickness of the film can be calc. by assuming that to each four Pt atoms there is one K atom, since the lattice const. of Pt is approx. half that of K. The variation of the photo-electric sensitivity for both gas-containing and outgassed Pt on which were deposited at. films of K (gas-containing and outgassed, respectively) with thickness of K film was investigated. A. J. M.

Radiation characteristics of oxide cathodes. W. T. MILLIS and E. F. LOWRY (Physical Rev., 1934, [ii], 45, 764). L. S. T.

Thermionic emission and electronic conductivity of solids. A. GEHRTS (Physikal. Z., 1935, 36, 764—767).—The thermionic emission of cathodes consisting of a metal covered with a monat. adsorption layer is a pure surface phenomenon just as in the case of homogeneous cathodes. The electron emission work is smaller for a Th-covered W cathode (monat. layer) than for a homogeneous Th cathode. The thicker is the Th film the more nearly do the consts.  $A$  and  $b$  of the thermionic emission equation,  $I = AT^2 e^{-b/T}$  ( $I$  = saturation current), approach those for a homogeneous Th cathode. A. J. M.

Effect of temperature on electron field currents from thoriated tungsten. A. J. AHEARN (Physical Rev., 1934, [ii], 45, 764—765; cf. A., 1933, 993).—The measurements made agree with the view that the field currents are const. and independent of temp., and that thermionic emission accounts for the observed variations with temp. L. S. T.

Electron emission from thoriated tungsten. W. B. NOTTINGHAM (Physical Rev., 1934, [ii], 45, 765).—Variation with temp. and electric field of electron emission from C-free thoriated W has been measured for surface coverings from zero to approx. a single layer. L. S. T.

Potential of an insulated screening grid in an electron stream. H. STRUBIG (Z. Physik, 1935, 97, 538).—Preliminary. A. B. D. C.

Born theory of the electron. A. BRAMLEY (Science, 1935, 82, 438—439).—A discussion. L. S. T.

After-effect of aluminium bombarded by electrons. M. TANAKA (Physical Rev., 1935, [ii], 48, 916).—Livingood's experiments (cf. this vol., 131) were performed using 250—300 kv. tube voltage and bombarding Al foil in high vac. with high-speed electrons. The Al afterwards emitted an electron radiation decaying with half-val. periods of about 7 sec., 40 sec., and 10 min. A similar effect was observed for other elements, including Ni, Cu, and Ag. N. M. B.

**Inelastic scattering of electrons from metals.** E. RUDBERG (Physical Rev., 1934, [ii], 45, 764).

L. S. T.

**Saturation ionisation current from high-speed electrons in air.** L. S. TAYLOR (Physical Rev., 1935, [ii], 48, 970).—A method previously reported (cf. *ibid.*, 1934, [ii], 45, 762) of plotting results of ionisation produced in liquids is extended to determine the ionisation produced in air at normal pressure by a heterogeneous beam of electrons of max. energy 150 electron kv.

N. M. B.

**Acceleration of electrons to high energies.** J. W. BEAMS and H. TROTTER, jun. (Physical Rev., 1934, [ii], 45, 849—850).—A method of accelerating electrons by means of effectively moving electrical fields is described.

L. S. T.

**Energy losses of electrons in helium, neon, and argon.** R. WHIDDINGTON and E. G. WOODROOFE (Phil. Mag., 1935, [vii], 20, 1109—1120).—An extension of work previously reported (cf. A., 1934, 825). Energy losses, relative probabilities, and interpretations of the excitations are tabulated.

N. M. B.

**Limitations of the theory of the positron.** W. H. FURRY and J. R. OPPENHEIMER (Physical Rev., 1934, [ii], 45, 903—904; cf. A., 1934, 468; 1935, 278).

L. S. T.

**Proton-proton forces in anomalous scattering and in nuclear binding.** R. D. PRESENT (Physical Rev., 1935, [ii], 48, 919—920).—In view of anomalies reported by White (cf. *ibid.*, 47, 573) on the scattering of protons in  $H_2$ , the scattering cross-section is calc. for  $45^\circ$  scattering, using the Feenberg-Knipp nuclear model (cf. this vol., 134) and assuming an additional attractive proton interaction.

N. M. B.

**Scattering of molecular rays in gases.** R. G. J. FRASER, H. S. W. MASSEY, and C. B. O. MOHR (Z. Physik, 1935, 97, 740—744).—The geometry of the crossed mol.-ray method is worked out for a primary beam of rectangular cross-section, and used to obtain collision cross-sections for Na-Hg and K-Hg.

A. B. D. C.

**High-current ion sources for nuclear investigations.** E. S. LAMAR, E. W. SAMSON, and K. T. COMPTON (Physical Rev., 1935, [ii], 48, 886—892).—Experiments are described with a capillary ion source designed by Tuve (cf. A., 1935, 1296), which has been modified by eliminating the auxiliary electrode for drawing ions out of the arc. The ion current for a 1.92 amp. arc was 4.2 milliamp.; currents up to 5 amp. have been used. The mass spectrograph, when the arc is operated in  $H_2$ , shows a preponderance of diat. and triat. ions with proton fractions 5—20% of the total ion current. There is evidence of the breaking up of the heavy ions into protons and neutral particles on collision at high speed with gas mols.

N. M. B.

**Positive rays. Application to the study of the Stark effect.** A. POIROT (Ann. Physique, 1935, [xi], 4, 533—645; cf. A., 1930, 657).—Morand's method (cf. A., 1927, 492) is extended to the emission of positive rays from Na, K, Ca, Ba, and Cr. The rays form a well-defined faintly luminous beam; the spectrum of the light emitted shows chiefly the lines of the

arc spectrum of the metal of the salt deposited on the anode. The phenomena observed can be explained by the electrolysis and partial volatilisation of the salt. The rays can be used for the study of the Stark effect, particularly in the case of metals which do not form stable volatile compounds for study by the discharge tube. The Stark effect for Li, the diffuse doublets of Na, and the singlets and triplets of Ba were observed.

N. M. B.

**At. wt. of neon.** A. VON ANTROPOFF [with R. JUNGBLUTH-FICHT and M. HOEPPENER] (Ber., 1935, 68, [B], 2389—2391).—Ne and He can be separated from one another by active C cooled in liquid air. The at. wt. of Ne, determined from its density, is 20.183.

H. W.

**Isotopic constitution of iron.** J. DE GIER and P. ZEEMAN (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 959—961).—The isotope 58 of Fe has been detected in  $Fe(CO)_5$  by the mass spectrograph, its abundance being about 0.5%.

J. W. S.

**Isotopic structure of iridium.** A. J. DEMPSTER (Nature, 1935, 136, 909).—A mass analysis of the Ir ions formed by a high-frequency spark between Pt-Ir electrodes confirms the existence (cf. A., 1935, 1295) of  $Ir^{191}$  and  $Ir^{193}$ , the latter more abundant.

L. S. T.

**Production of  $H^3$  by a canal-ray discharge in deuterium.** G. P. HARNWELL, H. D. SMYTH, S. N. VAN VOORHIS, and J. B. H. KUPER (Physical Rev., 1934, [ii], 45, 655—656, 769).— $H^3$  has been accumulated by running a high-voltage discharge in  $D_2$  at low pressure and passing the resulting canal rays into  $D_2$  at a higher pressure. Circulation of the gas for 3 hr. increased the  $H^3$  content from 1 in  $2 \times 10^5$  to 1 in 5000 parts of  $D_2$ .

L. S. T.

**Prediction of isotopes.** J. H. BARTLETT, jun. (Physical Rev., 1934, [ii], 45, 847).—A list is given.

L. S. T.

**Inhomogeneous fields for mass spectrography.** S. H. BAUER (Physical Rev., 1935, [ii], 48, 917).—Mathematical.

N. M. B.

**Radioactivity of samarium and "columnar ionisation."** D. LYFORD and J. A. BEARDEN (Physical Rev., 1934, [ii], 45, 743—744).—3.9  $\alpha$ -particles, range 1.28 cm., are emitted per sq. cm. per min. from a  $Sm_2O_3$  surface.

L. S. T.

**Radioactivity of the rare-earths. I. Distribution of radioactivity in the fractionation of cerium earths.** L. MAZZA (Gazzetta, 1935, 65, 993—1008; cf. A., 1934, 578).—By means of an automatic Geiger counter the distribution of radioactivity in the various fractions resulting from the fractionation of rare-earth mixtures has been measured. La-Ce-Pr, Pr-Nd, and Nd-Sm mixtures, respectively, were used. Both La and Ce retain traces of radioactive elements very tenaciously and are themselves inactive. The Pr-Nd fractions are all feebly active, probably due to the radioactivity of Nd. In the Nd-Sm mixtures the radioactivity is due chiefly to Sm, although here also impurities of radioactive elements tend to become conc. in the more sol. fractions.

O. J. W.

**Interaction between  $\alpha$ -particles.** J. A. WHEELER (Physical Rev., 1934, [ii], 45, 746). L. S. T.

**Ionisation curves of single  $\alpha$ -particles.** H. ALFVEN (Z. Physik, 1935, 97, 718—724).—The current due to the ionic sheath surrounding an  $\alpha$ -particle track in a homogeneous electric field has the form of the Bragg curve (cf. A., 1935, 1048). A. B. D. C.

**Range of  $\alpha$ -rays from polonium and its dependence on intensity of the radiation, age of the preparation, and nature of the substrate.** B. KARLIK and E. RONA (Sitzungsber. Akad. Wiss. Wien, IIA, 1934, 143, 217—221; Chem. Zentr., 1935, i, 2773).—Strong preps. show inhomogeneity, which increases on ageing, and is  $>$  corresponds with self-absorption. The range decreases steadily on keeping in CO<sub>2</sub>. Penetration of Ni or Pd substrates does not occur with weak sources. J. S. A.

**Excitation of K-radiation of nitrogen, oxygen, and neon by alpha-particles.** W. RIEZLER (Ann. Physik, 1935, [v], 24, 714—718).—The excitation function for K-radiation of N<sub>2</sub>, O<sub>2</sub>, and Ne by  $\alpha$ -particles was investigated for  $\alpha$ -particles of range 13—35 mm. in air. The curve between range of  $\alpha$ -particle and excitation function is analogous to the Bragg curve for total ionisation by  $\alpha$ -particles, although the max. is much flatter. The Ne curve does not reach a max. in the range considered. A. J. M.

**Recoil by  $\beta$ -decay.** F. BLOCH and C. MÖLLER (Nature, 1935, 136, 911—912).—Theoretical. L. S. T.

**X-Ray levels of radioactive elements with applications to  $\beta$ - and  $\gamma$ -ray spectra.** F. A. MAXFIELD and A. E. RUARK (Physical Rev., 1934, [ii], 45, 744). L. S. T.

**Magnitude and composition of the absorption coefficients of hard  $\gamma$ -rays.** W. GENTNER (Physikal. Z., 1935, 36, 810—812).—The variation with  $\lambda$  of the absorption coeff. for  $\gamma$ -rays in Pb, and for  $\gamma$ -rays from Th-C'' ( $h\nu=2.65 \times 10^6$  e.v.) the variation with at. no., have been determined. A. J. M.

**Magnetic moment of the neutron.** D. R. INGLIS and A. LANDÉ (Physical Rev., 1934, [ii], 45, 842; cf. A., 1935, 278).—Theoretical. L. S. T.

**Production of neutrons by annihilation of protons and electrons according to Fermi's theory.** F. BLOCH and C. MÖLLER (Nature, 1935, 136, 987).—Theoretical. L. S. T.

**Experiments with slow neutrons.** P. I. LUKIRSKI and T. V. ZAREVA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 393—396).—A detailed account of work already noted (A., 1935, 1441).

**Production of secondary  $\gamma$ -rays by neutrons.** R. FLEISCHMANN (Physikal. Z., 1935, 36, 806—808).— $\gamma$ -Rays were produced by the action of slow neutrons on paraffin, Fe, Cu, Cd, and Pb. In the case of the metals the slow neutrons were produced by the preliminary passage of neutrons through paraffin. The efficiency is in all cases one quant per neutron. A. J. M.

**Absorption of residual neutrons.** L. SZILARD (Nature, 1935, 136, 950—951).—Slow neutrons

(paraffin) from a Rn-Be source filtered by thick Cd sheets are strongly absorbed by In and some other elements. Cd absorbs the bulk of the unfiltered beam more strongly than does In. The residual neutrons from the Cd filter are scarcely absorbed by Cd itself. They show marked selective absorption effects, and in some elements are more absorbable than the unfiltered beam. The results are contrary to the current theory of radiative capture. L. S. T.

**Scattering of neutrons by H<sub>2</sub>O, D<sub>2</sub>O, paraffin, lithium, boron, and carbon, and the production of radioactive nuclei by neutrons found by Fermi.** J. R. DUNNING and G. B. PEGRAM (Physical Rev., 1934, [ii], 45, 768—769).—The scattering of Rn-Be neutrons by these substances shows that for light in contrast to heavy nuclei the cross-section for neutron-nucleus collision does not vary greatly with the nuclear charge or nuclear mass. Mg gives an induced radioactivity with a period of approx. 3 hr. L. S. T.

**Slowing down of neutrons by collisions with protons.** H. VON HALBAN, jun., and P. PREISWERK (Nature, 1935, 136, 951—952).—The degree of activation produced in a Ag plate by neutrons from a Rn-Be source slowed down by passage through various thicknesses of H<sub>2</sub>O, EtOH, C<sub>6</sub>H<sub>6</sub>, and a liquid paraffin has been observed. The differences in the effect of these liquids on the intensity of slow neutrons cannot be ascribed to differences in the amounts of H, C, or O which the liquids contain. Mol. structure appears to be a factor. L. S. T.

**Energy distribution of neutrons from fluorine.** T. Y. WU (Physical Rev., 1934, [ii], 45, 846—847).—Theoretical. L. S. T.

**Geiger-counter characteristics with applied potentials reversed.** D. B. COWIE (Physical Rev., 1935, [ii], 48, 883—885).—Counters in which the cylinder potential is positive with respect to the wire operate with a reduced efficiency for which an explanation is discussed. N. M. B.

**Search for radioactivity induced by 800-kilo-volt electrons.** J. J. LIVINGOOD and A. H. SNELL (Physical Rev., 1935, [ii], 48, 851—854).—About 50 elements were bombarded with 850-kv. electrons and examined with a Geiger counter for induced radioactivity. No positive results were obtained, indicating that the yield is  $< 1$  activation per  $10^{12}$  electrons. N. M. B.

**Radioactivity produced by artificially-accelerated particles.** H. R. CRANE and C. C. LAURITSEN (Physical Rev., 1934, [ii], 45, 746). L. S. T.

**Disintegration of beryllium with fast protons.** B. ZIPPRICH (Z. Physik, 1935, 96, 337—341).—This disintegration produces  $\alpha$ -particles. A. B. D. C.

**Artificial radioactivity using carbon targets.** L. R. HAFSTAD and M. A. TUVE (Physical Rev., 1934, [ii], 45, 902—903).—The production from C bombarded with protons of a radio-element which has a decay period the same as that of C bombarded with deuterons (cf. A., 1935, 1442) is due to deuterons contaminating the proton beam. L. S. T.

Induced radioactivity which follows bombardment of targets by deuterium ions. L. R. HAFSTAD and M. A. TUVE (Physical Rev., 1934, [ii], 45, 767—768).—Delayed emission effects produced in a series of targets by deuteron bombardment are described. L. S. T.

Protons from the disintegration of lithium by deuterons. L. A. DELSASSO, W. A. FOWLER, and C. C. LAURITSEN (Physical Rev., 1935, [ii], 48, 848; cf. *ibid.* 47, 971).—The range distribution of the  $\alpha$ -particles and protons emitted in the disintegration of Li by 700-kv. deuterons was determined. The calc. energy released in the disintegration is 4.3 m.e.v.; the calc. masses are  $\text{Li}^8$  8.0185, and  $\text{Be}^8$  8.0072 =  $2\text{He}^4 + 0.5 + 1.0$  m.e.v. N. M. B.

Radioactivity induced in oxygen by deuteron bombardment. H. W. NEWSON (Physical Rev., 1935, [ii], 48, 790—796).—An induced radioactivity of half-life 1.16 min. was observed after the bombardment of  $\text{O}_2$  or its compounds by 3-mv. deuterons. The disintegration particles were positrons, and the active substance an isotope of F. The probable reactions are:  $\text{O}^{16} + \text{D}^2 = \text{F}^{17} + n^1$ ;  $\text{F}^{17} = \text{O}^{17} + e^+$ . The activation function of O was measured, and the drop in the excitation curve at low deuteron energies is explained by assuming that the energy of reaction is the negative of the threshold energy; the estimated val. is -1.8 mv. This is approx. verified by measuring the max. angle between the direction of the deuteron beam and the paths of the radioactive recoil atoms when  $\text{SiO}_2$  and graphite were separately bombarded. N. M. B.

Two radioactive substances from magnesium after deuteron bombardment. M. C. HENDERSON (Physical Rev., 1935, [ii], 48, 855—861).—Mg bombarded by 3.3 m.e.v. deuterons became radioactive with emission of negative electrons and  $\gamma$ -rays, and with two decay periods,  $10.25 \pm 0.24$  min., and  $15.8 \pm 0.5$  hr., characteristic of  $\text{Mg}^{27}$  and  $\text{Na}^{24}$ . The reactions are:  ${}_{12}\text{Mg}^{26} + {}_1\text{H}^2 = {}_{12}\text{Mg}^{27} + {}_1\text{H}^1$ ;  ${}_{12}\text{Mg}^{26} + {}_1\text{H}^2 = {}_{11}\text{Na}^{24} + {}_2\text{He}^4$ ;  ${}_{12}\text{Mg}^{27} = {}_{13}\text{Al}^{27} + \beta + \gamma$ ;  ${}_{11}\text{Na}^{24} = {}_{12}\text{Mg}^{24} + \beta + \gamma$ . The measured voltage excitation functions of the two activities follow different laws. At 3 m.e.v. one atom becomes  $\text{Na}^{24}$  for each 9.6 atoms becoming  $\text{Mg}^{27}$ . The thick target yield of  $\text{Mg}^{27}$  atoms is about 5 per  $10^7$  deuterons. The nuclear cross-section ( $\text{Mg}^{26}$ ) at 3 m.e.v. is approx.  $2.4 \times 10^{-26}$  sq. cm. N. M. B.

Collisions of  $\alpha$ -particles with neon nuclei. W. W. EATON (Physical Rev., 1935, [ii], 48, 921—928).—Using a special projection method, collisions with nuclei were investigated from photographs of 700,000  $\alpha$ -particle tracks due to a source of Th active deposit. The Wilson chamber contained Ne 85%, air 10%, and  $\text{H}_2$  5%. Range-velocity curves for recoil atoms give no evidence of disintegrations of nuclei with emission of protons or neutrons. The probability of disintegrating  $\text{Ne}^{20}$  with  $\alpha$ -particles of < 6 cm. range in air is small; from this the calc. lower limit for the mass of  $\text{Na}^{23}$  is 22.99945. N. M. B.

Proton spectra of magnesium, silicon, and sulphur on bombardment with fast  $\alpha$ -particles. O. HAXEL (Physikal. Z., 1935, 36, 804—806).—The

proton spectra of Mg, Si, and S when bombarded with  $\alpha$ -particles of 8.6 cm. range are very similar. This result is discussed on the basis of the nuclear structure of the three atoms. The spectra are those of the most abundant isotopes,  $\text{Mg}^{24}$ ,  $\text{Si}^{28}$ , and  $\text{S}^{32}$ . From the energies of the emitted proton groups, the energies of the excited nuclei of Al, P, and Cl can be obtained. These energies are identical for the three nuclei, and the excitation probabilities for all three elements are approx. equal. This can be explained if the nuclei differ from each other by only one  $\alpha$ -particle. A. J. M.

Evidence for a resonance level in the nucleus of  $\text{B}^{10}$ . E. POLLARD (Physical Rev., 1934, [ii], 45, 746).—The protons emitted by B under  $\alpha$ -particle bombardment consist of a group of 18 cm. range superposed on the 14-cm. group observed by Heidenreich. The new group is due to a broad resonance level through which  $\alpha$ -particles of 1.2—1.7 cm. range can enter the nucleus. L. S. T.

Methods and types of artificial transformation of atoms. W. BOHRÉ (Physikal. Z., 1935, 36, 776—779).—A review of the types and products of nuclear reactions. The highest known stable isotope of any given at. no. must contain an even no. of neutrons. A. J. M.

Artificial disintegration. III. D. VAN DER VEEN (Chem. Weekblad, 1936, 33, 16—21).—A further review (see A., 1934, 826).

Chemical detection of artificial transmutation of elements. F. A. PANETH and H. LOLEIT (Nature, 1935, 136, 950).—He produced by bombardment of Me borate with neutrons from a Rn-Be source has been observed spectroscopically and the vol. measured. One millicurie of Rn, mixed with Be, produces  $\approx 3 \times 10^3$  neutrons per sec. L. S. T.

Excitation of nuclei by neutrons. W. EHREBERG (Nature, 1935, 136, 870; cf. A., 1935, 141).—Neutrons, apparently of medium velocity, from a Rn-Be source produce an increased activity in Ag and I and a decreased activity in Si and Al when the source is surrounded by a Ag shield. Collisions of neutrons with Ag nuclei lead either to excitation of the nucleus without capture or to capture with formation of a radioactive element. L. S. T.

Radioactivity induced by neutron bombardment. A. BRAMLEY (Physical Rev., 1934, [ii], 45, 901—902).—Nuclear reactions are discussed. L. S. T.

Effect of substances containing hydrogen on artificial radioactivity excited by neutrons. II. E. FERMI, B. PONTECORVO, and F. RASETTI (Ric. sci. Prog. tec., 1934, 5, II, 380—381; Chem. Zentr., 1935, i, 2492).—The collision area of the atoms of various elements is derived from the relative activity of Rh, embedded in paraffin wax, activated through a screen of the element in question. Elements of large collision area, except Li and B, show high activation by slow neutrons. Li and B probably form stable isotopes or emit very soft  $\beta$ -rays. J. S. A.

Artificial radioactivity excited by neutron bombardment. VI. E. AMALDI, O. D'AGOSTINO, and E. SEGRÉ (Ric. sci. Prog. tec., 5, 381—382;

- Chem. Zentr., 1935, i, 2492—2493; cf. A., 1934, 1284).—In all cases (F, Na, Al, Cl, Ga, Ag, In, Cs, Pr, Pt, Re) where the radioactive species could be separated chemically from material activated with slowed-down neutrons, the active atom was isotopic with the starting material. New half-life periods are reported for F, Al, Cl, Pr, and Pt. J. S. A.
- Problems of ultra-radiation. P. M. S. BLACKETT (Physikal. Z., 1935, 36, 773—776).—A review. A. J. M.
- Transmission of ultra-radiation through matter. H. KULENKAMPFF (Physikal. Z., 1935, 36, 785—787).—Coincidence determinations have been carried out using counter tubes placed horizontally above each other with absorbing layers above and between the tubes. A secondary corpuscular radiation with a range of about 35 cm. of Fe is found to be produced by  $\gamma$ -radiation of which the absorption coeff. in Fe is 0.009 cm.<sup>-1</sup> A. J. M.
- Showers of rays which produce bursts of cosmic-ray ionisation. C. G. MONTGOMERY and D. D. MONTGOMERY (Physical Rev., 1935, [ii], 48, 786—789).—An expression for the probability that a shower of a given no. of rays will discharge a no. of Geiger-Müller counters is derived and verified experimentally. Results indicate that there is no marked discontinuity between small and large showers. N. M. B.
- Compensation method for simultaneous measurement of ionisation collisions and intensity of cosmic rays. A. GASTELL (Z. Physik, 1935, 97, 403—413). A. B. D. C.
- Ionisation collisions of cosmic rays. A. GASTELL (Z. Physik, 1935, 97, 414—435).—The gas in the ionisation chamber has little effect on collision measurements. The no. of collisions is sensitive to barometric pressure. A. B. D. C.
- Investigation of ionisation by ultra-radiation with a double chamber. W. MESSERSCHMIDT (Physikal. Z., 1935, 36, 788—789).—A double ionisation chamber was used for the investigation of the absorption of Hoffmann "stösse" (A., 1934, 235). A half-val. thickness of 3.5 cm. Pb was obtained. The connexion between the shower groups observed by the cloud-chamber method and the "stösse" is discussed. A. J. M.
- Solar components of ultra-radiation. J. BARNÓTHY and M. FORRÓ (Physikal. Z., 1935, 36, 789—791). A. J. M.
- Analysis of corpuscular cosmic radiation under a screen of 28 m. of soil. P. AUGER and A. ROSENBERG (Compt. rend., 1935, 201, 1116—1118; cf. A., 1935, 560).—Soft cosmic radiation was almost completely eliminated at this depth. H. J. E.
- Sign and nature of the ultra-penetrating particles of cosmic radiation. L. LEFRINCE-RINGUET (Compt. rend., 1935, 201, 1184—1187).—The most penetrating cosmic particles have been investigated in a large Wilson chamber working in a magnetic field. The majority have the paths of fast electrons. One third of the particles have such high energies that the sense of the deflexion of their paths could not be ascertained. From the measurable paths, the ratio of positive to negative particles is 2 : 1, and their energies are > 700 m.e.v. T. G. P.
- What fraction of the primary cosmic radiation is positive? T. H. JOHNSON (Physical Rev., 1934, [ii], 45, 758). L. S. T.
- Ionisation spurts resulting from cosmic-ray entities. W. F. G. SWANN and W. E. RAMSEY (Physical Rev., 1934, [ii], 45, 758). L. S. T.
- Azimuthal effect of cosmic rays. R. GUNN (Physical Rev., 1934, [ii], 45, 900—901).—Theoretical. L. S. T.
- Orbit of electric particles in field of a magnetic dipole, with application to the theory of cosmic radiation. C. STØRMER (Avh. Norske Vid. Akad. Oslo, 1933, No. 11; Chem. Zentr., 1935, i, 2774).—The author's auroral theory is applied to cosmic radiation. J. S. A.
- Stellar theory. W. NERNST (Z. Physik, 1935, 97, 511—534).—A physical interpretation for the formation of stars is given. A. B. D. C.
- Neutrino theory of light. O. SCHERZER (Z. Physik, 1935, 97, 725—739). A. B. D. C.
- Decisive forces in the structure of the atomic nucleus. C. V. VON WEIZSÄCKER (Physikal. Z., 1935, 36, 779—785).—Theoretical discussion. A. J. M.
- The Geiger counter and gas discharges as space-charge problems. A. VON HIPPEL (Z. Physik, 1935, 97, 455—481).—The conception of space charge is developed and applied to the region between initiation and continuous discharge; this gives an accurate definition of initiation potential. Extension to inhomogeneous fields gives a description of the properties of the Geiger counter. A. B. D. C.
- Possibility of a metallic modification of hydrogen. E. WIGNER and H. B. HUNTINGTON (J. Chem. Physics, 1935, 3, 764—770).—The energy of a body-centred lattice of H<sub>2</sub>, calc. as a function of the lattice const., assumes its min. val. for a lattice const. which corresponds with a density many times > that of the ordinary mol. lattice of solid H<sub>2</sub>, and with a pressure of approx. 250,000 atm., beyond the range of present technique. N. M. B.
- $\infty s$  orbits of the elements. E. FERMI and E. AMALDI (Mem. R. Accad. Italia, 1934, 6, 119—149).—Mathematical. The calculation of the proper functions of elements, using the Thomas-Fermi statistics, is described, and applied to the  $\infty s$  functions of 14 elements. O. J. W.
- Tables for determining atomic wave functions and energies. P. M. MORSE, L. A. YOUNG, and (Miss) E. S. HAURWITZ (Physical Rev., 1935, [ii], 48, 948—954). N. M. B.
- Value of the electronic charge. R. T. BIRGE (Physical Rev., 1935, [ii], 48, 918).—Kellström's result (cf. A., 1935, 1455) for the viscosity of air leads to the val.  $4.816 \pm 0.013 \times 10^{-10}$  for  $e$ , compared with  $4.8036 \pm 0.0005 \times 10^{-10}$  e.s.u. by abs. X-ray  $\lambda$  measurements. These results, however, still leave in doubt

any set of vals. of the interrelated consts.  $e$ ,  $e/m$ , and  $h$  that would satisfy all the experimental results.

N. M. B.

Quantised field theory and the mass of the proton. M. BORN (Nature, 1935, 136, 952—953).

L. S. T.

Statistic perturbation theory. I. Perturbation calculations with the Thomas-Fermi theory excluding exchange. P. GOMBAS (Z. Physik, 1935, 97, 633—654).

A. B. D. C.

Majorana's exchange energy. G. BREIT and E. WIGNER (Physical Rev., 1935, [ii], 48, 918—919).—Mathematical. Anomalies arising from the differences in mass of the neutron and proton are corr.

N. M. B.

Absorption of high-energy particles by matter. J. SOLOMON (Compt. rend., 1935, 201, 1110—1112).—Theoretical.

H. J. E.

Characteristic constants of the atomic sphere. L. LABOCETTA (Ric. sci. Prog. tec., 1934, 5, II, 376—377; Chem. Zentr., 1935, i, 2491).—Theoretical.

J. S. A.

Intra-nuclear forces. E. FEENBERG and J. K. KNIPP (Physical Rev., 1935, [ii], 48, 906—912).—Mathematical. The H and He isotopes are considered.

N. M. B.

Interaction of nuclear particles. L. A. YOUNG (Physical Rev., 1935, [ii], 48, 913—915; cf. *ibid.*, 47, 972).—Mathematical. Calculations of the ranges and strengths indicate that the interactions are of an exchange nature with approx. range  $2.8 \times 10^{-13}$  cm.; the neutron-neutron and proton-proton interactions are approx. equal, the former depending probably on spin orientation. A di-neutron or di-proton may be dynamically stable, but unstable with respect to  $\beta$ -decay.

N. M. B.

Application of the Dirac matrix method to the theory of metals. S. SCHUBIN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 15—18).—Theoretical. The Dirac matrix method is applied to the problem of the motion of electron gas under the influence of an alternating electric field.

A. J. M.

Elements of the quantum theory. VI. Hydrogen atom. S. DUSHMAN (J. Chem. Educ., 1935, 12, 529—539; cf. this vol., 7).

L. S. T.

Electrostatic field and energy conditions in neighbourhood of a lattice edge. W. KLEBER (Zentr. Min., 1935, A, 45—52; Chem. Zentr., 1935, i, 2644—2645).—Theoretical.

J. S. A.

Quadratic Zeeman effect. G. RACAH (Nuovo Cim., 1934, [ii], 11, 723—724; Chem. Zentr., 1935, i, 2775).—Relativistic treatment of the problem gives the same results as the use of Schrödinger's equation.

J. S. A.

Mass of the neutron from the nuclear reaction  $H^2 + H^2 \rightarrow He^3 + n^1$ . H. H. GOLDSMITH and V. W. COHEN (Physical Rev., 1934, [ii], 45, 850).—A discussion.

L. S. T.

Extensive results of the classical simplest elastic hydrogen atom. L. ZEHNDER (Physikal. Z., 1935, 36, 820—822).—The structure of the atom is

considered from the viewpoint of the "principle of greatest simplicity."

A. J. M.

Deviation of electrical charge distribution from spherical symmetry for some atomic nuclei. H. SCHÜLER (Physikal. Z., 1935, 36, 812—814).—There is an asymmetry of the charge distribution in the nuclei of  $^{63}_{29}\text{Cu}$ ,  $^{65}_{29}\text{Cu}$ ,  $^{201}_{80}\text{Hg}$ ,  $^{209}_{83}\text{Bi}$ , the vals. of which are calc. The results are discussed with reference to nuclear structure (cf. A., 1935, 1051).

A. J. M.

Emission spectrum of the oxide of tellurium TeO. C. S. PIAW (Compt. rend., 1935, 201, 1181—1183).—TeO has a system of about 30 bands, degraded towards the red, between 3190 and 3820 Å., analogous to those of SO and SeO. The energy of dissociation of the normal mol. is 5.70 volts.

T. G. P.

Rotational structure of the D and E band systems of CuCl. J. TERRIEN (Compt. rend., 1935, 201, 1029—1030).—The bands, produced in a discharge tube containing CuCl, are complex, since the frequencies of vibration and anharmonic factors of the two states are similar, and each atom has two isotopes. The E band,  $v'=0$ ,  $v''=0$ ,  $\lambda=4333.19$ , and the D band,  $v'=0$ ,  $v''=0$ ,  $\lambda=4353.86$ , have been investigated.

T. G. P.

Absorption spectrum of  $\text{SnI}_4$  vapour. A. V. BANOV (Acta Physicochim. U.R.S.S., 1935, 2, 733—736; cf. A., 1935, 807).—The continuous absorption of  $\text{SnI}_4$  between  $130^\circ$  and  $280^\circ$  shows max. at 3570, 2800, and 2450 Å. The first two are associated with the dissociation into  $\text{SnI}_3 + \text{I}$ , and  $\text{SnI}_3 + \text{I}^*$ , respectively. The dissociation energy of  $\text{SnI}_4$  into  $\text{SnI}_3 + \text{I}$  is 2.6 volts. The 2450 Å. max. is probably associated with  $\text{SnI}_4 \rightarrow \text{SnI}_2 + 2\text{I}$ .

T. G. P.

Absorption spectrum of tellurium dibromide vapour. J. LARIONOV (Acta Physicochim. U.R.S.S., 1935, 2, 67—80).—The spectrum consists of diffuse bands without heads, grouped in triplets, of which the 8 most characteristic lie between 6255 and 5684 Å. Heats of dissociation of  $\text{TeBr}_2$  have been calc. from thermochemical data, and the possible dissociation processes are discussed in relation to the band spectrum.

R. S.

Absorption spectra of the vapours, and determination of the heats of sublimation of (I) the monoxides, (II) the monosulphides, of copper, iron, nickel, and cobalt. H. TRIVEDI (Proc. Acad. Sci. Agra and Oudh, 1935, 5, 27—33, 34—40).—I. The spectrum of the vapours of CuO and FeO showed only one region, and of NiO and CoO two regions, of continuous absorption. The long- $\lambda$  limits are: FeO 2500; NiO 3270, 2380; CoO 2750, 2100; CuO 2410 Å. The difference between the limits of the two regions was approx. 32 kg.-cal. in each case; this may be due to dissociation into the metal atom and O ( $^3P$ ) and O ( $^1D$ ). The calc. heats of vaporisation of FeO, CoO, and NiO are 97.5, 101.5, and 111.5 kg.-cal., respectively.

II. The vapours of the sulphides showed continuous absorption from a long-wave limit, resulting in photo-dissociation into two normal atoms; after the first absorption there is a retransmitted patch and



a second absorption. The energy difference 1.31 volts is attributed to the difference  ${}^3P \rightarrow D$  of S. The heats of vaporisation, determined indirectly, were FeS 93, NiS 101.6, CoS 89, and CuS 84 kg.-cal.

N. M. B.

**Continuous absorption spectrum of hydrogen bromide.** C. F. GOODEVE and A. W. C. TAYLOR (Proc. Roy. Soc., 1935, A, 152, 221—230).—The extinction coeffs. of HBr have been measured over a wide range of conditions, and the approx. upper potential energy curve has been calc. from the eigenfunction of the ground state and the observed extinctions. The results favour the dissociation into normal atoms.

L. L. B.

**Absorption spectrum of water in the ultra-violet.** E. HAAS (Biochem. Z., 1935, 282, 224—229).—A method for determination of the absorption of  $H_2O$  is described and tables summarise the results. The dissociation const. of  $H_2O$  is  $0.6 \times 10^{-14}$  at  $17^\circ$  and  $2.5 \times 10^{-14}$  at  $37^\circ$ . By raising the temp. to  $20^\circ$ , the  $[OH^-]$  increases from  $0.77 \times 10^{-7}$  to  $1.58 \times 10^{-7} N$ . Since  $10^{-7}$ — $10^{-6} N$ -NaOH absorbs as does  $H_2O$ , and since saturation with  $CO_2$  has little effect on the absorption, the effect of temp. on absorption cannot be explained in terms of dissociation.

P. W. C.

**Ultra-violet absorption of mixtures of  $NO$ ,  $NO_2$ , and  $H_2O$ .** E. H. MELVIN and O. R. WULF (J. Chem. Physics, 1935, 3, 755—759).—In the presence of a trace of  $O_2$  or  $NO_2$  in  $NO$ , a continuous absorption in the ultra-violet obscures the absorption of  $NO$  and part of that of  $NO_2$ ; the behaviour of this absorption relative to temp. and partial pressure of the constituents points to  $N_2O_3$ . When, in addition, traces of  $H_2O$  vapour are present, a group of bands appears in the region 4000—3000 Å., decreasing in intensity with rise of temp.; there is evidence of a predissociation process in the carrier, probably HONO.

N. M. B.

**Effect of heavy water of crystallisation on the line absorption spectrum of chrome alum.** G. JOOS and H. BÖHM (Physikal. Z., 1935, 36, 826—827).—Replacement of  $H_2O$  in K Cr Se alum by  $D_2O$  causes considerable displacement of the absorption lines.

A. J. M.

**Influence of pressure and foreign gases on the optical absorption of chromyl chloride.** M. KANTZER (Compt. rend., 1935, 201, 1030—1031; cf. A., 1934, 472).—Absorption by the A series increases with pressure, whilst that of the B and C series diminishes. Addition of  $H_2$  up to 1 mol. proportion increases the general absorption, especially at longer  $\lambda$ . Similar effects observed with A,  $N_2$ ,  $CO_2$ ,  $SO_2$ , and  $SF_6$  decrease regularly with increasing mol. wt.

T. G. P.

**Absorption, optical activity, and configuration of metal complexes.** J. P. MATHIEU (Compt. rend., 1935, 201, 1183—1184; cf. A., 1934, 944).—Examination of the visible absorption bands of 20 Co, Cr, and Ir complexes of the type  $[Co en_2 A A']$  shows that the  $\lambda$  of the max. increases with the mobility of the groups A or A' in the order I, Br, Cl, CNS,  $NO_2$ . Absorption shows a principal and a feeble subsidiary band, confirmed by measuring the circular dichroism,

which is also a means of comparing the configurations of active ions.

T. G. P.

**Paramagnetism. III. Light absorption in paramagnetic crystals and solutions.** S. DATTA and M. DEB (Phil. Mag., 1935, [vii], 20, 1121—1136; cf. A., 1934, 832).—Absorption spectra data are given for anhyd. and hydrated crystals of paramagnetic halides of the Fe group and their solutions at different temp. in  $H_2O$ , EtOH, or conc. HCl. The absorption max. for solutions of  $CrCl_3$ ,  $CoCl_2$ , and  $NiCl_2$  are shifted, relative to the max. in aq. solutions, to the longer- $\lambda$  side when the solvent has dielectric const.  $<$  that of  $H_2O$ , or when it contains excess of HCl; for the latter type of solutions, at low temp. the bands recede towards the shorter- $\lambda$  side and agree with those of the hydrated complexes, as in the aq. solutions. For powdered anhyd. chlorides the absorption max. lie in the longer- $\lambda$  side relative to those of the corresponding hydrated complexes, and agree fairly well with the positions for EtOH and HCl solutions at higher temp. Results are discussed relative to a theory of absorption by a transition group ion forming part of a complex ion or of an undissociated mol.

N. M. B.

**Absorption spectra of nitrophenylhydrazines.** A. K. MACBETH and J. R. PRICE (J.C.S., 1935, 1563—1567).—The absorption spectra of *o*-, *m*-, and *p*- $NO_2 \cdot C_6H_4 \cdot NH \cdot NH_2$  in EtOH and aq. EtOH (20%) have been compared with those of *o*-, *m*-, and *p*- $NO_2 \cdot C_6H_4 \cdot NH_2$  and  $-NO_2 \cdot C_6H_4 \cdot NMe_2$  (cf. A., 1934, 997). It is shown that the long-wave absorption is probably due to electronic excitation of the  $\cdot NO_2$  influenced by the nuclear  $\cdot NH_2$  or  $\cdot NH \cdot NH_2$ . This is supported by the fact that bands due to each influenced  $\cdot NO_2$  still persist in 4:6-dinitrotolyl- and 2:4-dinitrophenyl-hydrazine, although displaced by  $2200 \text{ cm}^{-1}$ . The band max. for 1:2:4- $C_6H_3(NO_2)_2 \cdot NH_2$  can be calc. from the *o*- and *p*- $NO_2 \cdot C_6H_4 \cdot NH_2$  vals. using this figure. The band displacements due to the change from EtOH to 20% EtOH solution are similar to those for the nitroamines.

R. S.

**Spectroscopy of amino-acids and their derivatives. I. Ultra-violet absorption of *l*-tyrosine, *dl*-phenylalanine, and *l*-tryptophan.** (Miss) K. FERAUD, M. S. DUNN, and J. KAPLAN (J. Biol. Chem., 1935, 112, 323—328).—*dl*-Alanine, *dl*-leucine, *l*-histidine dihydrochloride, *l*-proline, and *l*-hydroxyproline show general, but  $C_6H_6$ , PhOH, indole, *l*-tyrosine, *dl*-phenylalanine, and *l*-tryptophan show selective, absorption (band max. given) in the ultra-violet region.

R. S. C.

**Flame spectra of some aromatic compounds.** W. M. VAIDYA (Proc. Indian Acad. Sci., 1935, 2, A, 352—357; cf. A., 1935, 279).—Investigations with a Smithells flame separator are extended to  $C_6H_6$ , PhMe, PhOH, resorcinol, pyrogallol, PhCHO, BzOH,  $Ph_2O$ ,  $NH_2Ph$ ,  $PhNO_2$ , and  $C_5H_5N$ . The bands attributed to HCO were found in the spectra of the flames of  $C_6H_6$  and other aromatic compounds, and are attributed to the double linking of the  $C_6H_6$  ring and the breaking up of oxygenated mols. formed by direct incorporation of the  $O_2$  mol. There is a gradual variation in the spectra of the flames of aliphatic series, and more uniformity in the spectra of aromatics.

Light is thrown on the mechanism of combustion of  $C_6H_6$  by the spectra of  $C_5H_5N$ ,  $NH_2Ph$ , and  $PhNO_2$  flames in which the CN bands and the  $\gamma$ -bands of NO appear; the rupture of the ring seems to take place at the N atom. A tentative scheme for the combustion of  $C_6H_6$  is given. N. M. B.

**Barium hydride spectra in the infra-red.** P. G. KOONTZ and W. W. WATSON (Physical Rev., 1935, [ii], 48, 937—938; cf. A., 1935, 427).—Analyses and frequency assignments of the (1,0), (1,1), and (2,1) bands of the  ${}^2\Sigma \rightarrow {}^2\Sigma$  system of BaH, and some details of the  ${}^2\Pi \rightarrow {}^2\Sigma$  band at 10,300 Å., are given. The spin doubling const. of the upper  ${}^2\Sigma$  state is  $-4.88$ , decreasing with increasing mol. rotation. N. M. B.

**Overtone absorption bands of gaseous HF.** D. E. KIRKPATRICK and E. O. SALANT (Physical Rev., 1935, [ii], 48, 945—948).—Measurements of the  $3 \leftarrow 0$  and  $4 \leftarrow 0$  vibration-rotation absorption bands are described and discussed, and mol. const. are tabulated. N. M. B.

**Photography of the third harmonic of hydrogen chloride.** A. P. CLEAVES and C. W. EDWARDS (Physical Rev., 1935, [ii], 48, 850).—The wave-no. of the band origin of the third harmonic at 9153 Å. is 10,922.7  $cm^{-1}$ . Vals. and const. calc. from previous available data are given. N. M. B.

**Infra-red absorption bands of methane.** A. H. NIELSEN and H. H. NIELSEN (Physical Rev., 1935, [ii], 48, 864—867; cf. following abstract).—The fundamental vibration-rotation bands at 3.3 and 7.7  $\mu$  have been remeasured, and, for the latter, additional complex rotational structure data are reported. The two combination bands at 4218 and 4315  $cm^{-1}$  have been partly resolved. N. M. B.

**Infra-red absorption spectrum of germane.** W. B. STEWARD and H. H. NIELSEN (Physical Rev., 1935, [ii], 48, 861—864; cf. A., 1935, 914).—Data and identifications in the range 1—13  $\mu$  of  $GeH_4$  are given for intense absorption regions, in order of intensity, at 4.74, 10.7, 3.4, and 2.3  $\mu$ ; there is a much weaker peak near 5.7  $\mu$ . Calc. vals. are: moment of inertia of the mol.  $7.0 \times 10^{-40}$  g.- $cm^2$ ; distances Ge—H  $1.37 \times 10^{-8}$ , H—H  $2.06 \times 10^{-8}$  cm. N. M. B.

**Symmetry considerations concerning the splitting of vibration-rotation levels in polyatomic molecules.** E. B. WILSON, jun. (J. Chem. Physics, 1935, 3, 818—821).—The max. no. of fine-structure components, their quantum wts. when nuclear spin is taken into account, and the selection rule for transitions are discussed in relation to the permutation symmetry of mols. containing several identical atoms. N. M. B.

**Raman spectra of the isotopic molecules  $H_2$ , HD, and  $D_2$ .** G. K. TEAL and G. E. MACWOOD (J. Chem. Physics, 1935, 3, 760—764).—Analyses are given for 42 lines excited at 3 atm. pressure by Hg  $\lambda$  2537. New vibrational const. calc. from the Raman and emission spectrum data of  $H_2$  and HD give calc. vals. of the positions of the rotational-vibration Raman lines in good agreement with observation. Contrary to theory, the 0,0 line of the Q vibrational band of HD was observed. N. M. B.

**Raman effect and molecular structure.** B. SUSZ (Ann. Guéhard-Séverine, 1935, 11, 12—25).—A summary of the theory and technique.  $N_2O_5$  in  $HNO_3$  affords the Raman frequencies 1050 and 1399  $cm^{-1}$ , in addition to those due to  $HNO_3$ . J. G. A. G.

**Raman spectra. I. Raman spectra of sulphuric, nitric, and nitrosylsulphuric acids.** W. R. ANGUS and A. H. LECKIE (Proc. Roy. Soc., 1935, A, 149, 327—340).—Raman spectra are recorded for conc.  $H_2SO_4$  and  $HNO_3$ , for solutions of nitrosylsulphuric acid ( $HNSO_5$ ) in  $H_2SO_4$ , and for solid  $HNSO_5$ . From the spectra of  $HNSO_5$  in various concns. of  $H_2SO_4$  it is concluded that in solutions of  $HNSO_5$  in  $H_2SO_4$  containing  $> 60\%$   $H_2SO_4$  the hydrolysis of  $HNSO_5$  is incomplete. The spectra of  $HNSO_5$ , both in solution and in the solid state, are characterised by a prominent frequency of 1045  $cm^{-1}$  assignable to  $HSO_4'$ . Another prominent frequency of 2340  $cm^{-1}$  in solutions and 2311  $cm^{-1}$  in the solid is shown, by analogy with band spectral data for iso-electronic groups, to arise from  $NO^+$ . Of the different mol. structures reviewed, only  $[HOSO_3][NO]'$ , nitrosyl sulphate, is in agreement with observed data. W. R. A.

**Raman spectrum of crystalline selenious acid.** C. S. VENKATESWARAN (Current Sci., 1935, 4, 309—310).—Transparent crystals give an intense Raman spectrum consisting of a large no. of sharp lines, in some cases the anti-Stokes being present. As in the case of  $HIO_3$  (cf. A., 1935, 1301), the spectrum of the solid differs markedly from that of the aq. solution. N. M. B.

**Raman effect of fluosilicic acid.** J. K. SIRKIN and M. V. VOLKENSTEIN (Acta Physicochim. U.R.S.S., 1935, 2, 308—312).— $H_2SiF_6$  shows a strong Raman line at 649  $cm^{-1}$  (cf. 314 and 337 for  $SnCl_6''$  and  $SbCl_6'$ , respectively; A., 1933, 113), but no other. This indicates the symmetrical vibration of six F atoms at the corners of a regular octahedron, in accord with X-ray data. J. W. S.

**Raman effect. XLIX. Mixture of phosphorus trichloride and tribromide.** O. BURKARD. L. Vibrational spectrum of benzene. K. W. F. KOHLRAUSCH (Z. physikal. Chem., 1935, B, 30, 298—304, 305—315).—XLIX. In the Raman spectra of mixtures of  $PCl_3$  and  $PBr_3$  the valency frequencies of  $PCl_3$  rise and those of  $PBr_3$  fall with falling  $[PCl_3]$ , whereas judged from the dipole moments the reverse would be expected. The intensity of the lines due to  $PCl_2Br$  is a max. in the mixture  $2PCl_3 + PBr_3$  (cf. A., 1931, 785).

L. Regarding  $C_6H_6$  and  $C_6D_6$  as valency force systems with the symmetry  $D_{6h}$  and applying Wilson's theory (A., 1934, 829), five of the six force const. necessary for stability have been calc. and have nearly the same vals. for each compound. From these have been deduced 16 of the 20 possible fundamental frequencies, and these and the selection rules are in almost quant. agreement with the observed vibrational spectrum (cf. A., 1935, 1301). For  $C_5H_5N$  the selection rules point to a ring system with "equalised" linkings and the symmetry  $C_{2v}$ . R. C.

**Raman spectra of solutions. II. Solutions of arsenic trichloride in methyl and ethyl alcohols.**

A. M. SACK and A. E. BRODSKI (Acta Physicochim. U.R.S.S., 1935, 2, 215—220).—In the Raman spectra of  $\text{AsCl}_3$  in EtOH and MeOH, respectively, the frequencies of the alcohols are unchanged; those of  $\text{AsCl}_3$  at 372 and 410  $\text{cm}^{-1}$  are lowered. Denoting the four mol. frequencies of  $\text{AsCl}_3$  (which is a regular pyramid) by  $\omega_1, \omega_2, \omega_3,$  and  $\omega_4$ , the ratio  $\omega_1\omega_2/\omega_3\omega_4$  remains almost const. The  $\text{AsCl}_3$  mol. is thus only slightly deformed by the alcohol dipoles, but the elastic binding force between  $\text{As}^{+++}$  and  $\text{Cl}^-$  changes by about 10% in alcoholic solutions. A. J. M.

**Raman spectrum of tetraethylammonium iodide.** J. K. SIRKIN and M. V. VOLKENSTEIN (Acta Physicochim. U.R.S.S., 1935, 2, 303—307).—The Raman spectrum of  $\text{NEt}_4\text{I}$  is compared with those of  $\text{NEt}_3$  and of EtI. None of the C-I or N-I frequencies are observed, indicating that the I of  $\text{NEt}_4\text{I}$  is ionically bound, and occurs outside the co-ordination sphere, in accord with the behaviour of  $\text{NEt}_4\text{I}$  as a binary electrolyte. The Raman spectrum observed is therefore that of  $\text{NEt}_4^+$ , and the strong lines of  $\text{NEt}_3$  occur, in some cases with modified frequency, with the exception of the 739  $\text{cm}^{-1}$  line. New strong frequencies are observed at 667 and 1231  $\text{cm}^{-1}$ . It is concluded that  $\text{NEt}_3$  is a pyramidal mol. with the N at the apex, whilst  $\text{NEt}_4^+$  is a regular tetrahedron with the N in the centre. J. W. S.

**Vibrations of benzene and Raman spectra of benzene-*d* and benzene-*d*<sub>2</sub>.** O. REDLICH and W. STRICKS (J. Chem. Physics, 1935, 3, 834).—Raman data are reported. Experimental error cannot account for the increase from 2270 (PhD) to 2279 ( $\text{C}_6\text{H}_4\text{D}_2$ ). A test relation applied to these and the results of Wood for  $\text{C}_6\text{D}_6$  (cf. A., 1935, 1189) shows that Wilson's correlations of frequencies to vibrations (cf. Physical Rev., 1934, [ii], 46, 146) cannot all be correct. N. M. B.

**Rotational Raman scattering in benzene.** S. BHAGAVANTAM (Proc. Indian Acad. Sci., 1935, 2, A, 342—344).—Contrary to the results of Sirkar (cf. A., 1935, 914), the intensity distribution in the rotation wing accompanying the Rayleigh lines is in exact agreement, using a high-dispersion spectrograph, with results by instruments of lower dispersion. N. M. B.

**Raman effect. LI. Benzene derivatives. IX.** K. W. F. KOHLRAUSCH, W. STOCKMAIR, and (GROSS-PRINZ) YPSILANTI. **LII. Benzene derivatives. X.** A. W. REITZ and W. STOCKMAIR. **LIII. Nucleus-substituted benzoyl chlorides.** K. W. F. KOHLRAUSCH, A. PONGRATZ, and W. STOCKMAIR (Monatsh., 1935, 67, 80—91, 92—103, 104—110; cf. A., 1935, 1190).—LI. Raman spectra of 1:3-dichloro-4-*X*-benzene ( $X=\text{NH}_2, \text{OH}, \text{Me}, \text{CN}, \text{Br}, \text{I}$ ), 1:4-dichloro-2-*X*-benzene ( $X=\text{NH}_2, \text{OH}, \text{Me}, \text{Br}, \text{I}$ ), and 4-chloro-2-*X*-toluene ( $X=\text{NH}_2, \text{OH}, \text{Br}, \text{I}$ ) have been measured.

LII. Raman spectra of the following are given:  $\text{CH}_2\text{PhX}$  ( $X=\text{NH}_2, \text{OH}, \text{Me}, \text{CN}, \text{SH}, \text{Cl}, \text{Br}$ ); *o*-, *m*-, and *p*- $\text{XC}_6\text{H}_4\cdot\text{NO}_2$  [ $X=\text{Cl}, \text{Br}, \text{OH}, \text{CN}$  (*m*-, *p*-), *F* (*p*-)];  $\text{PhNO}_2$ ;  $\text{PhSO}_2\text{Cl}$ .

LIII. Raman spectra of *o*-, *m*-, and *p*- $\text{XC}_6\text{H}_4\cdot\text{COCl}$  ( $X=\text{Me}, \text{Cl}, \text{Br}, \text{COCl}, \text{p-Ome}$ ) are given. The results are discussed theoretically. F. L. U.

**Raman spectra of hydroxy-acids and their esters and salts. I.** PEYGHÈS (Bull. Soc. chim., 1935, [v], 2, 2195—2209; cf. A., 1935, 146).—Data are recorded for  $\text{AcOH}, \text{KOAc}, \text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}, \text{CCl}_3\cdot\text{CO}_2\text{H}, \text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}, \text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$ , and lactic acid,  $(\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2, [\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}]_2$ , their Et esters and Na salts. The results are discussed from the point of view of the structure of the  $\cdot\text{CO}_2\text{H}$  group and of the tartaric acid mol. and anion. F. L. U.

**Raman spectra of glasses.** T. G. KUJUMZELIS (Z. Physik, 1935, 97, 561—569).—Raman spectra of different Jena glasses show different characteristic features; a displacement of approx. 800  $\text{cm}^{-1}$  is present in all glasses examined independent of the presence or absence of the  $\text{SiO}_2$  group. A. B. D. C.

**Polarisation of scattered Raman light.** W. HANLE and F. HEIDENREICH (Physikal. Z., 1935, 36, 851—853).—The edges of the Rayleigh lines are polarised in quite a different manner from the centres. The inversion factor (ratio of left to right circularly polarised light) is 6 if there is only rotational widening of the lines, whereas the experimental val. for PhMe is 1.7. There are, therefore, causes of widening of the lines other than rotation. The circular polarisation of the Raman lines of some substances has been determined, and from the inversion factor, *U*, the degree of depolarisation  $\rho_n$  has been calc. from Placzek's formula. The same vals. for  $\rho_n$  were found for right circularly polarised lines as for linearly polarised rays, but there were differences for left circularly polarised light. The rotational widenings of the Raman lines are always left circularly polarised, whilst the centres are right circularly polarised. The dispersion of polarisation of the scattered Raman light was investigated, the results disagreeing with those of Sirkar. The degree of polarisation is independent of  $\lambda$  outside the regions of absorption. Assuming that, in general, the polarisation of the line due to the same vibration in different substances is the same, the Raman lines of a no. of org. Cl-derivatives are assigned to their different mol. vibrations. A. J. M.

***U* Centres in alkali halide crystals.** P. TARTAKOVSKI and V. PODDUBNI (Z. Physik, 1935, 97, 765—773).—NaCl heated to 550—600° absorbs intensely near 1.2  $\mu$ , corresponding with electron transition from the ground to the *U* level. Electrons in this level can combine with  $\text{Cu}^+$  ions to colour the crystal red. A. B. D. C.

**Thermal formation of colour centres and their life-period.** R. HILSCH (Physikal. Z., 1935, 36, 735—737).—The equilibrium between the *U* and *F* centres in KBr crystals with a stoichiometric excess of K is examined. The variation of the "degree of dissociation" of the *U* centres with temp. and concn. is determined by means of absorption experiments. The life-period of the *F* centres is also found. (Cf. this vol., 139.) A. J. M.

**Thermal diffusion of colour centres.** O. STASIW (Physikal. Z., 1935, 36, 737—740).—The diffusion const. of *F* centres in KCl crystals in which the stoichiometric excess of K existed only in the form of these centres has been determined. From the

diffusion const. and the known mobility of the colour centres in an electric field, the mobility of the positive charges in the crystal is determined. The positive charges move more rapidly than electrons at temp.  $>700^\circ$ . Below this temp. retardation of electrons occurs owing to the positive charges. A. J. M.

**Photodissociation of stannous chloride vapour in the Schumann region.** H. NEUJMIN (Acta Physicochim. U.R.S.S., 1935, 2, 595—602; cf. A., 1934, 1286).—Fluorescence is excited in  $\text{SnCl}_2$  vapour in the visible region by  $\lambda$  1700—1800, and in the ultra-violet by  $\lambda$  1500—1700 Å. Analysis of the observed spectrum indicates photodissociation into Cl and excited  $\text{SnCl}$ . The energy required is calc. to be 90 kg.-cal. per mol. F. L. U.

**Correspondence between absorption and luminescence spectra of dilute solutions of dyes. IV. Effect of temperature and solvents.** V. L. LEVSHIN (Acta Physicochim. U.R.S.S., 1935, 2, 221—238; cf. A., 1935, 808).—Absorption and luminescence spectra of eosin B in  $\text{H}_2\text{O}$ , isoamyl alcohol, and  $\text{COMe}_2$ , and of erythrosin and rhodamine 6G in  $\text{H}_2\text{O}$  and  $\text{COMe}_2$ , have been investigated with respect to temp. and solvent. The symmetry of form of the two spectra is maintained in all cases. Change of solvent causes displacement of both absorption and luminescence spectra, the max. undergoing equal displacements. The direction of the displacement is not determined by the dielectric const. of the solvent. The area of the absorption spectrum is approx. the same for all solvents, although the luminescence efficiency,  $\eta$ , varies greatly. The variation of  $\eta$  with temp. is independent of dye concn. and of the properties of the solvent. A. J. M.

**Fluorescence spectra of chlorophyll pigments.**—See this vol., 125.

**Spectrographic investigation of the thermoluminescence of felspar.** S. IMORI and E. IWASE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 28, 147—151).—The position of the thermoluminescence bands is unaffected by treatment with X-rays, but their intensity is increased. Data are given for 12 Japanese felspars. The bands generally lie in the yellow and blue. R. S.

**Induced chemiluminescence of mercury in the carbon monoxide-oxygen flame.** V. KONDRATEEV (Acta Physicochim. U.R.S.S., 1935, 2, 126—128).—Hg becomes chemiluminescent in  $\text{CO} + \text{O}_2$  at 650—700°. Since the line 2537 Å. is below the shortest  $\lambda$  of the CO flame spectrum, it is concluded that the activation must be due to collision with excited  $\text{CO}_2$ . A similar mechanism is proposed for the activation of  $\text{N}_2$  in the explosion of  $\text{CO} + \text{O}_2 + \text{N}_2$  at high pressures. R. S.

**Quantum equivalence of photo-electric conductivity in rock-salt crystals.** Z. GYULAI and P. TOMKA (Z. Physik, 1935, 96, 350—354).—Arsenjeva's results (A., 1926, 782) showing non-equivalence of absorbed light and conductivity are due to colloidal particles in the test-piece. A. B. D. C.

**Electronic conduction in silver and thallium halide crystals. I. Electron yield on light**

**absorption in spectral regions of high absorption. II. Photo-electric secondary current.** W. LEHFELDT (Nachr. Ges. Wiss. Göttingen, 1935, [ii], 1, 171—186; Chem. Zentr., 1935, i, 2322).—I. In electric fields giving saturation of the primary current in  $\text{TlBr}$  at  $-70^\circ$ , and in  $\text{AgCl}$  at  $-170^\circ$ , all photo-electrons move to the anode, the positive charge remaining stationary. In the ultra-violet absorption region the quantum yield is 0.1—0.5.

II. Crystals with long displacement paths for primary photo-electrons tend to give rise to secondary current, due to electrons drawn from the cathode. J. S. A.

**Electronic conduction of cuprous oxide.** W. SCHOTTKY and F. WAIBEL (Physikal. Z., 1935, 36, 912—914).—The sign of the Hall effect and the mechanism of conduction of specimens of  $\text{Cu}_2\text{O}$  with and without excess of  $\text{O}_2$  are discussed. A. J. M.

**Conductance of salt crystals.** W. H. RODEBUSH and T. G. COOKE (J. Chem. Physics, 1935, 3, 834).—Jost's expression (cf. A., 1934, 11) is inadequate to account for the conductance behaviour of various salts throughout the whole temp. range; it can be obtained by merely general considerations. N. M. B.

**Rate of migration of cations in alkali halide crystals.** O. STASIW (Nachr. Ges. Wiss. Göttingen, 1935, [ii], 1, 147—152; Chem. Zentr., 1935, i, 2318—2319).—The cation mobility increases exponentially with rise of temp., and equals that of electrons at 600—700°. H. J. E.

**Problems of ionic and electronic conduction in non-metallic solids.** B. GUDDEN and W. SCHOTTKY (Physikal. Z., 1935, 36, 717—721).—The different types of ionic conduction are discussed. The mechanism of electronic conduction on the basis of permitted and forbidden energy states is considered and applied to semi-conductors. The energy states may be determined by means of the photo-electric effect and the fine structure of X-ray absorption edges. A. J. M.

**Disorder phenomena in ionic lattices as a basis for ionic and electronic conduction.** C. WAGNER (Physikal. Z., 1935, 36, 721—725).—The types of disarrangement in the crystal lattice giving rise to the possibility of conduction are discussed. The conductivity ( $\kappa$ ) of oxides varies with the pressure ( $p$ ) of  $\text{O}_2$  above them. In this connexion, three classes of oxides may be considered: (1) those for which  $\kappa \propto p^{-1/4}$ , e.g.,  $\text{ZnO}$ ,  $\text{CdO}$ ; (2) those for which  $\kappa \propto p^{1/7}$ , e.g.,  $\text{Cu}_2\text{O}$ ,  $\text{FeO}$ ; (3) those for which  $\kappa$  is independent of  $p$ , e.g.,  $\text{CuO}$ ,  $\text{Fe}_3\text{O}_4$ . The behaviour of oxides of class (1) is governed by dissociation of the oxide giving an excess of metal in solid solution in the oxide phase. With class (2), places with electron defect are formed in the lattice. Electron-defect conductivity is to be expected in those cases where the ions are in an intermediate valency state, whereas electron-excess conductivity is found where the ion is exerting its max. valency. The behaviour of  $\text{Co}_3\text{O}_4$  is explained on the basis of its lattice structure. A. J. M.

**Theory of electron motion in non-metallic crystal lattices.** F. HUND (Physikal. Z., 1935, 36, 725—729).—The description of the states of electrons

in solids is discussed from the viewpoint of quantum mechanics. The arrangement of energy bands in non-metallic ideal and distorted lattices is considered.

A. J. M.

**Electronic conduction in alkali halide crystals.** R. W. POHL (Physikal. Z., 1935, 36, 732—735).—The electronic conduction of a KBr crystal with a stoichiometric excess of K (part of the Br replaced by electrons) is considered. The excess of metal may exist as  $U$  (ultra-violet absorption) centres, or as  $F$  (visible absorption) centres. The production of, and thermal equilibrium between, these centres are discussed. The movements of electrons to the anode can be followed with the eye by means of the  $F$  centres. Crystals with  $U$  centres are semi-conductors. It is possible with the KBr crystal under consideration to determine the variation of both the no. and mobility of the electrons with temp. Crystals with  $U$  centres behave as photo-electric conductors for which the law of the quantum equiv. holds accurately.

A. J. M.

**Electrical conduction in melts of alkali salts with a stoichiometric excess of alkali metal.** E. MOLLWO (Physikal. Z., 1935, 36, 740—742).—The optical properties of alkali salts with a stoichiometric excess of metal indicate that the excess metal is dissolved in the form of neutral atoms. Electron conductivity was not found.

A. J. M.

**Formation of opposing potentials in solid ionic conductors.** A. SMEKAL (Physikal. Z., 1935, 36, 742—749).—Results previously obtained on the decrease with time of the d.c. conductivity of purely ionic conductors are summarised. The Maxwell-Wagner theory of dielectric anomalies, and the Jaffé theory of ions with retarding atm. (A., 1933, 338) fail to account for the facts. The most satisfactory explanation is based on the distortion conduction theory, according to which the formation of the opposing potential is due to retardation of the conducting ions in the structurally inhomogeneous crystal.

A. J. M.

**Electrical conduction in semi-conductors.** W. MEYER (Physikal. Z., 1935, 36, 749—755).—The nature of the consts.  $a$  and  $B$  in the equation  $\kappa = ae^{-B/T}$  connecting conductivity,  $\kappa$ , with abs. temp.,  $T$ , is discussed. No numerical val. can be assigned to  $a$  which will hold for all semi-conductors.  $\log \kappa = -kB$ , where  $k$  is const., is true as a first approximation. The connexion between  $a$  and  $\kappa$  was investigated for  $\text{TiO}_2$ .

A. J. M.

**Calculation of the magnitude and pressure dependence of ionic-disorder energy and mobilities in crystals.** W. JOST (Physikal. Z., 1935, 36, 757—760).—A rough calculation of the disorder energy of ions in crystals is possible from a consideration of the polarisation effect. The effect of pressure on the conductivity and degree of disorder is discussed. If the degree of disorder is affected by temp. it should be possible to arrive at disorder energies from consideration of sp. heats.

A. J. M.

**Electrical conductivity of cuprous oxide in equilibrium with its adjacent phase.** F. WAIBEL (Physikal. Z., 1935, 36, 760—764).—The cold con-

ductivity of  $\text{Cu}_2\text{O}$  plates in equilibrium with Cu after having been heated to temp. between  $10^\circ$  and  $1000^\circ$  was determined and plotted against temp. A max. occurs at a tempering temp. of  $400$ — $500^\circ$ , corresponding with a similar max. in the same curve for  $\text{Cu}_2\text{O}$  in equilibrium with  $\text{CuO}$ . The formation of the rectifying layer of  $\text{Cu}_2\text{O}$  rectifiers is discussed on the basis of this investigation. The amount of  $\text{O}_2$  dissolved in the  $\text{Cu}_2\text{O}$  was determined.

A. J. M.

**Specific resistance of cuprous oxide.** W. H. BRATTAIN (Physical Rev., 1934, [ii], 45, 745).—The sp. resistance of  $\text{Cu}_2\text{O}$  grown on Cu at  $1030^\circ$  in air is not uniform, but varies exponentially in the direction of growth of the oxide.

L. S. T.

**Determination of the metal-cuprous oxide contact resistance.** J. ROULLEAU (Compt. rend., 1935, 201, 947—948).—The factors controlling the Cu- $\text{Cu}_2\text{O}$  contact resistance were studied. High resistances occur only for cryst. surfaces.

H. J. E.

**Effect of cooling on the electrical properties of resistances which vary with temperature.** H. LUEDER and E. SPENKE (Physikal. Z., 1935, 36, 767—773).—The effects of cooling in various ways (e.g., at the edges, at the front of a plate, etc.) have been examined.

A. J. M.

**Conductivity of glasses.** R. L. MÜLLER (Acta Physicochim. U.R.S.S., 1935, 2, 103—125; cf. A., 1935, 567).—The Frenkel theory of electrical conductivity has been applied to glasses. Alkali-rich glasses approach the ion-lattice type, whilst alkali-poor glasses approx. to liquid salt solutions. The influence of the association of polar mols. on the conductivity has been studied in various glasses.

R. S.

**Dielectric coefficients of volatile compounds of fluorine and boron.**  $\text{CF}_4$ ,  $\text{NF}_3$ ,  $\text{CHF}_3$ ,  $(\text{CF}_3\text{N})_2$ ,  $\text{B}_2\text{H}_6$ , and  $\text{B}_3\text{N}_3\text{H}_6$ . K. L. RAMASWAMY (Proc. Indian Acad. Sci., 1935, 2, A, 364—377).—Data for dielectric coeffs. measured at different temp. are quoted, and give vals. of the electric moments 0, 0.21, 1.59, 0.46, 0, and  $0.67 \times 10^{-18}$ , respectively. Accurate vals. of compressibilities at room temp. by refractometric studies, and approx. vals. at low temp. by studying variations of dielectric coeffs. are given.

N. M. B.

**Discontinuity in the dielectric constant of liquids and their saturated vapours at the critical temperature.** J. MARSDEN and O. MAASS (Canad. J. Res., 1935, 13, B, 296—307).—A dielectric cell of small dimension for simultaneous liquid and gas measurements in the crit. temp. region is described. The electrodes were sealed in by frozen Hg capillary seals. Data are given for  $\text{Me}_2\text{O}$  and  $\text{C}_3\text{H}_6$  from room temp. to  $8^\circ$  above the crit. temp. The dielectric consts.,  $\epsilon$ , of liquid and gas were not identical at the crit. temp. Above the crit. temp. (for up to  $8^\circ$ ) a difference in  $\epsilon$  persisted between the medium above and below the position where the liquid meniscus was last seen, in spite of stirring of the medium.

H. J. E.

**Dependence of dielectric constants of anisotropic liquids on field strength and frequency.** W. KAST (Physikal. Z., 1935, 36, 869—873).—The

decrease of dielectric const.,  $\epsilon$ , of anisotropic liquids, e.g., *p*-azoxyanisole, with increase of field strength reaches a saturation val. at approx. 1000 volts per cm., and is regarded as a dipole saturation effect. Calculation shows that the saturation val. of  $\epsilon$  should be equal to the val. for the solid substance, but actually it is considerably greater, since not only does the mean moment of the mol. groups contribute to the orientation polarisation, but the single polar mols. within the groups are sufficiently movable to take part.

A. J. M.

Electrical moments of *p*-benzoquinone and related compounds. D. L. HAMMICK, G. C. HAMPSON, and G. I. JENKINS (Nature, 1935, 136, 990—991).—The following vals. of  $P_{A+O}$  (c.c.) have been obtained: *p*-benzoquinone 8.9 in  $C_6H_6$ , 9.6 in  $CCl_4$ , and 8.6 in  $n-C_6H_{14}$ ; and in  $C_6H_6$  2:5-dimethyl- 9.4, and 2:5-dichloro-1:4-benzoquinone 8.8, and tetramethylcyclobutane-1:3-dione 11.0. These vals. are apparently due either to a general effect of the solvent or to an abnormally large atom polarisation. L. S. T.

Dipole moments of cyclohexa-1:4-dione, cyclopentadienebenzoquinone, benzoquinone, carbon suboxide, and carbonyl chloride. C. G. LE FÈVRE and R. J. W. LE FÈVRE (J.C.S., 1935, 1696—1701).—The dielectric consts.,  $d$ , and  $n$ , of solutions of the above substances in  $C_6H_6$  and  $CCl_4$  have been determined, and the total polarisations, mol. refractivities, orientation polarisations, and dipole moments of the solutes have been calc. The dipole moment of cyclohexa-1:4-dione is 1.3 *D*, indicating a comparatively low *cis*-content. The mol. refractivity (27.8) shows that it is entirely ketonic. The dipole moment of cyclopentadienebenzoquinone is 1.39 *D*, and of *p*-benzoquinone 0.69 *D*. The orientation polarisation of the latter is approx. the same in  $C_6H_6$  and  $CCl_4$ , and does not vary with temp., results which may be due to the solute mols. not being completely rigid when bombarded by solvent mols. The orientation polarisation of  $C_3O_2$  is approx. 10 c.c., showing that in  $C_6H_6$  solution very little of the cyclic form can exist. The possible structures are reviewed. The dipole moment of  $COCl_2$  in  $CCl_4$  is 1.099 *D*. The size of the Cl-C-Cl angle is discussed.

A. J. M.

Relation between molecular orientation polarisation of substances in the liquid, dissolved, and gaseous states. C. G. LE FÈVRE and R. J. W. LE FÈVRE (J.C.S., 1935, 1747—1751).—The relationship  ${}_oP_1/{}_oP_2 = K(\epsilon_2 + 2)/(\epsilon_1 + 2)$ , where  ${}_oP_1$  and  ${}_oP_2$  are the orientation polarisations developed by a mol. when surrounded by media of dielectric const.  $\epsilon_1$  and  $\epsilon_2$ , respectively, has been tested with a no. of pairs of solutions, solutions and solutes in the vapour state, solutions and liquid solutes in bulk, and substances in the pure liquid and gaseous state. It has no general applicability, since probably the mutual influences of mols. in conjunction with their shapes should be taken into account.  ${}_oP_{liq.}/{}_oP_{gas}$  should be given by  $1 - (\epsilon - 1)/(\epsilon + 2)f$ , where  $f$  depends on the shape and polarisability of the mols.

A. J. M.

Optical dispersion of HCl in the infra-red. R. ROLLEFSON and A. H. ROLLEFSON (Physical Rev.,

1935, [ii], 48, 779—785).—In view of the large discrepancy between the temp. invariant part of the dielectric const. of HCl and  $n_{\infty}^2$ , attributed to the contribution of infra-red vibration bands to  $n$ , the optical dispersion of HCl was measured over 1—10  $\mu$ . The val.  $1.00 \pm 0.05 \times 10^{-10}$  e.s.u. obtained for the effective charge of the rotator-vibrator shows that the contribution of the latter to  $n_{\infty}$  is too small to explain the discrepancy, which appears to be due to uncertainty in the dielectric const. measurements.

N. M. B.

Refractivity of cellulose as function of the degree of swelling. M. MEYER and A. FREY-WYSSLING (Helv. Chim. Acta, 1935, 18, 1428—1435).—Measurements of  $n_a$  by the immersion method show  $n$  to decrease regularly, although very slightly, with the H<sub>2</sub>O content of the fibre. Kanamaru's results (A., 1934, 1292) are attributed to displacement of H<sub>2</sub>O by the immersion medium. Reasons for the negligible influence of the adsorbed H<sub>2</sub>O on  $n$  are discussed.

J. S. A.

Magnetic birefringence of nitric oxide. H. BIZETTE and T. BELLING (Compt. rend., 1935, 201, 955—956).—Measurements are recorded at 16.5°/80—180 atm.

H. J. E.

Quantum-mechanical calculation of polarisability and dispersive powers. H. HELLMANN (Acta Physicochim. U.R.S.S., 1935, 2, 273—290).—Mathematical.

J. W. S.

Constitution of diborane. E. WIBURG (Z. anorg. Chem., 1935, 225, 262—269).—A crit. discussion of published work.

E. S. H.

Constitution of complex metallic salts. III. Parachors of palladium and mercury in simple and complex compounds. F. G. MANN and D. PURDIE (J.C.S., 1935, 1549—1563; cf. A., 1934, 640).—The parachor of Pd in homologous series of the type  $[(R_2S)_2PdCl_2]$ ,  $[(R_3P)_2PdCl_2]$ ,  $[(R_3As)_2PdCl_2]$  decreases and becomes negative with increasing length of alkyl chain.  $HgEt_2$  and  $Hg(n-C_5H_{11})_2$  do not exhibit this behaviour, whilst in the Hg mercaptides the parachor of Hg decreases to a const. at  $R=n$ -heptyl. Since the parachors of compounds of the type  $CRR'(SEt)_2$  show no abnormality, the above decrease cannot be due to the formation of a group  $\cdot S \cdot X \cdot S \cdot$ . It is shown that the parachors of the metal in ketonic derivatives of Tl, Be, and Al (cf. Sugden, "The Parachor and Valency," 1930) also decrease as the homologous series is ascended, and it is suggested that the effect is due to a diminution in the vol. of the mol. as a whole owing to increased compression resulting from the operation of "strain factors" (cf. A., 1929, 1219). Dipole moments of  $[(Et_3S)_2PdCl_2]$ ,  $[(Et_3P)_2PdCl_2]$ , and  $[(Et_3As)_2PdCl_2]$  have been determined, and it is concluded that these are stable *trans*-compounds, although  $[(Me_3As)_2PdCl_2]$  may have the *cis*-configuration. Densities, surface tensions, and parachors of the following compounds are given:  $Pr^a$ ,  $Bu^a$ , and *n*-amyl sulphides, *di-n*-amyl sulphoxide, m.p. 60°, *n*-hexyl, heptyl, and octyl sulphide, *Ph Bu^a*, b.p. 137—139°/12 mm., and *Bu^b* sulphide, b.p. 126—127°/12 mm.,  $\alpha\gamma$ -bis(phenylthiol)propane, b.p. 264°/12 mm. [from PhSH and

$\text{CH}_2(\text{CH}_2\text{Br})_2$ ];  $\alpha'$ -bis(phenylthiol)acetone, m.p. 43°, similarly prepared from  $\text{CO}(\text{CH}_2\text{Cl})_2$ ; acetone bisethyl mercaptol, b.p. 84.5–85°/20 mm.; *Me Et ketone bisethyl mercaptol*, b.p. 99–100°/18.5 mm.;  $\text{Pr}^a$ ,  $\text{Bu}^a$ , *n*-amyl, hexyl, and heptyl thiols; *Et*,  $\text{Pr}^a$ ,  $\text{Bu}^a$ , and *n*-amyl phosphines, *tri-n-amylphosphine oxide*, m.p. 59°;  $\text{Et}_3$  phosphite, b.p. 55°/19 mm.;  $\text{AsMe}_3$ ,  $\text{AsEt}_3$ ,  $\text{AsPr}^a_3$ , and  $\text{AsBu}^a_3$ . *Bis(dialkylsulphide)palladium compounds* were prepared by addition of a sulphide to aq.  $(\text{NH}_4)_2\text{PdCl}_4$ . The *Me*, *Et*,  $\text{Bu}^a$ , and *isoamyl* dichlorides are described, also the *Me Et dichloride*, m.p. 67°, decomp. on heating,  $\text{Pr}^a_2$  dichloride, m.p. 59°,  $\text{Pr}^b_2$  dichloride, m.p. 163°,  $\text{Bu}^a_2$  dichloride, m.p. 32°, *diisoamyl dichloride*, m.p. 41°; the *n*-heptyl and *n*-octyl derivatives obtained were impure; the *divinyl dichloride*, orange, decomposes at room temp., the *Ph Bu^a dichloride* has m.p. 118°, and the  $\text{Bu}^b$  compound melts at 96°;  $\text{Ph}_2$  dichloride, orange, m.p. 170°, *dibenzyl dichloride*, orange, m.p. 154°, *bis(diethyl sulphide)palladium dibromide*, deep red, m.p. 103°, *di-iodide*, m.p. 107–108° (decomp.). Grinding the corresponding dichloride with aq.  $\text{NaNO}_2$  gave pale yellow dinitrites:  $\text{Me}_2$ , m.p. 137–138°,  $\text{Et}_2$ , m.p. 161–163° (slight decomp.),  $\text{Pr}^a_2$ , m.p. 163–164°,  $\text{Bu}^a_2$ , m.p. 165–166°, *di-n-amyl*, m.p. 163°. The following *bis(trialkylphosphine)palladium compounds* were similarly prepared:  $\text{Et}_3$  dichloride, m.p. 139°, sublimes 140° in vac.,  $\text{Pr}^a_3$  dichloride, m.p. 96° (crystallographic data given);  $\text{Bu}^a_3$  dichloride, m.p. 66°, *dibromide*, m.p. 73°, and *di-iodide*, dark orange, m.p. 64–65°, *tri-n-amyl dichloride*, m.p. 47°. Alcoholic solutions of the dichlorides gave dinitrites with  $\text{NaNO}_2$ ;  $\text{Pr}^a_3$  dinitrite, m.p. 167–168° (decomp.). The following *bis(trialkylarsine)palladium salts* are described:  $\text{Me}_3$ , golden-yellow crystals, m.p. 235° (crystallographic data given),  $\text{Et}_3$ , m.p. 116°,  $\text{Pr}^a_3$ , m.p. 55°,  $\text{Bu}^a_3$ , m.p. 54°, and *tri-n-amyl dichloride*, m.p. 10–11°;  $\text{Pr}^a_3$  *dibromide*, orange prisms, m.p. 49°,  $\text{Et}_3$  dinitrite, m.p. 176–177°. Addition of a thiol in  $\text{CHCl}_3$  to  $(\text{NH}_4)_2\text{PdCl}_4$  gave deep reddish-orange *Pd mercaptides*; *Et* derivative, decomp. 250°,  $\text{Pr}^a$ , m.p. 209–210° (crystallographic data given),  $\text{Bu}^a$ , m.p. 142°, *n-amyl*, m.p. 83°, whilst the amorphous vermilion  $\text{Ph}_2$  derivative is formed when  $\text{PhSH}$  is added to  $\text{EtOH}$  or  $\text{COMe}_2$  solutions containing  $[(\text{R}_2\text{S})_2\text{PdX}_2]$ , and gives *Pd* on heating. *Pd* can be determined in this way. Addition of a thiol to  $\text{HgO}$  gave the *Hg alkyl mercaptides*: *Et*, m.p. 77°,  $\text{Pr}^a$ , m.p. 67°,  $\text{Bu}^a$ , m.p. 85°, *n-amyl*, m.p. 66°, *n-hexyl*, m.p. 58°, *n-heptyl*, m.p. 75°, and *n-octyl*, m.p. 71°.  $[\text{Et}_2\text{S}, \text{HgCl}_2]$  has m.p. 77.5–78.5°.

R. S.

**Physical identity of enantiomerides. I. Rotatory dispersion of *l*-borneol, enantiomeric camphors, camphoric acids, sodium camphorates, camphoric anhydrides, and camphorimides.** B. K. SINGH and I. MAHANTI (Proc. Indian Acad. Sci., 1935, 2, A, 378–396).—In view of reported slight deviations in rotatory powers of *d*- and *l*-forms, suggested by wave mechanics, high-precision data for a no. of carefully purified compounds over a range of concns. in various solvents are tabulated. Results indicate that, within the limits of experimental error, Pasteur's principle is quantitatively strictly obeyed.

N. M. B.

**Maximum valency of elements and atomic structure. III, IV.** B. ORMONT (Acta Physicochim. U.R.S.S., 1935, 2, 533–546, 547–556; cf. A., 1935, 1058).—III. The dependence of the stability of the homopolar hydrides on the structure and valency of the central atoms (quantum states of the extranuclear electrons) is discussed.

IV. The stability of organo-metallic compounds containing homopolar linkings is discussed.

O. J. W.

**Maximum valency of elements and atomic structure. V. Maximum valency in the formation of hydrides, organometallic compounds, oxides, and halogen compounds.** B. ORMONT (Acta Physicochim. U.R.S.S., 1935, 2, 689–694; cf. preceding abstract).—Discussion. T. G. P.

**Natural classification of chemical compounds.**

II. F. M. SCHEMJAKIN (Acta Physicochim. U.R.S.S., 1935, 2, 421–426; cf. A., 1931, 287).—Analogies are observed between the physical properties of compounds of similar structural arrangement and between compounds in which the sums of the atomos. of the constituent atoms are equal. J. W. S.

**Valency strength and the magnetism of complex salts.** J. H. VAN VLECK (J. Chem. Physics, 1935, 3, 807–813).—The anomalously low susceptibilities of ferro- and ferri-cyanides and certain other complex salts, compared with the predictions of the Bose-Stoner "spin only" formula, can be interpreted by Pauling's directed wave functions, or by the cryst. potential method (cf. Schlapp, A., 1933, 212), or by Mulliken's method of mol. orbitals (cf. A., 1932, 562).

N. M. B.

**Group relation between the Mulliken and Slater-Pauling theories of valency.** J. H. VAN VLECK (J. Chem. Physics, 1935, 3, 803–806).—By means of the group theory of characters, an intimate relation and transformation between Mulliken's mol. orbitals and the Slater-Pauling directed wave functions is shown.

N. M. B.

**Molecular structure of dielectrics.** (Sir) W. H. BRAGG (J. Inst. Electr. Eng., 1935, 77, 737–748).—Kelvin Lecture.

**New formulation of the Pauli principle for bond problems.** A. A. SCHUCHOVITSKI (Acta Physicochim. U.R.S.S., 1935, 2, 81–90).—Mathematical. R. S.

**Interaction between vibration and rotation for symmetrical molecules.** M. JOHNSTON and D. M. DENNISON (Physical Rev., 1935, [ii], 48, 868–883).—Mathematical. Teller's explanation of the anomalous fine structure of the infra-red bands of symmetrical mols. is developed. Expressions for the spacing const. of axially symmetrical and of tetrahedral mols. are derived, the internal angular momenta associated with the  $\perp$  frequencies of the axial mol.  $\text{YX}_3$  are calc., and results are applied to  $\text{NH}_3$  and  $\text{ND}_3$ . The axial mol.  $\text{ZXY}_3$  is treated, and the moments of inertia of  $\text{MeF}$ ,  $\text{MeCl}$ ,  $\text{MeBr}$ , and  $\text{MeI}$  are calc. as 5.61, 5.35, 5.44, and  $5.44 \times 10^{-40}$ , respectively. Results for overtones and combinations of two  $\perp$  frequencies are applied to  $\text{NH}_3$  and  $\text{MeCl}$ .

The calc. moment of inertia of  $\text{CH}_4$  is  $5.47 \times 10^{-40}$ . The overtones of  $\text{YX}_4$  are investigated. N. M. B.

Partial calculation of the potential energy function of the benzene molecule on the hypothesis of plane hexagonal symmetry. C. MANNEBACK (Ann. Soc. Sci. Bruxelles, 1935, 55, B, 237—252; cf. A., 1935, 1057).—Coeffs. of the potential function of  $\text{C}_6\text{H}_6$  have been calc. with the aid of the Raman and infra-red spectra of  $\text{C}_6\text{H}_6$  and  $\text{C}_6\text{D}_6$ . It is shown that interaction occurs between non-adjacent C, giving a trellis-like elastic system. R. S.

Heat of dissociation of nitrogen. W. W. LOZIER (Physical Rev., 1934, [ii], 45, 840).—A discussion. L. S. T.

Dissociation energy of carbon monoxide. P. GOLDFINGER, V. LASAREV, and B. ROSEN (Compt. rend., 1935, 201, 958—960).—The dissociation energy of CO of 9.10 e.v. is consistent with related spectroscopic and thermochemical data. H. J. E.

Dissociation energy of CO. D. COSTER and F. BRONS (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 961—964; cf. A., 1934, 237).—The energy of predissociation in the fourth positive group of CO indicates that the energy of dissociation of the CO mol. is 8.41 volts (193.9 kg.-cal. per g.-mol.). From this the heat of sublimation of solid C is 107.6 kg.-cal. per mol. J. W. S.

Surface tension near the critical point. A. W. PORTER (Phil. Mag., 1935, [vii], 20, 1163—1166).—A quant. discussion of surface flattening in a small tube near the crit. temp. N. M. B.

Surface tension of liquid metals. D. V. GOGATE and D. S. KOTHARI (Phil. Mag., 1935, [vii], 20, 1136—1144).—Mathematical. An electron theory of surface tension is developed. Results agree with observed vals. N. M. B.

Surface tension of mercury and its alloys. M. LEMARCHANDS and L. CONVERS (J. Chim. phys., 1935, 32, 657—669).—The drop-wt. method of determining the surface tension ( $\sigma$ ) of Hg in air leads to variable results owing to the adsorption of gases by the surface. The val. of  $\sigma$  determined by the same method in a vac. is 434 dynes per cm. This method applied to Ca amalgam was unsuccessful owing either to superficial oxidation or to the formation of a surface film of solid amalgam. J. W. S.

Contribution of X-ray analysis to the question of electron terms in ionic lattices. R. DE L. KRONIG (Physikal. Z., 1935, 36, 729—732).—Two chief factors determine the fine structure of the X-ray absorption bands for ionic crystals: (1) the inability of electrons moving in a definite direction to take up certain quanta of energy on account of the zonal structure of the energy spectrum; this is a factor depending on the type of lattice, and (2) the effect of the modulation of the wave function on the probability of transition, depending on the variation of potential within the lattice cell. The various types of fine structure of the  $K$ -absorption edges encountered experimentally are discussed.

A. J. M.

X-Ray interference for contact of the source of rays and the crystal. H. SEEMANN (Physikal. Z., 1935, 36, 837—841).—Results obtained by the single-crystal anticathode method (cf. A., 1935, 1306) in which the crystal and X-ray source are one and the same are improved by separating the crystal from the source by a short distance. A. J. M.

Conditions determining the intensity of X-ray reflexions from microcrystalline layers. J. BRENTANO (Nature, 1935, 136, 988).—A discussion (cf. A., 1935, 1306; this vol., 45). L. S. T.

Relation between the mechanical strain and the intensity of X-rays reflected by a quartz plate. II. E. FUKUSHIMA (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 1199—1204; cf. this vol., 15).—The intensity of the reflected X-rays approaches a max. as the applied force is increased. R. S.

Face-centred lattices with incompletely arranged cations. E. J. W. VERWEY (Chem. Weekblad, 1935, 32, 721—726).—A discussion of crystals, the lattice structure of which is determined by the face-centred arrangement of the large anions, the cations being relatively very small. D. R. D.

State of electrons in crystal lattices. F. HUND (Physikal. Z., 1935, 36, 888—890).—Theoretical. The position of the energy bands in some simple types of crystal lattice is calc. A. J. M.

Recrystallisation processes. I. Single particle recrystallisation of deformed single crystals. II. Recrystallisation of single crystals. III. Compressed powdered rock-salt. H. G. MÜLLER (Z. Physik, 1935, 96, 279—306, 307—320, 321—327).—I. The speed of growth of visible particles and their rate of formation both follow a van 't Hoff law from 270° to 790°, and for pure NaCl are independent of time; as these both follow the one law there can be no special nuclei formation.

II. Recrystallisation of powdered NaCl to a single crystal gives this microscopic and amicroscopic defects.

III. The tensile strength of tempered compressed NaCl varies with temp. and time of tempering in the same manner as compressed metals. A. B. D. C.

Crystal growth and dissolution under local stress. G. A. RUSSELL (Amer. Min., 1935, 20, 733—737).—Experiments with halite and alum show that stresses may be localised in crystals as well as in amorphous material, and that the solubility of a part of the crystal is related to local stress. Material dissolved from one part on account of local stress may be redeposited on a less strained part of the same crystal. L. S. T.

Lattice constants of beryllium. E. A. OWEN and L. PICKUP (Phil. Mag., 1935, [vii], 20, 1155—1158).—In view of discrepancies between results previously obtained with a focussing camera (cf. A., 1934, 136) and those of other authors, determinations were made with a special type of spectrum camera, and data were analysed by a new method. Results for Be annealed in vac. were  $a$  2.2810,  $c$  1.5682 Å., in close agreement with the previous vals. N. M. B.



**Tetragonal martensite in carbon steels.** Z. NISHIYAMA (Sci. Rep. Tôhoku, 1935, 24, 517—522).—The lattice const. of tetragonal or  $\alpha$ -martensite, calc. from the effective radii of Fe and C atoms, is in accord with vals. observed in quenched steel. This is interpreted as confirming that martensite is a solid solution of C in Fe. J. W. S.

**Metals and alloys. XVIII. Lattice structure of LiAl.** E. ZINTL and G. WOLTERS DORF (Z. Elektrochem., 1935, 41, 876—879; cf. A., 1934, 356).—LiAl has space-centred cubic lattice of the NaTl type with a 6.360 Å. The radius of both atoms is 1.38 Å. The lattice dimensions are determined solely by the Al atoms, the size of which remains unchanged, whilst the Li atoms undergo a large contraction. F. L. U.

**Structural type of aluminium boride (AlB<sub>2</sub>).** W. HOFMANN and W. JANICHE (Naturwiss., 1935, 23, 851).—The structure of AlB<sub>2</sub> (hexagonal leaflets) has been determined by the Laue, powder, and rotating-crystal methods. The unit cell has  $a$  3.00,  $c$  3.24 Å., and contains 1 mol. of AlB<sub>2</sub>. The Al atoms lie at the corners of the cell, and thus form planes parallel to the leaflet plane. The B form a lattice analogous to the C in graphite. A. J. M.

**Stabilised cubic iron sesquioxide.** A. MICHEL and G. CHAUDRON (Compt. rend., 1935, 201, 1191—1193).—Cubic Fe<sub>2</sub>O<sub>3</sub> is stable in presence of the ferrites of Na, Be, Ag, and K. Its virtual Curie point obtained by extrapolation of the system Na<sub>2</sub>O—Fe<sub>2</sub>O<sub>3</sub> is 675° ± 10°. T. G. P.

**Crystal structure of hydrogen peroxide.** F. FEHÉR and F. KLÖTZER (Z. Elektrochem., 1935, 41, 850—851; cf. A., 1935, 806).—H<sub>2</sub>O<sub>2</sub> has tetragonal structure with  $a=b=4.02$ ,  $c$  8.02 Å. The unit cell contains 4 mols. F. L. U.

**Structure of ferric phosphate.** V. CAGLIOTTI (Atti R. Accad. Lincei, 1935, [vi], 22, 146—149).—FePO<sub>4</sub>, prepared by the action of Na<sub>2</sub>HPO<sub>4</sub> on FeCl<sub>3</sub> in presence of NaOAc, crystallises in one phase isomorphous with quartz:  $a_0$  5.035,  $c_0$  5.588 Å.,  $d_{\text{obs}}$  3.1. O. J. W.

**Crystal parameters of copper ammonium bromide.** A. SILBERSTEIN (Compt. rend., 1935, 201, 970—971).—CuBr<sub>2</sub>·2NH<sub>3</sub>·Br·2H<sub>2</sub>O is quadratic,  $a$  7.98,  $c$  8.41 Å.; 2 mols. in unit cell; space-group  $P4/mmm$  ( $D_{4h}^{11}$ ). H. J. E.

**Crystal structure of cerium tungstate.** J. BEINTEMA (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 1011—1015).—Ce<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> is tetragonal-bipyramidal, possessing a scheelite-like structure with  $a_0$  5.336,  $c_0$  11.620 Å., and contains 4/3 Ce<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> in the unit cell. It is isomorphous with PbWO<sub>4</sub>, with which it forms a complete range of mixed crystals, but only 2/3 of the positions occupied by Pb in PbWO<sub>4</sub> are occupied by Ce, the remainder being void. J. W. S.

**Crystal structure and composition of sodium dihydropyrostibiate.** J. BEINTEMA (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 1015—1020).—Na<sub>2</sub>H<sub>2</sub>Sb<sub>2</sub>O<sub>7</sub>·5H<sub>2</sub>O crystallises in the tetragonal-bipyramidal form, the unit cell having  $a_0$  8.005,

$c_0$  7.868 Å. and containing 4 Na atoms. Cations and anions form a NaCl-like lattice, and in each anion Sb is surrounded by 6 O in almost octahedral configuration. The structure is in accord with the view that the composition is NaSb(OH)<sub>6</sub>. J. W. S.

**Structure and configuration of certain diamminopalladium compounds.** F. G. MANN, (MISS) D. CROWFOOT, D. C. GATTIKER, and (MRS.) N. WOOSTER (J.C.S., 1935, 1642—1652).—The deep red cryst. [(NH<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub>] (I) which is produced when the rate of formation is slow is chemically identical with the usual yellow form, which is a *trans*-compound. (I) is twinned,  $a$  8.0,  $c$  7.8 Å., and has 4 mols. per unit cell. Both forms give the pale greenish-white *oxalate* (darkens 175—185°) on shaking with aq. K<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, and X-ray measurements indicate that this is a *cis*-compound having a planar configuration. The *trans*-dinitrite, pale yellow, m.p. 231—232° (decomp.), is formed in a similar manner and shows a planar co-ordination about the central Pd. Addition of [(NH<sub>3</sub>)<sub>4</sub>Pd]Cl<sub>2</sub> to aq. NaNO<sub>2</sub> gives *cis*-diamminopalladium dinitrite, blackens at 234°, which is converted into the *trans*-dinitrite by slow recrystallisation. Since treatment of K palladonitrite with aq. NH<sub>3</sub> gives the *trans*-dinitrite, the production of the *cis*-form must be ascribed to the presence of NaCl or NaNO<sub>2</sub>. The *cis*-dinitrite gives an immediate brown ppt. with CS(NH<sub>2</sub>)<sub>2</sub>, whilst the *trans*-form does not. [(NH<sub>3</sub>)<sub>4</sub>Pd]Cl<sub>2</sub> ppts. canary-yellow tetramminopalladium palladonitrite from aq. K palladonitrite, m.p. 224—225° (decomp.). Recrystallisation converts this into the *trans*-dinitrite, which gives yellow diamminopalladium di-iodide with aq. KI. Treatment with COMe<sub>2</sub> yields a reddish-blue octahedral form which shows a new type of repeated polysynthetic twinning. X-Ray photographs indicate that it is internally highly heterogeneous and that the I are arranged irregularly along the  $c$ -axis. When the di-iodide is dissolved in aq. NH<sub>3</sub>, [(NH<sub>3</sub>)<sub>4</sub>Pd]I<sub>2</sub> is formed, which dissociates on keeping and deposits red crystals identical with the yellow pptd. di-iodide. The di-iodide may also be formed by the action of aq. KI on the dichloride. Diamminopalladium oxalate, when treated with KI, does not give the expected *cis*-di-iodide, but chocolate-brown tetramminopalladium palladoiodide, which may also be obtained from the palladochloride or from NH<sub>4</sub> palladoiodide and [(NH<sub>3</sub>)<sub>4</sub>Pd]Cl<sub>2</sub>. Further crystallographic properties of the compounds are given in detail. R. S.

**X-Ray diagrams of sugar carbon submitted to various thermal treatments.** P. CORRIEZ (Compt. rend., 1935, 201, 1189—1191; cf. A., 1934, 1088).—X-Ray diagrams of sugar C heated for 2 hr. at 1200°, 1400°, 1600°, 1800°, and 2000° indicate that the structure approaches nearest to that of graphite in the specimen heated at the highest temp. T. G. P.

**Structure of cellulose.** F. WORSCHITZ (Magyar Chem. Fol., 1934, 40, 60—64; Chem. Zentr., 1935, i, 2825).—A series of fibre diagrams obtained from Canadian Pappel and Pe-mou (*Fokiana hodgensii*, A. Henry), and differing from the normal, are given. In one case the diagram points to orientation of the cellulose crystals along the  $a$ -axis. H. N. R.

**X-Ray analysis of the structure of iridescent shells. II. *Haliotide*.** S. RAMASWAMY (Proc. Indian Acad. Sci., 1935, 2, A, 345—351; cf. A., 1935, 1194).—X-Ray diffraction patterns were investigated, and orientations of the aragonite crystals obtained. Results are compared with those for *Turbo* and *Trochus* shells. N. M. B.

**Orientation of the CO<sub>3</sub> groups in the ammonium [and potassium] hydrogen carbonate crystal.** A. MOOKHERJEE (Physical Rev., 1934, [ii], 45, 844).—Magnetic anisotropy measurements confirm Mooney's conclusions (A., 1933, 1234) concerning NH<sub>4</sub>HCO<sub>3</sub>. KHCO<sub>3</sub> exhibits a much feebler anisotropy, showing that the planes of the different CO<sub>3</sub> groups in the unit cell must be considerably inclined to each other. L. S. T.

**Anomalies in the diffraction of fast-moving electrons.** H. MARK and H. MOTZ (Monatsh., 1935, 67, 13—23).—Further experiments confirm the conclusion previously reached (A., 1935, 813, 820), that anomalous interference lines obtained with electrons of 20—30 kv. are due to the presence of traces of fatty material of high mol. wt. on the surface of the specimen. F. L. U.

**Deflexion of slow electrons by sublimed tungsten.** V. I. KASSATOTSHKIN (Acta Physicochim. U.R.S.S., 1935, 2, 317—336).—The deflexion of 40—400-volt electrons by a film of micro-cryst. sublimed W indicates that the inner potential of W is  $10.5 \pm 2$  e.v. A second group of deflexion max. correspond with electron diffraction at the surface of the W crystals. The results are in accord with measurements with single W crystals (cf. A., 1933, 549). J. W. S.

**Variation in the lattice constant of zinc oxide.** V. E. COSSLETT (Nature, 1935, 136, 988—989).—A ZnO film prepared from a granulated Zn melt had  $a$   $3.234 \pm 0.005$ ,  $c$   $1.615 \pm 0.005$  Å. when freshly prepared and  $a$   $3.279$ ,  $c$   $1.637$  Å. 18 and also 20 months later. Au films remained const. over this period. ZnO films prepared as described should not be used for high-voltage calibration or measurement. L. S. T.

**Diffraction of electrons by metal crystals and by mica.** J. A. DARBYSHIRE and E. R. COOPER (Proc. Roy. Soc., 1935, A, 152, 104—123).—An examination has been made of spot patterns produced when an electron beam of velocity  $\sim 30$  kv. is transmitted through thin cryst. films of Cd, Zn, and Bi, and through thin curved sheets of mica. The reciprocal lattice picture of electron diffraction is presented in a form suitable for discussing the results. The crystals of the metals were prepared by withdrawing the surface oxide film from the molten metals in air and in N<sub>2</sub>; these films produced Debye-Scherrer patterns due to the oxide and spot patterns due to occluded metal crystals. The spot patterns are caused chiefly by distortion of the metal crystals. This view is supported by the results obtained with mica. Forbidden spectra, probably due to successive reflexions by different crystallites in an aggregate, were observed. L. L. B.

**Molecular structures of sulphur dioxide, carbon disulphide, and carbonyl sulphide.** P. C. CROSS and L. O. BROCKWAY (J. Chem. Physics, 1935, 3, 821—824).—Mol. structure data obtained by the electron diffraction method are: SO<sub>2</sub>, S—O,  $1.46 \pm 0.02$ ; CS<sub>2</sub>, C—S,  $1.54 \pm 0.03$ ; COS, C—O,  $1.16 \pm 0.02$ , C—S,  $1.56 \pm 0.03$  Å. In SO<sub>2</sub> the mol. resonates between structures having single-double and double-single linkings between S and the two O, with a linking angle  $122^\circ \pm 5^\circ$ . CS<sub>2</sub> is a linear mol. having the two double linkings predominating over the single and triple linking structure. In COS the double-double linking arrangement and the structure having the triple C—O linking predominate. N. M. B.

**Molecular structure of nickel carbonyl.** L. O. BROCKWAY and P. C. CROSS (J. Chem. Physics, 1935, 3, 828—833).—Electron diffraction by Ni(CO)<sub>4</sub> vapour leads to a mol. model in which the four CO have a tetrahedral arrangement about the Ni with Ni—C,  $1.82 \pm 0.03$ , and C—O,  $1.15$  Å., corresponding with resonance between two electronic structures in which the C—O linking resonates between triple and double electron pair linkings, and the N—C linking between single and double electron pair linkings. N. M. B.

**Diffraction of electrons by chloroform and its molecular structure: the Urbain and tetrahedral models.** C. DEGARD (Compt. rend., 1935, 201, 951—952).—The Cl—Cl and C—Cl interat. distances in CHCl<sub>3</sub> were  $2.95 \pm 0.03$  and  $1.76$  Å., respectively. This is consistent with either the tetrahedral formulation or Urbain's co-ordinate formula CCl<sub>2</sub>.HCl. H. J. E.

**Formation of molecular swarms in liquids.** R. GANS (Physikal. Z., 1936, 37, 19—22).—Theoretical. The calculation of the size and shape of mol. swarms in liquids by the determination of the degree of depolarisation of light scattered by the liquid is considered, the method of Krishnan (A., 1935, 11) being extended. A. J. M.

**Theory of influence of pressure on electrical resistance of metals.** M. H. LENSSEN and A. MICHELS (Physica, 1935, 11, 1091—1107). H. J. E.

**Resistance of very thin films of foreign substances in metallic contacts.** R. HOLM and B. KIRCHSTEIN (Physikal. Z., 1935, 36, 882—888).—Metallic surfaces become covered, in air, with a film of foreign matter of definite resistance. The resistance of very thin films may be calc. using the tunnel effect. Such calculation shows that the resistance is independent of temp. and obeys Ohm's law up to 0.5 volt, in agreement with experiment. A. J. M.

**Variation of electrical resistance and reflecting power of metallic mirrors condensed at low temperatures.** R. SUHRMANN and G. BARTH (Physikal. Z., 1935, 36, 843—845).—The resistance of mirrors of Cu, Ag, Au, Cd, Tl, and Pb deposited at 20—80° abs. decreases on warming to room temp. and there is a simultaneous increase in the reflecting power. The resistance of Bi mirrors deposited at 80° abs. increases with rise of temp. The results are analogous to the resistance changes which occur when the liquid metal solidifies, and therefore indicate that

rise of temp. from 80° abs. to room temp. involves an increase in the orderly arrangement of atoms in the lattice.

A. J. M.

**Longitudinal resistance changes in a magnetic field according to elementary theory.** A. SOMMERFELD and B. W. BARTLETT (*Physikal. Z.*, 1935, **36**, 894—899).—Mathematical. Previous calculations of the longitudinal resistance change in a magnetic field (current and magnetic field parallel) led to a zero val. If the electron orbits are quantised a finite result is obtained.

A. J. M.

**Dielectric investigations on crystals of Seignette's salt.** R. DAVID (*Helv. phys. Acta*, 1934, **7**, 647—649; *Chem. Zentr.*, 1935, **i**, 2779).—The dependence of the dielectric const. on elastic deformation of the crystal has been investigated. The charge-field strength curves exhibit hysteresis and saturation. Non-homogeneous deformation produces highly asymmetric hysteresis curves, which are attributed to internal stresses in the crystal.

J. S. A.

**Magnetisation of single crystals of nickel at various temperatures.** K. HONDA, H. MASUMOTO, and Y. SHIRAKAWA (*Sci. Rep. Tôhoku*, 1935, **24**, 391—410).—The magnetisation of single Ni crystals has been measured by the ballistic method between -252° and 370°. The magnetisation along the (111) axis at 20° increases rapidly at first and slowly later with increasing field strength to a saturation val. of about 503 gauss. At higher temp. magnetisation occurs more readily in weak fields, but the saturation val. is lower. The magnetisation along the (100) and (110) axes behaves similarly at higher temp., but at low temp. saturation is not reached with fields up to 1000 oersteds. The estimated val. of the magnetisation of Ni at 0° abs. is 533 gauss.

J. W. S.

**Cessation of spin in ferromagnetic crystals under the influence of mechanical strains.** R. GANS (*Ann. Physik*, 1935, [v], **24**, 680—696).—Theoretical.

A. J. M.

**Directions of discontinuous changes of magnetisation in a rotating monocrystal of silicon-iron.** L. W. MCKEEHAN and R. F. CLASH, jun. (*Physical Rev.*, 1934, [ii], **45**, 839—840; cf. *A.*, 1935, 287).

L. S. T.

**Action of X- and  $\gamma$ -rays on piezo-electric crystals.** F. SEIDL and E. HUBER (*Z. Physik*, 1935, **97**, 671—680).—Quartz and Rochelle salt show an increase in electrical conductivity when irradiated with X- or  $\gamma$ -rays, but the piezo-const. does not always change in one direction.  $\gamma$ -Rays colour Rochelle salt yellow.

A. B. D. C.

**Magnetostriction volume effect for nickel and magnetite.** M. KORNETZKI (*Z. Physik*, 1935, **97**, 662—666).

A. B. D. C.

**Inversion of quartz to tridymite.** I. Natural tridymite. II. X-Ray distinction between tridymite and cristobalite. S. KONDO and T. YAMAUCHI (*J. Soc. Chem. Inst. Japan*, 1935, **38**, 651—652B).—I. For natural tridymite (I)  $n_D$  varies from 1.477 to 1.479. Interplanar spacings and intensities have been calc. for 29 lines in the diffraction pattern.

II. Artificial (I), and natural and artificial cristobalite (II), have  $n_D$ , respectively, 1.469—1.474, 1.482, 1.484. (I) and (II) can be distinguished by the X-ray pattern.

T. W. P.

**Dynamic theory of crystal optics.** G. MOLIERE (*Ann. Physik*, 1935, [v], **24**, 591—608).—Mathematical. Laue's method for X-rays is extended to longer  $\lambda$  and expressions for double refraction and optical activity are derived; the vals. calc. are in agreement with those obtained from the Born-Ewald lattice theory.

W. R. A.

**Negative cohesion pressure.** V. JACYNA, S. DEREVJANKIN, and A. OBNORSKI (*Z. Physik*, 1935, **97**, 774—776).—Weiss and Bridgman's revision of van der Waals' equation of state (cf. *A.*, 1935, 1064) gives results that accord well with Jacyna's theory (*A.*, 1934, 1070).

A. B. D. C.

**Lattice distortion and coercive force in single crystals of nickel-iron-aluminium.** W. G. BURGERS and J. L. SNOEK (*Physica*, 1935, **11**, 1064—1074).—In the state of max. coercive force, the segregation of the supercooled metastable  $\alpha$ -phase into a stable  $\alpha$ - and a  $\gamma$ -phase has reached only a preliminary stage. The  $\gamma$ -phase is not in evidence in the X-ray diagrams. A highly stressed state occurs in the lattice.

H. J. E.

**Crystal plasticity.** IV. **Dynamic plasticity law.** E. OROWAN (*Z. Physik*, 1935, **97**, 573—595).—Plastic flow of Zn crystals shows that the stress varies with the rate of slip and not with the actual displacement (cf. *A.*, 1934, 949).

A. B. D. C.

**Plasticity of bismuth.** W. F. BERG and L. SANDLER (*Nature*, 1935, **136**, 915).—Crystals of Bi grown in a vac. or under atm. pressure in  $N_2$ ,  $H_2$ , or  $CO_2$  by the Andrade-Roscoe method are all soft, *i.e.*, they slip in tensile tests at room temp. The hypothesis that the gas is responsible for the softness (*A.*, 1934, 722) is untenable.

L. S. T.

**Strength of crystals towards pressure.** M. SCHULER and A. DIMPKER (*Z. Instrument.*, 1935, **55**, 63—70; *Chem. Zentr.*, 1935, **i**, 2490).—Spheres and cones of materials (sapphire, ruby, diamond, quartz) used for construction of knife edges, pressed against the same material, crack readily, but require much higher loads for breakage. Steel spheres behave as required by the Hertz theory.

J. S. A.

**Elastic behaviour of tin single- and polycrystals.** W. BOAS (*Helv. phys. Acta*, 1934, **7**, 878—883; *Chem. Zentr.*, 1935, **i**, 2312).—Elastic moduli calc. from the Voigt formula for polycryst. Sn agree fairly well with published data. For single crystals, Bridgman's results are much > those calc.

J. S. A.

**Electrical evaluation of recovery in compressed rock-salt crystals.** J. BOROS and Z. GYULAI (*Z. Physik*, 1935, **96**, 355—358).—Sudden changes in electric conductivity of NaCl under pressure are associated with recovery.

A. B. D. C.

**Explosive antimony.** II. **Structure, electrical conductivity, and rate of crystallisation.** C. C. COFFIN (*Proc. Roy. Soc.*, 1935, **A**, 152, 47—63; cf. *A.*, 1934, 1297).—A microscopic examination of

polished and etched surfaces shows that the explosive electrolytic deposit of Sb possesses a heterogeneous gel-like structure definitely oriented with respect to the cathode receiving surface. This oriented phase is probably an  $\text{SbCl}_3\text{-Sb}$  complex resulting from the deposition of a complex ion; the other phase is probably amorphous Sb. The electrical properties of the deposits are non-metallic in that the conductivity is very small and has a positive exponential temp. coeff. Ohm's law is obeyed, but Faraday's law is not involved, although a small polarisation is built up at the higher temp. At temp. too low to initiate explosion the deposits crystallise at a rate which is independent of the extent to which they have already crystallised. The rate of crystallisation increases exponentially with rise of temp. L. L. B.

**Two new phenomena [transitions produced in bismuth and phosphorus] at very high pressure.** P. W. BRIDGMAN (Physical Rev., 1934, [ii], 45, 844—845).—At approx. 25,000 kg. per sq. cm. and room temp., a new modification is produced reversibly from ordinary solid Bi with a vol. decrease of approx. 9%. At 35,000 kg. per sq. cm., black P is formed at room temp. from the modification of white P stable at atm. pressure only below  $-80^\circ$ . The transformation is not complete;  $d$  is 2.59, as compared with 2.69 for the usual form of black P.

L. S. T.

**Effects of high shearing stress combined with high hydrostatic pressure.** P. W. BRIDGMAN (Physical Rev., 1935, [ii], 48, 825—847).—With mean pressures up to 50,000 kg. per sq. cm., the effect of shearing stresses up to the plastic flow point was investigated for a no. of substances in the form of thin discs. Normally stable substances which detonated were: celluloid,  $\text{CHI}_3$ ,  $\text{PbO}_2$ ,  $\text{KMnO}_4$ ,  $\text{Ag}_2\text{O}$ ,  $\text{MnO}_2$ ,  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ ,  $\text{AgNO}_3$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Cr}_2(\text{SO}_4)_3$ ,  $\text{K}_2\text{SO}_4$  cryst. and anhyd.,  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{CuCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot 2\text{H}_2\text{O}$ . Rubber changed to a hard horn-like mass, paper, wood, and linen cloth changed to translucent horn-like substances, thymol-blue became insol., amorphous Se partly became metallic, cryst. S appeared to become amorphous,  $\text{PbO}$  decomposed to Pb without detonation, red  $\text{HgO}$  changed to black, and red P changed to the black form. Combinations of substances normally inert to each other which reacted explosively were  $\text{Cu}+\text{S}$ ,  $\text{Fe}_2\text{O}_3+\text{Al}$ ,  $\text{SiO}_2+\text{Mg}$ ,  $\text{K}_2\text{C}_2\text{O}_4+\text{Al}$ , and  $\text{Si}+\text{MgO}$ . Single substances giving negative results were: graphite, mica,  $\text{NH}_4\text{NO}_3$ , sugar, rosaniline,  $\text{CuS}$ ,  $\text{SiO}_2$ , tremolite,  $\text{NH}_4\text{F}$ ,  $\text{CuO}$ ,  $\text{MgO}$ ,  $\text{Ag}_2\text{S}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{LiF}$ ,  $\text{AgCl}$ ,  $\text{K}_2\text{C}_2\text{O}_4$ ,  $\text{NaBrO}_3$ ,  $\text{Si}$ ,  $\text{Na K tartrate}$ ,  $\text{HgNO}_3$ , and  $\text{K}_2\text{Cr}_2\text{O}_7$ . Polymorphic transitions under these stresses could be detected by a break in the shearing stress—pressure curve; out of 57 elements examined, breaks were found for Li, Sr, Ca, Ba, Cd, Zn, V, Mn, Sb, Te, I, La, Ce, Cr, Tl, Bi, Th, Sn, Yt, and Pr.

N. M. B.

**Polymorphism, principally of the elements, up to 50,000 kg.** P. W. BRIDGMAN (Physical Rev., 1935, [ii], 48, 893—906).—A new technique is described for applying to solids pressures up to 50,000 kg. per sq. cm. and measuring the parameters of transitions. Results of examination for polymorphism of a no. of elements are given; new modifications

were found for Bi, Hg, Tl, Te, Ga, and I, and transition parameters were measured. KCl, KBr, and KI at about 20,000 kg. per sq. cm. appear to assume the CsCl type of structure.

N. M. B.

**Coalescence in stages between two drops of a liquid.** M. KATALINIĆ (Nature, 1935, 136, 915—916; cf. A., 1935, 1062).

L. S. T.

**Recrystallisation accompanying an allotropic change.** C. F. ELAM (Nature, 1935, 136, 917; cf. A., 1935, 1452).—Such changes in  $\text{NH}_4\text{NO}_3$ ,  $\text{KNO}_3$ , and  $\text{AgNO}_3$  can be followed under the microscope using crossed Nicols.

L. S. T.

**Softening of vitreous substances.** E. RENCKER (Ann. Chim., 1935, [xi], 4, 523—566; cf. A., 1934, 17, 480).—Determinations of the softening temp. and the transformation point of vitreous substances are discussed. A kinetic interpretation of the phenomena is advanced, and it is shown that the properties of "tempered" glasses cannot be ascribed to a persistence in the interior of the conditions which exist above the transformation temp.

R. S.

**Highly polymerised compounds. CXXV. Mol. wt. determinations with highly complex polyethylene oxides.** H. STAUDINGER and H. LOHMANN. CXXVI. Comparison of the osmotic and viscosimetric methods of determining mol. wt. in polymeric-homologous series. CXXVII. Osmotic determinations in solutions of rod-like and spherical particles. H. STAUDINGER and G. V. SCHULZ. CXXVIII. Abnormal mol. wts. of highly complex compounds. H. STAUDINGER, W. KERN, and J. J. HERRERA. CXXIX. Polymerisation as chain reaction. H. STAUDINGER and W. FROST. CXXX. Conception of mol. wt. of simple and complex compounds. H. STAUDINGER (Ber., 1935, 68, [B], 2313—2319, 2320—2335, 2336—2346, 2346—2350, 2351—2356, 2357—2362).—CXXV. Determination of the mol. wt. of hemicolloidal polyethylene oxides (concordant data for which are obtained by the cryoscopic, terminal group, and viscosimetric methods) shows that Brintzinger's process gives abnormal vals.; marked divergences are noted with relatively simple products the diffusion of which is not impeded by the too small diameter of the membrane pores. Diffusion of thread-like particles differs therefore from that of spherical particles, to which alone the expression  $K=\lambda\sqrt{M}$  can be applied. The osmotic and viscosimetric methods give approx. concordant results, proving that extrapolation of the viscosity equation is permissible and that the mol. wt. of complex materials with thread mols. can be determined viscosimetrically.

CXXVI. The relationship between mol. wt. and osmotic pressure is expressed by the equation  $M=RTc/p_c[1-c(K/p_c)^{1/\nu}]$ , in which  $K$  and  $\nu$  are constants for all members of a given polymeric-homologous series and, if determined for mesocolloidal members can be applied to eucolloids in solutions in which the van 't Hoff relationship does not hold good. The mol. wts. of cellulose acetates (I) and nitrates (II) and methylcelluloses (III) are thus determined and the results applied in the calculation of viscosimetric data.  $K_m$  has the same val. for (II) in COME,

(III) in  $H_2O$ , and (I) in  $COMe_2$  or *m*-cresol, proving that  $\eta_{sp.}$  of solutions of thread mols. depends only on the length of the mol. and the concn. and is independent of particular structure. With balata and hydro-caoutchouc the differences between the mol. wt. determined osmotically and viscosimetrically are considerable. With approx. eucolloidal polyethylene oxides the agreement between the determinations by the two methods is scarcely so close as with the cellulose derivatives. Observations with polystyrenes are greatly influenced by the manner in which polymerisation has been effected; it is assumed that unknown complications, particularly at higher temp., cause branching of the thread mols. Similar results are obtained with other synthetic polymerides formed by chain reactions; these, therefore, differ from the natural products which are polymeric-uniform and permit the determination of mol. length and hence mol. wt. by measurement of viscosity.

CXXVII. The cryoscopic and ebullioscopic methods are trustworthy for the determination of mol. wt. of relatively simple substances with thread-like mols., but their applicability to similarly constructed hemi-, meso-, and eu-colloids is difficult to assess, although the behaviour of cellulose derivatives suggests that they are trustworthy in very dil. solution. Determinations of osmotic pressure of polymeric-homologous caoutchoucs, polyethylene oxides, and cellulose nitrates show that in each series the additional pressure increases with increasing concn. more rapidly as the mol. wt. is greater. Additional pressure is not observed with spherical-colloidal ovalbumin and serum-albumin, whereas gelatin appears to have thread-like particles. In osmotic behaviour, spherocolloids conform approx. to van 't Hoff's law and  $p_c/c$  is const., whereas with linear colloids the  $p_c/c$  vals. increase with increasing concn.

CXXVIII. The depression of the f.p. of  $C_{10}H_8$  by five fractions of complex polyanetholes, the mol. wt. of which is determined concordantly by the viscosimetric and ultra-centrifugal methods, increases more slowly than expected with increasing concn., and the mol. wts. calc. on the assumption that Raoult's laws are followed are much smaller in dil. than in conc. solution, in some cases being < that of the fundamental mol. The observations are similar to those of Hess with cellulose esters and ethers in AcOH.

CXXIX. The view that polymerisation is a chain reaction and not a poly-condensation process is strengthened by the observation that intermediate products are not observed during the polymerisation of acrylic acid or styrene. The rate of polymerisation depends on the rates of activation, growth, and of "final" reaction leading to the formation of non-reactive positions at the end of the thread mols. The second process takes place very rapidly in comparison with the first and third. Catalysts accelerate the initial, but generally also the final, action, so that in general the products are less complex than those formed by slow polymerisation in absence of catalyst. Acceleration of the first change without affecting the third is achieved by polymerisation in soap emulsion, and the addition of a catalyst is here permissible, since it does not penetrate into the interior of the mol.

CXXX. The importance of discriminating between the physical mol. wt. (which does not involve the internal structure of the particles) and the chemical mol. wt. (sum of the wts. of all the atoms united by main valencies in a particle) in the case of highly polymerised compounds is stressed. H. W.

Conductivity of the Bunsen flame measured with direct and alternating current. H. ULLMANN (Z. Physik, 1935, 97, 496—510).—D.-c. and a.-c. conductivity has been determined for the pure Bunsen flame, and for one containing  $Na_2CO_3$ . Probe measurements show that the effect of electrodes is small for the pure flame, but high for the salt flame. The conductivities are 1 and  $14 \times 10^4$  for d.c. and a.c. in the pure flame, and 36 and  $173 \times 10^4$  sec.<sup>-1</sup> in the salt flame. A. B. D. C.

Electrical conductivity of compressed metal vapours. W. BRAUNBEK (Z. Physik, 1935, 97, 482—495).—Bloch's theory predicts a large pressure variation for the conductivity of metal vapours, but measurements on Hg and K vapours at 730° and 1200° and up to 35 and 10 atm., respectively, gave negative results. A. B. D. C.

Effect of ultra-violet light on the electrical conductivity of quartz. R. RADMANCHE (Compt. rend., 1935, 201, 1021—1022).—The conductivity of quartz increases with time of irradiation to a max., and falls gradually to the original val. after removing the light source. T. G. P.

Superconductivity and other low-temperature phenomena. A discussion (Proc. Roy. Soc., 1935, A, 152, 1—46).—J. C. McLENNAN discussed new methods of liquefying He: (1) in which the cooling is produced by the adiabatic expansion of compressed He gas, (2) in which the gas is pre-cooled with liquid  $N_2$  and in expanding is made to do external work on an expansion engine which is included in the gas cycle. Discontinuities in certain physical properties of liquid He, the lowest temp. which has been reached with liquid He alone (0.71° abs.), and the temp. reached by the method of adiabatic demagnetisation (0.0044° abs.) were mentioned. Up to the present, the following elements have been shown to become superconducting: Nb, Pb, Ta, Hg, Sn, In, Tl, Ti, Th, Al, Ga, Zn, Mg, Zr, Cd, Hf. The magnetic fields around superconductors, superconductivity in thin films, the Hall effect in superconductors, thermal conductivity at low temp., the anomalous behaviour of certain alloys, low-temp. calorimetry applied to radioactive measurements, sp. heats, and the electric magnetic theory of superconductors were also considered.

J. D. COCKCROFT discussed Kapitza's method for the liquefaction of He.

D. SHOENBERG reviewed the magnetic properties of superconductors.

W. H. KEESOM discussed the lambda-phenomena in liquid He, the thermodynamic temp. scale below 0.9° abs., the heat capacity of electrons in metals, and the calorimetry of superconductors.

W. MEISSNER. The magnetic effects occurring on transition to the superconducting state.

R. DE L. KRONIG. The propagation of electro-

magnetic waves in metallic conductors, and its bearing on the problem of superconductivity.

L. BRILLOUIN. Superconductivity and the difficulties of its interpretation.

N. KURTI and F. SIMON. The sp. heat of  $\text{Fe NH}_4$  alum below  $1^\circ$  abs. and a preliminary determination of the thermodynamic temp. scale.

R. PEIERLS. The residual resistance of superconducting metals.

F. LONDON. The macroscopical interpretation of superconductivity.

K. MENDELSSOHN. The induction and energy content in various superconducting substances.

N. F. MOTT. The heat capacity of certain elements at low temp.

L. L. B.

**Superconductivity.** M. VON LAUE, F. LONDON, and H. LONDON (*Z. Physik*, 1935, 96, 359—364).—Theoretical.

A. B. D. C.

**Superconductivity of the elements. III. Origin and range of validity of a proposed criterion for superconductivity.** Z. A. EPSTEIN (*Z. Physik*, 1935, 96, 386—409).—Theoretical (cf. A., 1930, 1242).

A. B. D. C.

**Electronic configuration of superconducting metals.** U. DEHLINGER (*Physikal. Z.*, 1935, 36, 892—894).—The composition of the outermost electron shells in the lattices of superconducting metals is considered. Only those elements are superconducting which possess a lattice with high co-ordination no., not too small at. radius, and, in their outermost shells,  $>$  one electron per atom. This holds for all elements, including the transition metals, with the exception of Ti and its congeners, which are weakly superconducting. The superconductivity of alloys is probably governed by a similar law. Thus, although Bi has a lattice too distorted to be superconducting,  $\text{Au}_2\text{Bi}$  has a highly co-ordinated lattice and is superconducting. The superconductivity of the carbides and nitrides of the transition elements may be explained in a similar way.

A. M.

**Effect of light on diamagnetic susceptibilities.**

H. C. BHUYAN (*Nature*, 1935, 136, 872).—Exposure to visible light temporarily increases the susceptibilities of  $\text{Cl}_2$ , Br, and I.

L. S. T.

**Magnetochemical investigations. XVIII.**

$\text{K}_2(\text{B}_2\text{H}_6)$  and  $\text{K}_2(\text{B}_2\text{H}_4[\text{OH}]_2)$ . L. KLEMM and W. KLEMM. XIX. Magnetic behaviour of potassium polyoxides and polysulphides. W. KLEMM and H. SODOMANN (*Z. anorg. Chem.*, 1935, 225, 258—261, 273—280; cf. A., 1935, 1312).—XVIII. Magnetochemical measurements support the above formulæ in preference to  $\text{KBH}_3$  and  $\text{KBH}_2\cdot\text{OH}$ .

XIX. Magnetochemical data do not suffice to differentiate between the formulæ  $\text{K}_2\text{O}_4$  and  $\text{KO}_2$ . The diamagnetic susceptibilities of  $\text{K}_2\text{S}$ ,  $\text{K}_2\text{S}_2$ ,  $\text{K}_2\text{S}_3$ ,  $\text{K}_2\text{S}_4$ , and  $\text{K}_2\text{S}_6$  have been determined at room temp. and  $-183^\circ$ .  $\text{K}_2\text{S}_3$  becomes ferromagnetic at  $-50^\circ$ .

F. S. H.

**Principal magnetic susceptibilities of  $\text{K}_3\text{Fe}(\text{CN})_6$ .** J. B. HOWARD (*J. Chem. Physics*, 1935, 3, 813—817).—The calc. magnitudes, anisotropy, and temp. dependence of the principal magnetic susceptibilities are in good agreement with experiment.

The relation of susceptibility to electron spin is discussed.

N. M. B.

**Magnetic susceptibilities of alkali and alkaline-earth halides.** U. VEIHEL (*Ann. Physik*, 1935, [v], 24, 697—713).—The susceptibilities of alkali and alkaline-earth halides and the halogen acids in aq. solution have been determined as a function of concn. The relationship is linear, in agreement with the Wiedemann additive law. The susceptibilities of the individual halides are considered in relation to their total nuclear charges. The results do not agree with Pascal's rule (extension of the Wiedemann law to mol. constituents). The mol. susceptibilities are used to calculate ionic susceptibilities. The effect of temp. on the susceptibilities of NaCl and KI solutions was determined. The temp.—susceptibility curves show only a small deviation from the curve for  $\text{H}_2\text{O}$ . This may be explained by assuming that the susceptibility of the salt does not vary with temp., although it causes an increase in the susceptibility of  $\text{H}_2\text{O}$  owing to a displacement of the equilibrium between the mol. complexes in  $\text{H}_2\text{O}$ .

A. J. M.

**Determination of paramagnetic susceptibilities of crystals of rare earths by measurement of the paramagnetic rotatory power.** J. BECQUEREL (*Compt. rend.*, 1935, 201, 1112—1115).—Measurements with the Et sulphates of Pr, Nd, Dy, and Er verify Van Vleck's prediction that the relation between the magnetisation and the paramagnetic rotation should be independent of temp.

H. J. E.

**Thermo-electric effect according to the new electron theory.** M. SATO (*Sci. Rep. Tôhoku*, 1935, 24, 523—536).—Mathematical.

J. W. S.

**Thermo-electric power, Peltier heat, and photo-potential of the element copper-cuprous oxide-copper.** G. MÖNCH (*Physikal. Z.*, 1935, 36, 755—757).—The deductions which can be made from the thermo-electric power, Peltier effect, and photo-potential of an element including a semi-conductor concerning the mechanism of conduction are discussed.

A. J. M.

**Diffraction of light by high-frequency sound waves. I, II.** C. V. RAMAN and N. S. N. NATH (*Proc. Indian Acad. Sci.*, 1935, 2, A, 406—412, 413—420).—Mathematical.

N. M. B.

**Propagation of ultrasonic waves in liquid media.** R. LUCAS (*Compt. rend.*, 1935, 201, 1172—1174).—Diffusion may account for the rapid diminution in amplitude of ultrasonic waves in liquid media.

T. G. P.

**Critical phenomena.** V. JACYNA (*Z. Physik*, 1935, 97, 669—670).—The indistinct crit. state of He is not due to impurities, but to the crit. point being a fiction applicable only to an unattainable ideal physical substance.

A. B. D. C.

**Entropy of deuterium.** K. CLUSIUS and E. BARTHOLOMÉ (*Z. physikal. Chem.*, 1935, B, 30, 258—264).—At  $298.1^\circ$  abs. the entropy calc. from thermal data is  $33.91_5$ , whilst the statistically calc. abs. val. is  $38.98_4$  g.-cal. per mol. per degree. The difference between these vals. may be accounted for by supposing that on cooling at  $10^\circ$  abs. the equilibrium between

*o*- and *p*-forms is "frozen in," but that down to 10° *p*-D<sub>2</sub> mols. rotate freely in the lattice with  $j_{rot}=1$ , the nuclear spin multiplicity of the *o*- and *p*-mols. being maintained. For practical thermodynamic calculations the abs. val. 34.62<sub>0</sub> should be used. At low temp. the chemical consts. of *o*-D<sub>2</sub> and normal D<sub>2</sub> and the v.-p. const. of normal D<sub>2</sub> are -0.68<sub>1</sub>, -0.522, and -0.67<sub>0</sub>, whilst above 200° abs. the chemical const. of *o*-D<sub>2</sub> and the v.-p. const. of normal D<sub>2</sub> are -2.61<sub>5</sub> and -2.76<sub>3</sub>, respectively. R. C.

**F.p. of organic compounds. XV. Esters of the fatty acids.** R. BILTERYS and J. GISSELEIRE (Bull. Soc. chim. Belg., 1935, 44, 567—586).—B.p., m.p., *d*, coeff. of expansion, viscosity, fluidity, surface tension, *n*, and mol. refractivity data are tabulated for *n*-heptioic acid, *n*-hexyl and *n*-heptyl alcohol, the Me, Pr<sup>a</sup>, Bu<sup>a</sup>, and *n*-C<sub>5</sub>H<sub>11</sub> esters of *n*-hexoic, *n*-heptioic, and *n*-octoic acids, and *n*-hexyl, *n*-heptyl, and *n*-octyl formate, acetate, propionate, *n*-butyrate, *n*-valerate, *n*-hexoate, *n*-heptoate, and *n*-octoate. The variation of the m.p. with the no. of C in the alcohol and acid radicals respectively is discussed. R. S.

**Relation between b.p., m.p., and mol. wt.** V. K. NIKIFOROV, N. V. ISMAILOV, and S. S. SANDO-MIRSKI (J. Chim. phys., 1935, 32, 670—677).—Statistical formulæ are deduced relating the b.p. and m.p. of org. compounds of mol. wt. 100—300 with the mol. wt. The formula  $T^2/M = \text{const.}$  holds for the alcohol and paraffin series. J. W. S.

**Normal reduced b.p.** R. LAUTIÉ (Bull. Soc. chim., 1935, [v], 2, 2234—2235).—The formula  $4T_c/T_c + 10T_c/T_c = 12.69$  ( $T_c = \text{crit. temp.}$  and  $T_c = \text{b.p. abs.}$ ) has been verified for a large no. of compounds of different types, within 0.3%. Hg and He are exceptions. F. L. U.

**International Bureau of Physico-chemical Standards. VII. Physical constants of twenty organic compounds.** J. TIMMERMANS and (MME.) HENNAUT-ROLAND (J. Chim. phys., 1935, 32, 589—617; cf. A., 1934, 480).—The following data for b.p./760 mm., m.p., and  $d^{15}$  have been determined: MeOBz 199.50°, -12.4°, 1.09334; EtOBz 212.45°, -34.7°, 1.05112; PhCN 191.10°, -13.8°, 1.00948; NH<sub>2</sub>Ph 184.40°, -6.1°, 1.02613; NPhMe 196.25°, -, 0.99018; NPhMe<sub>2</sub> 194.15°, 2.45°, 0.96012; *o*-200.40°, -16.4°, 1.00279, and *m*-toluidine 203.40°, -31.25°, 0.99302; PhNO<sub>2</sub> 210.80°, 5.70°, 1.20824. Other data recorded include the variation of b.p. with pressure, coeffs. of dilatation,  $r_v^{15}$ , viscosity coeffs., surface tensions, and crit. solution temp. in suitable solvents. Previous data are tabulated. J. W. S.

**B.p. of normal paraffin series.** E. R. COX (Ind. Eng. Chem., 1935, 27, 1423—1425).—From C<sub>3</sub>H<sub>8</sub> to C<sub>8</sub>H<sub>18</sub> (except C<sub>4</sub>H<sub>10</sub>) results calc. from  $\log_{10} B = 1.07575 + 0.949128 \log_{10} m - 0.101 \log_{10}^2 m$  ( $B = \text{b.p. abs.}$ ;  $m = \text{mol. wt.}$ ) agree with observation. Disagreement in the cases of CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> is attributed to their not being true aliphatic compounds (cf. Rossini, A., 1934, 1071). J. W.

**Specific heat of iron carbide, Fe<sub>3</sub>C.** G. NAESER (Mitt. Kaiser-Wilh. Inst. Eisenforsch., 1934, 16,

207—210; Chem. Zentr., 1935, i, 2325).—The mean sp. heat (*h*) of cementite, obtained electrolytically from Fe with 0.9% C, has been measured between -188° and 765°. *h* reaches a max., nearly const. val. at 250°. The heat of formation and of the magnetic transformation are calc. J. S. A.

**Heat capacity of gadolinium sulphate from 1.0° to 20.5° abs.** C. W. CLARK and W. H. KEESOM (Physica, 1935, 11, 1075—1079).—The anomalous thermal behaviour of Gd<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·8H<sub>2</sub>O observed by Kurti (A., 1933, 449) was verified down to 1° abs. H. J. E.

**Phase equilibria in hydrocarbon systems. IX. Specific heats of *n*-butane and -propane.** B. H. SAGE and W. N. LACEY (Ind. Eng. Chem., 1935, 27, 1484—1488).—*c* was determined for both compounds in the gaseous and the condensed state; both *c<sub>p</sub>* and *c<sub>v</sub>* were determined. Apparatus is described. J. W.

**Calorimetric and thermal properties of condensed deuterium.** K. CLUSIUS and E. BARTHOLOMÉ (Z. physikal. Chem., 1935, B, 30, 237—257).—The following data are recorded: latent heat of vaporisation at 194.5 mm., 302.3; heat of sublimation at 0° abs., 274.0; latent heat of fusion 47.0 g.-cal.; characteristic temp. of Debye function for *c<sub>p</sub>*, 89°; m.p., 18.65° abs.; slope of fusion curve at triple point, 40.5 kg. per sq. cm.; mol. vol. of liquid at triple point, 23.14; mol. vol. of solid at triple point, 20.48 c.c.; zero-point energy of lattice, ~215 g.-cal. The considerable differences between these vals. and the corresponding figures for H<sub>2</sub> are qualitatively accounted for if it is assumed that H<sub>2</sub> and D<sub>2</sub> have the same intermol. forces but different zero-point energies and anharmonicities of lattice vibration. R. C.

**Absolute zero, and the sub-zero region of temperatures and reactions.** P. N. PAVLOV (Ukrain. Chem. J., 1935, 10, 285—294).—Theoretical. The possibility of temp. < 0° abs. is envisaged, and the properties of matter in this region are discussed. R. T.

**Theory of the equation of state.** S. RAY (Kolloid-Z., 1935, 73, 269—272).—Ray's theory (A., 1931, 1117) is extended to saturated vapours and the liquid phase. E. S. H.

**Vapour pressures of some alkyl sulphides.** H. W. THOMPSON and J. W. LINNETT (Trans. Faraday Soc., 1935, 31, 1743—1747).—The v.p. of EtSH, Me<sub>2</sub>S, MeEtS, and Et<sub>2</sub>S have been determined at several temp. up to the b.p. The vals. of Trouton's const. deduced are normal, indicating non-association. J. W. S.

**Vapour pressure of drops.** S. V. GORBATSCHEV (Kolloid-Z., 1935, 73, 263—267).—Mathematical. E. S. H.

**Influence of degree of dispersion on physico-chemical constants.** V. E. COHEN and J. J. A. BLEKKINGH, jun. (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 978—982; cf. this vol., 20).— $d^{25}$  for *o*-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H is 1.4340, independently of crystal size between 0.01 and 1 mm. J. W. S.

**Fluctuations in density at the critical point.** J. YVON (Compt. rend., 1935, 201, 1099—1102).—Theoretical. H. J. E.

**Röntgenographic thermal expansion of very pure sodium chloride.** W. RECK and A. SMEKAL (Helv. phys. Acta, 1934, 7, 876; Chem. Zentr., 1935, i, 2783).—Measurements between  $-175^{\circ}$  and  $725^{\circ}$  show uniform expansion. Saini's anomaly (A., 1935, 436) is illusory. J. S. A.

**Thermal expansion of rock-salt and of pure sodium chloride.** H. SAINI (Helv. phys. Acta, 1934, 7, 877; Chem. Zentr., 1935, i, 2783).—The conclusion of Reck and Smekal (cf. preceding abstract) is acknowledged. J. S. A.

**Joule-Thomson effect of methane, nitrogen, and their mixtures.** J. H. PERRY and C. V. HERRMANN (J. Physical Chem., 1935, 39, 1189—1195).—Joule-Thomson coeffs. of  $\text{CH}_4$ ,  $\text{N}_2$ , and of 25, 50, and 75% mixtures at five temp. are calc. from the Beattie-Bridgeman equation. F. L. U.

**Viscosity and constitution of organic liquids.** S. PAPKOV (Z. physikal. Chem., 1935, 174, 445—448).—For an org. compound the val. of  $S = M \sqrt[3]{\eta/d}$ , where  $M$  is the mol. wt. and  $d$  the viscosity,  $\eta$ , are for  $20^{\circ}$ , is additively made up of characteristic vals. for the constituent atoms. Degrees of association of various liquids have been calc.  $S$  varies with temp. R. C.

**Square root law of fluidity. I. Hydrocarbons.** R. LAURIE (Bull. Soc. chim., 1935, [v], 2, 2187—2192; cf. A., 1935, 1064).—The law proposed is  $\sqrt{\phi_t} = \sum I_i$ , where  $\phi$  is the fluidity at  $t^{\circ}$ , and  $I_i$  denotes increments appropriate to the atoms, types of linking, etc. in the compound considered. Examples are given for saturated and unsaturated cyclic hydrocarbons, and for paraffins. For mixtures of normal liquids of not too low or too high viscosity ( $\eta$ ), which show little vol. change on mixing, the law  $100\sqrt{\eta} = \sum m_x \sqrt{\eta_x}$  (where  $m_x$ ,  $\eta_x$  indicate the mol.-% and viscosity coeff. of the several constituents) applies closely. F. L. U.

**Viscosity in the system chlorine-sulphur.** V. A. MAZEL (J. Gen. Chem. Russ., 1935, 5, 1066—1072).—The  $\eta$ -composition curves of the system  $\text{Cl}_2$ - $\text{SCl}_2$  have been studied at  $-15^{\circ}$ ,  $0^{\circ}$ , and  $25^{\circ}$ . R. T.

**Viscosity of the system  $\text{KAlSi}_3\text{O}_8$ - $\text{NaAlSi}_3\text{O}_8$  and of perthite at high temperatures.** K. KANI (Proc. Imp. Acad. Tokyo, 1935, 11, 324—336).—The data refer to  $1300$ — $1450^{\circ}$  and the entire range of concns. of the system  $\text{KAlSi}_3\text{O}_8$  (I)- $\text{NaAlSi}_3\text{O}_8$ . Log  $\eta$  increases with concn. of (I), and the slope of the line connecting log  $\eta$  and temp. is the same for all mixtures. J. G. A. G.

**Thermal expansion of the binary system  $\text{Na}_2\text{B}_4\text{O}_7$ - $\text{B}_2\text{O}_3$  in the molten state.** M. P. VOLAROVITSCH (Acta Physicochim. U.R.S.S., 1935, 2, 695—710; cf. A., 1935, 24).—The sp. vols. of  $\text{Na}_2\text{B}_4\text{O}_7$ - $\text{B}_2\text{O}_3$  melts have been determined between  $500^{\circ}$  and  $1200^{\circ}$  in a Pt-Ir dilatometer. Fluidity varies linearly with temp. above  $820^{\circ}$ ; the large divergence at lower temp. is attributable to association. T. G. P.

**Dipole induction and the solvent effect in dipole moment measurements.** F. C. FRANK (Proc. Roy. Soc., 1935, A, 152, 171—196).—On the

basis of Weigle's formula (A., 1934, 12), a theory is developed to account for the effect of the solvent on the measured val. of the dipole moment of a solute. Examples of solvent effect are classified according to mol. geometry. The empirical laws advanced by Müller (A., 1932, 1077) and others apply only to a single class. The theory leads to important conclusions regarding dipole induction in radicals forming part of the polar mol.; in general, the more positive is the radical effect, the more negative is the solvent effect, and vice versa. The attraction of solvent mols. by dipole forces, the effect of anisotropic anisotropic polar solvents, the bearing of the dielectric constant of aq. solutions on the structure of zwitterions, and the form of the dispersion curve in polar liquids are discussed in the light of the above theory. L. L. B.

**Dielectric polarisation and molecular-compound formation in solution. I. Structures of the compounds of ethers with halogeno-methanes and -ethanes. II. Structures of the compounds of acetone, quinoline, and dioxan with halogenomethanes.** D. P. EARP and S. GLASSTONE (J.C.S., 1935, 1709—1719, 1720—1723).—I. The dielectric polarisations of binary mixtures of  $\text{Et}_2\text{O}$ ,  $\text{Pr}^n\text{O}$ , and  $(\text{CH}_2\text{Cl}-\text{CH}_2)_2\text{O}$  with halogen derivatives of  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  have been determined. The molecular polarisations of the constituents suggest that compound formation in such mixtures involves the introduction of a new co-ordinate linking, which contributes to the dipole moment. A method for calculating the proportion of compound present has been developed. In compounds of the type  $\text{R}_2\text{O}\cdot\text{CHX}_3$ , co-ordination occurs between O and H attached to C. When chemical interaction does not occur, polarisations are additive, even in mixtures of two polar substances, when allowance is made for variation of dielectric const.

II. Compound formation occurs which is analogous to that observed with ethers. The nature of the linking, which generally involves co-ordination with H, is discussed. E. S. H.

**Dipole theory of solutions.** N. BARBULESCU (J. Chim. phys., 1935, 32, 639—656).—The theory described leads to a formula for the osmotic pressure which corresponds with van der Waals' equation. Deviations of real from ideal solutions at high concn. are explained by mol. polarisation, the existence of permanent electric moment causing deactivation of the solute in some cases and of the solvent in other cases. The formulæ are verified by experiment for mixtures of  $(\text{CH}_2\text{Cl})_2$  and  $\text{C}_6\text{H}_6$ ,  $\text{CCl}_4$  and  $\text{C}_6\text{H}_6$ ,  $\text{O}_2$  and  $\text{N}_2$ ,  $\text{EtOAc}$  and  $\text{EtI}$ ,  $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$  and  $\text{Et}_2\text{O}$ , and for  $\text{CHCl}_3$  and  $\text{COMe}_2$ . J. W. S.

**Surface tensions of binary liquid mixtures containing benzene.** J. W. BELTON (Trans. Faraday Soc., 1935, 31, 1642—1648).—The surface tensions of  $\text{C}_6\text{H}_6$ - $\text{AcOH}$  and  $\text{C}_6\text{H}_6$ - $\text{CS}_2$  mixtures have been measured at  $20^{\circ}$  and  $35^{\circ}$  and those of  $\text{C}_6\text{H}_6$ - $\text{CCl}_4$  mixtures at  $50^{\circ}$ , the surface adsorption being calc. from Gibbs' equation. The adsorbed layer is always  $<$  unimol. and varies with concn. Only with  $\text{C}_6\text{H}_6$ - $\text{AcOH}$  mixtures of low  $[\text{C}_6\text{H}_6]$  is  $\text{C}_6\text{H}_6$  adsorbed. J. W. S.



**Surface tensions of ternary solutions. III.** J. W. BELTON (Trans. Faraday Soc., 1935, 31, 1648—1652; cf. A., 1935, 1316).—The surface tensions of solutions containing sucrose and NaCl, HCl and NaCl, and HCl and KCl have been measured and the surface adsorption of H<sub>2</sub>O is calc. The adsorption for sucrose and NaCl is  $\ll$  the sum of the adsorptions which each solute produces separately, but a [HCl] which has inappreciable effect on the surface tension of H<sub>2</sub>O greatly decreases the adsorption of H<sub>2</sub>O on a salt solution. J. W. S.

**Calculation of various physical constants of heterogeneous substances. I. Dielectric constants and conductivities of mixtures of isotropic substances.** D. A. G. BRUGGEMAN (Ann. Physik, 1935, [v], 24, 636—664).—Theoretical. Dielectric consts. and thermal and electrical conductivities are calc. by a unitary method from the consts. of the homogeneous constituents of the mixture. The accuracy of older formulæ is discussed and previously undetermined consts. in these formulæ are evaluated. W. R. A.

**Calculation of various physical constants of heterogeneous substances. I (cont.). Dielectric constants and conductivities of mixtures of isotropic substances.** D. A. G. BRUGGEMAN (Ann. Physik, 1935, [v], 24, 665—679).—The above theory is applied to the conductivity of binary heterogeneous alloys. For Pt-Ag alloys the experimental results are in qual. agreement with theory. The dielectric consts. of compressed powdered KCl (KCl-air mixture) and of emulsions are considered in the light of the new theory. For salt-air mixtures experiment agrees with theory, but Piekara's results on emulsions of small concn. are best explained by the Rayleigh formula, although more conc. emulsions would probably be covered by the new theory. A. J. M.

**Vapour pressure of solutions of acids and salts in liquid ammonia at 15°.** A. I. SCHATTENSTEIN and L. S. USKOVA (Acta Physicochim. U.R.S.S., 1935, 2, 337—344; cf. A., 1934, 838).—The v.p. and *d* of solutions of NH<sub>4</sub>Cl, NH<sub>4</sub>Br, NH<sub>4</sub>I, NH<sub>4</sub>NO<sub>3</sub>, NH<sub>4</sub>OAc, NaCl, and NaNO<sub>3</sub> in liquid NH<sub>3</sub> have been determined for wide ranges of concn. at 15°, and for the NaCl solutions also at 10°. The osmotic coeffs. of these solutes follow the order NH<sub>4</sub>I > NH<sub>4</sub>NO<sub>3</sub> > NaNO<sub>3</sub> > NH<sub>4</sub>Br > NaCl > NH<sub>4</sub>Cl > NH<sub>4</sub>OAc. J. W. S.

**Numerical relationships in binary metallic systems.** D. STOCKDALE (Proc. Roy. Soc., 1935, A, 152, 81—104).—The work of Hume-Rothery and others on the depression of the f.p. and m.p. of Cu and Ag by the addition of elements of the B sub-groups, and the solubility limits in these alloys (A., 1934, 725), are discussed. It is shown that there are probably other simple integral relationships between the no. of atoms in a binary alloy, and the following empirical rules are adduced: (a) the solute and solvent atoms are present in a simple integral ratio in a saturated solid solution at the temp. of the eutectic or peritectic horizontal; (b) in a eutectic mixture the elements are present in a simple integral at. ratio; (c) in a eutectic mixture the ratio of the no. of atoms, irrespective of their kind, in the phases is

simple. It is improbable that rules (b) and (c) are both exact, but if either is true, then, in seven systems investigated, the other is true to within 1 part in 200.

L. L. B.

**Effect of thermal agitation on atomic arrangement in alloys. III.** E. J. WILLIAMS (Proc. Roy. Soc., 1935, A, 152, 231—252; cf. this vol, 24).—Mathematical. The equilibrium equations for a general case are derived from the Boltzmann distribution formula and from the principle of min. free energy. By comparing the dependence of the entropy of the at. arrangement on the order of nearest neighbours with its dependence on the superlattice order, the quant. relation of Bethe's treatment (A., 1935, 1193) to that of Bragg and Williams (*loc. cit.*) becomes evident. L. L. B.

**Methods of investigating the constitution [of alloys].** G. GRUBE (Z. Metallk., 1935, 27, 194—195).—Dilatometric and magnetometric methods are briefly described and a detailed description is given of a delicate apparatus for measuring the magnetic susceptibility of metals at temp. up to 1400°; it consists of a micro-electric furnace in the middle of two inclined poles of a powerful electro-magnet, the specimen being suspended in the furnace by means of a lever system the movement of which is compensated for by a small coil, the current through which, measured by a milliammeter, is  $\propto$  the susceptibility. A. R. P.

**Relation between diffusion and structure in solid alloys.** W. SEITH and A. KEIL (Z. Metallk., 1935, 27, 213—215).—In alloys which form homogeneous solid solutions  $\log D = A - Q/RT$ , where *D* is the rate of diffusion and *A* and *Q* are material consts., *Q* being the equiv. of the heat of activation in chemical reactions. The diffusion of small amounts of one metal into another takes place the more readily the greater is the amount of distortion produced and less readily the greater the tendency to form solid solutions; the addition of metals which reduce the m.p. of the base metal increases the rate of diffusion in this metal. Transformation and recrystallisation, as well as the passage of a d.c. through the alloy, increase the rate of diffusion, the effect of the current being due to electrolytic transport. A. R. P.

**Electrical conductivity and equilibrium diagram for binary alloys. XVII. System lithium-aluminium.** G. GRUBE, L. MOHR, and W. BREUNING (Z. Elektrochem., 1935, 41, 880—883; cf. A., 1935, 23).—The solid phases in the successive ranges are: 0—30 at.-% Li,  $\alpha$ -mixed crystals; 30—60%, LiAl; 60—78%,  $\beta$ -mixed crystals of LiAl with excess of Li; 78—100%, compound Li<sub>2</sub>Al. Between 44.5 and 60.0 at.-% of Li at 698° there are two liquid phases. F. L. U.

**Constitution and properties of iron-carbon-beryllium alloys.** M. BALLAY (Compt. rend., 1935, 201, 1124—1126).—The effect of Be (0—4%) on an alloy with C 3—4.45, Mn 0.25, Si 0.25, S 0.02, and P 0.05% is reviewed. Be<sub>2</sub>C is almost insol. in austenite. The temp. of the Ac transformation is only slightly affected by Be. Data for the hardness of a series of these alloys are given. H. J. E.

**X-Ray analysis of the homogeneous phase in the system Mg-Ni.** E. F. BACHMETEV (*Acta Physicochim. U.R.S.S.*, 1935, 2, 567—570).—Preliminary. Two hexagonal homogeneous phases have been observed, one of which (I), probably  $Mg_3Ni$ , has  $a$  5.26,  $c$  about 13.3 Å., whilst the other (II) has  $a$  4.87,  $c$  about 16 Å. The unit cell of (I) contains 16, and of (II) 48, atoms. F. L. U.

**Is an intermetallic homogeneous phase formed in the system Mg-Mn?** E. F. BACHMETEV and J. M. GOLOVTSCHINER (*Acta Physicochim. U.R.S.S.*, 1935, 2, 571—574).—Preliminary. Crystals separating from a Mg-Mn alloy containing 36—51 at.-% Mn have cubic symmetry, and X-ray examination indicates that they consist of  $\beta$ -Mn. F. L. U.

**Modified aluminium-silicon alloys. II.** J. A. KLJATSCHKO (*J. Gen. Chem. Russ.*, 1935, 5, 1299—1301).—The silicide content of Si-Al alloys is reduced from 0.4 to 0.2% by treatment with Na. R. T.

**Physico-chemical investigation of the gold-manganese alloys.** V. A. NEMILOV and A. A. RUDNICKI (*Compt. rend. Acad. Sci. U.R.S.S.*, 1935, 3, 351—354).—The thermal properties, hardness, and electrical resistance of Au-Mn alloys have been investigated. AuMn exists in the molten alloy, whilst  $AuMn_3$  and  $Au_3Mn$  separate from the solid solutions formed on cooling. R. S.

**Nickel-manganese system. II.** S. VALENTINER (*Z. Physik*, 1935, 97, 745—757).—The electrical resistance in magnetic fields shows that alloys with 25—30% of Mn are abnormal (cf. A., 1935, 576). A. B. D. C.

**Mechanism of precipitation [in silver-copper alloys].** U. DEHLINGER (*Z. Metallk.*, 1935, 27, 209—212).—The particles of Ag which first separate during the decomp. of a quenched supersaturated solid solution of Ag in Cu do not act as nuclei for further pptn. The process of pptn. must therefore be propagated by lattice distortion probably at the boundaries of mosaic blocks. At these points thin films of Ag first separate and gradually coalesce into grains which are visible under the microscope. After deformation and recrystallisation decomp. of the solid solution is accelerated, probably owing to the concn. of an "active factor" at the boundaries of regions in which pptn. has already commenced. A. R. P.

**System copper-nickel-iron.** W. KÖSTER and W. DANNOHL (*Z. Metallk.*, 1935, 27, 220—226).—The system has been investigated by thermal, magnetometric, and electrical resistance methods. The  $\alpha$ - $\gamma$  transformation occurs in all alloys the composition of which lies on the Fe side of a straight line joining the Cu corner of the ternary diagram to the 28% Ni point on the Fe-Ni side. The miscibility gap in the Fe-Cu system is gradually closed by addition of Ni and disappears entirely with 27% Ni at 1220° and with 82% Ni at 20°; alloys within this range are therefore amenable to pptn.-hardening, and such treatment gives rise to interesting magnetic properties. The equilibria in the system are showed in ternary diagrams and in numerous sectional diagrams for const. Ni contents and const. Fe : Cu ratio. A. R. P.

**X-Ray analysis of crystal formation in the ternary system Cu-Al-Ti.** E. F. BACHMETEV, N. G. SEVASTIANOV, and N. I. KOTOV (*Acta Physicochim. U.R.S.S.*, 1935, 2, 561—566).—In an alloy of composition Cu 40, Al 40, Ti 20 wt.-%, a preliminary examination has established the existence of two homogeneous phases, viz., cubic, with  $a$  3.94 (or 7.88) Å., and hexagonal, with  $a$  5.05,  $c$  8.06 Å. F. L. U.

**Magnetic investigations of precipitation-hardening.** H. AUER (*Physikal. Z.*, 1935, 36, 880—882).—The mechanism of the improvement of the mechanical properties of an alloy by suitable heat-treatment whereby a new phase is produced is discussed. The variation of susceptibility,  $\chi$ , of Cu-Al alloys during such a process is determined. There is a considerable decrease in  $\chi$  during the transition, and this fact can be used to follow the velocity of transition under different conditions of temp., concn., supersaturation, and previous heat-treatment. The mean transition velocity,  $u$ , is connected with abs. temp.,  $T$ , by  $\log u = A/T + B$  ( $A$  and  $B$  const.). The final val. of  $\chi$  depends in a discontinuous manner on the tempering temp. The points at which the discontinuities occur give points on the diagram of state. The val. of  $\chi$  shows that the separating phase is  $CuAl_2$ . An extended Curie law holds for the alloys when equilibrium is attained, but the considerable deviations found at the transition point are to be connected with supersaturation in the mixed crystal phase. A. J. M.

**Rate of diffusion in metallic crystals and atomic structure.** W. SEITH (*Z. Elektrochem.*, 1935, 41, 872—876; cf. A., 1935, 158, 1205).—The rates of diffusion of metals in solid Pb show the same dependence on their at. radius and no. of valency electrons as do their solubilities. F. L. U.

**Shape of critical temperature curves of binary systems.** R. V. MERZLIN (*J. Gen. Chem. Russ.*, 1935, 5, 1073—1076).—Stachorski's formula (A., 1928, 472) corresponds more closely with experimental surface tension data than do those of Pawlewski (A., 1882, 915; 1883, 176) or Strauss (Ber., 1881, 14, 510). R. T.

**Desaturation experiments on aqueous carbonic acid.** Y. KAUKO and H. KOMMUSAR (*Ann. Acad. Sci. fenn.*, 1934, A, 39, No. 8; *Chem. Zentr.*, 1935, i, 2767).—With good mixing of gas and liquid, the rates of saturation and desaturation of  $CO_2$  in  $H_2O$  are reproducible. J. S. A.

**Solubility of lime in water.** G. L. LAROCQUE and O. MAASS (*Canad. J. Res.*, 1935, 13, B, 276—279; cf. A., 1933, 897).—Conductivity data at 0—30° are given for a series of  $Ca(OH)_2$  solutions. Vals. for the solubility and degree of dissociation of  $Ca(OH)_2$  are calc. Equilibrium between aq. solutions and solid  $Ca(OH)_2$  is established very slowly. H. J. E.

**Solubilities of *l*-proline and *l*-hydroxyproline in water, the calculated heats of dissolution, and the partial molal volume of *l*-hydroxyproline.** T. TOMIYAMA and C. L. A. SCHMIDT (*J. Gen. Physiol.*, 1935, 19, 379—382). F. A. A.

**Solubilities of certain salts in liquefied ammonia. III. Solubility of ammonium chloride,**

and vapour pressure of the solution. S. ABE, K. WATANABE, and R. HARA (J. Soc. Chem. Ind. Japan, 1935, 38, 642—646b).—Solid phases in the  $\text{NH}_4\text{Cl}-\text{NH}_3$  system are  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Cl}\cdot 3\text{NH}_3$ , which coexist at  $5.9^\circ$ . Solubilities between  $-20^\circ$  and  $25^\circ$  are recorded, and also v.p. of the saturated and unsaturated solutions. Heats of dissolution are calc.

J. S. A.

Absorption of hydrogen sulphide and sulphur dioxide from a current of air. V. A. PIANKOV (J. Gen. Chem. Russ., 1935, 5, 1112—1118).—The velocity of adsorption of  $\text{H}_2\text{S}$  by wood C is doubled at  $20^\circ$ , and quadrupled at  $40^\circ$ , by treatment with I, whilst for  $\text{SO}_2$  it is increased 1.8 times at  $20^\circ$  and  $40^\circ$ .

R. T.

Distribution of hydrogen sulphide between benzene and water. S. A. SCHTSCHUKAREV and I. B. CHACHAM (J. Gen. Chem. Russ., 1935, 5, 1056—1058).—The high vals. of the partition coeff. of  $\text{H}_2\text{S}$  between  $\text{C}_6\text{H}_6$  and  $\text{H}_2\text{O}$  are ascribed to anomalously low solubility in  $\text{H}_2\text{O}$ .

R. T.

Distribution of (A) saturated monocarboxylic fatty acids between glycerol and other organic solvents, (B) hexoic acid between two contiguous liquid phases. N. A. DE KOLOSOVSKI (J. Gen. Chem. Russ., 1935, 5, 1041—1044, 1048—1055).—(A) [with F. S. KULIKOV]. Data are recorded for  $\text{EtCO}_2\text{H}$  with  $\text{CHCl}_3$  and for  $\text{Bu}^n\text{CO}_2\text{H}$  with  $\text{CHCl}_3$ ,  $\text{PhMe}$ , and  $\text{PhNO}_2$ , at  $25^\circ$ .

(B) [with M. O. LEVITAS]. Data are recorded for the systems  $\text{H}_2\text{O}-\text{C}_6\text{H}_6$ ,  $-\text{PhMe}$ ,  $-\text{decahydronaphthalene}$ ,  $-\text{CCl}_4$ ,  $-\text{MeI}$ ,  $-\text{PhBr}$ ,  $-\text{PhOMe}$ , and  $-\text{PhNO}_2$ , at  $25^\circ$ . The val. of 1/partition coeff. approaches the same figure when the concn. of hexoic acid in the entire system approaches 7.8 g.-equiv. per litre.

R. T.

Points of intersection of curves representing distribution of solutes between two liquid phases. N. A. DE KOLOSOVSKI (J. Gen. Chem. Russ., 1935, 5, 1045—1047).—The curves connecting the total concn. of  $\text{Bu}^n\text{CO}_2\text{H}$  with the partition coeff. between a no. of org. solvents and  $\text{H}_2\text{O}$  intersect at the origin and at another point. The phenomenon is shown to be general when the solubility of the solute is unlimited in one, and limited in the other, solvent.

R. T.

A partition paradox. N. A. DE KOLOSOVSKI and F. S. KULIKOV (J. Gen. Chem. Russ., 1935, 5, 1037—1040).—It is shown mathematically that the concn. of a solute in each layer of a binary liquid mixture may increase as the result of the addition of a small amount of one of the solvents, owing to changes in the mutual solubility of the solvents themselves.

R. T.

Sorption of sulphur dioxide by active charcoal. VI. Rate of sorption. K. ARII (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 1210—1232; cf. A., 1935, 577).—Rates of sorption and desorption determined between  $-20^\circ$  and  $-40^\circ$  are in agreement with Bangham's equation.

R. S.

Heterogeneous catalysis. II. Adsorption on graphite and diamond. E. STORFER (Z. Elektrochem., 1935, 41, 868—872; cf. A., 1935, 696).—Adsorption isotherms have been determined for  $\text{N}_2$ ,

$\text{CH}_4$ ,  $n\text{-C}_6\text{H}_{14}$ , cyclohexane, and  $\text{C}_6\text{H}_6$  on graphite and diamond at  $155^\circ$  and  $205^\circ$ . The first two exhibit stepped adsorption at low pressures, and are adsorbed in quantities approx.  $\propto$  the sp. surface. The three last are adsorbed by graphite more strongly than can be accounted for by its higher sp. surface. Heats of adsorption are calc.

F. L. U.

Van der Waals, activated, and atomic adsorption of hydrogen on copper and nickel, and their influence on the photo-effect. O. I. LEIPUNSKI (Acta Physicochim. U.R.S.S., 1935, 2, 737—760).—The adsorption of  $\text{H}_2$  on Cu and Ni has been investigated. The presence of a steric factor (Leipunski, A., 1935, 578) is generally characteristic of activated adsorption, which therefore involves a diffusion process, contrary to other views (cf. Taylor *et al.*, A., 1934, 1181). There is no activated adsorption on Cu which has been distilled in vac. or has been once oxidised and then reduced. Ni adsorbs  $\text{H}_2$  by two different processes according to the temp. The heats of adsorption are 4, 13, and 16—17 kg.-cal. per mol. at  $-183^\circ$ ,  $0^\circ$ , and  $100^\circ$ , respectively. At the higher temp. the activation energy is 3 kg.-cal. per mol. The surface of Ni is not homogeneous and only 10% of it is active. The activated adsorption at low temp. is a localised phenomenon, and each active area is heterogeneous. Neither adsorption process influences the photo-effect. At. H is adsorbed by Cu and Ni at  $-183^\circ$  to an extent corresponding with a layer 3 mols. thick. The kinetics of desorption of at. H from Ni at  $-106^\circ$  suggest that the process may be due to recombination of atoms in the surface followed by desorption of the mols. The energy of activation of the surface diffusion process is 23.8 kg.-cal. per mol.

T. G. P.

Adsorption of indium and thallium atoms on tungsten oxide. C. F. POWELL and R. L. MERCER (Phil. Trans., 1935, A, 235, 101—124).—The adsorption and desorption of In and Tl atoms have been studied thermionically on a film of  $\text{WO}_3$  on W,  $10^{-4}$  cm. thick, at  $656-765^\circ$ . The condensation coeff. is independent of the fraction of surface covered ( $\theta$ ) and of the temp., and is probably 1. In contrast with the behaviour of Cs on W, the adsorbed phase is always uniform. From the ratio ( $r$ ) of positive ion to neutral atom emission the electronic work function ( $V$ ) of a bare surface is calc. to be 6.13 and 6.25 volts, using In and Tl, respectively. Surface migration and diffusion into the interior of the oxide film have been studied at approx.  $200^\circ$  below emission temp. The ratio  $r$  increases with  $\theta$ , and  $V$  for the partly covered surface decreases linearly with increasing  $\theta$ . The ratio of the dipole moments associated with adsorbed Tl and In is 0.80. Similar experiments with Ga are not possible, since this is too strongly adsorbed, and appreciable emission occurs only at temp. at which  $\text{WO}_3$  decomposes; Ga acts as a poison towards the adsorption of In and Tl. The oxides of Ni, U, Fe, and Mo have been studied as sources of positive ions,  $\text{Fe}_2\text{O}_3$  being most similar to  $\text{WO}_3$ .

R. S. B.

Sorption and diffusion of ammonia in analcime. A. TISELIUS (Z. physikal. Chem., 1935, 174, 401—423; cf. A., 1934, 726).—Langmuir's isotherm is

valid if the amount sorbed is not too great, and this equation yields a val. for the amount of  $\text{NH}_3$  sorbed at saturation which approximates to the val. calc. from the equiv. max.  $\text{H}_2\text{O}$  content; in the temp. range studied ( $302\text{--}385^\circ$ ) this does not vary with temp. The const.  $b$  of the isotherm is  $\propto e^{Q/RT}$ , where  $Q$  is the heat of sorption. Each sorbing centre corresponds with a vol. which is of the order of magnitude of a mol. vibrating in the lattice rather than of a mol. able to move freely in the whole sorption space. The heat of sorption is 16,640 g.-cal. At  $302^\circ$  the diffusion coeff. in a single crystal is  $1.3 \times 10^{-8}$  (sq. cm., sec.). Diffusion apparently takes place by jumps along the canals in which the  $\text{H}_2\text{O}$  mols. are present (cf. *ibid.*, 947) and its rate determines that of the sorption as a whole; the energy of activation is 14,480 g.-cal., irrespective of the direction. R. C.

**Selective adsorption of heavy water.** A. KING, F. W. JAMES, C. G. LAWSON, and H. V. A. BRISCOE (J.C.S., 1935, 1545—1549; cf. A., 1934, 1062).—Steam from London tap- $\text{H}_2\text{O}$  was passed over  $\text{SiO}_2$  gel and various charcoals until equilibrium was attained, and the  $\text{H}_2\text{O}$  fractionally desorbed. The isotopic enrichment ratio, determined by measurement of  $d$ , is greatest (about 1.4) in the last fraction and is independent of the activity of the charcoal. An experiment with pure charcoal and  $\text{H}_2\text{O}$  containing 4% of  $\text{D}_2\text{O}$  gave a similar result, the % of  $\text{D}_2\text{O}$  being determined in this case from the f.p. It is suggested that the difference in the adsorption of  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$  is due to a difference in polarisability. R. S.

**Adsorption of anions by precipitated barium sulphate.** T. P. CHAO, K. H. HSIUNG, and Y. L. CHU (J. Chinese Chem. Soc., 1935, 3, 325—342).—The order of adsorption of anions by  $\text{BaSO}_4$  is  $\text{NO}_3' > \text{ClO}_3' > [\text{Fe}(\text{CN})_6]''' > [\text{Fe}(\text{CN})_6]'' > \text{NO}_2' > \text{CNS}' > \text{Cl}' > \text{Br}'$ . The Schulze-Hardy law is only qualitatively valid. The amount of adsorption is governed by the nature of the ion, its valency, and the solubility of its Ba compound. The less sol. are more strongly adsorbed.  $\text{NO}_3'$  and  $\text{ClO}_3'$  are particularly strongly adsorbed, and their presence in the quant. pptn. of  $\text{SO}_4'$  is to be avoided. A. J. M.

**Absorption of sodium hydroxide by cellulose.** S. M. NEALE (J. Physical Chem., 1935, 39, 1245; cf. A., 1930, 417, 1249).—The concn. of adsorbed aq.  $\text{NaOH}$  removed from cellulose by powerful centrifuging decreases as centrifuging proceeds. This effect is compatible with the assumption that  $[\text{OH}']$  in the adsorbed solution is determined by membrane equilibrium. F. L. U.

**Absorption of dyes by cellulose. VI. Effect of modification of the cellulose and a theory of the electrolyte effect.** J. HANSON, S. M. NEALE, and W. A. STRINGFELLOW (Trans. Faraday Soc., 1935, 31, 1718—1730; cf. A., 1934, 1169).—Increased motion of the absorbent relative to the dye-bath increases the rate of absorption of sky-blue FF considerably in the case of yarns and fabrics and slightly for Cellophane. Swollen cellulose takes up more dye than natural cellulose in a ratio which is independent of the concn. of added  $\text{NaCl}$ . Oxidation of cellulose reduces the absorption of dye, especially

at low  $[\text{NaCl}]$ . These effects are attributed to Donnan equilibria, and a theoretical equation is deduced which is in accord with the observed variation of the absorption with  $[\text{NaCl}]$  and dye concn. An extension of the theory embracing the ionisation of the  $\text{CO}_2\text{H}$  groups of oxycellulose is in qual. agreement with experiment. J. W. S.

**Adsorption of cyclopentanone by cellulose nitrate.** J. DESMAROUX, R. VANDONI, and (MLE.) T. PETITPAS (Compt. rend., 1935, 201, 1392—1393).—The adsorption of cyclopentanone by nitro-cotton (12.13 and 13.52% N) has been examined. It is independent of the N content. R. S. C.

**Adsorption problems. I.** TRAUBE (Trans. Faraday Soc., 1935, 31, 1730—1739).—Anthracene,  $\text{C}_{10}\text{H}_8$ ,  $\text{NHPh}_2$ , phthalic acid, and charcoal, added to aq. solutions of  $\text{C}_8\text{H}_{17}\cdot\text{OH}$  or  $\text{C}_7\text{H}_{15}\cdot\text{CO}_2\text{H}$  adsorb such small quantities of the solute that the Langmuir theory may be applicable, but if such adsorbents are added to  $\text{H}_2\text{O}$ -sol. or  $\text{H}_2\text{O}$ -insol. substances in an emulsified state, the emulsified substances are adsorbed to a very high degree and very firmly. This is attributed to the lower diminution of surface tension produced by colloid particles than by dissolved mols. The adsorption is generally accompanied by flocculation owing to linking of the adsorbent particles through the adsorbed substances, and this flocculation is compared with electrolytic flocculation of colloids by ions, coagulation by gelatinous colloids, and flocculation of ores by surface-active org. substances. J. W. S.

**Formation and constitution of crystals of lead salts containing water-soluble colloid.** F. D. MILES (Phil. Trans., 1935, A, 235, 125—164).—The adsorption of neutral dextrin, gum-arabic, and gelatin, and their influence on the crystal habit, have been studied with  $\text{PbCl}_2$ ,  $\text{PbBr}_2$ ,  $\text{PbI}_2$ ,  $\text{PbN}_6$ , and  $\text{PbSO}_4$  during slow and rapid crystallisation from aq. solution. At low concn. of colloid the crystal edges are curved, but the internal structure, as revealed by optical measurements, is almost unaffected up to 5% of adsorbed colloid. The max. adsorption is 10%. Colloids retard the formation of  $\beta$  crystals of  $\text{PbN}_6$  from the  $\alpha$  form, whereas dyes have the opposite effect. Adsorption occurs in the order  $\text{PbSO}_4$  and  $\text{PbN}_6 > \text{PbCl}_2 > \text{PbI}_2$  at  $20^\circ$ , i.e., in the order of increasing polarisability of the anion. Maltose is not adsorbed. From conductivity measurements on solutions of Pb salts in presence of dialysed dextrin it is inferred that no association occurs in solution. X-Ray studies on  $\text{PbSO}_4$  and  $\text{PbN}_6$  show that the lattice dimensions are unaffected, but that the particle size decreases with increasing content of colloid. With  $\text{PbN}_6$  the introduction of colloid causes the deposition of a colloidal Pb compound. It is inferred that at  $< 5\%$  adsorption the crystallites are approx. in the same crystallographic orientation and are separated by a layer of dextrin, the mols. being attached to the crystallites by some of their OH groups. At  $> 5\%$  adsorption the same orientation is not maintained throughout the crystal. R. S. B.

**Exchange adsorption on colloidal vanadium pentoxide.** V. A. KARGIN and H. B. KLIMOVITZKAJA

(Acta Physicochim. U.R.S.S., 1935, 2, 33—50; cf. A., 1935, 1069).—The pptn. of  $V_2O_5$  sol by  $BaCl_2$ ,  $CaCl_2$ , and  $MgCl_2$  has been studied and the changes in ionic concn. in the filtrate determined by gravimetric and potentiometric methods. The amounts of  $Ba^{++}$ ,  $Ca^{++}$ , and  $Mg^{++}$  adsorbed are not themselves equiv. nor are they equiv. to the total cations ( $H^+$  and  $NH_4^+$ ) released, whilst the amount of acid in the filtrate is approx. const. The intermicellar ionic concns. have been determined by analysis of the ultrafiltrate and the true adsorption calc., but the cation exchanges are again not equiv. Vanadic acids derived from the dissolution of the sol are present in the intermicellar liquid in approx. const. concn. The non-equivalence of the cation exchange and the fact that cation adsorption is also independent of sol concn. over a limited range are attributed to the formation of insol. Ba, Ca, or Mg salts of the intermicellar vanadic acids. R. S.

Adsorption of grass and butter carotenes on alumina. A. E. GILLAM and M. S. EL RIDI (Nature, 1935, 136, 914—915).—A double adsorption of pure  $\beta$ -carotene (I) from grass changes it partly into a substance resembling  $\alpha$ -carotene (II). This process is reversible, since re-adsorption changes this substance in part to (I).  $Ca(OH)_2$ , but not  $MgO$ , effects a similar change in (I), but less readily than does  $Al_2O_3$ . Pure (II) from palm oil is also changed by repeated adsorption on  $Al_2O_3$ . The possibility of changes brought about by chromatographic adsorption itself must thus be considered in work on the carotenes. L. S. T.

Electrokinetics. XVII. Surface charge and ion antagonism. L. S. MOYER and H. B. BULL (J. Gen. Physiol., 1935, 19, 239—247).—The surface charges of cellulose in contact with various salts are calc. from previously published data. The surface charge in contact with  $NaCl$  plotted as a function of temp. is discontinuous at  $39^\circ$ . Mixtures of Na, K, Mg, and Ca chlorides give lower surface charges at a given anion concn. than the single chlorides, thus showing ion antagonism. F. A. A.

Affinities between proteins and fatty acids, fats, and lipins. S. J. VON PRZYŁECKI, E. HOFER, and S. FRAJBERGER-GRYNBERG (Biochem. Z., 1935, 282, 362—373).—Paraffins adsorb ovalbumin, serum-albumin, and edestin very readily, but caseinogen, gelatin, and peptone only slightly. Suspensions of cholesterol (I) behave similarly. Possibly the non-polar  $NH_2$ -acid residues (especially leucyl) are responsible for the adsorption, but the adsorption which occurs on acids and esters seems to be due to the polar groups of the proteins. The union with (I) may be partly strengthened by its  $CH_2CH$  and  $OH$  groups. W. McC.

Theory of adsorption. H. BRADLEY (Trans. Faraday Soc., 1935, 31, 1652—1655).—The author's formula (A., 1927, 821), identical with that of Miyamoto (A., 1935, 578), is in accord with the observed adsorption of  $CO$  or  $A$  by coconut charcoal, of  $N_2$  by charcoal, of  $H_2O$  vapour by cotton, and of  $COMe_2$  in  $H_2O$ ,  $Br$  in  $H_2O$ ,  $iso-C_5H_{11} \cdot OH$  in  $H_2O$ , or  $BzOH$  in  $C_6H_6$  by blood charcoal. J. W. S.

Formula for the rate of evaporation of adsorbed atoms and mols. J. K. ROBERTS (Trans. Faraday Soc., 1935, 31, 1710—1713).—A formula derived from kinetic considerations is consistent with the behaviour of adsorbed films of  $O$  and  $H$  atoms on  $W$ , and with that of  $O_2$  mols. adsorbed on isolated  $W$  atoms left bare during formation of the at.  $O$  film. The theory is also applied to the case where the adsorbed atoms are the same as those in the surface, and an equation for v.p. is derived which is in good accord with experiment. J. W. S.

Application of force-fields to the derivation of special thermodynamic relations, especially a general sorption equation and a new electrocapillary equation. B. DERJAGUIN (Acta Physicochim. U.R.S.S., 1935, 2, 377—384).—Mathematical. J. W. S.

Surface forces at the gas-liquid interface. VI. Method for determining the potential difference at still surfaces. M. GEROVITSCH and A. FRUMKIN (Acta Physicochim. U.R.S.S., 1935, 2, 1—8).—The potential developed when a rapid stream of  $0.01N$ - $KCl$  is passed over a still surface of the same in air has been determined and compared with the result given by a radioactive probe. Good agreement is obtained, and it is shown that ionisation of the air does not affect the results for very dil. solutions. The potential and the sensitivity given by the stream method vary linearly with the height of the stream above the surface. R. S.

Solid-liquid interface. W. CLAYTON (J. Oil Col. Chem. Assoc., 1935, 18, 412—429).—A lecture on dielectric properties, polar groups, the electric double layer, adsorption, crystal growth, and surface films. E. S. H.

Determinations of surface tension of solutions of potassium and lithium salts of higher fatty acids by the ring method with exclusion of atmospheric carbon dioxide and with special regard to other disturbing influences. II. A. LOTTERMOSER and E. GIESE (Kolloid-Z., 1935, 73, 276—288; cf. this vol., 26).—The surface tensions,  $\sigma$ , of several aq. K and Li soap solutions have been determined, using the precautions previously described. With rising temp.,  $\sigma$  decreases linearly as a rule; the causes of deviations have been traced. In certain soaps  $\sigma \propto \log$  concn. The cation has no influence on surface activity. At low concns. ( $10^{-5}$ — $10^{-4}$  g. per c.c.) Traube's rule holds qualitatively. E. S. H.

Surface tension between aqueous and isopropyl ether solutions of acetic acid. F. M. BROWNING and J. C. ELGIN (Ind. Eng. Chem. [Anal.], 1935, 7, 399—400).—Data for surface tension and  $d$  for dil. solutions at  $20^\circ$  are recorded. E. S. H.

Graphical representation of the angle of wetting relations by the maximum bubble pressure method. E. LANGE and K. NAGEL (Kolloid-Z., 1935, 73, 268—269).—Mathematical. E. S. H.

Heat of wetting and the physical significance of the constants in Rodewald's equation. P. J. ANDRIANOV (Kolloid-Z., 1935, 73, 328—334).—Theoretical. E. S. H.

**Constitution of the capillary layer in solutions of malachite-green.** (MLLE.) M. T. SALAZAR (Compt. rend., 1935, 201, 1120—1123).—The difference between the surface tension of  $H_2O$  ( $\sigma_w$ ) and that of the malachite-green solution ( $\sigma_s$ ) is const. for concns.  $> 6.5$  g. in 100 c.c. At lower concns. (c) the relation  $\sigma_w - \sigma_s = ac^b$  holds ( $a=15.14$ ,  $b=0.26$ ). The Gibbs equation is applied to these solutions. Above a certain concn. corresponding with the completion of a unimol. surface layer of solute, the quantity of solute absorbed in the surface is const. H. J. E.

**Investigation of unimolecular films.** I. LANGMUIR and K. B. BLODGETT (Kolloid-Z., 1935, 73, 257—263).—A discussion of technique. E. S. H.

**Semipermeability and neutral salts.** T. Y. CHANG and S. T. CH'IAO (J. Chinese Chem. Soc., 1935, 3, 308—320).—Experiments have been made to discover a possible relationship between semipermeability and the lyotropic series, due to the dehydration effect of the ions. Such an effect, leading to change of adsorption, provides an alternative theory to that of Zsigmondy on the variation of permeability with the nature of the solution. When increasing amounts of a neutral salt were added to an acid dye hydrosol, a collodion membrane became permeable at first, but later became impermeable. The effect of different salts was not in the order of the lyotropic series, and it appears that the effect is not simply a dehydration, but that discharge of the  $H_2O$  layer in the pore-wall and coagulation by the salts also intervene. Basic dye hydrosols were similarly examined. The membrane did not become permeable to the sol when neutral salt was added. The effect of tannin and EtOH was also studied.

A. J. M.

**Influence of a solid phase on the f.p. of water and of dilute aqueous solutions. I. Quartz sand-water.** A. V. RAKOVSKI, D. N. TARASENKOV, and A. V. KOMANDIN (J. Gen. Chem. Russ., 1935, 5, 1273—1278).—The f.p. of  $H_2O$  is depressed by  $SiO_2$  to an extent varying exponentially with the  $H_2O$  content of the mixture, and directly with the  $SiO_2$  surface. The phenomenon is not affected by the presence of 0.1N- $Na_2CO_3$  or - $Ca(NO_3)_2$ . The results indicate that surface forces act at a distance of  $< 10,000$  mol. diameters.

R. T.

**Electrical investigation of solutions of stearanilide in paraffin wax.** W. JACKSON and F. C. FRANK (Trans. Faraday Soc., 1935, 31, 1700—1706).—The dielectric loss and d.c. conductivity of dil. solutions of stearanilide in molten and solid paraffin wax indicate the presence of polar groups containing  $< 10$  stearanilide mols. It is suggested that the mols. in the groups may approach a liquid crystalline formation, and that they adsorb ionic impurities.

J. W. S.

**Kinetic treatment of formation of nuclei in supersaturated vapours.** R. BECKER and W. DÖRING (Ann. Physik, 1935, [v], 24, 719—752).—Theoretical.

A. J. M.

**Theory of physico-chemical periodic processes.** F. M. SCHEMJAKIN and A. A. VITT (Acta Physicochim. U.R.S.S., 1935, 2, 171—176).—For certain periodic

reactions, the law of mass action and Fick's law of diffusion are together sufficient to explain the periodicity.

A. J. M.

**Formation of microscopic Liesegang rings.** E. C. BOTTI, O. W. LINK, and B. P. CALDWELL (J. Chem. Educ., 1935, 12, 540—541).—Details for the production of periodic ppts. of  $Ag_3AsO_4$  and  $Ag_2CrO_4$  in gelatin on a microscope slide are recorded; the advantages of the method are pointed out. L. S. T.

**Investigation of periodic reactions by application of physico-chemical analysis.** F. M. SCHEMJAKIN and P. F. MICHALEV (Acta Physicochim. U.R.S.S., 1935, 2, 427—432; cf. A., 1934, 363).—The product of the distance between successive bands and the velocity of diffusion for Liesegang ring type periodic structures produced with  $K_2Cr_2O_7$  and  $AgNO_3$  diffusing in gelatin varies with the concn. of the gel and of the electrolytes. Periodic ptns. have also been observed with  $K_2Cr_2O_7$  and neutral-red,  $K_4Fe(CN)_6$  and methylene-blue, and with  $K_2Cr_2O_7$  and Me-violet, all in gelatin. J. W. S.

**Physico-chemical analysis of periodic reactions. VI.** F. M. SCHEMJAKIN, E. A. FOKINA, and P. F. MICHALEV (J. Gen. Chem. Russ., 1935, 5, 1145—1157).—The val. of the periodicity const.  $K=\lambda v$  ( $\lambda$ =distance between rings,  $v$ =velocity of propagation) rises with increasing dilution of the internal electrolyte when aq.  $Pb(NO_3)_2$  diffuses into aq. KI,  $Na_2CO_3$  into  $HgCl_2$  or  $BaCl_2$ ,  $AgNO_3$  into  $K_2CrO_4$ , and  $K_2CrO_4$  into  $CuSO_4$ . At the same time  $\lambda$  rises,  $v$  falls, whilst the no. of crystallites present in the ring falls, and the radius of the diffusion field increases. Periodic ptn. occurs in the reaction  $Na_2HPO_4 + CaCl_2 \rightarrow CaHPO_4 + 2NaCl$  at  $p_H$  0.5—12.9. In general,  $\lambda$  and  $K$  fall with increasing dilution of the  $Na_2HPO_4$  and with increasing deviation from  $p_H$  7. R. T.

**Liesegang phenomenon in the precipitation of iodine in the absence of a gel.** B. N. SEN (Monatsh., 1935, 67, 10—12).—The rhythmic ptn. of I by the reduction of aq.  $KIO_3$  by  $As_2O_3$  in presence of  $CaCl_2$  is described.

F. L. U.

**Viscosity and plasticity of disperse systems. VIII. Application of Batschinski's formula to the viscosity of hydrogenated fats.** M. P. VOLAROVITSCH and G. B. RAVITSCH (Kolloid-Z., 1935, 73, 339—342; cf. A., 1935, 1318).—The viscosity of sunflower-seed oil and of two hydrogenated fats has been determined at 50—140°. The results are in accordance with Poiseuille's law. At high temp. there is a linear relation between fluidity and sp. vol.

E. S. H.

**Dispersion of multi-disperse solutions by Nistler's apparatus.** J. FAUTREZ (Bull. Acad. roy. Belg., 1935, [v], 21, 927—936).—Measurements of the variations of  $\lambda\lambda$  of the scattered light in colloidal suspensions of various colouring matters support the theory of multi-dispersion.

N. M. B.

**Light scattering in gold sols in relation to particle size and shape.** D. S. SUBBARAMAIA (Proc. Indian Acad. Sci., 1935, 2, A, 358—363; cf. A., 1935, 821).—Measurements of the depolarisation obtained with unpolarised light and with per-

pendicular and parallel polarisation are reported. Results show that the particles in Faraday's sols are much  $<$  those in the other red sols prepared by using nuclear sols and  $H_2O_2$  as the reducing agent; those in the blue sols are relatively the largest. The size and anisotropy of the particles increase with increase in rate of growth caused by raising the temp. during prep. Addition of  $K_2CO_3$  to the mixture before reduction has the reverse effect.

N. M. B.

**Cryolysis, diffusion, and particle size. III. Investigations with gum-arabic and polyacrylic acid.** C. ENDOH, F. E. M. LANGE, and F. F. NORD (Ber, 1935, 68, [B], 2004—2011; cf. A., 1935, 932).—Determinations of the conductivity of solutions of polyacrylic acid (I) show no difference between the frozen and unfrozen solutions. Proof that the purely chemical properties of (I) are not influenced by freezing is still more firmly established by conductometric titration of the acid with NaOH. The irreversible nature of the action of freezing lyophilic colloids is established, since a 2% solution of (I) diffuses more slowly after freezing than when unfrozen and the difference persists when the dilution is increased to 0.1%. A 0.1% solution after being frozen at  $-17^\circ$ , however, diffuses more rapidly than an unfrozen solution. Similar results are obtained with gum-arabic.

H. W.

**Viscometric investigations of structure formation in  $V_2O_5$  sols. III. Action of anions.** G. SCHUMANN (Acta Physicochim. U.R.S.S., 1935, 2, 792—808; cf. A., 1935, 1073).—The viscosity-pressure curves of three  $V_2O_5$  sols in presence of Na salts have been determined. Structure formation is influenced in the order  $Cl' > NO_3' > Br' > SO_4'' > CrO_4''$ . All the salts depress the viscosity during the first day after addition. The results are discussed.

T. G. P.

**Structure in hydrosols of aluminium oxide and the lyotropic effect of ions.** A. RABINERSON and Z. ARISTOVA (Acta Physicochim. U.R.S.S., 1935, 2, 585—594; cf. A., 1935, 700).—Undialysed hydrosols of  $Al(OH)_3$  (from the acetate) show normal viscosity ( $\eta$ ), whilst dialysis causes  $\eta$  to vary with the rate of shear owing to formation of structural elements. Comparison of the effects of various neutral salts in promoting structure-viscosity shows that the effect increases with hydration not only of the cation but also of the anion. It is inferred that sols of  $Al(OH)_3$  and  $Fe(OH)_3$  owe their stability in part to hydration, and that the action of electrolytes is not exclusively electrical.

F. L. U.

**Mechanism of coagulation of sols by electrolytes. V. Sulphur sol.** H. B. WEISER and G. R. GRAY (J. Physical Chem., 1935, 39, 1163—1175; cf. A., 1933, 23).—Pptn. vals., adsorption, and capacity for displacing  $H^+$  of  $Th^{+++}$ ,  $Nd^{+++}$ ,  $Al^{+++}$ ,  $Ba^{++}$ ,  $Sr^{++}$ , and  $Ca^{++}$ , have been measured for Raffa and Selmi S sols. Contrary to the results of Bassett and Durrant (A., 1932, 19) and of Bolam and Muir (A., 1933, 1011), neither the adsorption vals. of the several cations nor the quantities of  $H^+$  displaced by them are equiv. at the respective pptn. conens. Cationic adsorption and coagulating power vary in opposite senses at the pptn. concn., but in the same sense at higher conens.

The results are interpreted, and a mechanism is suggested, in terms of the theory of the diffuse double layer.

F. L. U.

**Structure of colloid particles of artificial atacamite.** A. A. MOROZOV (Kolloid-Z., 1935, 73, 288—299).—Investigations of the kinetics of formation of the sol from  $Cu(OAc)_2$  and NaCl, the behaviour on dilution, the conductivity, the charge on the particles, and the coagulation by electrolytes suggest the structure  $n\{[Cu([OH]_2Cu)_3]Cl_2\}_x CuCl_2, mCu^{++}, 2mCl^-$ .

E. S. H.

**Coagulation of ferrocyanide sols containing varying amounts of potassium ferrocyanide.** N. CHATTERJEE (J. Indian Chem. Soc., 1935, 12, 671—685).—The coagulating concn. (a) of various electrolytes on ferrocyanide sols freed as far as possible from intermicellar ions, and (b) of KCl on ferrocyanide sols in presence of (adsorbed)  $K_4Fe(CN)_6$ , has been determined. With (b) if the concn. of added  $K_4Fe(CN)_6$  ( $c_1$ ) is small the coagulating concn. of total K ions ( $c_2$ ) increases with  $c_1$ , and stability increases with dilution of sol. For greater vals. of  $c_1$ , max. and min. appear in the curves of  $c_1$  against  $c_2$  [Prussian-blue and  $Cd_2Fe(CN)_6$ ] or the coagulating val. increases continuously (U, Cu, Al, and Zn ferrocyanides). These complicated results explain the disagreements between published observations. The sp. conductivity ( $\kappa$ ) of  $Cu_2Fe(CN)_6$  sols and their ultrafiltrates and the  $p_H$  of the latter have been determined;  $\kappa$  increases with the dilution of the sol. The cataphoretic velocity for these Cu sols passes through a max. with increasing  $c_1$  and decreases with increasing dilution for low  $c_1$ . These results are correlated with the phenomena of coagulation.

R. S. B.

**Effect of light on the flocculation of colloidal solutions in fluorescent media.** A. BOUTARIC (Ann. Guébbard-Séverine, 1935, 11, 25—34).—In general, fluorescent substances accelerate the flocculation of colloids only in the presence of visible or ultra-violet light and added electrolytes. The fall ( $\Delta t$ ) in the time of flocculation of colloidal  $As_2S_3$  which is associated with the addition of eosin, uranine, or erythrosin, diminishes as the fluorescing power of the dye is decreased by the added electrolyte. Oxidation inhibitors and dyes which diminish the fluorescing power have a similar influence on  $\Delta t$ .

J. G. A. G.

**Electrolyte coagulation of weakly solvated sols and electrolyte activity.** W. OSTWALD (Kolloid-Z., 1935, 73, 301—328).—A new theory of electrolyte coagulation of sols is put forward, in which attention is directed to the rôle of the dispersion medium. Coagulation is supposed to occur, not when the particles reach a certain state of charge, but when the intermicellar electrolyte reaches a certain physico-chemical state. The importance of the activity coeff. of the coagulating ions is emphasised and the interpretation of the valency rule and other regularities in coagulation is discussed. A large amount of published data is re-examined in the light of the theory.

E. S. H.

**Variation of viscosity during the coagulation of colloid aluminium hydroxide by potassium chloride solutions.** S. S. JOSHI and K. P. N.

PANNIKAR (Proc. Acad. Sci. Agra and Oudh, 1935, 5, 41—45; cf. A., 1935, 164).—The  $\eta$ -time curves for 0.5*N*—0.025*N*-KCl solutions show initial discontinuity in the progress of coagulation at low concns. The time corresponding with the viscosity at the first min. on the curve is independent of the concn., indicating that the min. may not denote a definite stage of coagulation. N. M. B.

**Gelatinised emulsions. I. Emulsifying power of different soaps. Thickness of [protective] layer. Rôle of water. L. KREMNEV** (Acta Physicochim. U.R.S.S., 1935, 2, 779—792).—Gelatinised emulsions are best prepared by manual shaking. The emulsification of  $C_6H_6$  by alkali oleates has been investigated. The emulsifying power decreases in the order  $Li > Na > K$ , and depends on the dispersion of the soap, being highest with 0.016*N* solutions, when an unsaturated monolayer covers the  $C_6H_6$  drops in the gelatinised emulsion. The influence of  $H_2O$  has been investigated, and the relationship between gelatinised and liquid emulsions is discussed. T. G. P.

**Thixotropy and allied phenomena, and their biological significance. H. FREUNDLICH** (Chem. Weekblad, 1935, 32, 739—745).—A lecture. E. S. H.

**Imbibition of hydrosols and of dye solutions through porous bodies. A. BOUTARIC** (J. Chim. phys., 1935, 32, 618—638, and Bull. Soc. Chim. biol., 1935, 17, 1522—1533).—The motion of the medium and of colloidal particles through filter-paper is in accord with the view that the particles are carried through the porous material mechanically by the medium unless adsorbed by the paper. The motion of the particles does not vary appreciably with the surface tension of the medium and has no direct relation with electric forces; the usual term "electro-capillary rise" is therefore a misnomer. J. W. S.

**X-Ray method for the study of "bound water" in hydrophilic colloids at low temperatures. W. H. BARNES and W. F. HAMPTON** (Canad. J. Res., 1935, 13, 218—227; cf. A., 1934, 597).—The X-ray camera (cf. this vol., 45) has been applied to the study of bound  $H_2O$  in gelatin between 0° and -50°. The presence of ice crystals due to free  $H_2O$  gives rise to randomly distributed diffraction spots on the photograph and causes a shift in the halo at 2 $\theta$  = 19—24°. The amount of bound  $H_2O$  decreases with fall of temp. to 0.44 g. per g. of dry gelatin at some temp. between -11.5° and -25.4°, below which it remains const. R. S.

**Time of setting of gels. M. PRASAD and M. U. PARMAR** (Current Sci., 1935, 4, 310—311).—Divergent times obtained by optical and various mechanical methods, in the case of  $H_2SiO_3$  gel, suggest that a precise definition is required for the term "time of setting," the process involving at least three stages. N. M. B.

**Dielectric constant and conductivity of gelatin sols and gels. A. PIEKARA and B. PIEKARA** (Kolloid-Z., 1935, 73, 273—276).—The dielectric const. of gelatin sols is  $>$  that of  $H_2O$ , increases with concn., and decreases with rising temp. The conductivity of the sol is  $>$  that of the gel. E. S. H.

**Hydroxide and oxide hydrate gels, and their amphoteric properties. R. FRICKE** (Kolloid-Z., 1935, 73, 300).—A criticism (cf. A., 1935, 1075). E. S. H.

**Anomalous dispersion of metallised gelatin. L. CAVALLARO** (Boll. Soc. ital. Biol. speriment., 1935, 10, 198—200).—The metastability of gelatin (I) and ovalbumin increases progressively with their purity during electro-dialysis, but reaches a max. before max. purity is attained, and falls considerably during the final stages of purification. The behaviour of  $\epsilon_{11,0}^{20}$  with increase of  $\lambda$  in metallised (I) is qualitatively similar to that of non-metallised (I), but  $\epsilon$  is increased in all cases. R. N. C.

**Colloid chemistry of edestin. II. K. HOLWERDA** (Biochem. Z., 1935, 282, 317—344; cf. A., 1935, 1203; Hollemann *et al.*, A., 1934, 842).—The composition of the coacervates produced by adding  $H_2O$  to edestin sols indicates that the peptisation is not chiefly dependent on the amount of  $H_2O$  introduced with the salts, although the degree of adsorption of univalent ions accords with viscosimetric results. In the zone of peptisation the adsorption is positive, whilst in the zone of salting out it is negative. When the concn. of salt is insufficient to cause peptisation the adsorption is positive. The controlling factor in the peptisation is the lowering of the surface tension caused by the addition of the salts, but intermicellar cohesive forces are involved, and such forces probably play a part in the salting-out process also. W. McC.

**Physico-chemical researches on the proteins. A. BOUTARIC and M. ROY** (Acta Physicochim. U.R.S.S., 1935, 2, 51—66).—Proteins as ordinarily prepared contain salt impurities which modify their colloidal properties. Pure preps. obtained by  $COMe_2$  pptn. have now been investigated. The optical density and  $n$  of coagulating mixtures of resorcinol (I) with serum-albumin and myxoprotein have been determined. (I) is fixed by the pptd. protein, and the solubility decreases to zero as the amount fixed approaches a limiting val. Absorption data for a no. of proteins on charcoal standardised against Na oleate are given and the influence of different protein concns. on the time of pptn. of  $Fe(OH)_3$  sol has been determined. It has been shown by both methods that the degree of polymerisation of albumin and myxoprotein obtained from various physiological secretions is the same. R. S.

**Colloidal model for illustration of biological processes. I.—See this vol., 232.**

**M.-p. curve of mixtures of heavy water and water. A. EUCKEN and K. SCHÄFER** (Z. anorg. Chem., 1935, 225, 319—320).—Contrary to Deželić's results (this vol., 30), but in agreement with those of other investigators, the authors have shown that the solidus-liquidus curves do not coincide, the max. distance apart being 0.02° for mixtures containing 42%  $D_2O$ . The m.-p. curve is not a straight line, but concave towards the concn. axis. Measurements have been made in a special apparatus recording variations of temp. of 0.00001°. M. S. B.



**Exchange equilibria between deuterium and ammonia.** K. WIRTZ (Z. physikal. Chem., 1935, B, 30, 289—297; cf. A., 1935, 1460).—A method which may in principle be used to calculate the equilibrium consts. of all the exchange reactions possible in a mixture of  $\text{NH}_3$  and  $\text{D}_2$  is described. As yet, however, the experimental accuracy is not great enough for it to be possible fully to follow this procedure. From spectroscopic data the equilibrium consts. of  $\text{NH}_3 + \text{NHD}_2 = 2\text{NH}_2\text{D}$  and  $\text{ND}_3 + \text{NDH}_2 = 2\text{NHD}_2$  at  $573^\circ$  abs. have been calc. to be 2.30 and 2.89, respectively. The distribution ratio of D between  $\text{H}_2$  and  $\text{NH}_3$  has also been determined. R. C.

**Maximum concentration of endothermic compounds at high temperatures; application to ozone and nitric oxide.** E. BRINER and B. SUSZ [with E. ROD] (Helv. Chim. Acta, 1935, 18, 1468—1478).—The equilibrium consens. of  $\text{O}_3$  and of NO in gas mixtures at high temp. have been recal. using more exact thermochemical data and equilibrium consts. Vals. so calc. are < those found previously. J. S. A.

**Equilibrium constants of the reaction of formation of ethyl chloride from ethylene and hydrogen chloride.** D. M. RUDKOVSKI, A. G. TRIFEL, and A. V. FROST (Ukrain. Chem. J., 1935, 10, 277—282).—The equilibrium const. for  $\text{C}_2\text{H}_4 + \text{HCl} \rightleftharpoons \text{EtCl}$  over the range  $170\text{—}230^\circ$  is given by  $\log K = 4.96 - 2925/T$ , and the heat of the reaction is 13.4 kg.-cal. R. T.

**Law of displacement of equilibrium.** P. RENAUD and E. BAUMGARDT (Compt. rend., 1935, 201, 1129—1131).—Polemical against Planck (A., 1934, 837). H. J. E.

**Thermodynamic potentials and affinity.** P. VAN RYSSELBERGHE (Compt. rend., 1935, 201, 1126—1128).—Theoretical. H. J. E.

**Thermodynamic problem.** A. SKRABAL (Z. Elektrochem., 1935, 41, 883—884; cf. A., 1935, 301, 446, 1204).—Further discussion. F. L. U.

**Thermodynamic problem.** R. LUTHER (Z. Elektrochem., 1935, 41, 884—885; cf. preceding abstract).—Discussion concluded. F. L. U.

**First dissociation constant of carbonic acid equilibrium.** Y. KAUKO (Ann. Acad. Sci. fenn., 1934, A, 39, No. 3; Chem. Zentr., 1935, i, 2767).— $K = [\text{H}^+][\text{HCO}_3^-]/[\text{CO}_2]$  is calc. at different temp. from published conductivity data, the uncertainty of  $K$  being principally dependent on the accuracy of the val. of the ionic conductivity of  $\text{H}^+$ . The heat of dissociation of  $\text{H}_2\text{CO}_3$  is calc. as 2500 g.-cal.  $K$  is determined independently by potentiometric measurements on aq.  $\text{CO}_2$  solutions. J. S. A.

**Dissociation constants of organic acids. XIII. Primary and secondary constants of some cyclic 1:1-dicarboxylic acids.** W. L. GERMAN, G. H. JEFFERY, and A. I. VOGEL (J.C.S., 1935, 1624—1630; cf. A., 1935, 1076).—Conductivity data are given for *cyclo*-propane-, -butane-, -pentane-, and -hexane-1:1-dicarboxylic acids and their Na salts, and the primary dissociation consts. calc. These have been confirmed by potentiometric titration of the acids using the quinhydrone electrode and the secondary dissociation consts. also obtained. The

distances between the  $\text{CO}_2\text{H}$  groups calc. from Bjerrum's expression are < those obtained by Gane and Ingold's method (A., 1931, 1126). R. S.

**Dissociation constants of monohalogenated anilines and phenols.** G. M. BENNETT, G. L. BROOKES, and S. GLASSTONE (J.C.S., 1935, 1821—1826).—The dissociation consts. of *o*-, *m*-, and *p*-fluoro-, chloro-, bromo-, and iodo-aniline and -phenol at  $25.0^\circ$  in 30 vol.-% EtOH have been determined by observations of  $p_{\text{H}}$ , using the glass electrode. The results are discussed. E. S. H.

**Mathematical and graphical treatment of the equilibrium base-carbon dioxide-water in dilute solutions.** Y. KAUKO (Ann. Acad. Sci. fenn., 1934, A, 39, No. 1; Chem. Zentr., 1935, i, 2766—2767).— $\text{CO}_2\text{—H}_2\text{O}$ -base equilibria are treated according to the classical and modern theories of solution, and a graphical method is described for the calculation of quantities involved in water-softening. The method is applicable also to quant. analysis of  $\text{H}_2\text{O}$ . J. S. A.

**Hydration of chromic chloride in heavy water.** G. CHAMPETIER (Compt. rend., 1935, 201, 1118—1120).—Measurements are recorded of the change in electrical conductivity with time of  $\text{CrCl}_3$  dissolved in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . The rate of change is slower and the final val. is lower in  $\text{D}_2\text{O}$ . The absorption spectra for the  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$  solutions appear to be the same. H. J. E.

**Ion hydration and aquo-complexes.** H. BRINTZINGER (Z. anorg. Chem., 1935, 225, 221—224).—The results of published work are discussed (cf. A., 1935, 1091, 1335). E. S. H.

**Complex ions [of ferro- and ferri-cyanides] and prussi- and prusso-compounds.** H. BRINTZINGER and H. OSSWALD (Z. anorg. Chem., 1935, 225, 217—220).—The ion wts. of  $[\text{Fe}^{\text{III}}\text{NO}_3(\text{CN})_5]''$ ,  $[\text{Fe}^{\text{III}}\text{NH}_3(\text{CN})_5]'''$ ,  $[\text{Fe}^{\text{III}}\text{NO}_2(\text{CN})_5]''''$ ,  $[\text{Fe}^{\text{II}}\text{NH}_3(\text{CN})_5]'''''$ ,  $[\text{Fe}^{\text{II}}\text{NO}_2(\text{CN})_5]''''''$ ,  $[\text{Fe}^{\text{II}}\text{H}_2\text{O}(\text{CN})_5]'''''''$ , and  $[\text{Fe}^{\text{II}}\text{AsO}_2(\text{CN})_5]''''''''$  have been determined by the dialysis method. E. S. H.

**Effect of temperature on borax solutions in the presence of polyhydric substances and organic acids.** S. M. MEHTA (Proc. Acad. Sci. Agra and Oudh, 1935, 5, 46—49).—Preliminary results are given of an extension of Meldrum's investigations (Proc. Ind. Sci. Cong., 1923, 108) to the hydrolysis of borax in presence of mannitol and of salicylic acid, and the system  $\text{H}_3\text{BO}_3\text{—NaOH}$ , over a wide temp. range. N. M. B.

**Stability of sodium aluminate solutions.** V. D. DJATSCHKOV and O. S. KOSHUCHOVA (J. Gen. Chem. Russ., 1935, 5, 1139—1143).—The stability of Na aluminate (I) is unaffected by presence of < 1.4 mols. of  $\text{Na}_2\text{O}$  per mol. of  $\text{Al}_2\text{O}_3$ ; in higher consens. of NaOH it rises linearly, but is always least in solutions which contain 120—180 g. of (I) per litre. Agar-agar and Na silicate stabilise the solutions. R. T.

**Isotope exchange between water and some organic compounds.** M. HARADA and T. TITANI (Bull. Chem. Soc. Japan, 1935, 10, 554—557).—Neglecting mols. of relatively low concn. the exchange of D between org. compounds and dil.  $\text{D}_2\text{O}$  proceeds

according to  $\text{RH}_n + \text{HDO} \rightleftharpoons \text{RH}_{n-1}\text{D} + \text{H}_2\text{O}$ . The equilibrium consts.  $K = [\text{RH}_{n-1}\text{D}][\text{H}_2\text{O}]/[\text{RH}_n][\text{HDO}]$ , and the distribution coeffs.  $k = (\text{at. concn. of D in exchangeable H in compound})/(\text{at. concn. of D in H}_2\text{O})$  are:  $\text{CHCl}_3$ ,  $\text{Et}_2\text{O}$ ,  $\text{PhCHO}$ , no exchange;  $\text{NH}_2\text{Ph}$   $k=K=1.11$ ;  $\text{PhOH}$   $k=1.07$ ,  $K=0.54$ ;  $\text{C}_6\text{H}_5\text{NH}$   $k=0.88$ ,  $K=0.44$ ;  $\text{BzOH}$   $k=1.04$ ,  $K=0.52$ ;  $\text{CH}_2\text{Ph-OH}$   $k=1.10$ ,  $K=0.55$ . R. S. B.

Exchange reactions of hydrogen with deuterium. I. Exchange in carboxyl groups of succinic acid and in hydroxyl groups of quinol. A. E. BRODSKI and O. C. SCARRE. II. Exchange in sulphuric acid and in sodium hydroxide. J. M. SCHERSCHEVER, A. E. BRODSKI, and M. M. SLUCKAJA (*Acta Physicochim. U.R.S.S.*, 1935, 2, 603—610, 611—614; cf. A., 1935, 44).—I. When  $(\text{CH}_2\text{CO}_2\text{H})_2$  or  $p\text{-C}_6\text{H}_4(\text{OH})_2$  is heated with  $\text{H}_2\text{O} + \text{D}_2\text{O}$  for 2—4 hr. in the absence of a catalyst, equilibrium is reached in which the coeff. of exchange between D and the H of the  $\text{CO}_2\text{H}$  or OH groups is approx. 1. The reverse change has been observed qualitatively.

II. The exchange coeff. of D between heavy water and dissolved  $\text{H}_2\text{SO}_4$  or  $\text{NaOH}$  has been found to be 1.0, thus affording direct evidence that in the production of  $\text{D}_2\text{O}$  by electrolysis acid or alkaline solutions the D content of the dissolved electrolyte changes *pari passu* with that of the water. F. L. U.

Physicochemical studies of complex formation involving weak acids. XIV. Complex formation between malonates of the heavy metals and of sodium. H. T. S. BRITTON and M. E. D. JARRETT (*J.C.S.*, 1935, 1728—1735; cf. A., 1935, 305, 449).—When Na malonate (I) is added to solutions of heavy-metal salts, the heavy metals remain in solution as feebly ionised basic hydromalonates; with excess of (I) complex anions are formed. Malonic acid solutions of heavy-metal bases do not contain definite complex acids. The prep. of  $\text{K}_3\text{Cr}[\text{CH}_2(\text{CO}_2\text{H})_2]_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{Na}_3\text{Al}[\text{CH}_2(\text{CO}_2\text{H})_2]_3$ , and  $\text{Na}_3\text{Fe}[\text{CH}_2(\text{CO}_2\text{H})_2]_3$  is described. The solubility product of Ag malonate at  $18^\circ$  is  $1.41 \times 10^{-7}$ . E. S. H.

Determination of weight of organic dye ions by the dialysis method. H. BRINTZINGER and A. SCHALL (*Z. anorg. Chem.*, 1935, 225, 213—216).—Apparatus for use with small amounts of liquid is described. Results are given for 6 dyes. E. S. H.

System lithium nitrite-water: the hydrate  $\text{LiNO}_2 \cdot 1.5\text{H}_2\text{O}$ . J. BUREAU (*Compt. rend.*, 1935, 201, 1193—1195).—Thermal analysis reveals the peritectic transformation of  $\text{LiNO}_2 \cdot 1.5\text{H}_2\text{O}$  into  $\text{LiNO}_2 \cdot \text{H}_2\text{O}$  at  $-7.95^\circ$ , of  $\text{LiNO}_2 \cdot \text{H}_2\text{O}$  into  $2\text{LiNO}_2 \cdot \text{H}_2\text{O}$  at  $30.9^\circ$ , and of  $2\text{LiNO}_2 \cdot \text{H}_2\text{O}$  into  $\text{LiNO}_2$  at  $94^\circ$ . T. G. P.

Existence of two hydrates of potassium thiocyanate. A. CHRISTEN and O. HOFFER (*Compt. rend.*, 1935, 201, 1131—1133).—The hydrates  $\text{KCN} \cdot 0.5\text{H}_2\text{O}$  and  $\text{KCN} \cdot 0.8\text{H}_2\text{O}$  are formed. The former is the stable solid phase at  $-29.5^\circ$  to  $6.8^\circ$ . The latter is always metastable. It is formed at  $-30^\circ$  to  $-17.75^\circ$ . H. J. E.

Vapour pressure of saturated solutions and hydrates of magnesium chloride. N. V. KON-

DIREV and G. V. BEREZOVSKI (*J. Gen. Chem. Russ.*, 1935, 5, 1246—1251).—V.-p. data are recorded for  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$  over a wide temp. range. R. T.

Dissociation pressures of nitrates and sulphates. IV. Sodium vanadates. B. NEUMANN and A. SONNTAG (*Z. Elektrochem.*, 1935, 41, 860—868; cf. A., 1933, 1246).— $\text{O}_2$  pressures of Na vanadates with varying ratios of  $\text{Na}_2\text{O} : \text{V}_2\text{O}_5$ , with and without admixture of  $\text{SiO}_2$ , have been measured.  $\text{SO}_2$  is oxidised with appreciable rapidity only at temp. at which the vanadate is partly decomposed. The influence of  $\text{SiO}_2$  is purely physical, in preventing sintering and compaction of the products. The pressure measurements show that the catalytic activity of Na vanadates in promoting oxidation of  $\text{SO}_2$  depends on the formation of a definite, at present unidentified, sulphate which is more labile than  $\text{VOSO}_4$ . F. L. U.

Thermodynamics of the liberation of oxygen from ferric oxide-ferrous oxide melts. J. KIELLAND (*Z. Elektrochem.*, 1935, 41, 834—838; cf. A., 1935, 1075).—An expression for the activity coeff. of the components is given. The calc. free energy change of the reaction  $\text{Fe}_2\text{O}_3 = 2\text{FeO} + 0.5\text{O}_2$  agrees with the observed val. (A., 1935, 1204). The standard entropy of  $\text{FeO}$  is calc. Mol. and partial mol. heats of mixing and free energies of liquid  $\text{Fe}_2\text{O}_3$  and  $\text{FeO}$  are given. F. L. U.

System calcium oxide-sulphur dioxide-water. I. Determination of vapour pressures and conductivities. G. W. GURD, P. E. GISHLER, and O. MAASS (*Canad. J. Res.*, 1935, 13, B, 209—217; cf. A., 1933, 897).—An apparatus is described in which pure  $\text{CaO}$ ,  $\text{H}_2\text{O}$ , and  $\text{SO}_2$  in accurately known amounts can be mixed at a const. temp. and the v.p. and conductivity determined. V.p. between  $25^\circ$  and  $130^\circ$  and conductivities between  $25^\circ$  and  $90^\circ$  are tabulated for  $[\text{SO}_2]$  up to 6% and  $[\text{CaO}]$  up to 2.5%. R. S.

System calcium oxide-sulphur dioxide-water. II. Calculation of ionic concentrations. P. E. GISHLER and O. MAASS (*Canad. J. Res.*, 1935, 13, B, 308—322; cf. preceding abstract).—Ionic concns. in the system  $\text{CaO-SO}_2\text{-H}_2\text{O}$  are calc. from earlier v.-p. and conductivity data. The existence of the compound  $\text{CaSO}_3 \cdot \text{Ca}(\text{HSO}_3)_2$  is deduced. Vals. of  $p_{\text{H}}$  up to  $90^\circ$  are extrapolated to  $140^\circ$ . H. J. E.

Reciprocal solubility of aluminium, sodium, potassium, and ferric nitrate in water in presence of nitric acid. II. A. J. SASLAVSKI, J. L. ETTINGER, and E. A. ESEBOVA (*Z. anorg. Chem.*, 1935, 225, 305—311; cf. A., 1935, 928).—Data are given for the quaternary system  $\text{Al}(\text{NO}_3)_3\text{-NaNO}_3\text{-HNO}_3\text{-H}_2\text{O}$  at  $0^\circ$  and  $20^\circ$ . The only solid phases are  $\text{NaNO}_3$  and the hydrates  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $8\text{H}_2\text{O}$ , and  $6\text{H}_2\text{O}$ . The composition of the solution at the transition points has been determined. M. S. B.

System  $\text{CaO-SiO}_2\text{-H}_2\text{O}$ . II. R. NACKEN and R. MOSEBACH (*Z. anorg. Chem.*, 1935, 225, 285—288; cf. A., 1935, 935).—Equilibrium data at  $23 \pm 1^\circ$  are given. E. S. H.

**System  $\text{CaO}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ .** R. NAACKEN and R. MOSEBACH (*Z. anorg. Chem.*, 1935, 225, 289—301).—Equilibrium data at  $23 \pm 1^\circ$  are given. E. S. H.

**Binary additive compounds in ternary systems. IX. Phenacetin-sulphonil-resorcinol.** F. ADAMANIS (*Rocz. Chem.*, 1935, 15, 383—390).—Equilibrium data are recorded for the system, which shows a 2:3 compound of phenacetin and resorcinol. R. T.

**Thermodynamic studies of silver and mercurous sulphate.** F. ISHIKAWA and H. HAGISAWA (*Bull. Inst. Phys. Chem. Res. Japan*, 1935, 14, 1205—1209).—The e.m.f. of the cell  $\text{Ag}|\text{Ag}_2\text{SO}_4(\text{s})| \text{aq. Ag}_2\text{SO}_4|0.0269M-\text{K}_2\text{SO}_4, \text{HgSO}_4(\text{a})|\text{Hg}$  has been determined at  $20^\circ, 25^\circ,$  and  $30^\circ$  and various thermodynamic quantities are calc. R. S.

**Heats of dissolution and specific heats of rhombic sulphur in carbon disulphide. Surface energy of solid rhombic sulphur.** A. R. WILLIAMS, F. M. G. JOHNSON, and O. MAASS (*Canad. J. Res.*, 1935, 13, B, 280—288).—The thermal data are recorded for  $20^\circ$  and  $25^\circ$  and for concns. of 6—17%. Modifications of the adiabatic rotating calorimeter are described (cf. A., 1928, 609). The surface energy of solid rhombic S, calc. from the heats of dissolution of coarse and finely-divided substance, is 1024 ergs per sq. cm. (accuracy approx. 30%). H. J. E.

**Thermodynamic properties of sulphur compounds. II. Sulphur dioxide, carbon disulphide, and carbonyl sulphide.** P. C. CROSS (*J. Chem. Physics*, 1935, 3, 825—827; cf. A., 1935, 569).—Vals. of free energy, entropy, and heat capacity are derived from the consts. obtained from electron diffraction and from Raman and infra-red spectra, and these are applied to several reactions involving the three compounds. The free energies of formation at  $298.1^\circ$  abs. are:  $\text{CS}_2$ , 15.24,  $\text{COS}$  —40.48 kg.-cal. N. M. B.

**Thermal decomposition of iron carbide  $\text{Fe}_3\text{C}$ .** G. NAESER (*Mitt. Kaiser-Wilh. Inst. Eisenforsch.*, 1934, 16, 211—212; *Chem. Zentr.*, 1935, i, 2336).—The decomp. of  $\text{Fe}_3\text{C}$ , studied by measurement of magnetic susceptibility, takes place at  $1050-1060^\circ$  with out-gassed material. Equilibria in the system cementite-pearlite-ferrite-graphite are recorded. J. S. A.

**Heat of formation and free energy of formation of boron nitride.** S. SATOH (*Bull. Inst. Phys. Chem. Res. Japan*, 1935, 14, 1233—1240).—The heat of formation and free energy of formation of BN calc. from the dissociation pressure and the sp. heats are 56,940 and 54,760 g.-cal., respectively. R. S.

**Heat of reaction between kaolin burnt at different temperatures and  $\text{Ca}(\text{OH})_2$ .** P. P. BUDNIKOV (*Compt. rend. Acad. Sci. U.R.S.S.*, 1935, 3, 355—359).—The heat evolved when burnt kaolin is added to aq.  $\text{Ca}(\text{OH})_2$  is a max. when the burning temp. is  $800^\circ$  and becomes zero when this is  $>1000^\circ$ . It is suggested that meta-kaolinite formed below  $1000^\circ$  reacts with  $\text{Ca}(\text{OH})_2$  giving a Ca aluminosilicate. R. S.

**Nature of conductivity of non-aqueous solutions.** M. USSANOVITSCH (*Acta Physicochim. U.R.S.S.*, 1935,

2, 239—271).—The conductivity and temp. coeff. of conductivity of solutions of  $\text{AsCl}_3$ ,  $\text{AsBr}_3$ ,  $\text{SbCl}_3$ , and  $\text{SbBr}_3$  in  $\text{Et}_2\text{O}$  have been determined. The conductivity is attributed to the formation of  $\text{Et}_2\text{O} \cdot \text{AsCl}_3$ ,  $\text{Et}_2\text{O} \cdot \text{AsBr}_3$ ,  $\text{Et}_2\text{O} \cdot 2\text{SbCl}_3$ , and  $\text{Et}_2\text{O} \cdot 2\text{SbBr}_3$ .  $\text{PCl}_3$  does not form a compound with  $\text{Et}_2\text{O}$ , and the solution is non-conducting. The conductivity of solutions of  $\text{AsCl}_3$  in  $\text{PhNO}_2$  and  $\text{C}_6\text{H}_5\text{N}$  is also due to compound formation. Data for  $\text{AcOH}-\text{H}_2\text{SO}_4$  and  $\text{HNO}_3-\text{H}_2\text{SO}_4$  confirm the existence of  $2\text{H}_2\text{SO}_4 \cdot \text{HNO}_3$  and  $\text{H}_2\text{SO}_4 \cdot \text{HNO}_3$ . In the system  $\text{HNO}_3-\text{H}_2\text{SO}_4$ , the  $\text{HNO}_3$  acts as a base. In the systems  $\text{H}_2\text{SO}_4-\text{Me}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4-\text{CCl}_3\text{CO}_2\text{H}$ , in which there is no compound formation, a new type of dependence of conductivity on concn. is found. When corr. for viscosity, the conductivities of both systems are identical, although the dielectric consts. are widely different. A. J. M.

**Mobility of the hydrogen and hydroxyl ions in aqueous solution. II.** G. WANNIER (*Ann. Physik*, 1935, [v], 24, 509—590; cf. this vol., 31).—An expression for the mean life of  $\text{H}^+$  and  $\text{OH}^-$  is obtained by a combination of the theory of Debye and Hückel and quantum mechanics. An equation is derived for the effect of temp. on the mobility of the ions which is in agreement with experiment. Calculation of the electric moment of the ions, however, does not agree with the experimental val. The mobility of  $\text{D}_2\text{O}^+$  is calc. A. J. M.

**Electrode potentials of sodium and potassium in liquid ammonia.** V. A. PLESKOV and A. M. MONOSSOV (*Acta Physicochim. U.R.S.S.*, 1935, 2, 615—620; cf. A., 1935, 1077).—Measurement of the e.m.f. of the cell  $\text{Hg}-\text{Na}|0.1N-\text{NaNO}_3(\text{sat. KNO}_3)|0.1N-\text{Pb}(\text{NO}_3)_2|\text{Pb}$  at  $-35^\circ$ , the salts being dissolved in liquid  $\text{NH}_3$ , has been used to calculate the normal potential of Na. Results for K have been obtained in a similar manner. The potentials, referred to  $\text{H}-0$ , are: Na —1.83 volt, K —1.98 volt. These vals., which are nearly 1 volt < the corresponding potentials in  $\text{H}_2\text{O}$ , are considered partly responsible for the slowness of the reaction of the metals with liquid  $\text{NH}_3$ . F. L. U.

**Electrode potentials in water and in liquid ammonia.** V. A. PLESKOV and A. M. MONOSSOV (*Acta Physicochim. U.R.S.S.*, 1935, 2, 621—632; cf. preceding abstract).—A method of comparing electrode potentials in  $\text{H}_2\text{O}$  and liquid  $\text{NH}_3$  by means of a dropping electrode is described, and results of measurements for K, Na, Zn, Cd, Pb, H, Cu, Ag, and Hg, from which normal potentials in the two solvents are calc., are given. The ionic solvation energies calc. on purely electrostatic grounds are, with the exception of K and Na, greatly at variance with the energies of transfer given by the experiments. The discrepancies show that an important part is played by homopolar chemical forces. F. L. U.

**Electrode potentials of halides in liquid ammonia.** V. A. PLESKOV (*Acta Physicochim. U.R.S.S.*, 1935, 2, 679—688).—In calculating the normal potentials of halides in liquid  $\text{NH}_3$  the energy of formation of the crystal solvate must be considered. Homopolar forces play a part in the solvation. Calculations from previous data show that the normal potentials of

different halides differ less in liquid  $\text{NH}_3$  than in  $\text{H}_2\text{O}$  (cf. Fredenhagen, A., 1927, 936). T. G. P.

**Measurement of capacity of polarised mercury electrodes.** P. P. PORPIROV (J. Gen. Chem. Russ., 1935, 5, 1077—1084).—The polarisation capacity  $P$  falls with increasing potential to a min. at about 1 volt, and then rises; with increasing c.d. the val. of  $P$  rises uninterruptedly, and the above min. becomes more abrupt. Using a.c. the val. of  $P$  is independent of the frequency, but  $\propto$  only to the p.d. R. T.

**Cathodic polarisation in the deposition of copper from solutions of its simple salts.** O. ESSIN and A. LEVIN (J. Gen. Chem. Russ., 1935, 5, 1302—1315).—Gordon's empirical equation (A., 1925, ii, 549),  $E = \Pi_0 + b \log(1 - kD)$ , where  $E$  is the polarisation potential, and  $b$  and  $k$  are consts., is confirmed by the data for the electrolysis of 0.3—1.0N- $\text{CuSO}_4$  in 0.1—0.2N- $\text{H}_2\text{SO}_4$ , at 25°, with a c.d.  $D$  of 1—110 m.amp. per sq. cm.;  $\Pi_0$  cannot be considered to be the initial polarisation. The difference between the actual  $E$  and that calc. for the concn. potential is best represented by Erdey-Gruz and Volmer's equation (A., 1930, 1376),  $E_x = 1/(a + k \log D)$ , indicating that  $E_x$  is ascribable to the retarded formation of crystal nuclei at the cathode. When the c.d. is increased gradually from 1 m.amp. per sq. cm., the potential becomes most negative at about 10 amp., but the potentials cannot be reproduced when the process is repeated or reversed. R. T.

**Hydrogen peroxide theory of electrolytic oxidation and the influence of the electrode surface on anodic polarisation.** S. GLASSTONE and A. HICKLING (Trans. Faraday Soc., 1935, 31, 1656—1660).—The anodic overpotentials at smooth Pt, platinised and otherwise prepared Pt, Au,  $\text{PbO}_2$ ,  $\text{MnO}_2$ , arc-gas C, and Ni electrodes cannot be simply correlated with their efficiencies in oxidation of  $\text{OAc}'$ ,  $\text{S}_2\text{O}_3''$ , and  $\text{SO}_3''$ . Difficulties in the discharged ion theory of anodic processes are pointed out, and it is shown that formation of  $\text{H}_2\text{O}_2$  from OH radicals is not improbable, since not only do catalysts for  $\text{H}_2\text{O}_2$  decomp. inhibit anodic oxidation, but the action of  $\text{H}_2\text{O}_2$  is in many cases qualitatively similar to that of electrolytic oxidation. Probably no one mechanism accounts for all types of anodic oxidation reactions. J. W. S.

**Significance of negative difference effect.** W. O. KROENIG and V. N. USPENSKAJA (Korros. u. Metallschutz, 1935, 11, 10—16; Chem. Zentr., 1935, i, 2781).—The negative difference effect is the increased H evolution from an Al electrode in acid (or a Mg electrode in salt solutions) on short-circuiting with a Pt cathode, and is associated with the oxide skin. Removal of the latter inhibits the negative and gives rise to a positive difference effect. The effect is due to destruction of the oxide skin by the augmented passage of ions into solution, the rate of dissolution of Al being thereby increased. J. S. A.

**Electrochemical behaviour of non-metallic inclusions in iron and its relation to corrosion.** E. CHYZEWSKI and A. SKĄPSKI (Z. Elektrochem., 1935, 41, 843—849).—The e.m.f., current strength, and internal resistance of cells of the type: non-metal electrode|0.005N- $\text{FeSO}_4$ +0.005N- $\text{MnSO}_4$ |Fe

have been measured at room temp. The non-metal electrodes were of FeO,  $\text{Fe}_2\text{O}_3$ , magnetite, fayalite, haematite, FeS, MnS, and MnO, and the solutions were saturated with air or  $\text{O}_2$ . The results show that only MnS, and to some extent its solid solutions, can give rise to electrochemical corrosion. FeS can under certain conditions exert a protective action.

F. L. U.

**Application of the barium amalgam electrode to the determination of the activity of barium ions in aqueous solutions.** Z. J. BERESTNEVA and V. A. KARGIN (Acta Physicochim. U.R.S.S., 1935, 2, 163—170).—The potential of a Ba-Hg electrode in  $N$ - to 0.001N- $\text{BaCl}_2$  has been determined. Addition of  $\text{Na}^+$  up to 0.1N has no effect on the potential of the electrode. The Ba-Hg electrode may be used to determine the activity of  $\text{Ba}^{++}$ , if its potential is first determined against a standard Ba solution.

A. J. M.

**Alkali amalgam electrodes and their application to the study of colloidal solutions.** Z. J. BERESTNEVA and V. A. KARGIN (Acta Physicochim. U.R.S.S., 1935, 2, 151—162).—An attempt has been made to use alkali-metal amalgam electrodes to investigate the adsorption of ions in the coagulation of  $\text{As}_2\text{S}_3$  sols by NaCl and KCl. The electrodes are, however, poisoned by products of hydrolysis of  $\text{As}_2\text{S}_3$ , and trustworthy results cannot be obtained.

A. J. M.

**Activity of hydrogen in complexes of alcohols with unsaturated organic compounds.** B. V. TRONOV and L. P. KULEV (J. Gen. Chem. Russ., 1935, 5, 1233—1239).—The e.m.f. developed when Pt and Na electrodes are immersed in primary alcohols is unaffected by addition of  $\text{C}_5\text{H}_5\text{N}$  or  $\text{PhNO}_2$ ; the same applies to *sec.*-alcohols, with the exception of  $\text{Pr}^2\text{OH}$ , which appears to form a highly dissociated compound with  $\text{C}_5\text{H}_5\text{N}$ . *tert.*-Alcohols and the homologues of cyclohexyl alcohol give considerably higher e.m.f. in presence of  $\text{C}_5\text{H}_5\text{N}$  and  $\text{PhNO}_2$ .  $\text{NH}_2\text{Ph}$  and  $\text{NPhMe}_2$  do not affect the e.m.f. given by aliphatic alcohols, but slightly raise that given by aromatic alcohols.

R. T.

**Mechanism of explosive reactions.** C. C. ANDREEV (Bull. Soc. chim., 1935, [v], 2, 2128—2134).—See A., 1935, 708.

F. L. U.

**Absolute rate of homogeneous atomic reactions.** H. EYRING, H. GERSHINOWITZ, and C. E. SUN (J. Chem. Physics, 1935, 3, 786—796; cf. A., 1935, 1205).—The abs. rate of recombination of 3 H atoms is calc. theoretically. The manner in which rotation determines the dimensions of the activated complex in cases having little or no activation energy is discussed. A result of the theory (cf. *ibid.*, 586) is that energy transfer occurs most effectively among particles which can react with each other, free atoms being more efficient than mols. A qual. application of potential surfaces to the problem of energy transfer is made.

N. M. B.

**Reality of chains in gas explosions.** M. POLJAKOV and I. MALKIN (Acta Physicochim. U.R.S.S., 1935, 2, 211—214).—Apparatus is described by means of which the theory that OH is an intermediate in the chain reaction occurring when a mixture of  $\text{H}_2$

and  $O_2$  in the vol. ratio 2:1 is exploded may be proved. It is supposed that two OH combine to form  $H_2O_2$ , which may be frozen out. 25 explosions gave sufficient  $H_2O_2$  to be detected. The amount of  $H_2O_2$  formed decreases with distance from the heated Pt spiral by which the explosion is started. This result is due to the removal of OH by the walls of the vessel. A. J. M.

**Influence of gas adsorbed by the vessel walls on the chain reaction of hydrogen-oxygen mixtures.** M. PRETTE (Compt. rend., 1935, 201, 962—964).—The initial rate of reaction of  $H_2$  and  $O_2$  at  $540^\circ$  in a glass vessel increases progressively when the vessel walls are allowed to adsorb (at  $540^\circ$ ) increasing quantities of  $H_2O$  vapour (5—70 mm. pressure) before carrying out the reaction. Preliminary treatment of the vessel with  $H_2$  at  $550^\circ$  retards the reaction and eliminates the induction period. H. J. E.

**Ignition limits of oxygen-hydrogen mixtures.** F. I. DUBOVITSKI (Acta Physicochim. U.R.S.S., 1935, 2, 761—778).—The reaction between stoichiometric proportions of  $H_2$  and  $O_2$  irradiated by a  $H_2$  tube at pressures and temp. close to the ignition limits has been investigated. The limits of ignition are not determined by the surface. A decrease in reaction rate at high pressures in presence of A indicates that chain breaking grows in consequence of increased probability of the triple collision  $O+H_2+M=H_2O+M$ . The primary process in the reaction is  $O_2+h\nu=O^*+O$ . The results obtained are combined with earlier data and interpreted through Semenov's chain theory. T. G. P.

**Experimental activation energies of elementary reactions between hydrogen and the halogens.** J. C. MORRIS and R. N. PEASE (J. Chem. Physics, 1935, 3, 796—802).—Available experimental data on reactions of the type  $H+X_2 \rightarrow HX+X$ ,  $X+H_2 \rightarrow HX+H$ , and  $H+HX \rightarrow X+H_2$  are analysed to give vals. of the activation energies of the intermediate reactions involved, and these are compared with calc. vals. N. M. B.

**Kinetics of oxidation of hydrides in the gaseous phase. I. Oxidation of silane.** P. S. SCHANTAROVITSCH (Acta Physicochim. U.R.S.S., 1935, 2, 633—646).—The lower ( $p_1$ ) and upper ( $p_2$ ) pressure limits for the ignition of mixtures of  $SiH_4$  and  $O_2$  have been determined. With falling temp.  $p_1$  increases and  $p_2$  diminishes. Ignition occurs the more readily, the smaller is the proportion of  $O_2$  below the stoichiometric ratio. Reducing the diameter of the vessel increases  $p_1$ , but has little effect on  $p_2$ . Addition of 0.1% of  $NO_2$  displaces the ignition curves towards lower temp. The kinetics of the reaction resemble those of  $H_2$ , CO,  $PH_3$ , etc., whilst differing entirely from those of hydrocarbons. At lower temp. an induction period is observed which is absent when  $t > 120^\circ$ , whence it is inferred that a chain mechanism is involved. F. L. U.

**Non-adiabatic reactions: decomposition of  $N_2O$ .** A. E. STEARN and N. EYRING (J. Chem. Physics, 1935, 3, 778—785; cf. A., 1935, 586).—The experimental and calc. abs. rates for the non-adiabatic decomp. of  $N_2O$  are in good agreement.

The amount of chemical inertia present in other reactions involving the singlet-triplet transition of  $O_2$  is examined. A convenient method of constructing potential functions for polyat. mols. is indicated, and employed for the  $N_2O$  mol. N. M. B.

**Heterogeneous oxidation of nitric oxide at the temperature of liquid air.** M. TEMKIN and V. PISHOV (Acta Physicochim. U.R.S.S., 1935, 2, 473—486).—The oxidation of NO by  $O_2$  at  $5 \times 10^{-3}$  to  $8 \times 10^{-2}$  mm. Hg and  $83-88^\circ$  abs. is a heterogeneous reaction between  $O_2$  mols. of the gas phase and NO mols. adsorbed on the surface. The reaction velocity  $v$  is given by  $v=4.2 \times 10^{-9} e^{4300/RT} S \cdot p_{O_2} \cdot p_{NO}$ , where  $S$ =area of surface in sq. cm.,  $p$ =partial pressure in mm. The reaction product has the composition  $N_3O_5$ . O. J. W.

**Thermal reaction between gaseous iodine monochloride and hydrogen.** W. D. BONNER, W. L. GORE, and D. M. YOST (J. Amer. Chem. Soc., 1935, 57, 2723—2724).—The kinetics of the reaction  $2ICl+H_2=I_2+2HCl$  at  $205-240^\circ$  have been investigated. A mechanism involving a slow and a rapid reaction is suggested. The energy of activation of the slow reaction is 33,900 g.-cal. E. S. H.

**Flame speeds during the inflammation of moist carbon monoxide-oxygen mixtures.** W. PAYMAN and R. V. WHEELER (Nature, 1935, 136, 1028).—A discussion. L. S. T.

**Critical explosion limits in oxidation of carbonyl sulphide and monosilane.** H. GUTSCHMIDT and K. CLUSIUS (Z. physikal. Chem., 1935, B, 30, 265—279).—The lower crit. limit for the stoichiometric mixture of COS and  $O_2$  in quartz and glass at  $190-480^\circ$  has been determined. The results agree well with Bawn's (A., 1933, 355) but are incompatible with Semenov's equation,  $\log(p_1+p_2)=A/T+B$ , ( $p_1, p_2$ =inflammation pressures of components) except over a very narrow temp. range. The effect of the diameter of the vessel,  $d$ , can be represented by  $(p_1+p_2)d^{9/7}=C$ , where  $C$  rises rapidly as the temp. falls. For mixtures of  $SiH_4$  and  $O_2$  in varying proportions the lower crit. limit has been determined at several temp. Semenov's equation,  $p_1 p_2 d^2 = \text{const.}$ , for the case where the chains break on the wall, does not hold. The probable cause of this discrepancy is that the course of the reaction varies with the composition of the mixture, for the form of the inflammation isotherms suggests the simultaneous occurrence of reactions yielding at least two different final products. No evidence of crit. limits could be obtained with mixtures of NO with  $CS_2$  vapour or  $PH_3$ . In all the examples of non-stationary chain reactions so far observed explosion involves no increase in the total no. of mols. present. R. C.

**Kinetics of the reaction between oxygen and sulphur. I. Reaction at  $240-280^\circ$ .** L. A. SAYCE (J.C.S., 1935, 1767—1774).— $SO_2$  is formed and chemiluminescence frequently occurs when a mixture of S vapour and 25—760 mm.  $O_2$  at  $200-280^\circ$  is cooled rapidly. The yield of  $SO_2$  is (i) greatest with air-cooling and least with very slow cooling, (ii) max. with 100—300 mm. of  $O_2$ , (iii) independent of  $[S]$  and initial temp. between  $240^\circ$  and  $280^\circ$ , but is very small at

< 220°. Effects due to this reaction were largely eliminated by a new static method for following the principal S-O<sub>2</sub> reaction. The latter is entirely heterogeneous at 240—280° and the velocity,  $k$ , on liquid S is 16-fold that on glass (cf. J.C.S., 1923, 123, 3203). The heat of activation on glass, and probably on liquid S, is 46,430 g.-cal., suggesting similar mechanisms on these surfaces. There is a linear relation between  $k$  and [O<sub>2</sub>], but with [O<sub>2</sub>] > 4 × 10<sup>-4</sup> g. per c.c. there is a marked acceleration probably owing to the development of a chain reaction. J. G. A. G.

**Esterification as a gas reaction.** C. A. WINKLER and C. N. HINSHELWOOD (Trans. Faraday Soc., 1935, 31, 1739—1743).—Reaction between MeOH and HCl vapours occurs readily at 450°, mainly on the surface of the reaction vessel. MeOH and AcOH do not react with appreciable velocity below the temp. at which decomp. of the MeOH becomes rapid. Reaction between MeOH, AcOH, and HCl to yield MeOAc occurs rapidly at 300°, probably in an adsorbed layer of MeOH where ionisation of the HCl can occur. Quant. results were irregular. The rate of esterification in a MeOH solution of AcOH and HCl decreases only slowly as the MeOH is replaced by CCl<sub>4</sub> until the [MeOH] reaches a small val., beyond which it  $\propto$  the [MeOH]. In this region the velocity of reaction  $\propto$  [AcOH]<sup>1/2</sup>. Some erratic behaviour is observed, related to the size of the liquid-vapour interface, so that adsorption at interfaces may play a part and thus the system becomes analogous to a gaseous system. J. W. S.

**Kinetics of ethylene polymerisation.** II. H. H. STORCH (J. Amer. Chem. Soc., 1935, 57, 2598—2601; cf. A., 1934, 369).—Addition of about 0.1% of EtSH to C<sub>2</sub>H<sub>4</sub> decreases the rate of polymerisation about 10-fold; the induction period is not eliminated, but its duration is markedly reduced. The induction period appears to be due to an intermediate compound, which survives cooling at -180° and subsequent re-activation into the reaction chamber at 393°. The polymerisation of C<sub>2</sub>H<sub>4</sub> is probably not a simple bimol. reaction. The activation energy is 43,500 g.-cal. E. S. H.

**Thermal decomposition of methyl hydrogen peroxide.** S. MEDVEDEV and A. PODJAPOLSKAJA (Acta Physicochim. U.R.S.S., 1935, 2, 487—504).—Decomp. of MeO<sub>2</sub>H in an atm. of N<sub>2</sub> gave the following products: MeOH, Me<sub>2</sub>O, CH<sub>2</sub>O, HCO<sub>2</sub>H, O<sub>2</sub>, CO, CO<sub>2</sub>, and H<sub>2</sub>O, but no H<sub>2</sub> or CH<sub>4</sub>. Two primary decomp. reactions take place, viz. (1) MeO<sub>2</sub>H → CH<sub>2</sub>O + H<sub>2</sub>O, and (2) 2MeO<sub>2</sub>H → 2MeOH + O<sub>2</sub>. At low temp. (1), which is followed by MeO<sub>2</sub>H + CH<sub>2</sub>O → MeO<sub>2</sub>·CH<sub>2</sub>·OH, predominates. The activation energies for (1) and (2) are 10,950 and 25,330 g.-cal., respectively. O. J. W.

**Abnormally small steric factors in chemical kinetics.** H. HELLMANN and J. K. SIRKIN (Acta Physicochim. U.R.S.S., 1935, 2, 433—466).—The wave-mechanical theory of collision processes presented is able to account for abnormally small steric factors (of the order of 10<sup>-5</sup>—10<sup>-8</sup>) in the velocity coeff. expression. The influence of tunnel effects on the steric factor is discussed. O. J. W.

**Polymorphism.** III. Linear velocity of the transformation of  $\alpha$ - into  $\beta$ -*o*-nitroaniline. N. H.

HARTSHORNE, G. S. WALTERS, and (in part) W. O. M. WILLIAMS (J.C.S., 1935, 1860—1873; cf. A., 1931, 1407).—Irregularities of the contour of the advancing interface between  $\alpha$ - and  $\beta$ -*o*-nitroaniline (I) are not due to local variations in the thickness of the film, although in very thin films the average velocity,  $v$ , is > in films 0.01—0.02 mm. thick. The decrease of  $v$  as the interface advances is not primarily due to impurities and is attributed to the progressive widening of the gap between the  $\alpha$ - and  $\beta$ -forms, since the  $d$  of  $\alpha$ - is < the  $d$  of  $\beta$ -(I). There were considerable variations in  $v$  with different specimens at the same temp., but there was no overlapping between the results at 0°, 20°, 30°, and 40°. No relation was found between  $v$  and the degree of purity of the specimens. The data are represented, in general, by the semi-empirical equation  $t = k_1 s^3 + k_2 s$ , where  $s$  is the linear displacement of the interface in time  $t$  from zero. The temp. coeff. between 20° and 40° leads to the activation energy 17—18 kg.-cal. per mol. This val. is in harmony with the view that  $v$  is controlled by the difference between the rates of evaporation of  $\alpha$ - and  $\beta$ -(I). J. G. A. G.

**Mechanism of polymerisation reactions.** I, II. H. DOSTAL (Monatsh., 1935, 67, 1—9, 63—79, 222).—I. Theoretical. The treatment previously developed (A., 1935, 1206) is extended to the stabilisation of growing chains, which is regarded as a unimol. process, the velocity coeff. of which may vary with the chain length.

II. The theory is applied to the dependence on time of the total quantity of polymeride, and to the influence of a steric factor, and of the combination of partly grown chains, on polymerisation. Stabilisation of chains, both spontaneously and in the presence of a foreign substance, is further considered. F. L. U.

**Activation energies of some reactions involving free radicals.** C. E. SUN (J. Chinese Chem. Soc., 1935, 3, 293—295).—The activation energy of reactions involving free radicals can be calc. by Eyring's method. The val. for a reaction in which there is a transfer of H from a C of the normal mol. to a free radical, the rest of the mol. remaining unaltered, is 17 kg.-cal. A. J. M.

**Kinetics of the reduction of (A) copper sulphate, (B) bismuth chloride, by hypophosphorous acid in aqueous solutions.** (A) G. S. VOZDVISHENSKI and A. F. GERASIMOV. (B) A. F. GERASIMOV and B. M. KOZUIREV (Trans. Butlerov Inst. Chem. Tech. Kazan, 1934, No. 1, 108—113, 126—133).—(A) The reaction was studied at 47°. The [Cu] at time  $t$  is given by  $\log [Cu] = 2.2932 - 0.48 \log t$ .

(B) The reaction was studied at 50°. The [Bi] at time  $t$  is given by  $\log [Bi] = -2.523 - 0.1 \log t$ .

CH. ABS. (e)  
**Velocity of decomposition of calcium carbonate solutions.** Y. KAUKO (Ann. Acad. Sci. fenn., 1934, A, 39, No. 9; Chem. Zentr., 1935, i, 2767).—The decomp. of Ca(HCO<sub>3</sub>)<sub>2</sub> at 0—15° by passage of CO<sub>2</sub>-free air follows the course HCO<sub>3</sub>' → OH' + CO<sub>2</sub>. At low [HCO<sub>3</sub>'] the velocity is determined by the velocity of diffusion of CO<sub>2</sub>. J. S. A.

**Polar effects of the halogens in aromatic combination.** G. BADDELEY, G. M. BENNETT, S. GLASTONE, and B. JONES (J.C.S., 1935, 1827—1830; cf. A., 1933, 1151).—Data previously considered and new data (see below) are interpreted by means of the following factors: an electromeric effect (if any), a mesomeric polarisation, an inductive effect and field effects all varying in the order  $F > Cl > Br > I$ , and a polarisability effect varying in the order  $I > Br > Cl > F$ . The nature of these effects is discussed. J. G. A. G.

**Intermediate stages in aldehyde oxidation. III. Kinetics of the reaction between peracetic acid and aldehydes in aqueous solution.** G. D. LUBARSKI and M. J. KAGAN (Acta Physicochim. U.R.S.S., 1935, 2, 665—678; cf. A., 1935, 1084).—The reaction has been studied in various concns. of aq. AcOH. The velocity coeff. in presence of  $H_2O$  is  $>$  in non-aq. solution due to acceleration of the second stage  $OH \cdot CHMe \cdot O \cdot OAc \rightarrow 2AcOH$ . In aq. MeCHO the velocity coeff. increases with  $H_2O$  content. The data do not support Wieland's hypothesis (A., 1932, 722). T. G. P.

**Kinetics of the bromination of benzaldehyde.** J. K. SIRKIN and A. T. GLADISCHEV (Acta Physicochim. U.R.S.S., 1935, 2, 467—472).—The velocity of the bromination of PhCHO in  $CCl_4$  solution in the dark has been measured at 30°, 35°, and 40°. Assuming that the reaction is bimol. the activation energy is calc. to be 32,900 g.-cal. Quinol and I do not influence the velocity. As the reaction is very slow a unimol. equation is obeyed approx. O. J. W.

**Dilatometric method for following the hydrolysis of sucrose.** D. I. HITCHCOCK and R. B. DOUGAN (J. Physical Chem., 1935, 39, 1177—1188).—The vol. change of sucrose (I) solutions undergoing inversion by HCl follows strictly a unimol. formula, and the velocity coeffs. agree with those obtained polarimetrically. The total contraction per mol. of (I) at infinite dilution, for complete hydrolysis and with the products in mutarotation equilibrium, is by extrapolation 6.92 c.c. at 25°. Results obtained with invertase are similar but less simple. The dilatometric method may be used with confidence in studying the hydrolysis of (I) in acid solutions, and for comparing the activities under optimum conditions of preps. of yeast-invertase. F. L. U.

**Velocities of reaction of  $\beta$ -arylethyl chlorides with potassium iodide.** G. BADDELEY and G. M. BENNETT (J.C.S., 1935, 1819—1821).—The data refer to  $p$ -X-C<sub>6</sub>H<sub>4</sub>-C<sub>2</sub>H<sub>4</sub>Cl, where X=H, MeO, I, Br, Cl, F, and NO<sub>2</sub>, in COMe<sub>2</sub> solution at 55° and 75°. The velocity coeff. at 75° is halogens  $>$  MeO  $>$  H.

J. G. A. G.

**Velocities of reaction of substituted benzyl chlorides in two reactions of opposed polar types.** G. M. BENNETT and B. JONES (J.C.S., 1935, 1815—1819).—The data refer to the  $o$ -,  $m$ -, and  $p$ -monohalogen- and NO<sub>2</sub>-, and  $p$ -Me-substituted benzyl chloride. The energy of activation,  $E$ , of the hydrolysis in 50% aq. COMe<sub>2</sub> is approx. 20.9 kg.-cal. between 70° and 85°. The velocity coeff.,  $k$ , is approx. const. in the  $m$ -halogen series, but in the  $o$ - and  $p$ -halogen series  $F \gg Cl > Br > I$ . The  $k$  of the reaction

with KI in COMe<sub>2</sub> at 0.1° and 20° has been determined.  $E$  is approx. 17.3 kg.-cal. for the  $o$ -compounds and 18.1 for the  $m$ - and  $p$ -derivatives. The anomalous vals. for  $k$  previously observed (A., 1925, i, 494) with  $o$ - and  $p$ -C<sub>6</sub>H<sub>4</sub>Br-CH<sub>2</sub>Cl are due to the presence of  $o$ - and  $p$ -C<sub>6</sub>H<sub>4</sub>Cl-CH<sub>2</sub>Br. The pure reagents were therefore prepared from the appropriate nuclear-substituted benzyl alcohol. J. G. A. G.

**Ester hydrolysis in pure water.** A. SKRABAL (Monatsh., 1935, 67, 118—128).—A discussion of papers by Kirmann (A., 1934, 847) and Poethlke (A., 1935, 938). F. L. U.

**Energies and entropies of activation of the reaction between bromoacetate and thiosulphate ions.** V. K. LA MER and M. E. KAMNER (J. Amer. Chem. Soc., 1935, 57, 2662—2668).—The temp. coeffs. of the reaction have been studied over a range of temp. and concn. to obtain data for the effect of temp. and ionic environment on the energy of activation and the action const.  $B$ . The increase in  $\log k$  produced by the addition of Na<sup>+</sup> is correlated with an increase of  $B$ . In presence of Ba<sup>++</sup> and La<sup>+++</sup> the energy of activation is increased, but is more than compensated by an increase in the entropy of activation. E. S. H.

**Influence of non-electrolytes on the kinetics of the reaction between bromoacetate and thiosulphate ions.** V. K. LA MER and M. E. KAMNER (J. Amer. Chem. Soc., 1935, 57, 2669—2673).—The velocity coeff. in H<sub>2</sub>O is increased by adding CO(NH<sub>2</sub>)<sub>2</sub>, sucrose, glycerol, or dioxan, although CO(NH<sub>2</sub>)<sub>2</sub> raises the dielectric const. and the remainder lower it. The energy of activation is unchanged by CO(NH<sub>2</sub>)<sub>2</sub>, but decreased by the other non-electrolytes. In 32% sucrose solutions the positive salt catalysis arises from an increase in the entropy of activation, which more than compensates the retarding influence of an increase in the energy of activation. E. S. H.

**Temperature dependence of the energy of activation in the de-aldolisation of diacetone alcohol.** V. K. LA MER and M. L. MILLER (J. Amer. Chem. Soc., 1935, 57, 2674—2680).—The velocity coeff. in presence of dil. NaOH has been determined at 5° intervals between 0° and 50°; the proportionality between velocity coeff. and [NaOH] has been confirmed over a limited concn. range at 25°. The energy of activation is a function of temp., increasing from 15,850 g.-cal. at 5° to 17,250 g.-cal. at 32.5°, and then decreasing by about 400 g.-cal. at 45°. Addition of 18.5% MeOH causes an increase of  $>$ 1700 g.-cal. The corresponding vals. for the action const.  $B$  in H<sub>2</sub>O and MeOH solutions are parallel. The data show the inadequacy of the collision theory and the importance of the entropy of activation. E. S. H.

**Kinetics of bimolecular reactions in solution. II. Formation of sulphonium salts.** J. K. SIRKIN and I. T. GLADISCHEV (Acta Physicochim. U.R.S.S., 1935, 2, 291—302).—The kinetics of the reaction between MeI and Et<sub>2</sub>S to yield SMeEt<sub>2</sub>I has been studied at 17°, 27°, and 37° in MeOH, EtOH, PrOH, and COMe<sub>2</sub> solutions. The calc. activation energies, corr. for the variation of frequency

of collision with viscosity, are 19,150, 20,760, 21,270, and 13,300 g.-cal. per mol., respectively. The velocities of reaction observed in alcohols are only about 0.01 of those calc. from the frequency of collision and activation energy, this being attributed to steric factors. In  $\text{COMe}_2$  the velocity is only  $4 \times 10^{-7}$  of the calc. val. This reaction in these solvents is intermediate between a normal and a slow reaction. The mechanism of reaction in  $\text{COMe}_2$  is discussed in detail.

J. W. S.

**Velocity of alkaline hydrolysis of crotonic esters.** E. SCHJÄNBERG (Z. physikal. Chem. 1935, 174, 465—471).—Branching of the C chain of the alkyl radical of the alcohol in the  $\alpha$ -position reduces the velocity coeff.,  $k$ , owing to fall in the action const.,  $\alpha$ . Comparison with the rates of hydrolysis of corresponding butyrates shows that an  $\alpha\beta$ -double linking in the acyl radical depresses  $k$ , whilst both the energy of activation,  $Q$ , and  $\alpha$  rise; the effect of the rise in  $Q$  outweighs that of the rise in  $\alpha$ , so that the net effect is a fall in  $k$ .

R. C.

**Coupled oxidation of alcohol.**—See this vol., 242.

**Relation between the apparent and true activation energy of heterogeneous reactions.** M. TEMKIN (Acta Physicochim. U.R.S.S., 1935, 2, 313—316).—Mathematical.

J. W. S.

**Reaction velocity in the system solid<sub>1</sub> + gas  $\rightarrow$  solid<sub>2</sub>.** G. S. GARDNER (J. Math. Phys. Mass. Inst. Tech., 1935, 14, 241—259).—Based on Langmuir's treatment and Fourier's law for heat conduction, an equation is derived for the rate of a solid-gas reaction and is integrated for six special cases covering all types of available data. Results are illustrated by curves using available data for the reaction of anhyd.  $\text{NH}_3$  with mixtures of powdered glass and  $\alpha$ - and  $\beta$ - $\text{C}_{10}\text{H}_7\text{OH}$ , phthalic acid, tartaric acid, and quinol, and for  $\text{NH}_3$ -anhyd.  $\text{CuSO}_4$ ,  $\text{N}_2$ - $\text{CaC}_2$ ,  $p$ -anisidine in  $\text{HCl}$ -air, and  $\psi$ -cumenol in  $\text{NH}_3$ -air.

N. M. B.

**Stability of solid pharmaceutical hydrogen peroxide preparations.**—See B., 1936, 74.

**Influence of fluid velocity on heterogeneous reactions. IV. Absorption of ammonia in wetted-wall towers.** S. UCHIDA and S. MAEDA. V. Model experiment of chemical change in packed towers. S. UCHIDA and S. SHONOYA (J. Soc. Chem. Ind. Japan, 1935, 38, 625B, 626—629B)—IV. Uchida's theoretical relationship (A., 1934, 1312) is roughly confirmed by experiment.

V. The factors governing the velocity of solid-liquid reactions in dynamic systems, where the rate of diffusion is predominant, have been correlated from experiments on the dissolution of sugar in packed columns.

J. S. A.

**Application of A. N. Schtschukarev's method of determining densities to the study of the reaction of polymorphic transformation of  $\beta$ -into  $\alpha$ -silver iodide.** V. LINITZKI (Ukrain. Chem. J., 1935, 10, 283—284).—The rate of transformation is determined by measuring the apparent change in wt. of a sample immersed in paraffin heated at  $148^\circ$ .

R. T.

**Velocity of absorption of oxides of nitrogen.** V. I. ATROSCITSCHENKO (Ukrain. Chem. J., 1935, 10, 295—304).—The relative velocity,  $V$ , of absorption of  $\text{NO}_2$  at  $20^\circ$  by various liquids is:  $\text{H}_2\text{O}$  1, 6 and 20%  $\text{HNO}_3$  0.84 and 0.79, 4.5 and 20%  $\text{NaOH}$  0.57 and 0.526, 17%  $\text{KOH}$  0.515, 90.2%  $\text{H}_2\text{SO}_4$  0.42, 10.6%  $\text{Na}_2\text{CO}_3$  0.375, and liquid paraffin 0.072. The corresponding figures for  $\text{NO-NO}_2$  mixture are 1, 0.85 and 0.65, 0.83 and 1.02, 1.05, 14.0, 0.134, and 0.0, and the corresponding ratios  $V_{\text{NO}_2}/V_{\text{NO}}$  are 4.2, 4.2, 5.0, 2.9, 2.2, 2.1, and 0.13 ( $\text{Na}_2\text{CO}_3$  and paraffin not given).

R. T.

**Kinetics of dehydration of gypsum.** P. P. BUDNIKOV and L. A. SCHTSCHUKAREVA (Kolloid-Z., 1935, 73, 334—339).—Determinations of loss of wt. show that the dehydration of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  at  $107^\circ$  follows the course of a unimol. reaction. The presence of small amounts of  $\text{NaCl}$  or  $\text{KCl}$  has a strong retarding action.

E. S. H.

**Deflagration of explosive substances by ultrasonic radiation.** N. MARINESCO (Compt. rend., 1935, 201, 1187—1189).—Substances very sensitive to shock, e.g.,  $\text{NI}_3$ , have been deflagrated by ultrasonic radiation. Others must be suspended in non-wetting liquids, when deflagration is induced by heating of the adhering air.

T. G. P.

**Kinetics of solid-phase reactions of certain carbonates with mullite, silica, and alumina.**—See B., 1936, 20.

**Reduction of iron oxides by gaseous reducing agents. I. Velocity of reduction of ferric oxide by hydrogen.** G. I. TSCHUFAROV and A. P. LOCHVITZKAJA (J. Phys. Chem. U.S.S.R., 1934, 5, 1103—1113).—Reduction of  $\text{Fe}_3\text{O}_4$  is not autocatalytic. The remaining stages are autocatalytic intersurface reactions. Data for the rates of reduction at 300—900° under various conditions are given. The porosity of the product is the greater the lower is the reduction temp.

CH. ABS. (c)

**Comparison between the effect of hydrogen-ion concentration on the rate of corrosion of steel in pure oxygen and air at  $25^\circ$ .** J. M. BRYAN (Trans. Faraday Soc., 1935, 31, 1714—1718; cf. A., 1933, 1251; 1935, 43).—The effect of a high  $[\text{O}_2]$  on the corrosion of Fe in citric acid containing varying amounts of Na citrate is to equalise the attack over most of the  $p_{\text{H}}$  range 2.4—5.5. Using fast-corroding steel the evolution of  $\text{H}_2$  is inhibited by pure  $\text{O}_2$  at high acidity, thus counterbalancing the increase in rate of corrosion through depolarisation. As the  $[\text{Fe}]$  in the solution increases its effect overshadows that of the direct action of  $\text{O}_2$  at the metal surface.

J. W. S.

**Rate of dissolution of iron in molten zinc.**—See B., 1936, 23.

**Explosive decomposition of tetryl.** A. LUKIN and S. ROGINSKI (Acta Physicochim. U.R.S.S., 1935, 2, 385—396; cf. J.C.S., 1921, 119, 721).—The time required for the explosion of tetryl to occur in a sealed vessel has been studied as a function of temp. and at  $156^\circ$  as a function of the amount of picric acid added.

J. W. S.

**Kinetics of the oxidation of fats and oils.**—See B., 1936, 27.



**Structure theory of chemical change. Complete system of doublet reactions.** A. A. BALANDIN (*Acta Physicochim. U.R.S.S.*, 1935, 2, 177—202; cf. A., 1929, 519, 890).—A complete system of "doublet" reactions in org. chemistry is drawn up. All have not been experimentally realised. The theory of structure of reactions may also be applied to heterogeneous reactions. Hydrogenation reactions are more fully discussed. A. J. M.

**Directions of reactions of decomposition and condensation.** A. A. BALANDIN (*Acta Physicochim. U.R.S.S.*, 1935, 2, 345—362; cf. preceding abstract).—The author's theory is extended to the determination of the different possible directions in which a complicated mol. can react. J. W. S.

**Application of the structure theory of reactions to Lebedev's synthesis of butadiene from alcohol and to Rice's theory of pyrolysis.** A. A. BALANDIN (*Acta Physicochim. U.R.S.S.*, 1935, 2, 363—376).—The author's theory (cf. preceding abstracts) is applied to the catalytic decomp. of EtOH at 450°, with special reference to the formation of (CH<sub>2</sub>:CH)<sub>2</sub>. Rice's theory of thermal decomp., which is in accord with the doublet mechanism of decomp., is developed and applied to cyclic hydrocarbons. The results are in qual. agreement with experiment. J. W. S.

**Inhibition of homogeneous reactions by small quantities of nitric oxide.** L. A. K. STAVELEY and C. N. HINSHELWOOD (*Nature*, 1936, 137, 29—30).—Small amounts of NO (0.1—1 mm.) reduce the rate of decomp. of Et<sub>2</sub>O, EtOPr, Pr<sup>β</sup><sub>2</sub>O, and EtCHO to a well-defined limit. MeOH, COMe<sub>2</sub>, and MeCHO give negative results. The effect is as though short reaction chains were broken up by the NO. L. S. T.

**Catalysis of hydrogen peroxide [decomposition] by iron salts.** N. JERMOLENKO and E. NOVIKOVA (*Z. anorg. Chem.*, 1935, 225, 333—336).—A study of the catalytic decomp. of H<sub>2</sub>O<sub>2</sub> by Fe salts of varying solubility and tendency to colloid formation indicates that catalysis is mainly due to colloidal Fe(OH)<sub>3</sub> containing adsorbed Fe<sup>+++</sup>. M. S. B.

**Efficiency of stabilisers used in the preservation of hydrogen peroxide.**—See B., 1936, 18.

**Homogeneous catalysis: decomposition of acraldehyde catalysed by iodine.** H. W. THOMPSON and J. J. FREWING (*Trans. Faraday Soc.*, 1935, 13, 1660—1668).—The decomp. of CH<sub>2</sub>:CH·CHO, catalysed by I, occurs 100° lower than in the absence of catalyst. The velocity of reaction  $\propto [I]^2$ . The reaction is only slightly retarded by packing the vessel, but is appreciably retarded by increasing [CH<sub>2</sub>:CH·CHO]. Probably catalysis occurs through I<sub>2</sub> mols. and the short chains are propagated and broken both by CH<sub>2</sub>:CH·CHO and I<sub>2</sub> mols. J. W. S.

**Kinetics of the autoxidation of pyrocatechol in presence of several foreign substances.** G. E. K. BRANCH and M. A. JOSLYN (*J. Amer. Chem. Soc.*, 1935, 57, 2388—2394).—Cysteine, K<sub>2</sub>SO<sub>3</sub>, and *o*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·OH inhibit the O<sub>2</sub> absorption of pyrocatechol (I), whilst quinol (II), resorcinol, pyrogallol (III), gallic acid, and *p*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·OH accelerate it.

In mixtures of (I) with (II) or (III) the rate increases almost to that for pure (II) or (III). A chain-exchanging mechanism is postulated. E. S. H.

**Behaviour of chromic oxide towards alkali halogenate solutions. II. Autocatalysis in the system chromic oxide-bromate and the influence of bromides in solution.** R. LYDÉN (*Z. anorg. Chem.*, 1935, 226, 46—56).—Oxidation of Cr<sub>2</sub>O<sub>3</sub> by neutral aq. KBrO<sub>3</sub> (cf. A., 1935, 834) is entirely prevented by the previous addition of alkali hydroxide or carbonate. The reaction is catalysed by H<sup>+</sup>, and since these are formed in the course of the reaction the latter is autocatalytic. The effect of added Br<sup>-</sup> is to depress the catalytic action of H<sup>+</sup>. F. L. U.

**Theory of heterogeneous catalysis.** P. D. DANKOV (*Compt. rend. Acad. Sci. U.R.S.S.*, 1935, 3, 253—256).—A theory which relates dispersion to catalytic activity renders possible the determination of the elementary catalysing area, indicates the connexion between the structure of the reacting mols. and the activity and structure of the catalyst, gives qualitatively new and quantitatively computable causes for the poisoning and promoting of catalysts, and points to new methods of interpreting and estimating chemical processes on the surface. W. R. A.

**Compact disperse materials. Action of hydrogen peroxide on ferric hydroxide.** H. W. KOHL-SCHÜTTER and H. SIECKE (*Z. Elektrochem.*, 1935, 41, 851—860; cf. A., 1933, 1019).—The catalytic activity (in decomp. H<sub>2</sub>O<sub>2</sub>) of pseudomorphic Fe(OH)<sub>3</sub> has been studied in relation to H<sub>2</sub>O content, degree of dispersion, and chemical reactivity. The results are discussed from the point of view of its structure. F. L. U.

**Reality of the chains in heterogeneous-homogeneous catalysis.** M. POLJAKOV and A. ELKENBARD (*Acta Physicochim. U.R.S.S.*, 1935, 2, 397—400).—When a Pt spiral is heated to > about 250° in a 3 : 1 H<sub>2</sub>-O<sub>2</sub> mixture contained in a vessel the walls of which are cooled in liquid air, H<sub>2</sub>O<sub>2</sub> is produced in a quantity which increases with rise of temp. of the Pt. If, however, a Pt gauze is interposed between the spiral and wall, H<sub>2</sub>O<sub>2</sub> formation is almost undetectable. The gauze therefore either eliminates the step in the reaction which gives rise to H<sub>2</sub>O<sub>2</sub> or causes stoppage of the chains. This observation proves the existence of a homogeneous process in this heterogeneous catalytic reaction, and also the chain mechanism of this process. J. W. S.

**Catalysis by fusions.** I. E. ADADUROV and P. D. DIDENKO (*J. Amer. Chem. Soc.*, 1935, 57, 2718—2722).—The catalytic activity of Sn in the oxidation of NH<sub>3</sub> by air increases with rise of temp. beyond the m.p.; thus the crystal lattice of Sn is not involved, but it is shown that the catalysis is actually due to SnO<sub>2</sub>. When Ag is used as the catalyst, no oxide is formed and the catalytic activity falls abruptly, with simultaneous change in the type of reaction, at the m.p. The bearing of these results on other catalytic reactions is discussed. E. S. H.

**Inflammability of ammonia in presence and absence of a catalyst.** H. ABESHAUS, N. TOKAREV, and N. NEKRASSOV (*Acta Physicochim. U.R.S.S.*,

1935, 2, 401—420).—The limiting pressures for the explosion of  $\text{NH}_3$ -air mixtures have been studied as a function of temp. and  $[\text{NH}_3]$  without a catalyst, and in presence of Pt gauze treated in various ways. The explosion region becomes narrower in presence of  $\text{H}_2\text{O}$  vapour, especially in decreasing the max.  $[\text{NH}_3]$  for explosion. The photochemical oxidation of  $\text{NH}_3$  has also been investigated, and the mechanism of the oxidation process is discussed.  
J. W. S.

**Velocity of decomposition of ammonia on thoriated tungsten.** I. MOTSCHAN, I. PEREVESEV, and S. ROGINSKI (*Acta Physicochim. U.R.S.S.*, 1935, 2, 203—210).—The addition of Th to a W surface has no effect on the catalytic activity of W in the decomp. of  $\text{NH}_3$ .  
A. J. M.

**Dependence of the structure of an ammonia catalyst on the conditions of its reduction.** A. M. STEFANOVSKI, E. S. TATARSKI, and N. V. SELJAKOV (*Compt. rend. Acad. Sci. U.R.S.S.*, 1935, 3, 21—24).—Higher temp. of prep. cause a diminution in activity associated with readjustment of the crystal lattice.  
C. W. G.

**Active oxides. LXXXVII. Active states of the systems cadmium oxide-iron oxide and beryllium oxide-iron oxide with regard to their catalytic activity in the decomposition of nitrous oxides.** G. F. HÜTTIG, G. SIEBER, and H. KITTEL (*Acta Physicochim. U.R.S.S.*, 1935, 2, 129—150).—Equimol. mixtures of  $\text{CdO}$  and  $\text{Fe}_2\text{O}_3$ , and  $\text{BeO}$  and  $\text{Fe}_2\text{O}_3$ , respectively, were heated at various temp. and the catalytic effect on the decomp. of  $\text{N}_2\text{O}$ , colour, and magnetic susceptibility was determined with respect to the temp. at which the systems were heated. The results of the catalytic action are expressed by  $\log \alpha = (-q/RT) + \log n'$ , where  $\alpha$  is the % of  $\text{N}_2\text{O}$  decomposed,  $T$  is the abs. temp. of heating, and  $q$  and  $n'$  are consts. for each system.  $q$  may be regarded as a heat of activation, whereas  $n' \propto$  the no. of active spots. The higher is  $q$ , the smaller is the activity of individual active spots. For the system  $\text{CdO}-\text{Fe}_2\text{O}_3$  there is no perceptible change in properties at temp.  $< 450^\circ$ . At about this temp. there is a slight colour change, accompanied by the commencement of catalytic action, which reaches a max. at about  $550^\circ$ . The magnetic susceptibility shows a sudden increase at about  $550^\circ$ , and reaches a max. at  $750^\circ$ . Similar results are obtained for the system  $\text{BeO}-\text{Fe}_2\text{O}_3$ , but in this case, unlike the first, the decrease in activity after the max. cannot be ascribed to compound formation. The ageing of active  $\text{MgO}$  (decrease of activity with time) has also been investigated.  
A. J. M.

**Acceleration of the reaction  $\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$  by the presence of some salts.** U. NISHIOKA (*Kinzo-Kenki.*, 1935, 12, 42—48).—Rates of formation of  $\text{CO}$  from  $\text{C}$  and  $\text{CO}_2$  at  $1000^\circ$  were measured with various carbonates and chlorides of alkali and alkaline-earth metals as catalysts. The catalytic activity increased with the at. wt. of the metal forming the salt.  
CH. ABS. (e)

**Catalytic oxidation of carbon.** J. E. DAY, R. F. ROBEY, and H. J. DAUBEN (*J. Amer. Chem. Soc.*, 1935, 57, 2725—2726).— $\text{LiCl}$ ,  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{CaCl}_2$ ,  $\text{SrCl}_2$ ,

$\text{BaCl}_2$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{Ba}(\text{OH})_2$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{K}_2\text{SO}_4$  catalyse the oxidation of films of deposited  $\text{C}$ . E. S. H.

**Kinetics of the reaction between carbon dioxide and hydrogen on platinum from the viewpoint of the adsorption theory of catalysis.** M. TEMKIN and E. MICHALOVA (*Acta Physicochim. U.R.S.S.*, 1935, 2, 9—32).—Previous results (*A.*, 1925, ii, 564; 1930, 551) are in error owing to poisoning of the Pt wire. The reaction, which has been studied in vessels at  $-78^\circ$  with filament temp. of about  $800^\circ$  abs., yields a small amount of  $\text{C}$  besides the main products  $\text{CO} + \text{H}_2\text{O}$ . The rate is given by  $dp_{\text{CO}}/dt = k_1 p_{\text{H}_2} / (k_2 p_{\text{H}_2} + p_{\text{CO}})$ , which has been derived from the assumption that the reaction velocity depends on the rate of evaporation of  $\text{CO}$  from the surface. Rates of evaporation observed at different temp. are in agreement with Langmuir's results (*A.*, 1921, ii, 629) and the activation energy of evaporation (22,000—25,000 g.-cal.) approximates to the heat of adsorption of  $\text{CO}$ . The application of adsorption equilibrium equations to heterogeneous reactions is not always valid.  
R. S.

**Dissociation of antimony trihydride: an autocatalytic heterogeneous reaction.** J. GUÉRON and A. LALANDE (*Bull. Soc. chim.*, 1935, [v], 2, 2240—2258).—An expression is derived for the velocity of an irreversible gaseous reaction catalysed by a solid, using Langmuir's adsorption equation. The expression is shown to represent the autocatalytic thermal decomp. (2—95%) of  $\text{SbH}_3$  if the reaction in the adsorbed phase is unimol.  
F. L. U.

**Nature of the surface of copper catalysts.** W. W. RUSSELL and L. G. GHERING (*J. Amer. Chem. Soc.*, 1935, 57, 2544—2552).—Determinations of the catalytic activity of poisoned (with  $\text{O}_2$  or  $\text{N}_2\text{O}$ ) and unpoisoned surfaces of  $\text{Cu}$  by means of the  $\text{C}_2\text{H}_4-\text{H}_2$  reaction at  $0^\circ$ , and of the heat of sorption of  $\text{O}_2$ , show that the  $\text{Cu}$  surface is non-uniform and that the above catalytic reaction proceeds almost exclusively on a relatively few surface types, probably of intermediate character.  
E. S. H.

**Promoter action of gases on hydrogenation catalysts.** K. ABLESOVA and S. ROGINSKI (*Z. physikal. Chem.*, 1935, 174, 449—464; cf. *A.*, 1935, 830).—The catalytic activity in respect of the hydrogenation of  $\text{C}_2\text{H}_4$  of  $\text{Ni}$  films formed by evaporation in presence of  $\text{H}_2$  passes through a marked max. with increase in the amount of  $\text{H}_2$  sorbed in the prep. of the film; this corresponds with  $\sim 1 \text{ H}_2$  mol. per 100  $\text{Ni}$  atoms. Such activated films are not affected by poisons, but, except at very low temp., are irreversibly deactivated by exposure to high vac. The promoter action of the sorbed gas is possibly due to its influence on activated sorption; the prevention of recrystallisation may also be an accessory factor.  
R. C.

**Activation of specific bonds in complex molecules at catalytic surfaces.** H. S. TAYLOR, K. MORIKAWA, and W. S. BENEDICT (*J. Amer. Chem. Soc.*, 1935, 57, 2735).—By following the reactions (1)  $\text{C}_2\text{H}_6 + m\text{D}_2 \rightarrow \text{C}_2\text{H}_x\text{D}_y$  (where  $x+y=6$  and  $m$  may be varied arbitrarily) and (2)  $\text{C}_2\text{H}_6 + \text{H}_2 = 2\text{CH}_4$ , which

involve, respectively, the C-H and C-C linkings, the specificity of catalyst surfaces may be studied.

E. S. H.

**Effect of adsorbed water on the catalytic decomposition of hydrocarbons (by a molecular beam method).** O. BEECK (*Nature*, 1935, 136, 1028—1029).—The catalytic decomp. of hydrocarbons at a hot Pt or C surface has been investigated by means of a mol. beam technique. No dehydrogenation of paraffins, olefines, or alcohols occurs unless traces of H<sub>2</sub>O are present. It is probable that this H<sub>2</sub>O is necessary to maintain a unimol. layer on the catalytic surface and that this layer is the true seat of dehydrogenation. Dehydrogenation is inhibited by an excess of H<sub>2</sub>O on the Pt in the lower temp. region and the temp. at which the reaction falls off thus depends on the H<sub>2</sub>O content of the gas investigated. Traces of air in presence of traces of H<sub>2</sub>O do not affect the reactions. There is evidence that H<sub>2</sub>O may be substituted by other mols. having H linkings with electronegative elements, e.g., H<sub>2</sub>S. The primary reaction appears to be the formation of free radicals by rupture of C-C, except in the case of CH<sub>4</sub>, which may decompose into H<sub>2</sub> and CH<sub>2</sub>. The presence of H<sub>2</sub>O is also necessary for the hydrogenation of unsaturated hydrocarbons. L. S. T.

**Decomposition of propane and n-butane at carbon filaments.** L. BELCHETZ and E. K. RIDEAL (*J. Amer. Chem. Soc.*, 1935, 57, 2466—2469).—The gases were passed at high steaming velocity and low pressure (0.1 mm.) over a heated C filament placed 2—3 mm. from a Te mirror, kept at 100°, with which any radicals formed could react. The first step is the production of H<sub>2</sub> and the complementary olefine. The latter can then dissociate to CH<sub>2</sub> and the next lower olefine, except with Δ<sup>2</sup>-butene, which may be further dehydrogenated to butadiene. CH<sub>2</sub> subsequently reacts with surrounding mols. The energies of activation for the two reactions are 94.2 and 93.2 kg.-cal., respectively. E. S. H.

**Reaction of hydrogen and deuterium with ethylene at a nickel surface.** T. TUCHOLSKI and E. K. RIDEAL (*J.C.S.*, 1935, 1701—1704).—The combination of H<sub>2</sub> and D<sub>2</sub> with C<sub>2</sub>H<sub>4</sub> on a Ni filament at > 0° is almost of zero order. At 0—140°, the velocity coeff., *k*, for H<sub>2</sub> is > for D<sub>2</sub> and the difference between the energies of activation decreases from approx. 0.79 to approx. 0.5 kg.-cal. with rise of temp. *k<sub>H</sub>* and *k<sub>D</sub>* have max. vals. at approx. 140° and 160°, respectively, and at 165—168°, *k<sub>H</sub>* and *k<sub>D</sub>* are almost identical. The results negative zur Strassen's interpretation (*A.*, 1934, 974) of the inversion of the temp. coeff., and a mechanism is suggested.

J. G. A. G.

**Hydrogenation of ethylene with nickel as a catalyst at low temperatures.** O. TOYAMA (*Proc. Imp. Acad. Tokyo*, 1935, 11, 319—321).—The velocity between -70° and 0° increases with the pressure of H<sub>2</sub> and decreases gradually with increasing pressure of C<sub>2</sub>H<sub>4</sub>. C<sub>2</sub>H<sub>6</sub> has little effect. The apparent heat of activation is approx. 6 kg.-cal. The rate of the initial reaction is increased by pretreating the catalyst with H<sub>2</sub>, but C<sub>2</sub>H<sub>4</sub> has a retarding effect. The

reaction is probably a bimol. combination of H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> at the Ni surface. J. G. A. G.

**Ferromagnetic transformation and catalytic activity. IV. Hydrogenation of carbon monoxide and ethylene over nickel, and formation of carbon dioxide from carbon monoxide over the Heusler alloy MnAlCu<sub>2</sub>.** J. A. HEDVALL and R. HEDIN (*Z. physikal. Chem.*, 1935, B, 30, 280—288; cf. A., 1935, 1467).—The course of each of these reactions changes abruptly when the ferromagnetic transformation of the catalyst occurs. R. C.

**Preparation of platinum oxide reduction catalysts.** W. F. SHORT (*J.S.C.I.*, 1936, 55, 14T).—The H<sub>2</sub>PtCl<sub>6</sub>-NaNO<sub>3</sub> fusion is conducted in a 50-c.c. Pyrex beaker resting in a cavity (47 mm. diameter, 25 mm. deep) in a Cu block (37—40 mm. high, 90 mm. diameter) provided with a thermometer pocket. By working at a definite temp. (usually 500—550°) catalysts of max. activity can be prepared with certainty.

**Catalytic properties of rhenium and of certain of its compounds.** S. B. ANISIMOV, V. M. KRASCHE-NIKOVA, and M. S. PLATONOV (*J. Gen. Chem. Russ.*, 1935, 5, 1059—1065).—The catalytic activity of Re (on kaolin) is small for reactions of hydrogenation, considerable for that of dehydrogenation of EtOH to MeCHO (max. yields at 300° and 600°, with a min. at 400°), and very small for those of oxidation, owing to formation of oxides of Re volatile at > 100°. Re is readily recovered from the catalyst by heating the mass at 200° in an atm. of O<sub>2</sub> in a sealed tube, when Re<sub>2</sub>O<sub>7</sub> condenses in the cooled upper part of the tube. R. T.

**Comparative action of mixed catalysts when used for the joint dehydration of ethyl alcohol and ammonia. I.** N. I. SCHUIKIN, A. A. BALANDIN, and Z. I. PLOTKIN. **Comparative action of mixed catalysts when used for the joint dehydration of ethyl alcohol and aniline. II.** N. I. SCHUIKIN, A. A. BALANDIN, and F. T. DIMOV (*J. Physical Chem.*, 1935, 39, 1197—1205, 1207—1216; cf. A., 1932, 1232).—I. Mixtures of Al<sub>2</sub>O<sub>3</sub> with ZnO (10%), SnO (10%), Cr<sub>2</sub>O<sub>3</sub> (20%), and Fe<sub>2</sub>O<sub>3</sub> (10%) have been compared with pure Al<sub>2</sub>O<sub>3</sub> with regard to their activity in ethylating NH<sub>3</sub>. All but the last-named decrease the reaction rate. The Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> mixture is superior to Al<sub>2</sub>O<sub>3</sub> in causing less decomp. of EtOH. The results are discussed theoretically.

II. The activity of the above mixtures and of Al<sub>2</sub>O<sub>3</sub>+NiO (5%) in promoting the formation of NPhEt and NPhEt<sub>2</sub> from EtOH and NH<sub>2</sub>Ph has been determined. All the mixtures studied are less active than Al<sub>2</sub>O<sub>3</sub>, but that with Fe<sub>2</sub>O<sub>3</sub> causes less decomp. of EtOH. NPhEt is formed almost exclusively. F. L. U.

**Production of hydrocarbons from fatty acids by [catalytic] hydrogenation.**—See B., 1936, 10.

**Kinetics of catalytic oxidation of hydrocarbons and their derivatives.**—See B., 1936, 10.

**Activation of kaolin for catalytic processes.**—See B., 1936, 18.

[Asymmetric] catalysis with organic fibres. II. G. BREDIG, F. GERSTNER, and H. LANG (Biochem. Z., 1935, 282, 88—98; cf. A., 1932, 1062).—When PhCHO was replaced by MeCHO, cinnamaldehyde, anisaldehyde, and piperonal, part of the product was levorotatory in all cases. Bases other than  $\text{NHEt}_2$  (24 tested) combined with cotton fibres to produce substances which catalysed the production of mandelonitrile (I), levorotatory (I) being obtained in many cases. Catalysts from *tert.* bases produced no asymmetry; those from *sec.* produced asymmetry more often than those from primary bases. Catalyst from optically active bases other than coniine produced no asymmetry. *cis-d*-Diaminotrimethylcyclopentane (II) forms with the fibres a very active catalyst but this produces no asymmetry. (II) without fibres is less active but produces asymmetry. The decarboxylation of optically active and inactive camphorcarboxylic acid and bromocamphorcarboxylic acid by the catalysts (from optically active or inactive bases) yields no asymmetric products. Decarboxylation caused by (II) produces no asymmetry but the effect is greater with than without fixation on the fibres.

W. McC.

Influence of electrolyte on the concentration of heavy water. A. E. BRODSKI and N. P. SKRINKOVA (Acta Physicochim. U.R.S.S., 1935, 2, 809—810; cf. this vol., 160).—The separation factors, determined by electrolyzing 100 c.c. of 0.2*N*-salt solutions in 0.1%  $\text{D}_2\text{O}$  between Pt electrodes and measuring the concn. of  $\text{D}_2\text{O}$  in the residual liquid (12.5 c.c.), increase from 5.6 for KOH through  $\text{H}_2\text{SO}_4$ , KCl, NaCl, and  $\text{K}_2\text{CO}_3$  to 10.6 for  $\text{Li}_2\text{SO}_4$ .

T. G. P.

Electrolytic separation of the oxygen isotopes. G. OGDEN (Nature, 1935, 136, 912).—Using Ni electrodes and 1.25*N*-NaOH as electrolyte, the val. found for the electrolytic separation coeff.,  $\alpha$ , for the O isotopes is 0.87. Calc. vals. for  $\alpha$  lie between 0.86 and 1, depending on the width and height of the energy barrier, and allowing for the possibility of "tunnelling" of these barriers by complexes such as  $\text{O}^{16}\text{H}$  and  $\text{O}^{18}\text{H}$ . With the most favourable val. of  $\alpha$ , the  $[\text{O}^{18}]$  in pure  $\text{D}_2\text{O}$  prepared by electrolytic methods can never be > approx. 0.6%. L. S. T.

Theory of combustion of graphite. IV. V. SHIVONEN (Suomen Kem., 1935, 8, B, 47—49; cf. A., 1935, 1210).—Further experiments on the electrolytic oxidation of graphite (I) in fused  $\text{NaKCO}_3$  show CO and  $\text{CO}_2$  to be primary oxidation products in addition to electrolytically liberated  $\text{CO}_2$ . (I) with poorly developed crystal structure is more readily attacked by electrolytic oxidation than highly cryst. (I), but the lamellar structure of the latter favours formation of graphitic oxide.

J. S. A.

Electrolysis of bromides and iodides of zinc, nickel, and cobalt in mixtures of water and ethyl alcohol. C. CHARMETANT (Compt. rend., 1935, 201, 1174—1176; cf. A., 1935, 1086).—The nature of the products of electrolysis has been determined in relation to  $[\text{EtOH}]$ .

T. G. P.

Instantaneous action of certain colloids on the electrolytic deposition of copper. P. JACQUET

(Compt. rend., 1935, 201, 953—955; cf. A., 1935, 294).—Gelatin and serum-albumin influence the electro-deposition of Cu from aq.  $\text{CuSO}_4$  even during the first few secs. of the electrolysis. This is due to adsorption of the colloid on the metal surface. Other colloids which are not adsorbed (*e.g.*, gum arabic) must first be accumulated around the cathode by electrophoresis. Their action is not instantaneous.

H. J. E.

Electrolytic conduction of a solid insulator at high fields. Formation of anodic oxide film on aluminium. E. J. W. VERWEY (Physica, 1935, 11, 1059—1063; cf. A., 1935, 1307).—The formation of the  $\text{Al}_2\text{O}_3$  film is due to concn. of O ions at the Al anode.  $\text{Al}^{+++}$  ions liberated from the metal are then drawn into the O lattice. As soon as the field, which decreases with increasing thickness of the  $\text{Al}_2\text{O}_3$  layer, is insufficient for appreciable mobility of the cations, growth of the oxide coating stops.

H. J. E.

Electrolysis under the microscope. X. Crystallisation centres in cathodic deposition of gold. A. GLAZUNOV and B. HONZA (Chem. Obzor, 1934, 9, 124—126; Chem. Zentr., 1935, i, 2651).—The no. of crystallisation centres during electrolysis of  $\text{AuCl}_3$  increases with the c.d. Formation of complex Au ions leads to the deposition of colloidal Au. In acid solution or in presence of org. compounds, a higher c.d. is required for such colloidal deposition.  $\text{PdCl}_2$  behaves similarly.

J. S. A.

Action of silent electric discharge on nitric oxide. Production of active nitrogen. C. ZENGHELIS and K. EVANGELIDIS (Praktika, 1934, 9, 266—267; Chem. Zentr., 1935, i, 2770).—Reaction takes place in three stages: (i) decomp. into  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{O}_3$ , active N, which forms  $\text{NH}_3$  from  $\text{H}_2\text{O}$  present, and  $\text{NO}_2$ , (ii) oxidation of NO to  $\text{NO}_3$  and  $\text{N}_2\text{O}_6$ , (iii) reaction of NO with  $\text{NO}_3$  to form  $\text{N}_2\text{O}_5$ . Only stage (iii) is accelerated by the discharge.

J. S. A.

Influence of inert additions on the lower limit of the photochemical explosion of the  $\text{H}_2 + \text{Cl}_2$  mixture. F. A. LAVROV and T. PERELMAN (Acta Physicochim. U.R.S.S., 1935, 2, 91—102).—The influence of excess of  $\text{H}_2$  or  $\text{Cl}_2$  and additions of  $\text{N}_2$ , A,  $\text{CO}_2$ , and HCl on the lower explosion pressure  $P$  of stoichiometric  $\text{H}_2 + \text{Cl}_2$  mixtures has been studied.  $P$  is a min. at 70%  $\text{Cl}_2$  and then increases linearly with the pressure of added gas in accordance with a theoretical equation. Assuming equal deactivation probabilities  $\epsilon$  in each case, the ratio addition concn./ $[\text{N}_2]$  for a given  $P$  has been calc. and good agreement obtained with experimental ratios, except in the case of HCl, when  $\epsilon_{\text{N}_2} = 2.2\epsilon_{\text{HCl}}$ . It is supposed that HCl becomes excited and may then activate another  $\text{Cl}_2$ . The occurrence of  $P_{\text{min}}$  at 70%  $\text{Cl}_2$  is ascribed to excited  $\text{Cl}_2$  in the rôle of chain carrier.

R. S.

Photochemical decomposition of nitric oxide. P. J. FLORY and H. L. JOHNSTON (J. Amer. Chem. Soc., 1935, 57, 2641—2651).—Using radiation from the Hg arc or from sparks between electrodes of Al, Zn, Cd, Ni, Cu, or Sn over the range 0.02—7 mm., the final reaction products are  $\text{N}_2$  and  $\text{O}_2$ . The rate of decomp.  $\propto$  the rate of light absorption for light of the effective wave-length and, at very low pressures,

$\propto$  pressure. The rate is not influenced by dilution with  $N_2$ . Evidence of a primary process of pre-dissociation is adduced.

E. S. H.

**An error in photographic photometry.** J. LAGRULA (Compt. rend., 1935, 201, 1025—1026).

T. G. P.

[Photographic] image reversal in silver iodide and mercury iodide [emulsions]. LÜPPO-CRAMER (Z. wiss. Phot., 1935, 34, 292—304).—Similarly to AgI emulsions,  $HgI_2$  emulsions (in gum arabic) give reversed images on development, if before or after the normal exposure to a 100-watt lamp they have been briefly exposed to diffuse daylight. Using either AgI or  $HgI_2$  emulsions, prolonged exposure to sunlight produced lower densities than normal exposure to diffuse daylight. These and other similar data are compared with the usual types of solarisation (with AgBr emulsions), and the theory of solarisation is discussed at length; the regression theory (re-formation of Ag halide) is still supported, as it is claimed that no other hypothesis can explain the inhibition of solarisation by the presence of halogen acceptors (nitrites, sulphites).

J. L.

**Structure of the latent Röntgen [photographic] image.** W. HOFMANN (Z. wiss. Phot., 1935, 34, 267—275, 276—292).—An ordinary light image is formed mainly in the surface of a photographic layer, but an X-ray image is formed equally throughout the layer. Various experiments have been made on different aspects of the Villard effect (reduction of sensitivity to light by pre-exposure to X-rays). It is suggested that X-rays produce two kinds of latent image, one (R I) similar to an ordinary light image, and the other (R II) consisting of very small nuclei ("ultranuclei"). R II is not affected by physical or chemical development; the former produces a loose branching structure, not an image, and the latter, by dissolution of AgBr, causes assimilation of R II nuclei to R I nuclei, the R II image being therefore lost. Ordinary light converts R II into a new kind of latent image, L II, which is not physically developable, but after primary fixing gives nuclei more widespread and more developable than an ordinary light image, when subsequently chemically developed. The theory is applied to explain the Villard effect.

J. L.

**Effect of wave-length on the iodine-sensitised decomposition of ethylene iodide in carbon tetrachloride solution.** R. G. DICKINSON and N. P. NIES (J. Amer. Chem. Soc., 1935, 57, 2382—2386).—For  $\lambda$  4358, 5461, and 5770 with 5790 Å., the relative vals. of the rate coeff. are 1 : 0.931 : 0.867. Light corresponding with continuous absorption in gaseous I is slightly more effective in dissociating I in solution than is light corresponding with discontinuous absorption.

E. S. H.

**Photochemical investigations. II. Photochemical decomposition of ethylene iodide in solutions of carbon tetrachloride.** R. E. DEIGHT and E. O. WING (J. Amer. Chem. Soc., 1935, 57, 2411—2415; cf. A., 1930, 180).—The apparent quantum yield with  $\lambda$  303 and 313  $m\mu$  is 0.76, including the photo- and any subsequent thermal reactions. The

mechanism discussed involves primary dissociation into  $C_2H_4I$  and I atoms.

E. S. H.

**Photochemical reaction between sodium formate and iodine, and a relation between chemical reactivity and light absorption.** N. R. DHAR and P. N. BHARGAVA (J. Physical Chem., 1935, 39, 1231—1244).—The reaction between  $HCO_2Na$  and aq. I in the absence of KI is unimol. in the dark and semimol. in the light. The velocity of the photochemical change  $\propto I^n$  ( $I$  = intensity,  $n = 0.75$ —1.5). Einstein's law is not obeyed, the quantum yield increasing with temp. and with frequency of the incident radiation. More light is absorbed by the mixture than by the reactants separately owing, it is suggested, to weakening of the binding forces.

F. L. U.

**Photochemical reactions of SH-compounds in solution.** J. WEISS and H. FISCHGOLD (Nature, 1936, 137, 71—72).—When aq. neutral or alkaline solutions of NaSH, EtSH, thioglycollic acid, cysteine, etc. are exposed to the radiation of a strong Hg arc  $H_2$  is produced with the simultaneous formation of the corresponding disulphide compound. The quantum efficiency with respect to  $H_2$  formation is always much  $< 1$ , indicating that reverse reactions occur. Some decomp. of RSH into RH and S also takes place. Many SH compounds react with fluorescent dyes in the dark at a measurable rate, and by irradiating with light which is absorbed by the dye, this reduction reaction is accelerated. The possible bearing of these results on the assimilation of  $CO_2$  by S bacteria is discussed.

L. S. T.

**Hydrolysis of glucosides and of certain organic compounds by ultra-violet rays.** A. GUILLAUME and G. TANRET (Compt. rend., 1935, 201, 1057—1060).—Various glucosides are hydrolysed by ultra-violet rays of  $\lambda$  1800—3100 Å., rise of temp. and acidity of the medium increasing the speed of hydrolysis. Certain esters and amides are also hydrolysed by ultra-violet rays but polypeptides and proteins are resistant.

W. O. K.

**Reduction of ferric chloride under the action of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -rays.** G. W. SPICER (Trans. Faraday Soc., 1935, 31, 1706—1710).—Complete reduction occurs when aq. or  $Et_2O$  solutions of  $FeCl_3$  are exposed to  $\alpha$ -rays, and when  $Et_2O$  solutions are exposed to  $\beta$ - and  $\gamma$ -rays. Partial reduction only is observed when solid anhyd.  $FeCl_3$  is exposed to  $\alpha$ -rays, but is probably complete in the thin layer penetrated by the radiation. No reduction is observed on exposing aq.  $FeCl_3$  solutions to  $\beta$ - and  $\gamma$ -rays.

J. W. S.

**Ortho-para-hydrogen conversion under the action of  $\alpha$ -particles.** P. C. CAPRON (Ann. Soc. Sci. Bruxelles, 1935, 55, B, 222—236).—The reaction has been studied at room temp. in presence of Hg, which exerts an inhibitory effect. The rate  $\propto$  [para-H][Rn], whilst  $M/I \propto$  [para-H] and is independent of the radiation intensity. It is probable that 1—2 H are formed per ion-pair and that H disappears according to a unimol. law. The possibility of the conversion being due to  $H^+$  has been considered, but the fact that no change occurs at  $-187^\circ$  suggests that H is the effective agent.

R. S.

**Chemical action caused by neutrons and  $\gamma$ -rays and the effects of these agents on colloids.** F. L. HOPWOOD and J. T. PHILLIPS (*Nature*, 1935, 136, 1026).—The effect produced by a pure  $\gamma$ -ray source,  $\text{RaSO}_4$  in Pt or Rn in glass surrounded by Pb, on the oxidation of  $\text{K}_2\text{S}_2\text{O}_5$  or of  $\text{NaHSO}_3$  and on the decomp. of  $\text{H}_2\text{O}_2$  is increased by using a source of equal strength which also emits neutrons. With hydrosols of Ag, Au,  $\text{As}_2\text{S}_3$ , CdS,  $\text{V}_2\text{O}_5$ , and  $\text{Fe}(\text{OH})_3$ , a source emitting  $\gamma$ -rays or  $\gamma$ -rays and neutrons increases the stability of the negatively charged sols and decreases that of the positively charged sols. Anomalous results are obtained when electrolytes are added to the sol before irradiation. The effect attributed to the neutrons alone is of the same order of magnitude as that due to the  $\gamma$ -rays, but the efficiency of the slow neutrons is much the greater. L. S. T.

**Sensitised decomposition of hydrogen with electrons of controlled energy.** G. GLOCKER and L. B. THOMAS (*J. Amer. Chem. Soc.*, 1935, 57, 2352—2357).— $\text{H}_2$  mols. have been dissociated by electrons of known speed, using Hg atoms as a sensitising agent. The reactions are analogous to the photochemical decomp. of  $\text{H}_2$ , using  $\lambda$  2537 Å. and Hg. At low pressures ( $\text{H}_2$  at 0.02 mm. and Hg at 0.002 mm.) the short-lived radiative states of Hg (4.9 and 6.7 e.v.) and the well-known metastable states ( $6^3P_{0,2}$ ) are not efficient or are too short-lived to cause reaction, but electrons of 7.7 e.v. energy can dissociate  $\text{H}_2$  in presence of Hg. The mechanism is discussed. E. S. H.

**Decomposition of  $\text{SO}_2$  through electron impacts.** N. NEKRASSOV and A. SCHNEERSON (*Acta Physicochim. U.R.S.S.*, 1935, 2, 711—732).—The crit. reaction potentials  $12.2 \pm 0.5$ ,  $15.7 \pm 0.5$ , and  $24.5$ — $26.5$  volts, corresponding with the changes  $\text{SO}_2 \rightarrow \text{SO}_2^+$ ,  $\text{SO}_2 \rightarrow \text{SO}^+ + \text{O}$  and double the potential of formation of  $\text{SO}_2^+$ , and the dependence of reaction velocity and electron yield on  $\text{SO}_2$  pressure and anode current, have been measured using a triode as a reaction chamber without freezing out the reaction products. The velocity of reaction is independent of temp. The conclusions of previous workers regarding reactions in electrical discharges are criticised as leaving out of account energetic relationships and ion recombination. T. G. P.

**Interaction of gases with solids.** H. W. MELVILLE (*Nature*, 1935, 136, 899—900). L. S. T.

**Use of topology and invariants to describe chemical reactions.** F. M. SCHEMJAKIN (*Acta Physicochim. U.R.S.S.*, 1935, 2, 557—558).—A preliminary note suggesting that chemical reactions may be classified according to geometric systems. O. J. W.

**Perchlorates. IV. Ammonia derivatives of alkali perchlorates.** C. SMEETS (*Natuurwetensch. Tijds.*, 1935, 17, 213—217).—Isotherms for systems of the type  $\text{MClO}_4 \cdot \text{NH}_3$  indicate the existence of the compounds,  $\text{LiClO}_4 \cdot 2\text{NH}_3$  (I),  $\text{LiClO}_4 \cdot 3\text{NH}_3$  (II),  $\text{LiClO}_4 \cdot 5\text{NH}_3$ ,  $\text{NaClO}_4 \cdot 4\text{NH}_3$ , and  $\text{NH}_4\text{ClO}_4 \cdot 3\text{NH}_3$ . Only (I) and (II) are stable at room temp.  $\text{KClO}_4$  does not combine with  $\text{NH}_3$  even at  $-79^\circ$ . D. R. D.

**Formation and composition of lithium aluminate.** H. A. HORAN and J. B. DAMIANO (*J. Amer.*

*Chem. Soc.*, 1935, 57, 2434—2436).—When  $\text{Al}^{+++}$  solutions, containing sufficient  $\text{Li}^+$ , are made alkaline with  $\text{NH}_3$ , a Li aluminate (at. ratio  $\text{Li} : \text{Al} = 1 : 2$ ) is pptd. almost quantitatively. After ignition to const. wt. the residue has the composition  $\text{Li}_2\text{O} \cdot 2\text{Al}_2\text{O}_3$ .

E. S. H.

**Chemical and mineralogical examination of the precipitate obtained from 50% NaOH and sodium sulphate.** D. BOBROVNIK (*Ukrain. Chem. J.*, 1935, 10, 320—330).—The solid phases separating when  $\text{Na}_2\text{SO}_4$  is added to 50% aq. NaOH, and the solution is cooled, are triple salts of  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{SO}_4$ , and NaCl, in the ratios 1 : 2 : 2, 1 : 2 : 4, 1 : 2 : 5, and 1 : 3 : 13. R. T.

**Decomposition of copper sulphate pentahydrate by heat.** O. BINDER (*Compt. rend.*, 1935, 201, 1035—1036; cf. this vol., 38).— $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  heated at  $650^\circ$  yields  $\text{SO}_3 \cdot 2\text{CuO}$  (I), which gives  $\text{SO}_3 \cdot 4\text{CuO} \cdot 4\text{H}_2\text{O}$  (II) +  $2\text{CuSO}_4$  with cold  $\text{H}_2\text{O}$ , and  $\text{SO}_3 \cdot 3\text{CuO} \cdot 2\text{H}_2\text{O}$  (III) +  $\text{CuSO}_4$  with boiling  $\text{H}_2\text{O}$ . X-Ray photographs of (I), (II), and (III) are reproduced. T. G. P.

**Organic cupric tetrachlorides and tetrabromides.**—See this vol., 212.

**Reactions between aqueous solutions of silver nitrate, lead nitrate, and potassium permanganate.** F. JIRSA (*Z. anorg. Chem.*, 1935, 225, 302—304).— $\text{AgNO}_3$  is oxidised by  $\text{KMnO}_4 + \text{KOH}$  to  $\text{Ag}_2\text{O}_2$ .  $\text{Pb}(\text{NO}_3)_2$  is oxidised by  $\text{KMnO}_4$  to  $\text{PbO}_2$ , and  $\text{Mn}_2\text{O}_3$  is formed. E. S. H.

**Hydrolysis of magnesium boride.** R. C. RAY and P. C. SINHA (*J.C.S.*, 1935, 1694—1695).—At  $>0^\circ$ , the hydrolysis of  $\text{Mg}_3\text{B}_2$  by  $\text{H}_2\text{O}$  or dil. aq. EtOH—HCl is essentially  $\text{Mg}_3\text{B}_2 + 6\text{H}_2\text{O} \rightarrow \text{Mg}_3\text{B}_2(\text{OH})_6$  (I) +  $3\text{H}_2$ , but at  $<-10^\circ$  the product is  $\text{H}_3\text{B}_2(\text{MgOH})_3$ , which has reducing properties and is hydrolysed by  $\text{H}_2\text{O}$  to (I) and  $\text{H}_2$ . J. G. A. G.

**Mechanism of hydrolysis in solutions of salts of heavy metals.** (MILLER) M. QUINTIN (*Compt. rend.*, 1935, 201, 1176—1178).—In  $\text{CdCl}_2$  solutions  $< 0.05M$  the activity of the Cd ion  $\propto [\text{H}^+]$ . The first stage in the hydrolysis of this and similar salts (A., 1927, 729; 1928, 241) therefore involves complex formation. T. G. P.

**Chemical curiosity.** F. P. DWYER (*J. Proc. Austral. Chem. Inst.*, 1935, 2, 318—320).—Vermiform growths are obtained by the action of Hg on  $\text{Hg}_2(\text{NO}_3)_2$ ,  $\text{Co}(\text{NO}_3)_2$ , and  $\text{Ni}(\text{NO}_3)_2$  in 60—70%  $\text{HNO}_3$ . J. S. A.

**Boron hydrides. XX. Potassium diborane,  $\text{K}_2(\text{B}_2\text{H}_6)$ .** A. STOCK, W. SÜTTERLIN, and F. KURZEN. XXI. Potassium compounds of  $\text{B}_4\text{H}_{10}$  and  $\text{B}_5\text{H}_9$ . A. STOCK, F. KURZEN, and H. LAUDENKLOS (*Z. anorg. Chem.*, 1935, 225, 225—242, 243—253; cf. A., 1934, 497).—XX.  $\text{K}_2(\text{B}_2\text{H}_6)$  (I) is prepared by agitating K amalgam with excess of  $\text{B}_2\text{H}_6$  and separating from Hg by distillation. It is stable at  $300^\circ$ , but decomposes at  $400^\circ$  as follows: (I) =  $\text{KB}_2\text{H}_2 + \text{K} + 2\text{H}_2$ . (I) is insol. in the usual org. solvents, but is hydrolysed by  $\text{H}_2\text{O}$ . The mechanism of hydrolysis has been investigated. With HBr the reaction (I) +  $2\text{HBr} = 2\text{KBr} + \text{B}_2\text{H}_6 + \text{H}_2$  occurs.

XXI.  $K_2(B_5H_{10})$  (II) has been prepared from  $B_5H_{10}$  and K amalgam. Separation from Hg is complicated by the ready decomp. of (II); at  $170^\circ$   $K_2(B_4H_8)$  is formed. (II) appears to be an intermediate product in the thermal decomp. of (I). Evidence for the formation of  $K_2(B_5H_9)$  from  $B_5H_9$  and K amalgam is given. E. S. H.

X-Ray investigation of potassium diborane and its hydrolysis products, especially potassium dihydroxydiborane. E. S. VON BERGKAMPF (Z. anorg. Chem., 1935, 225, 254—257).—The mechanism of hydrolysis of  $K_2(B_2H_6)$  (cf. preceding abstract) is confirmed. E. S. H.

Boron halide additive compounds of anomalous composition. II. Action of phosphine on boron fluoride. E. WIBERG and V. HEUBAUM (Z. anorg. Chem., 1935, 225, 270—272; cf. A., 1933, 917).— $PH_3$  and  $BF_3$  react at  $-145^\circ$  to form  $PH_3 \cdot BF_3$ . E. S. H.

Conditions for the formation and existence of kernite,  $Na_2B_4O_7 \cdot 4H_2O$ . H. MENZEL, H. SCHULZ, and H. DECKERT (Naturwiss., 1935, 23, 832—833).—The chemical properties, artificial prep., and range of stability of kernite have been investigated. With  $H_2O$  it gives  $Na_2B_4O_7 \cdot 10H_2O$  or the metastable  $Na_2B_4O_7 \cdot 5H_2O$ . The formation of kernite starts from a dihydrate. It may be prepared artificially by heating  $Na_2B_4O_7$  with 4.5—6 mols. of  $H_2O$  at  $140^\circ$  for 20 hr. in a sealed tube. Its temp. range of existence is approx.  $58—152^\circ$ . A. J. M.

Somatoids. II. Influence of other dissolved constituents on the forms exhibited by monobasic aluminium sulphite. III. Topochemical reactions on aluminium sulphite somatoids. K. HUBER (Helv. Chim. Acta, 1935, 18, 1316—1326, 1327—1335; cf. A., 1935, 1072).—II. The influence of (a) mineral acids, and their hydrolysable heavy metal salts, (b) chromic sulphite, and (c)  $NaOAc$ ,  $Na_2HPO_4$ , and  $UO_2(OAc)_2$  on the form of the somatoids of monobasic Al sulphite (I) has been investigated. From the absence of sp. effects, and the similarity of the effects to those produced by temp. and concn. changes in the absence of foreign salts, it is concluded that disturbances in the  $Al_2O_3-H_2O-SO_2$  equilibrium and in the intermediate formation of  $Al(OH)_3$  are involved.  $Cr^{+++}$  and  $UO_2^{++}$  are taken up by the (I) lattice without altering its structure or dimensions.

III. The effects of heat, hydrolysis by  $H_2O$  and alkali, and oxidation on somatoids of (I) show the presence of a lamellar structure, and a differentiation between the outer skin and the centre of the somatoids. By ignition at  $400—500^\circ$ , (I) is converted directly into  $\alpha-Al_2O_3$ . Evidence is advanced of inhomogeneities in the internal structure. J. S. A.

Preparation of aluminium carbide,  $Al_4C_3$ . O. RUFF (Chem.-Ztg., 1936, 60, 28).—Al and C are heated in  $H_2$  at  $2000^\circ$  for 30 min. E. S. H.

Compounds of aluminium bromide with lithium, copper, and silver bromides. V. A. PLOTNIKOV and E. J. GORENBEIN (J. Gen. Chem. Russ., 1935, 5, 1108—1111).—The compounds  $LiBr \cdot AlBr_3$ , m.p.  $192^\circ$ ,  $CuBr \cdot AlBr_3$ , m.p.  $241^\circ$ , and  $2AgBr \cdot 3AlBr_3$ ,

m.p.  $180—185^\circ$  (decomp.), are obtained by crystallising the mixed salts from EtBr. R. T.

Volatilisation of silicic acid and silicon as silicon sulphide. P. DOLCH (Chem. Fabr., 1935, 8, 512—514).—Published evidence of reactions involving the above is reviewed. E. S. H.

Reaction of titanium tetrachloride with phenol. G. P. LUTSCHINSKI [with E. S. ALTMANN] (Z. anorg. Chem., 1935, 225, 321—326).— $TiCl_4$  reacts vigorously with PhOH forming a dark red cryst. compound,  $TiCl_3 \cdot OPh$ . It fumes in moist air and reacts with  $H_2O$  giving PhOH and  $Ti(OH)_4 \cdot H_2O$ . Mixtures of  $TiCl_4$  and PhOH in  $CHCl_3$  solution show a max. light absorption for the equimol. mixture. The selective light absorption obeys the Lambert-Beer law and the reaction might be used for the colorimetric determination of either compound. M. S. B.

Reactions between solids. A. ALBERTO (Ann. Acad. brasil. Sci., 1934, 6, 49—52; Chem. Zentr., 1935, i, 2486).— $NH_4ClO_4$  is quoted as a very stable  $NH_4$  salt. J. S. A.

Slow action of fuming nitric acid vapour on metals. E. MONTIGNIE (Bull. Soc. chim., 1935, [v], 2, 2260—2261).—At  $15^\circ$  the vapour of fuming  $HNO_3$  reacts only with Na, Ag, and Hg. F. L. U.

Action of heat on the ortho-, pyro-, and meta-arsenates of calcium and strontium. H. GUÉRIN (Compt. rend., 1935, 201, 1133—1135).—Neutral arsenates of Ca and Sr may be heated in vac. to  $1200^\circ$  without change. Products containing excess of  $As_2O_5$  lose  $As_2O_3$  and  $O_2$  at  $>1000^\circ$ , forming neutral orthoarsenate. The pyroarsenates form orthoarsenates at  $>800^\circ$ ,  $As_2O_3$  and  $O_2$  being liberated. The two meta-arsenates yield the pyroarsenates at  $500—800^\circ$ , and the orthoarsenates at higher temp. H. J. E.

Quantitative separation of protoactinium from pitchblende by means of titanium oxide. CHENG DA-CHANG (J. Chinese Chem. Soc., 1935, 3, 381—387).—Pa can be quantitatively pptd. with  $TiO_2$  from a solution of pitchblende in HCl to which  $TiCl_4$  is added. The  $TiO_2$  deposited on hydrolysis contains all the Pa present in the mineral. The  $\alpha$ -ray activity of the ppt. gives the quantity of Pa present. Pa salts are shown to be readily hydrolysed in acid solution, easily soluble in dil. HF, and completely pptd. by aq.  $NH_3$  in absence of HF. A. J. M.

Ductile chromium. W. KROLL (Z. anorg. Chem., 1935, 226, 23—32).—Cr powder, obtained by the action of twice distilled Ca on  $Cr_2O_3$  in molten  $CaCl_2 + BaCl_2$  and in an atm. of A, is degassed in a vac. at  $1300^\circ$  and sintered at  $1600—1700^\circ$ . The resulting mass can be rolled at  $1250^\circ$ . Rolled Cr is brittle at room temp., but deformable at  $180^\circ$ . F. L. U.

Action of hydrogen sulphide on chromates. Potassium dichromate. H. B. DUNNICLIFF, G. S. KOTWANI, and M. A. HAMID (J. Physical Chem., 1935, 39, 1217—1229; cf. A., 1932, 133).—The brown solid formed during the action of  $H_2S$  on 5% aq.  $K_2Cr_2O_7$  consists of  $CrO_2$ ,  $Cr(OH)_3$ ,  $Cr_2(S_4O_6)_3$ , a Cr thiosulphate, and S, whilst the filtrate contains unchanged  $K_2Cr_2O_7$ ,  $K_2S_2O_3$ , and  $K_2S_4O_6$ . The final

products are a ppt. of  $\text{Cr}(\text{OH})_3$ , S, and a complex Cr thiosulphate, and a solution containing  $\text{K}_2\text{S}_2\text{O}_3$  and  $\text{K}_2\text{S}_x$ . The course of the reactions is discussed.

F. L. U.

**Preparation of potassium molybdo- and molybdi-cyanides.** H. H. WILLARD and R. C. THIELKE (J. Amer. Chem. Soc., 1935, 57, 2609—2611).— $\text{K}_4\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$  (I) is prepared by pptg.  $\text{Mo}^{\text{IV}}$  pyridine thiocyanate in aq.  $\text{NH}_3$  and treating the ppt. with KCN. A quant. yield of  $\text{K}_3\text{Mo}(\text{CN})_6$  is obtained by oxidising (I) with  $\text{KMnO}_4$  in acid solution.

E. S. H.

**Lower oxides of tungsten.** F. EBERT and H. FLASCH (Z. anorg. Chem., 1935, 226, 65—81).— $\text{WO}_3$  treated with active H at room temp. for 13—30 hr., is completely converted into the compound  $\text{W}_4\text{O}_{10}(\text{OH})_2$ . By isobaric dehydration at 0.001 mm., the latter substance yields the compound  $\text{W}_{12}\text{O}_{32}(\text{OH})_2$  (I), which is stable between  $150^\circ$  and  $500^\circ$ , above which it passes into  $\text{W}_4\text{O}_{11}$  (A., 1934, 378). The identity of the compounds has been established by chemical and X-ray analysis. The following lattice consts. are given:  $\text{W}_4\text{O}_{10}(\text{OH})_2$ , tetragonal,  $a$  3.79,  $c$  3.74 Å.;  $\text{W}_{12}\text{O}_{32}(\text{OH})_2$ , tetragonal,  $a$  3.85,  $c$  3.65 Å.;  $\text{W}_4\text{O}_{11}$ , monoclinic,  $a$  3.85,  $b$  3.79,  $c$  3.85 Å.,  $\beta$   $79.45^\circ$ . (I) is also formed in the reduction of  $\text{WO}_3$  by mol.  $\text{H}_2$  at  $500$ — $550^\circ$ , and it is suggested that such addition of H is a general preliminary stage in the reduction of higher oxides by  $\text{H}_2$ .

F. L. U.

**Composition and properties of potassium phosphotungstate.** E. A. NIKITINA (J. Gen. Chem. Russ., 1935, 5, 1133—1138).—The salts pptd. by adding KOH or NaOH to aq. phosphotungstic acid have the composition  $\text{K}_3\text{H}_4[\text{P}(\text{W}_2\text{O}_7)_6]$  (I) or  $\text{Na}_3\text{H}_4[\text{P}(\text{W}_2\text{O}_7)_6]$  (II); their solubilities in  $\text{H}_2\text{O}$  and in aq. acids have been determined at  $0$ — $90^\circ$ . That of (II) > that of (I); for both salts it falls with increasing acidity, but more so for (I), which is insol. in 18% HCl at  $0$ — $43^\circ$ . At the same time, elimination of alkali metal from the solid phases takes place, to yield successively the  $\text{M}_2$  and  $\text{M}_1$  salt. The results obtained for the determination of K in presence of Na are high, owing to pptn. of some (II) from solutions of the acidity necessary to ensure complete pptn. of (I).

R. T.

**Reduction of 1-phospho-18-tungstic acid by ascorbic acid.**—See this vol., 255.

**Fluorine and its compounds.** A. DAMIENS (Bull. Soc. chim., 1936, [v], 3, 1—22).—A lecture.

**Bromine.** I. Preparation of bromine dipyridine perchlorate and bromine dipyridine nitrate. II. Preparation, properties, and constitution of an aquo-pyridine compound of bromine monoxide. H. CARLSOHN (Ber., 1935, 68, [B], 2209—2211, 2212—2214).—I (cf. Uschakov *et al.*, A., 1935, 857).—Addition of Br in  $\text{CHCl}_3$  to  $\text{AgNO}_3$  in  $\text{CHCl}_3$ — $\text{C}_5\text{H}_5\text{N}$  at  $15$ — $20^\circ$  followed by removal of AgBr and addition of the filtrate to  $\text{Et}_2\text{O}$  containing a little  $\text{C}_5\text{H}_5\text{N}$  gives the hygroscopic Br dipyridine nitrate (I) in 75—80% yield. Br dipyridine perchlorate is obtained by adding Br in  $\text{CHCl}_3$  to Ag dipyridine perchlorate (from  $\text{AgNO}_3$ ,  $\text{C}_5\text{H}_5\text{N}$ , and  $\text{NaClO}_4$  in  $\text{H}_2\text{O}$ ) in  $\text{CHCl}_3$ — $\text{C}_5\text{H}_5\text{N}$ .

II. Treatment of (I) with 0.4N-NaOH gives a pale yellow ppt. which when rapidly dried on porous clay and then for 1 hr. in a vac. over KOH has the composition  $\text{Br}_2\text{O} \cdot \text{H}_2\text{O} \cdot \text{C}_5\text{H}_5\text{N}$ . The constitution  $[\text{BrC}_5\text{H}_5\text{N}(\text{OH}_2)]\text{OBr}$  is suggested.

H. W.

**Reaction of atomic iodine with quartz glass.** G. BRAUER (Z. physikal. Chem., 1935, 174, 435—440).—Thermally dissociated  $\text{I}_2$  vapour forms from quartz glass Si, but if the O formed is not removed a film of  $\text{SiO}_2$  results. Optically dissociated  $\text{I}_2$  behaves similarly.

R. C.

**Iron, even when impure, is not oxidised in salt solutions.** P. RONCERAY (Bull. Soc. chim., 1935, [v], 2, 2171—2174; cf. A., 1935, 834).—Corrosion of impure Fe in NaCl solutions does not occur in the absence of foreign material in the surface.

F. L. U.

**Iron, when impure but rigorously freed from surface contamination, does not effervesce in dilute acids.** P. RONCERAY (Bull. Soc. chim., 1935, [v], 2, 2174—2178; cf. preceding abstract).—Impure Fe effervesces in 1%  $\text{H}_2\text{SO}_4$  only when the surface of the Fe is contaminated with certain "extrinsic" materials. A reaction, however, still takes place. An antagonism between the effervescent and quiet reactions is observed.

F. L. U.

**Iron, even when impure, is not oxidised at the ordinary temperature in pure distilled and aerated water.** P. RONCERAY (Bull. Soc. chim., 1935, [v], 2, 2179—2182; cf. preceding abstract).—Impure Fe, if suitably cleaned, is not attacked by  $\text{H}_2\text{O}$  containing dissolved  $\text{O}_2$ . Localised rusting is due to extrinsic impurities, and the rust spreads from the primary corrosion centres thus formed.

F. L. U.

[Iron, even when impure, is not oxidised in air saturated with moisture.] L. GUITTON (Bull. Soc. chim., 1935, [v], 2, 2258—2260).—A criticism of experiments and conclusions published by Ronceray (A., 1935, 834).

F. L. U.

**Action of carbonic acid on ferrous sulphide.** Y. KAUKO and P. HAULIO (Suomen Kem., 1935, 8, B, 49—50).—From the relevant equilibrium consts., aq.  $\text{CO}_2$  should be able to convert FeS into sol.  $\text{Fe}(\text{HCO}_3)_2$ , from which  $\text{FeCO}_3$  is pptd.

J. S. A.

**Action of oxidising agents on sodium hypoferrite.** X. THIESSE (Compt. rend., 1935, 201, 1135—1137; cf. A., 1935, 314).—In 35% aq. NaOH solution,  $\text{Cl}_2$  causes pptn. of  $\text{Fe}(\text{OH})_3$ . In 40% NaOH a mixture of olive-green crystals and of hydrated  $\text{Fe}_2\text{O}_4$  is formed. The product from  $\text{Cl}_2$  and a 50% NaOH solution at  $130$ — $140^\circ$ , when washed and dried, is  $\text{Fe}(\text{ONa})_3 \cdot 10\text{H}_2\text{O}$ ; at  $170$ — $180^\circ$  with 60—70% NaOH it is  $\text{Na}_2\text{Fe}_2\text{O}_4$ .  $\text{Pb}(\text{OH})_2$  in presence of 50% NaOH yields  $\text{Fe}(\text{ONa})_3$ .

H. J. E.

**Dehydration of hydrated cobaltic oxide.** H. A. PAGEL, W. K. NOYCE, and M. T. KELLEY (J. Amer. Chem. Soc., 1935, 57, 2552—2553).—Dehydration occurs slowly at  $< 90^\circ$ , but rapidly at  $100$ — $180^\circ$ . The rate varies greatly with differences in the physical state of the oxide.

E. S. H.



**Topochemical reactions of compact-disperse materials. IV. Mixed precipitation of nickel-zinc and cobalt-zinc hydroxides.** W. FEITKNECHT and W. LOTMAR (Helv. Chim. Acta, 1935, 18, 1369—1388).—Pptn. of aq.  $\text{Co}(\text{NO}_3)_2\text{-Zn}(\text{NO}_3)_2$  or  $\text{Ni}(\text{NO}_3)_2\text{-Zn}(\text{NO}_3)_2$  mixtures with  $\text{NaOH}$  yields completely unordered, partly amorphous, ppts.  $(\text{Ni,Zn})(\text{OH})_2$  low in Zn passes on ageing at room temp. into cryst.  $\text{Ni}(\text{OH})_2$ , type C6, in which  $\gt 15\%$  of Ni atoms may be replaced by Zn, with some expansion of the lattice. From 15 to 65% of  $\text{Zn}(\text{OH})_2$ , a new hexagonal double hydroxide is formed, having a 3.07, c 8.2 Å., and consisting of sheets of  $\text{Ni}(\text{OH})_2$  in which Ni is partly replaced by Zn, intercalated with unordered  $\text{Zn}(\text{OH})_2$ . By heating freshly pptd.  $(\text{Ni,Zn})(\text{OH})_2$ , mixed crystals with up to 25% of  $\text{Zn}(\text{OH})_2$  may be obtained, which pass on prolonged heating into a new double hydroxide of type C6. Similar results are obtained by copptn. of Zn and Co; an unstable double hydroxide of very imperfect structure is formed in presence of 40—60% of  $\text{Zn}(\text{OH})_2$ . J. S. A.

**Structure of complex compounds.** H. BRINTZINGER and H. OSSWALD (Z. anorg. Chem., 1935, 225, 312—318).—The anions  $\text{SO}_4''$ ,  $\text{C}_2\text{O}_4''$ ,  $\text{PO}_4''$ ,  $\text{AsO}_4''$ ,  $\text{F}'$ , etc. are capable of forming the complex anions containing a central complex cation, e.g.,  $[\{\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}\}(\text{SO}_4)_4]''''$ , the existence of which is shown by dialysis (A., 1935, 1091, 1471; this vol., 40). Other anions, viz.,  $\text{NO}_3'$ ,  $\text{Cl}'$ ,  $\text{S}_2\text{O}_8''$ ,  $\text{S}_2\text{O}_3''$ ,  $\text{CrO}_3''$ ,  $\text{MoO}_4''$ ,  $[\text{Co}(\text{CN})_6]''''$ , etc., do not form such complex anion. A necessary condition of formation appears to be the possession, by either the partaking cation or anions, of a large electrostatic potential, i.e., residual valencies, recognisable by the formation in aq. solution of aquo-complexes of the type  $[\text{Mn}(\text{H}_2\text{O})_6]''$ ,  $[\text{Fe}(\text{H}_2\text{O})_{18}]''''$ ,  $[\text{C}_2\text{O}_4(\text{H}_2\text{O})_4]'$ ,  $[\text{HPO}_4(\text{H}_2\text{O})_6]''$ , etc., as demonstrated by dialytic methods. M. S. B.

**New group of complex compounds: complex compounds of which the central ion is a complex cation. IV. Double-shelled arsenato-complex compounds with complex cobalt cations as central ions.** H. BRINTZINGER and H. OSSWALD (Z. anorg. Chem., 1935, 225, 365—368; cf. A., 1935, 1091, 1471; this vol., 40).—A no. of complex Co amines, slightly sol. in  $\text{H}_2\text{O}$ , are sol. in aq. arsenate, or, if decomposed by  $\text{H}_2\text{O}$ , are stable in aq. arsenate. Dialysis indicates that a complex anion is formed and consists of a central complex Co cation surrounded by a shell of arsenate anions; e.g.,  $[\text{Co}(\text{NH}_3)_6]''''$  gives  $[\{\text{Co}(\text{NH}_3)_6\}(\text{HASO}_4)_4]''''''$  and  $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)]''$  gives  $[\{\text{Co}(\text{NH}_3)_5(\text{NO}_3)\}(\text{HASO}_4)_4]''''''$ . M. S. B.

**Nucleus formation on crystals of nickel sulphate heptahydrate.** W. E. GARNER and W. R. SOUTHOON (J.C.S., 1935, 1705—1709).—The nuclei formed by dehydrating  $\text{NiSO}_4\cdot 7\text{H}_2\text{O}$  crystals in vac. consist of half-ellipses with one direction of growth on the crystal surface and the other into the interior at an angle of  $45^\circ$  to the surface. Before nuclei become visible, there is an induction period,  $t_i$ , which decreases with rise of temp. (1— $22^\circ$ ) and varies, within limits, from crystal to crystal, probably owing to variations in surface structure and the nature of the imperfections leading to nucleation. The rate of

growth of nuclei of diameter  $> 0.02$  mm. is linear, but is much smaller during  $t_i$ . After  $t_i$ , the no. of nuclei,  $N$ , increases with time,  $t$ , according to  $N = (t - t_i)^x$ , where  $x$  is 2, approx. The activation energy calc. from the temp. coeffs. of  $t_i$  and the linear rate of growth is 19.0 kg.-cal., approx. The interpretation of the results is discussed. J. G. A. G.

**Complex dipyridyl salts of nickel and copper.** F. M. JAEGER and J. A. VAN DIJK (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 972—977).—Addition of 3 equivs. of dipyridyl (I) to  $\text{Ni}(\text{NO}_3)_2$  solution, followed by slow evaporation, yields red crystals of the compound  $[\text{Ni}(\text{dipy})_3](\text{NO}_3)_2\cdot 5\text{H}_2\text{O}$  (II). With 2 equivs. of (I) some (II) is first obtained and then the violet compound  $[\text{Ni}(\text{dipy})_2](\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$  (III). When only 1 equiv. of (I) is used, some (II) is deposited and then the compound  $[\text{Ni}(\text{dipy})(\text{H}_2\text{O})_2](\text{NO}_3)_2\cdot \text{H}_2\text{O}$ , in an impure state.  $\text{NiCl}_2$  similarly yields the compounds  $[\text{Ni}(\text{dipy})_3]\text{Cl}_2\cdot 7\text{H}_2\text{O}$  (IV) and  $[\text{Ni}(\text{dipy})(\text{H}_2\text{O})_2]\text{Cl}_2$ . The crystal structures of (II), (III), (IV), and  $[\text{Cu}(\text{dipy})_3]\text{Cl}_2\cdot 7\text{H}_2\text{O}$  are detailed. J. W. S.

**Affinity. LXVI. Rhodium sulphides.** R. JUZA, O. HÜLSMANN, K. MEISEL, and W. BILTZ (Z. anorg. Chem., 1935, 225, 369—385).—By direct combination of Rh with S, by v.-p. measurements, and by X-ray analysis, the existence of  $\text{Rh}_2\text{S}_3$ ,  $d_4^{25}$  6.40, and  $\text{Rh}_2\text{S}_5$ ,  $d_4^{25}$  5.00, 4.92, has been confirmed, but not that of  $\text{RhS}$  and  $\text{RhS}_2$  as given by earlier investigators. The compounds  $\text{Rh}_3\text{S}_8$ ,  $d_4^{25}$  7.51, and  $\text{Rh}_3\text{S}_4$ ,  $d_4^{25}$  6.33, have also been obtained.  $\text{Rh}_2\text{S}_5$  has a pseudo-pyritic structure. M. S. B.

**Alkali bromo-salts and bromo-pyridine derivatives of rhodium.** P. POULENC (Ann. Chim., 1935, [xi], 4, 567—657).—The preparation of the following compounds is described:  $[\text{RhBr}_3][\text{Na}_3\cdot 12\text{H}_2\text{O}]$ , deep red crystals;  $[\text{RhBr}_5]\text{Li}_2\cdot 6\text{H}_2\text{O}$ , a deep red hygroscopic powder;  $[\text{Rh}_2\text{Br}_9](\text{NH}_4)_3$ , green hexagonal micro-crystals;  $[\text{Rh}_2\text{Br}_9]\text{K}_3$ , green hexagonal micro-crystals;  $[\text{Rh}_2\text{Br}_{10}]\text{K}_4\cdot 6\text{H}_2\text{O}$ , deep red octahedra, decomp.  $120^\circ$ ;  $[\text{Rh}_2\text{Br}_{11}]\text{K}_5\cdot 6\text{H}_2\text{O}$ , deep red plates, unstable;  $[\text{Rh}_2\text{Br}_9]\text{Rb}_3$ , deep green micro-crystals, insol.;  $[\text{Rh}_2\text{Br}_{10}]\text{Rb}_4\cdot 6\text{H}_2\text{O}$ ;  $[\text{Rh}_2\text{Br}_{11}]\text{Rb}_5\cdot 6\text{H}_2\text{O}$ ;  $[\text{Rh}_2\text{Br}_9]\text{Cs}_3$ , deep green hexagonal micro-crystals, insol.;  $[\text{Rh}_2\text{Br}_{11}]\text{Cs}_5\cdot 6\text{H}_2\text{O}$ ;  $[\text{RhCl}_{4.5}\text{Br}_{1.5}]\text{K}_3\cdot \text{H}_2\text{O}$ , deep violet crystals; and  $[\text{Rh}_2\text{Cl}_{1.5}\text{Br}_{9.5}]\text{K}_5\cdot 6\text{H}_2\text{O}$ . The structures of the compounds and the influence of the halogen and the metallic ion, respectively, on the type produced are discussed. Compounds described by previous authors (A., 1908, ii, 200; 1911, ii, 45) could not be obtained. The following pyridine (Pyr) compounds have been prepared:  $[\text{Rh}_2\text{Br}_9]\text{Pyr}_3\text{H}_3\cdot 3\text{H}_2\text{O}$ , dark prisms;  $[\text{Rh}_2\text{Br}_9]\text{Cs}_3$ ,  $[\text{Rh}_2\text{Br}_9]\text{Pyr}_3\text{H}_3$ ;  $[\text{Rh}_2\text{Br}_{10}]\text{Pyr}_4\text{H}_4\cdot 9\text{H}_2\text{O}$ , insol. octahedra;  $[\text{RhPyrBr}_5]\text{Pyr}_2\text{H}_2$ , deep red prisms;  $[\text{RhPyrBr}_5]\text{CsPyrH}$ , red needles;  $[\text{RhPyrBr}_5][\text{RhCl}(\text{NH}_3)_5]$ ,  $[\text{RhBr}_6]\text{Pyr}_2\text{H}_3$ , green powder decomp. in solution yielding  $[\text{Rh}_2\text{Br}_9]\text{Pyr}_3\text{H}_3$ , and giving  $[\text{Rh}(\text{H}_2\text{O})\text{Br}_5]\text{Cs}_2$ , green prisms, with  $\text{CsOH}$  and wine-red  $[\text{Rh}(\text{H}_2\text{O})\text{Br}_5][\text{RhCl}(\text{NH}_3)_5]$  with  $[\text{RhCl}(\text{NH}_3)_5]\text{Cl}_2$ . Treatment of  $\text{RhBr}_3$  with  $\text{C}_5\text{H}_5\text{N}$  led to the following compounds and derivatives:  $[\text{RhPyr}_2\text{Br}_4]\text{PyrH}$ , red crystals, giving orange crystals of  $[\text{RhBr}_3\text{Pyr}_3]$  in  $\text{EtOH}$ ,  $[\text{RhPyr}_2\text{Br}_4]\text{K}\cdot \text{H}_2\text{O}$ , brick-

red crystals,  $[RhPyr_2Br_4]NH_4.H_2O$ , brick-red needles, and  $[RhPyr_2Br_4]Cs.H_2O$ , brick-red needles, all of which give buff-coloured needles of  $[RhBr_3(H_2O)Pyr_2].2H_2O$  in  $H_2O$ , and  $[RhBr_3Pyr_3]$  orange crystals, insol. The thermal and photo-decomp. of aq. and alcoholic  $[RhBr_2Pyr_4]Br$  has been studied. Three forms of  $[RhBr_3Pyr_3]$  are produced, viz., orange prisms, buff crystals, and octahedra, characterised by different solubilities and X-ray diagrams. Addition of  $H_2O$  to their  $C_5H_5N$  solutions yields identical prisms. Similar forms of  $[RhCl_3Pyr_3]$  have been obtained and it is supposed that the octahedra and the buff crystals are the two possible isomerides whilst the prisms constitute a third cryst. form.  $[RhBr(C_2O_4)Pyr_3]$  forms orange prisms, insol., reddens on heating and decomposed by light. Addition of  $C_5H_5N$  to excess of  $RhBr_3$  yields orange-yellow prisms of  $[RhBr_2Pyr_4]Br.6H_2O$ , which gives the double salt  $[RhPyr_2Br_4]_2$ , and which is converted in presence of Br into isomeric orange prisms having a different solubility and a different X-ray diagram. Treatment of  $[RhBr_2Pyr_4]Br$  with  $AgNO_3$  yields  $[RhBr_2Pyr_4]NO_3.HNO_3$ , yellow prisms, which forms yellow crystals of  $[RhBr_2Pyr_4]NO_3$  in  $H_2O$  and  $[RhBr_2Pyr_4Ag](NO_3)_2$  (I), yellow crystals, giving insol. yellow needles of  $[RhBr_2Pyr_4Ag]Br_2$  with  $HBr$ . (I) is unstable, yielding chiefly  $[Rh(NO_3)BrPyr_4]NO_3$ , orange crystals, and on prolonged treatment with  $AgNO_3$   $[Rh(NO_3)_3Pyr_3]$ , lozenge-shaped orange crystals, very sol. in  $H_2O$ . R. S.

**Spectral analytical investigations of W. Kraemer.** (A) W. GERLACH. (B) W. KRAEMER (Z. anal. Chem., 1935, 103, 356; cf. A., 1934, 981).—(A) Polemical. Kraemer's identifications of spectral lines are largely erroneous.

(B) The cogency of Gerlach's criticism is admitted. J. S. A.

**Determination of the [metal] content of a mineral by measuring its density.** E. BORGHESEAN (Reso. assoc. min. sarda, 1935, 40, No. 2, 14—17).—If  $S_0$  is the  $d$  of the pure mineral ( $\rightarrow T_0\%$  of metal), and if  $S_x$  is the  $d$  of a mixture containing  $x$  vol.-% of pure mineral and  $(100-x)\%$  of rock of  $d=s$ , the average content of metal in the mixture is  $T_x = T_0(S_x - s) / S_0(S_0 - s)$ . CH. ABS. (e)

**Areometric analysis. Technique in determining small amounts of heavy precipitates.** V. R. DAMERELL and M. AXELROD (J. Amer. Chem. Soc., 1935, 57, 2724—2725).—Compact, circular piles of ppt. of reproducible dimensions are obtained in the centre of the flask bottom. The areas of these spots are measured and compared with areas produced by known amounts of ppt. E. S. H.

**Reaction rates and indicator acidities.** L. P. HAMMETT (Chem. Rev., 1935, 16, 67—79).—An argument for the expression of acidity in terms of measurement with a basic indicator. CH. ABS. (e)

**Colorimetric determination of hydrogen-ion concentration in aqueous solution.** M. KILPATRICK (Chem. Rev., 1935, 16, 57—66).—A summary and discussion. CH. ABS. (e)

**Simplification of optical bathmometry by application of "spectral mixed-colour colorimetry"**

and other improvements. A. THIEL and H. LOGEMANN (Angew. Chem., 1935, 48, 799—802).—A colorimetric method for  $p_H$  determination is described. E. S. H.

**Photometric determination of hydrogen-ion concentration.** A. G. DE ALMEIDA (Diss., Lisbon, 1935).—By plotting dominant hue, determined colorimetrically and expressed as a  $\lambda$ , against  $p_H$ , for a series of indicators, curves are obtained from which the  $p_H$  of an unknown solution can be determined more accurately than by electrometric methods. D. R. D.

**Determination of  $p_H$  by means of the glass electrode.** D. WOLFERS (Bull. Soc. Chim. biol., 1935, 17, 1559—1572).—The glass electrode may be used to determine the  $p_H$  of solutions of strong acids, e.g.,  $HNO_3$  or  $HCl$  from 2N to 0.0001N. Vals. for the  $p_H$  of urine are  $<$  those obtained using the quinhydrone electrode. A. L.

**Titration of a dibasic acid in stages.** S. KILPI (Z. physikal. Chem., 1935, 174, 441—444).—In the potentiometric titration of a weak or moderately strong acid the jump in potential is a max. or a min. at the first stoichiometrical equiv. point according as  $K_1/K_2$  is  $>$  or  $<$  13.93. If  $K_1/K_2$  is large the  $[H^+]$  at the point of max. potential jump is equal to that at the first equiv. point, independently of the strength of the acid. R. C.

**Application of organic redox systems to analysis. I, II.** L. KULBERG (J. Gen. Chem. Russ., 1935, 5, 1085—1090, 1240—1245).—The application of redox indicators to the detection and determination of inorg. oxidising and reducing substances is discussed, and formulæ determining their applicability are given. R. T.

**Step-photometric determination of free chlorine in chlorinated water.**—See B., 1936, 46.

**Determination of chlorate and perchlorate in presence of large amounts of nitrate.** E. S. TOMULA (Z. anal. Chem., 1935, 103, 427—430).— $ClO_3'$  is reduced by warming the material with 40% aq.  $CH_2O$  in presence of  $FeCl_3$  as catalyst. Na salts are pptd. with an excess of  $HCl$ , and the  $HCl$  solution is evaporated to dryness.  $Cl'$  is removed by treating the residue with the calc. quantity of  $Ag_2SO_4$ , and  $ClO_4'$  is reduced with a Zn-Cd couple in presence of  $Ti^{IV}$ .  $Ti^{III}$  is oxidised with  $KMnO_4$ , and  $Cl'$  in the resulting solution is finally titrated with  $AgNO_3$ .  $ClO_3'$  in a separate portion is reduced with Zn and  $H_2SO_4$ . J. S. A.

**Qualitative reaction for bromates.** I. M. KORENMAN (Z. anal. Chem., 1935, 103, 269—271).— $BrO_3'$  but not  $IO_3'$ ,  $ClO_3'$ ,  $NO_3'$ , or  $S_2O_8''$  in 4N-HCl solution decolorises Me-orange rapidly. The reaction is very much faster than with  $Cr_2O_7''$ ,  $Fe(CN)_6'''$ , or  $NO_2'$ .  $BrO_3'$  may be so detected in presence of a large excess of these ions. The reaction of  $ClO_3'$  with Me-orange is catalysed by  $BrO_3'$ ; 10<sup>-6</sup> g. of  $BrO_3'$  per c.c. may be so detected. J. S. A.

**Detection of small amounts of bromide in sodium chloride.** R. C. LÓPEZ (Farm. moderna, 1935, 46, 55—57).—One drop of fuchsin solution

(0.2%) (I) in 10 c.c. of  $H_2O$  is decolorised by aq.  $Cl_2$ , added drop by drop. To 10 c.c. of the test solution are added 1 drop of (I) and twice the no. of drops of aq.  $Cl_2$  solution required above. Presence of  $Br^-$  is shown by a pink colour, which becomes purple, perhaps with pptn., if sufficient  $Br^-$  is present. 0.0001 g. of  $KBr$  in 10 c.c. of 20% aq.  $NaCl$  may be detected. The reaction is prevented by  $I^-$ ,  $SO_3^{2-}$ ,  $NO_2^-$ ,  $S_2O_3^{2-}$ ,  $CN^-$ ,  $SCN^-$ , and  $Fe(CN)_6^{4-}$ . Alkaline-reacting salts must be neutralised prior to the test.

CH. ABS. (p)

**Action of perchloric acid on iodine and iodine derivatives.** Determination of iodine in organic substances. E. KAHANE and T. TOMESCO (Compt. rend., 1935, 201, 1195—1198).— $HClO_4$  oxidises I compounds at 200—210° quantitatively to  $HIO_3$ . I may be determined in 2—10 mg. of substance by oxidation with  $HNO_3$ — $H_2SO_4$ — $HClO_4$ , followed by addition of  $As_2O_3$ , the whole of the I liberated in the processes being distilled into aq.  $Br$ , the excess of  $Br$  removed by boiling after acidification with  $AcOH$ , and the resulting  $HIO_3$  determined with  $Na_2S_2O_3$  after addition of  $KI$ .

T. G. P.

**Determination of fluorine in water by Sanchis' method.** E. H. DUCLOUX (Anal. Assoc. Quím. Argentina, 1935, 23, 63—66).—Modifications of the  $Zr(NO_3)_4$ -alizarin method (A., 1934, 500) are described.

F. R. G.

**Detection of small amounts of hydrogen peroxide.** J. PLANK (Magyar chem. Fol., 1934, 40, 105; Chem. Zentr., 1935, i, 2412).—Fresh  $Ce_2(SO_4)_3 + K_2CO_3$  detects 1 part of  $H_2O_2$  in 160,000 parts of solution.

J. S. A.

**Colour reaction between nitroprusside and sulphites (Bödeker's reaction).** G. SCAGLIARINI (Atti R. Accad. Lincei, 1935, [vi], 22, 155—159).—The formation of the complex ion  $[Fe(CN)_5NOSO_3]^{4-}$  in the above reaction has been demonstrated by measurements of the oxidation-reduction potential of the process  $[Fe(CN)_5NO]^{3-} + SO_3^{2-} + 2e = [Fe(CN)_5NOSO_3]^{4-}$ . The normal val. for 0.1M solutions at 21° is 0.468 volt.

O. J. W.

**Potentiometric titration of sulphite and sulphoxylate, etc.** E. MÜLLER (Z. anal. Chem., 1935, 103, 340—341).—Polemical against Löbering (A., 1935, 1092). Reduction of  $Cr_2O_7^{2-}$  to  $Cr^{II}$  by  $SO_3^{2-}$  or  $HSO_2^-$ , and consequently the analytical method based thereon, is impossible.

J. S. A.

**Potentiometric titration of sulphite and sulphoxylate alone and in presence of hyposulphite.** A. MUTSCHIN (Z. anal. Chem., 1935, 103, 342—348).—Polemical against Löbering (A., 1935, 1092; cf. also preceding abstract). The reaction between  $Cr_2O_7^{2-}$  and  $SO_3^{2-}$  or  $HSO_2^-$  is neither quant. nor stoichiometric, and cannot be used analytically.

J. S. A.

**Washing strontium sulphate precipitate with its saturated solution.** A. M. VASILIEV and O. S. TSCHMUIR-KORSUNSKA (Trans. Kirov Inst. Chem. Tech. Kazan, 1935, No. 3, 73—77).—The amount of  $SO_4^{2-}$  pptd. as  $SrSO_4$  by addition of excess of  $SrCl_2$  to approx. 0.05N- $H_2SO_4$  is equal to that pptd. by  $BaCl_2$  if the excess of  $SrCl_2$  renders the solution

N in respect of  $Sr$ . The ppt. must be washed with saturated aq.  $SrSO_4$ .

CH. ABS. (p)

**Accuracy of the titration of thiocyanate with mercuric mercury.** I. M. KOLTHOFF and J. J. LINGANE (J. Amer. Chem. Soc., 1935, 57, 2377—2379).— $KCNS$  is a satisfactory standard when the accuracy required is  $\pm 0.05\%$ . The sources of errors are traced to side reactions; the formation of  $NH_4^+$  was detected.

E. S. H.

**Determination of traces of gases in air with Cauver's absorption tubes.** E. QUITMANN (Z. anal. Chem., 1935, 103, 258—261; cf. this vol., 47).—The quant. absorption of traces of  $NH_3$ ,  $I$ ,  $HCl$ , and  $O_3$  in air is described.

J. S. A.

**Determination of total oxidising power, nitrite, ozone, and total chlorine content of ordinary and foetid air.** I. [Total oxidising power.] H. CAUER (Z. anal. Chem., 1935, 103, 321—334).—For air low in total oxidants, 100—200 litres of air are sucked through a wash-tube containing 3 c.c. of aq.  $KI$ , at  $p_H < 2.8$ , containing  $3 \times 10^{-5}$  g. of  $I^-$ , using the apparatus described previously (this vol., 47).  $I$  is thereby liberated and volatilised away. Complete absorption of  $HNO_2$  is detected by a wash-bottle of Ilosvay's reagent following the  $KI$  tube. 0.3 c.c. of the  $KI$  solution is treated with  $H_2SO_4$  containing  $NaNO_2$ , and is then emulsified with 0.02 c.c. of  $CHCl_3$ . The  $CHCl_3$  is separated centrifugally, and the amount of residual  $I$  determined colorimetrically by matching the  $CHCl_3$  drop against those from similarly treated solutions of known  $[I]$ . With air of higher oxidising power, larger initial amounts of  $KI$  and smaller vols. of air are used.

J. S. A.

**Determination of oxides of nitrogen in gaseous mixtures.** A. N. ZEITLIN (Ukrain. Chem. J., 1935, 10, 362—366).—The  $NO + NO_2$  is absorbed by 4%  $KBrO_3$  in  $N-H_2SO_4$  in an Orsat apparatus ( $< 10$  min.), and the difference in vol. of the sample is read.

R. T.

**Determination of phosphoric acid by precipitation as ammonium phosphomolybdate.** H. TERLET and A. BRIAU (Ann. Falsif., 1935, 28, 546—555; cf. B., 1935, 198).—Scheffer's method (J. Officiel, Aug. 30, 1934), which consists in the titration of the pptd.  $NH_4$  phosphomolybdate with aq.  $NaOH$  in presence of  $CH_2O$ , is trustworthy and accurate, provided steps are taken to remove  $H_2MoO_4$ , which is co-pptd. Procedures are outlined for the examination of natural  $Ca_3(PO_4)_2$ , fertilisers containing org. matter, superphosphates and the like, basic slag, and alkali phosphates.

E. C. S.

**Eliminating the effects of  $PO_4$  radical in qualitative analysis.** I—V. S. ISHIMARU (Sci. Rep. Tôhoku, 1935, 24, 426—438, 439—447, 448—460, 461—472, 473—480).— $I. PO_4^{3-}$  can be removed completely from a solution rendered just acid to Me-orange by addition of  $Fe(NO_3)_3$ . This method is more convenient in analysis than the  $Pb$  method, which can be applied satisfactorily only after removal of the  $Al$  group and  $Mn$ .

II. Pptn. with  $Bi^{III}$  leads to less occlusion and adsorption of other ions by the ppt. than the  $Fe$

method, but is unsatisfactory in presence of a high  $[\text{Fe}^{+++}]$ . The Zr method yields gelatinous ppts. and is of equal merit to the Fe method.

III. Pptn. with Sn leads to loss of Fe and Cr, but can be adopted after removal of the Al group and Mn. Reynoso's procedure (Ann. chim. phys., 1852, 34, 320) is the most satisfactory.

IV, V. Of analytical methods in which  $\text{PO}_4^{4-}$  or  $\text{C}_2\text{O}_4^{2-}$  are added in excess to eliminate the effects of  $\text{PO}_4^{4-}$  already present Smith's phosphate method (A., 1933, 479) is the most satisfactory. J. W. S.

**Rapid determination of assimilable phosphoric acid in freshly prepared superphosphates.**—See B., 1936, 58.

**Graphite formation. I. Determination of graphite.** A. E. BALFOUR and H. L. RILEY (J.C.S., 1935, 1723—1728; cf. A., 1935, 453).—The  $\text{CO}_2$  evolved when a steady stream of air is bubbled through a suspension of 1 g. of C, graded between 60 and 100 I.M.M. sieves, in 50 c.c. of  $\text{CrO}_3\text{-H}_3\text{PO}_4$  (10 g. of  $\text{K}_2\text{Cr}_2\text{O}_7 + 50$  c.c. of  $\text{H}_3\text{PO}_4$ ,  $d$  1.75) at  $100^\circ$  is an approx. measure of the extent to which the sample is graphitised; e.g., electrode graphite, diamond, and sucrose carbonised at  $900^\circ$  gave 1600, 43, and 16 mg. of  $\text{CO}_2$ , respectively, under similar conditions. The differentiation disappears as the  $[\text{H}_3\text{PO}_4]$  is diminished and is small with conc.  $\text{H}_2\text{SO}_4$ .  $\text{H}_3\text{PO}_4$  probably reacts with graphitic C under sp. conditions. Coal carbonised at approx.  $650^\circ$  has a max. moisture absorption and a min. rate of wet oxidation, consistent with the view that graphitisation commences at approx.  $700^\circ$ . J. G. A. G.

**Preservation of standard solutions of oxalic acid and sodium oxalate. II.** S. ISHIMARU (Sci. Rep. Tôhoku, 1935, 24, 411—425).—Either colourless or black bottles can be used safely for the storage of unacidified 0.2N- $\text{Na}_2\text{C}_2\text{O}_4$  or pure 0.5N- $\text{H}_2\text{C}_2\text{O}_4$  or of 0.01N- $\text{Na}_2\text{C}_2\text{O}_4$  and 0.01N- $\text{H}_2\text{C}_2\text{O}_4$  if 100 c.c. of conc.  $\text{H}_2\text{SO}_4$  are added per litre. 0.01N- $\text{Na}_2\text{C}_2\text{O}_4$  is also stable with 20 c.c. of  $\text{H}_2\text{SO}_4$  per litre in a black bottle. J. W. S.

**Rapid determination of certain gases or vapours  $[\text{CO}_2, \text{HCN}]$  in air.**—See B., 1936, 46.

**Spectrophotometric determination of potassium chloride in sylvines.** R. ROMANN and C. SPEITEL (Bull. Soc. chim., 1935, [v], 2, 2168—2170).—An aq. solution of a known wt. of the specimen is saturated with K picrate, and the concn. of the latter, which is determined by the ratio K : Na in the specimen, is measured spectrophotometrically. The results agree with those obtained by the perchlorate method. F. L. U.

**Determination of alkalis in silicates.**—See B., 1936, 21.

**Colorimetric determination of small amounts of silver with *p*-dimethylaminobenzylidenerhodanine.** I. C. SCHOONOVER (J. Res. Nat. Bur. Stand., 1935, 15, 377—384).—Feigl's method (A., 1928, 1108) gives satisfactory results for Ag in concns. of 0.06—9 mg. per litre when  $\text{Cl}^-$ ,  $\text{Cu}^+$ , and  $\text{Hg}^+$  are absent and fused  $\text{SiO}_2$  vessels are used. Soft glass vessels adsorb appreciable amounts of Ag, but Pyrex adsorbs very little unless the solution is boiled. A. R. P.

**Gravimetric determination of calcium and magnesium.** A. M. VASILIEV and L. A. VASILIEVA (Trans. Kirov Inst. Chem. Tech. Kazan, 1935, No. 3, 67—72).—Appreciable quantities of  $\text{CaC}_2\text{O}_4$  are dissolved by washing with  $\text{H}_2\text{O}$ .  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  should be substituted. Pptd.  $\text{MgNH}_4\text{PO}_4$  should be washed with a saturated solution of this salt, instead of with aq.  $\text{NH}_3$ , which causes losses. CH. ABS. (p)

**Determination of barium silicofluoride in insecticidal powders.**—See B., 1936, 36.

**Determination of the [radium] content of substances containing radium.** A. E. KORVEZEE (Chem. Weekblad, 1935, 32, 726—731).—A lecture. D. R. D.

**Volumetric micro-determination of magnesium with methylene-blue following its precipitation as magnesium picrolonate.** A. BOLLIGER (J. Proc. Roy. Soc. New South Wales, 1935, 69, 68—74).—Solutions ( $> 0.01N$ ) of Mg salts with Li picrolonate at  $100^\circ$  afford Mg picrolonate in which the picronic acid is determined; alternatively, the excess of the acid used is titrated (cf. A., 1934, 1017). Alkali picrolonates in concns.  $< 0.01N$  do not interfere; in larger concns., they are pptd. and the error involved is determined by a differential titration. A modification for determining Ca and Mg separately in the same sample is described. J. L. D.

**Organic compounds as analytical reagents. IV. *p*-Nitrobenzeneazoresorcinol as a reagent for magnesium.** L. NEWELL, N. R. PIKE, and J. B. FICKLEN (Z. anorg. Chem., 1935, 225, 281—284; cf. A., 1935, 951).—The reagent is sp. for Mg when the ions of groups I, II, and III, and  $\text{NH}_4^+$  are removed. The sensitivity is 1 in 500,000. E. S. H.

**Determination of traces of heavy metals in mineral waters.**—See B., 1936, 46.

**Organic flocculating agents in the quantitative precipitation of zinc sulphide.** J. R. CALDWELL and H. V. MOYER (J. Amer. Chem. Soc., 1935, 57, 2372—2374).—Gelatin (0.5—2 mg.) or agar (2—5 mg.) produces immediate and complete flocculation of  $\text{ZnS}$  suspensions (0.3 g. in 300 c.c.). The solution may be filtered within 15 min. after pptn. Satisfactory separation from all metals but Co is obtained. E. S. H.

**Separation of zinc from cobalt based on a new method for reducing post-precipitation.** J. R. CALDWELL and H. V. MOYER (J. Amer. Chem. Soc., 1935, 57, 2375—2377).— $\text{ZnS}$  ppts., formed in presence of hydrophilic colloids (cf. preceding abstract), are not contaminated with Co when acetaldehyde is added. E. S. H.

**Determination of small quantities of zinc.** H. LUX (Z. anorg. Chem., 1935, 226, 1—20).—The method, which is intended for the examination of biological material, consists first in the incineration of the latter at a temp.  $> 550^\circ$ . The metal sulphides, pptd. from a  $\text{HNO}_3$  solution of the ash in presence of  $\text{CaCO}_3$ , are then oxidised in air at  $650\text{--}700^\circ$ , and the resulting oxides are heated in  $\text{H}_2$ . Zn volatilises and is condensed in a capillary, which is then drawn out to a conical end into which the whole of the Zn is driven. The Zn cone is measured microscopically. The method

is accurate to within  $\pm 2\%$  and can be used for quantities down to  $10^{-6}$  mg. Zn of biological origin obtained in this way is shown to contain  $< 0.1\%$  of Cd.  
F. L. Ü.

**Organic reagent for cadmium.** A. W. SCOTT and E. G. ADAMS (J. Amer. Chem. Soc., 1935, 57, 2541—2542).—The prep. of *N*-2 : 6-dihydroxyphenyl-*N'*-allylthiocarbamide, decomp.  $230^\circ$ , *N*-2-hydroxy-5-nitrophenyl-*N'*-allylthiocarbamide, m.p.  $122^\circ$ , and 1-(2-quinolyl)-4-allylthiosemicarbazide (I), m.p.  $158^\circ$ , is described. A saturated solution of (I) in 50% EtOH, in presence of KI, gives a yellow ppt. with solutions containing 1 part of  $\text{Cd}^{++}$  in  $10^6$  parts. E. S. H.

**Determination of small amounts of lead by photometric titration.** S. HIRANO (J. Soc. Chem. Ind. Japan, 1935, 38, 648—650B).—Pb is titrated photometrically with  $\text{Na}_2\text{S}$  (A., 1934, 856) in presence of AcOH and  $\text{NH}_4\text{OAc}$ . Pb may be first isolated as  $\text{PbSO}_4$ , which is dissolved in aq.  $\text{NH}_4\text{OAc}$  for titration. J. S. A.

**Separation of lead as sulphate.** A. M. VASILIEV (Trans. Kirov Inst. Chem. Tech. Kazan, 1935, No. 3, 61—65).—Washing  $\text{PbSO}_4$  ppts. with dil.  $\text{H}_2\text{SO}_4$  followed by 50% EtOH causes losses. Washing with saturated aq.  $\text{PbSO}_4$  gives accurate results.

CH. ABS. (p)

**Extraction of lead by means of diphenylthiocarbazono.** D. C. GARRATT (Analyst, 1935, 60, 817).—In the examination of org. substances for Pb by wet oxidation with  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  followed by extraction of the Pb with diphenylthiocarbazono and  $\text{CHCl}_3$ , errors are caused by the dissolution of resistant  $\text{NO}_2$ -compounds in the  $\text{CHCl}_3$ ; these may be avoided by evaporating the first extract to dryness, heating with 2 c.c. of  $\text{H}_2\text{SO}_4$  and 10 c.c. of 6%  $\text{H}_2\text{O}_2$  until acid fumes are evolved, adding 2 g. of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , and continuing the heating for 30 min.; after cooling the Pb is extracted as before and comparison made with the standards. A. R. P.

**Determination of lead in official [B.P.] compounds and preparations.**—See B., 1936, 76.

**Determination of lead dioxide.** IV.—See B., 1936, 59.

**Volumetric determinations in strongly alkaline solutions.** III. Titration of thallium and cerium with hypobromite. O. TOMÍČEK and M. JAŠEK (J. Amer. Chem. Soc., 1935, 57, 2409—2411; cf. A., 1935, 838, 1094).—The titration of  $\text{Tl}^{\text{III}}$  salts with  $\text{NaOBr}$  is described.  $\text{NaOBr}$  solutions may be standardised by using  $\text{Tl}_2\text{CO}_3$  or  $\text{Tl}_2\text{SO}_4$  as standard.  $\text{Ce}^{\text{III}}$  salts can be titrated with  $\text{NaOBr}$  in 20—30%  $\text{K}_2\text{CO}_3$  solution, from which  $\text{O}_2$  has been removed, but the  $\text{K}_3\text{Fe}(\text{CN})_6$  method is preferred. E. S. H.

**Inorganic complex compounds in analytical chemistry.** III. Detection and determination of copper. C. MAHR (Z. anorg. Chem., 1935, 225, 386—392).— $\text{Cu}^{++}$ , freed from Hg, Ag, and Tl, is reduced to  $\text{Cu}^+$  by  $\text{K}_2\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$  in aq. HCl. A drop of  $\text{NH}_4[\text{Cr}(\text{CNS})_4(\text{NH}_3)_2] \cdot \text{H}_2\text{O}$  in HCl is added and a yellow ppt.,  $\text{Cu}[\text{Cr}(\text{CNS})_4(\text{NH}_3)_2]$ , cryst. from warm solution, is formed. The method is very sensitive. One part of Cu in 15,000 of Bi, 10,000 of Cd, 20,000 of Zn, or 50,000 of Pb can be detected. The applic-

ation of the method to the determination of small quantities of Cu in the presence of a large no. of different metals is described. M. S. B.

**Determination of small amounts of mercury by photometric titration.** S. HIRANO (J. Soc. Chem. Ind. Japan, 1935, 38, 646—647B).—Hg, present in neutral solution as chloride or nitrate, is titrated photometrically (cf. A., 1934, 856) with 0.01*N*- or 0.001*N*- $\text{Na}_2\text{S}$ , using gum arabic as protective colloid. Cu and As do not interfere. J. S. A.

**Determination of small amounts of mercury with dithizone.** H. FISCHER and G. LEOPOLDI (Z. anal. Chem., 1935, 103, 241—257).—For the colorimetric determination of Hg, the Hg in dil.  $\text{HNO}_3$  solution, containing  $> 5 \times 10^{-6}$  g. of Hg per c.c., is extracted quantitatively with successive portions of a  $\text{CCl}_4$  solution of diphenylthiocarbazono (I). The excess of (I) is washed out of the united  $\text{CCl}_4$  extracts with very dil. aq.  $\text{NH}_3$ . The orange Hg-(I) compound is decomposed with slightly acid aq. KI, and the green colour of (I) remaining is either matched against that produced similarly with known amounts of Hg, or measured photometrically. Small amounts of Hg may be determined colorimetrically from the mixed orange-green colour of the original  $\text{CCl}_4$  extract. Volumetrically, Hg is extracted as before with a measured small excess of a solution of (I) previously standardised against Ag. The excess of (I) is bound by adding a standard solution of  $\text{Ag}^+$ , and the excess of  $\text{Ag}^+$  is titrated back with (I).  $\text{Cl}^-$  in large excess does not interfere. In presence of Zn, Cd, Pb, or Bi, Hg alone is extracted from acid solution. Any Zn etc. dissolved is removed by washing with 0.2*N*-acid. In presence of Cu, Hg is extracted preferentially, and may be determined volumetrically, but not colorimetrically. J. S. A.

**Electrocapillary method of detection of the cations of the first sub-group of group IV.** A. F. ORLENKO (J. Gen. Chem. Russ., 1935, 5, 1091—1092).—Al electrodes are placed on wet filter-paper, crystals of  $\text{K}_4\text{Fe}(\text{CN})_6$ , pyrogallol (I),  $\text{K}_2\text{Cr}_2\text{O}_7$ , and KI are placed at different points around the cathode, and drops of the solution, containing  $\text{Hg}^{++}$ ,  $\text{Cu}^{++}$ ,  $\text{Bi}^{+++}$ , and  $\text{Cd}^{++}$ , are placed around the anode, and a current is passed. A few min. later the  $\text{K}_4\text{Fe}(\text{CN})_6$  turns pink, and then brown, and the (I) red, pointing to the presence of  $\text{Cu}^{++}$ . A yellow stain due to formation of  $\text{BiO}_2 \cdot \text{Cr}_2\text{O}_7$  then forms around the  $\text{K}_2\text{Cr}_2\text{O}_7$ , and a pink coloration due to  $\text{HgI}_2$  around the KI crystal. The entire procedure requires 10—15 min. R. T.

**Spectral analysis of complex mixtures.** B. J. DAIN, I. V. GRANOVSKI, and E. S. PUZENKIN (J. Gen. Chem. Russ., 1935, 5, 1093—1097).—A system of standard Co-Mn mixtures giving invariant homologous pairs of spectral lines is proposed. The relative intensity of the lines is unaffected by Na, K, Ba, Al, and Ni, but the Mn lines are relatively more damped by Fe, and more so by Fe+Al, whence it follows that Fe must be eliminated from the mixtures for spectral analysis. R. T.

**Step-photometric determination of manganese in waters.**—See B., 1936, 46.

**Analytical applications of 8-hydroxy-5-methylquinoline.** C. E. GIETZ and A. SÁ (Anal. Asoc. Quím. Argentina, 1935, 23, 45—57).—The detection of traces of the following is described:  $\text{Fe}^{+++}$ ,  $\text{Cu}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Pd}^{++}$ ,  $\text{Ti}^{+++}$ ,  $\text{Zn}^{++}$ ,  $\text{Fe}^{++}$ ,  $\text{Cd}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{VO}_3'$ ,  $\text{MoO}_4''$ ,  $\text{WO}_4''$ . F. R. G.

**Influence of silicic acid on the magnetic behaviour of dissociated mixtures with ferric oxide.** W. LEITGEBEL and K. BOCKEMÜHL (Z. anorg. Chem., 1935, 225, 209—212).—The amount of  $\text{Fe}_3\text{O}_4$  formed under different conditions has been determined by magnetic measurements. E. S. H.

**Detection of traces of iron in mercury salts.**—See B., 1936, 59.

**Determination of iron and aluminium by Crispo's method in natural phosphates.**—See B., 1936, 18.

**Determination of small amounts of nickel and cobalt in iron ores.**—See B., 1936, 63.

**Rapid determination of nickel in high-chromium steels and alloys.**—See B., 1936, 64.

**Importance of hydrogen-ion concentration in determination of molybdenum and vanadium by the 8-hydroxyquinoline method and solubility of 8-hydroxyquinoline in various solvents.** H. GOTO (J. Chem. Soc. Japan, 1935, 56, 314—321).—Complete pptn. of Mo occurs in the  $p_{\text{H}}$  range 3.3—7.6 and that of V at  $p_{\text{H}}$  2.7—6.1. The solubility of 8-hydroxyquinoline in the EtOH-COME<sub>2</sub> mixture is small at  $p_{\text{H}}$  5.5—8.5. CH. ABS. (p)

**Iodometric titration of tin.** F. L. OKELL and J. LUMSDEN (Analyst, 1935, 60, 803—810).—Low results in Sn titrations are shown to be due to  $\text{O}_2$  dissolved in the I solution and not to incomplete exclusion of air from the flask. In the analysis of Sn ores the presence of Ti gives erratic results; this is ascribed to its acting as a negative catalyst for the oxidation of  $\text{Sn}^{++}$  by dissolved  $\text{O}_2$ . No interference of Ti occurs if O-free I is used for titration. Reduction with Al turnings is recommended in ore analysis. A. R. P.

**Quantitative spectral analysis. IV.** R. BREKROP and A. MEVIS (Ann. Soc. Sci. Bruxelles, 1935, 55, B, 266—292; cf. A., 1935, 719).—The spectral determination of Ti, V, Cr, Mn, Co, Ni, Mo, and In using a Cu base is discussed and tables of data are given. The Cu line previously described as 2480.13 Å. is actually 2479.8 Å. and coincident with an Fe line persistent at feeble amperages. R. S.

**Colorimetry of titanium. IV.** H. GINSBERG (Z. anorg. Chem., 1935, 226, 57—64; cf. A., 1933, 566).—Errors in the colorimetric determination of  $\text{TiO}_2$  are discussed. By using a Pulfrich photometer 0.07 mg. of  $\text{TiO}_2$  per 100 c.c. can be determined within  $\pm 10\%$ . F. L. U.

**Determination of zirconium.** G. A. AMPT (J. Proc. Austral. Chem. Inst., 1935, 2, 321—334).—A review of analytical methods for the determination of Zr and complete analysis of Zr minerals. J. S. A.

**Determination of the zirconium-hafnium ratio.** G. WERNIMONT and T. DE VRIES (J. Amer.

Chem. Soc., 1935, 57, 2386—2387).—An equation for the calculation of the mol. ratio Hf : Zr in mixtures, when the effect of a known wt. of the mixed oxides on the rotation of certain reference tartrate solutions has been measured, is given. Results on two samples of mixed oxides are compared with those obtained by other methods. The procedure is not more accurate, but is rapid and convenient. E. S. H.

**Potentiometric determination of metavanadates with silver nitrate.** P. SPACU (Z. anal. Chem., 1935, 103, 422—424).— $\text{VO}_3'$  is titrated potentiometrically with  $\text{AgNO}_3$  in 20% aq. EtOH solution. J. S. A.

**Electrometric determination of vanadium in (A) high-chromium steels, (B) slags.**—See B., 1936, 65.

**Determination of antimony in white metals.**—See B., 1936, 64.

**Determination of bismuth with 8-hydroxyquinoline.** F. HECHT and R. REISSNER (Z. anal. Chem., 1935, 103, 261—269).—Determination of Bi as  $\text{C}_9\text{H}_6\text{N}\cdot\text{OH}\cdot\text{HBiI}_4$  (cf. A., 1927, 847) is unsatisfactory, the ppt. undergoing partial decomp. during washing. Pptn. with 8-hydroxyquinoline from AcOH solution at 70° under the exact conditions described gives good macro- and micro-results. The ppt. is dried at 105° and weighed as  $\text{Bi}(\text{C}_9\text{H}_6\text{ON})_3\cdot\text{H}_2\text{O}$ . J. S. A.

**Colorimetric assay of bismuth pharmaceuticals.**—See B., 1936, 43.

**Potentiometric determination of quadrivalent osmium with chromous sulphate.** W. R. CROWELL and H. L. BAUMBACH (J. Amer. Chem. Soc., 1935, 57, 2607—2609).—Apparatus and technique for (1) storing and titrating  $\text{CrSO}_4$  solutions, (2) standardising  $\text{CrSO}_4$  with  $\text{K}_3\text{Fe}(\text{CN})_6$  and  $\text{K}_2\text{Cr}_2\text{O}_7$ , and (3) determining Os in  $\text{K}_2\text{OsBr}_6$  and  $\text{K}_2\text{OsCl}_6$  by potentiometric titration are described. E. S. H.

**Separation of the six platinum metals from one another and their gravimetric determination.** R. GILCHRIST and E. WICHERS (J. Amer. Chem. Soc., 1935, 57, 2565—2573).—Os is isolated by distilling  $\text{OsO}_4$  from  $\text{HNO}_3$  solution. Ru is next isolated by distilling  $\text{RuO}_4$  from a solution of the sulphates in dil.  $\text{H}_2\text{SO}_4$  containing  $\text{NaBrO}_3$ . A suitable reagent for absorption of  $\text{OsO}_4$  or  $\text{RuO}_4$  is 6N-HCl saturated with  $\text{SO}_2$ . The separation of Pt, Pd, Rh, and Ir is effected by controlled hydrolytic pptn. In the recovery and determination of these metals, Os, Ru, and Ir are pptd. as hydrated oxides, ignited, and weighed as metal; Rh and Pt are obtained as sulphides and ignited to metal; Pd is recovered as the glyoxime compound, which may be weighed directly or ignited and weighed as metal. The accuracy is equal to that of the best analytical procedures. E. S. H.

**Comparison of some platinum thermometers with the helium thermometer between 0° and -183°.** W. H. KEESOM and B. G. DAMMERS (Physica, 1935, 11, 1080—1090).—A  $\text{C}_5\text{H}_{12}$  cryostat for use at 0° to -150° is described. H. J. E.

**Construction of platinum thermometers and determination of their basic points.** W. H. KEESOM and B. G. DAMMERS (Physica, 1935, 11,

1051—1058).—The construction and calibration are described. The optimum annealing temp. was 840—850°.  
H. J. E.

**Micro-determination of m.p.** M. MEZENER and S. WEHRLI (Helv. Chim. Acta, 1935, 18, 1281—1283).—A sealed m.-p. tube is used, the specimen being observed through a low-power microscope.  
J. S. A.

**Calorimeter for measurement of continued heat effects.** W. SWIENTOSELAWSKI (Rocz. Chem., 1935, 15, 343—350).—A flow calorimeter is described in which heat effects of the order of 1—400 g.-cal. per hr. are determined by measuring the difference in temp. between a liquid entering and leaving the calorimeter at const. velocity. Efficient heat exchange is achieved by surrounding the reaction vessel and the thermometer with labyrinths through which the liquid circulates.  
R. T.

**Thermocouples from 2° to 90° abs.** J. E. AHLBERG and W. O. LUNDBERG (J. Amer. Chem. Soc., 1935, 57, 2722—2723).—Methods of calibration are discussed.  
E. S. H.

**Precision thermostat for use down to -20°.** G. A. BENFORD (J. Sci. Instr., 1936, 13, 4—6).—A commercial refrigerating element acts in opposition to a controlled heater.  
C. W. G.

**Thermal conductivity method for following the electrolytic separation of hydrogen isotopes.** W. C. NEWELL, R. H. PURCELL, H. S. GREGORY, and H. J. T. ELLINGHAM (Nature, 1936, 137, 69—70).—A method, accurate to approx. 0.1% of D<sub>2</sub>, using gas at 10 cm. pressure is described.  
L. S. T.

**Determination of transformation points [in alloy systems].** H. NIPPEN and E. LIPS (Z. Metallk., 1935, 27, 242—243).—An apparatus for the automatic registration of the torsion angle of wires at various temp. is described; a sharp change in the direction of the resulting curve indicates a change in the constitution of the alloy. The use of the apparatus in determining the solidus of Cu-Ag alloys is illustrated.  
A. R. P.

**Physical methods in the chemical laboratory. XXVII. Application of röntgenographic methods to chemical problems.** R. BRILL and H. HALLE (Angew. Chem., 1935, 48, 785—795).—X-Ray methods for the study of gases, liquids, crystals, fibres, etc. are reviewed.  
R. S.

**Accurate determination of glancing angles and lattice constants by the method of Debye and Scherrer.** M. STRAUMANIS and A. IEVINS (Naturwiss., 1935, 23, 833).—The usual method is improved by a different arrangement of the film in the camera.  
A. J. M.

**Subjective photometer.** W. D. WRIGHT and J. H. NELSON (J. Sci. Instr., 1935, 12, 373—377).—The intensity of a patch viewed by the left eye is compared with that of one viewed by the right, in order to measure the variation in sensitivity of the eye for different conditions of the visual mechanism.  
C. W. G.

**Use of a selenium photo-electric cell for the measurement of solar ultra-violet radiation near 3200 Å.** G. LIANDRAT (Compt. rend. Acad. Sci.

U.R.S.S., 1935, 3, 19—20).—A surface of 30 sq. cm. is used, behind a Ag filter.  
C. W. G.

**Cuprous oxide "sperrschicht" photo-electric cell as precision sunshine recorder.** H. MAYER (Meteorol. Z., 1935, 52, 15—18; Chem. Zentr., 1935, i, 2565).—The photo-electric cell has advantages over the glass-sphere instrument.  
J. S. A.

**X-Ray powder camera for specimens at various known temperatures.** W. H. BARNES and W. F. HAMPTON (Canad. J. Res., 1935, 13, 73—81).—The specimen is placed over a hole in a Cu block through which the X-rays are directed by a pinhole system. The temp. of the block is maintained const. by circulation of COMe<sub>2</sub> or other liquid, which passes through two coils at -78° and is then warmed to any desired temp. between 0° and -60° by an electric heater.  
R. S.

**Mapping ultra-violet absorption spectra, using a special hydrogen lamp and a microphotometer.** H. C. GULL and A. E. MARTIN (J. Sci. Instr., 1935, 12, 379—388).—The spectra are photographed with a H<sub>2</sub> lamp, of const. output. They are traversed in the microphotometer by a series of lines corresponding with known extinction coeffs.  
C. W. G.

**Square reagent glasses for comparators.** H. BAUSCH (Woch. Brau., 1935, 52, 397).—A reagent tube, part of which has a square cross-section, is described. The uniformity and enlargement of the field which are thus made possible facilitate colorimetric comparisons.  
I. A. P.

**Spectrograph with high illumination for Raman spectra.** G. DUPONT and J. TABUTEAU (Bull. Soc. chim., 1935, [v], 2, 2152—2156).—Apparatus and method of working are described.  
F. L. U.

**Sedimentometer.** J. MILBAUER (Z. anal. Chem., 1935, 103, 419—422).—A photo-electric cell is employed to measure velocity of sedimentation.  
J. S. A.

**Photo-electric half-shadow method for determination of rotational dispersion.** O. SCHÖNROCK and E. EINSPOHN (Physikal. Z., 1936, 37, 1—12).—The method employs a single photo-electric cell.  
A. J. M.

**Observing fluorescence.** D. W. DANA (Rev. Sci. Instr., 1935, [ii], 6, 417).—Corning glass No. 038, "Noviol A," may be used when the source of excitation extends into the visible violet.  
C. W. G.

**Resolving power of the two-crystal X-ray spectrometer.** L. G. PARRATT (Rev. Sci. Instr., 1935, [ii], 6, 387—399).—The physical meaning of resolving power when the shape of the diffraction pattern is unknown has been studied experimentally. New criteria of spectrometric perfection of calcite crystals are proposed.  
C. W. G.

**Illuminator for printing Laue photographs.** C. H. DWIGHT and H. KERSTEN (Rev. Sci. Instr., 1935, [ii], 6, 418; cf. A., 1935, 1340).—The priority of Trendelenburg and Franz (A., 1934, 504) is admitted.  
C. W. G.

**Double ionisation chamber for detection of corpuscular particles.** B. ZIPPRICH (Z. Physik, 1935, 96, 328—336).  
A. B. D. C.

**Mechanism of action of solid rectifiers.** V. P. SHUSÉ (Physikal. Z. Sovietunion, 1935, 7, 1—18).—A method for making rectifiers with blocking layers of  $\text{SiO}_2$ ,  $\text{B}_2\text{O}_3$ ,  $\text{NaCl}$ ,  $\text{S}$ , glass, and bakelite, and with rectification coeffs. up to 100 is described.

CH. ABS. (e)

**Measurement of electromotive force and very weak direct current by means of electron tubes.** F. MÜLLER and W. DÜRICHEN (Z. Elektrochem., 1936, 42, 31—43).—A review.

**Magnification of currents of the order of  $10^{-13}$  amp.** H. ALFVÉN (Z. Physik, 1935, 97, 708—717).—The valve circuit described automatically differentiates, with respect to time, the potential of the first grid, and so records the true form of the applied small current.

A. B. D. C.

**Hydraulic counter for elementary rays and photo-electrons.** H. GREINACHER (Helv. phys. Acta, 1934, 7, 514, 641; Chem. Zentr., 1934, ii, 2096; 1935, i, 2319).

J. S. A.

**Further hydroelectric counter for elementary rays and photo-electrons. III.** H. GREINACHER (Helv. phys. Acta, 1935, 8, 89—96; Chem. Zentr., 1935, i, 2852).—Elementary rays or photo-electrons initiate a discharge between a liquid surface and an Fe point electrode. The counter has advantages over the author's hydraulic counter (see above).

J. S. A.

**Further improvements in the Curie-Chéneveau magnetic balance.** F. W. GRAY, A. CLOW, and J. H. CRUIKSHANK (J. Sci. Instr., 1936, 13, 13—20).—Alterations in apparatus and technique are described (cf. Gray *et al.*, *ibid.*, 1932, 9, 1).

C. W. G.

**Routine gas analysis apparatus.** H. K. SEN, K. ROY, and P. ROY (J. Indian Chem. Soc., 1935, 12, 654—658).—The method of fractional combustion is employed.

R. S. B.

**Gas micro-analysis [apparatus] for following the course of oxidation of hydrocarbons.**—See B., 1936, 50.

**Container for analysing gases by combustion.** V. MATSCHKARIN (Novo. Tech., Seri. Gorn. Prom., 1935, No. 2, 13).—The sealed-in Pt wires of the explosion vessel are cooled by Hg, contained in glass tubes sealed to the outside of the vessel. Risk of cracking at the seals is thus eliminated.

CH. ABS. (e)

**Manometric device for gas analysis.**—See this vol., 259.

**Air analysis apparatus.**—See this vol., 259.

**Apparatus for determining the concentration of ammonium fluoride solutions.** M. SCRÜTZA (Woch. Brau., 1935, 52, 405—406).—The described apparatus minimises the difficulties met with in titrating  $\text{NH}_4\text{HF}_2$  solution (I) with 0.1N-Ba(OH)<sub>2</sub> solution (litmus). The concn. of free HF varies in commercial samples of (I) from 29 to 33%, and a correction table is therefore supplied for the elimination of errors due to this variation.

I. A. P.

**Modified Rehberg burette for use with titrating solutions which react with mercury.** B. B. LONGWELL and R. M. HILL (J. Biol. Chem., 1936, 112, 319—321).—The Rehberg micro-burette (A.,

1925, i, 852) is modified so that Hg does not touch the titrating fluid.

H. D.

**Logarithmic head correction in viscometry.** G. BARR (J.C.S., 1935, 1793—1795).—The effects of several shapes of bulbs on the "head correction" for viscosimeters are evaluated. Bury's procedure (A., 1934, 1195) is modified.

J. G. A. G.

**Microscopical method for measuring the viscosity of a liquid.** F. HIRATA (Bull. Chem. Soc. Japan, 1935, 10, 507—524).—The velocity of flow of liquids under a known pressure through a capillary is observed under a microscope by using particles of C and SiC, 0.1—0.002 mm. in diameter, as indicators of flow. The particles have no effect on  $\eta$  within the experimental error.  $\eta$  has been measured for glycerol and for solutions of cellulose acetate in  $\text{COMe}_2$ , results agreeing with those obtained with the Oswald viscosimeter, and with theory.

R. S. B.

**Regulation of liquid flow by capillary tubes.** I. HVIDBERG (Kem. Maanedsl., 1934, 15, 152; Chem. Zentr., 1935, i, 2409).—A simple device for fine flow regulation is described.

J. S. A.

**Sulphuric acid hygrometer.** A. BLACKIE (J. Sci. Instr., 1936, 13, 6—9).—The change of pressure of air at const. vol. on drying is measured.

C. W. G.

**Simple humidity chamber.** F. C. MEAD (J. Sci. Instr., 1935, 12, 394—395).—Suitable solutions are placed inside an air thermostat controlled by a bi-metallic regulator.

C. W. G.

**Obtaining and controlling high humidities at high temperatures.** W. LETHERSICH (J. Sci. Instr., 1935, 12, 388—391).—Separate heating is provided for a dish of  $\text{H}_2\text{O}$  inside a heated oven.

C. W. G.

**Chemical hygrometer.** T. M. CARPENTER (J. Biol. Chem., 1935, 112, 123—133).—An apparatus, on the principle of that used in gas analysis, for the determination of  $\text{H}_2\text{O}$  vapour by vol. in air is described. The vols. before and after removal of  $\text{H}_2\text{O}$  by  $\text{Mg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$  are read against a const. vol. kept dry by  $\text{P}_2\text{O}_5$ . The agreement with results obtained by wt. of the absorbed  $\text{H}_2\text{O}$  is within 0.02%.

J. N. A.

**Development of air-driven spinning top as transparent centrifuge.** J. W. MCBAIN and C. M. O'SULLIVAN (J. Amer. Chem. Soc., 1935, 57, 2631—2641).—Apparatus and technique are described.

E. S. H.

**Mercury float-valves [taps] for high-vacuum work.** H. LUX (Z. anorg. Chem., 1935, 226, 21—22).—The greaseless taps devised by Stock (A., 1915, ii, 339; 1925, ii, 1195) have been modified by using floats provided with thin sintered glass plates, thus permitting rapid evacuation.

F. L. U.

**Rapid weighings with a Troemner solution balance.** E. T. BARTHOLOMEW and E. C. RABY (Science, 1935, 82, 468).—Modifications to ensure quicker and more convenient weighing with a 20-kg. capacity balance are described.

L. S. T.

**Modern developments in chemical balances.** J. L. BUCHAN (J. Sci. Instr., 1936, 13, 1—4).—Historical.

C. W. G.



**Determination of low gas pressures.** H. KLUMB and T. HAASE (Physikal. Z., 1936, 37, 27—32).—An apparatus for determining low gas pressures uses an electrically heated bimetal strip (invar-constantan), the loss of heat, varying with the pressure of the gas, being measured by the bending of the strip. The instrument is useful for pressures down to  $10^{-4}$  mm., and may also be used for determining the composition of a gas, since the effect is dependent on mol. wt. A. J. M.

**Laboratory apparatus.** A. OSTROGOVICH (Annali Chim. Appl., 1935, 25, 563—568).—Apparatus for drying substances in a vac., a reflux condenser, and a flask with neck adaptable to reflux condenser or distillation head are described and illustrated. F. O. H.

**Device for drilling oriented holes in spheres required in the construction of crystal structure models.** M. J. BUERGER (Rev. Sci. Instr., 1935, [ii], 6, 412—416).—Full constructional diagrams are given. C. W. G.

**Simple oil micromanometer.** O. BEECK (Rev. Sci. Instr., 1936, [ii], 6, 399—400).—Movement of Hg is magnified by transfer to movement of oil in a capillary. C. W. G.

**Apparatus for studying the elastic properties of filamentous materials.** I. J. SAXL (Rev. Sci. Instr., 1935, [ii], 6, 409—412).—Chainomatic wt. application is used. C. W. G.

**Making extremely thin films.** K. LARK-HOROVITZ, J. D. HOWE, and E. M. PURCELL (Rev. Sci. Instr., 1935, [ii], 6, 401—403).—The film is deposited on a layer of material such as camphor which is subsequently removed by vaporisation. C. W. G.

**Apparatus for the determination of colloid osmotic pressure in small amounts of fluid.** R. DUBACH and R. M. HILL (J. Biol. Chem., 1936, 112, 313—318).—The Krogh-Nakazawa osmometer (A., 1927, 1104) is modified by using brass parts, thus dispensing with washers around the membrane and allowing a view of the latter when in place. H. D.

## Geochemistry.

**Gases of the borate-carrying soffioni, with special reference to their content of helium and other noble gases.** U. SBORGI (Mem. R. Accad. Ital., Cl. Sci. fis. mat., 1934, 5, 667—713; Chem. Zentr., 1935, i, 2792).— $O_2$  is absent from soffioni gases, which vary little in composition from different sources. He and A are present, with little Ne. The Rn : He ratio is not const. J. S. A.

**Mineral composition of atmospheric dust collected at Baton Rouge, Louisiana.** R. D. RUSSELL (Amer. J. Sci., 1936, [v], 31, 50—66).—Samples from the dust storms of April, 1934 (and April, 1935) were compared. The vol. % size of particles is 0.050—0.100, < 1 (1); 0.025—0.050, 4 (9); 0.005—0.025, 30 (50); < 0.005 mm., 65 (40). The material was separated into lighter and heavier portions by centrifuging in  $CHBr_3$ , and particles > 0.01 mm. were identified and counted under the microscope. The lighter portion contained volcanic glass 42 (24), plant fragments etc. 18 (5), quartz 21 (53)%; and 11 other minerals were identified. In the heavier portion ( $d > 2.88$ ; 1% of the whole) 35 minerals were identified, including "black metallies" 25 (22), hematite with some limonite 18 (25), epidote 21 (27)%, etc. The relative abundance of volcanic glass is evidently due to its concn. by suspension in the air. The 1934 dust came from the northern plains, and that of 1935 from the south. L. J. S.

**Concentration of  $D_2O$  in natural ice.** II. E. BARONI and A. FINK (Monatsh., 1935, 67, 131—136; cf. A., 1935, 953).—Results of determinations of  $D_2O$  in samples of ice taken systematically from definite parts of glaciers (Caucasus) are given. Variations of —50 to +25% from the normal are recorded. F. L. U.

**Mineral waters of Harrogate.** A. WOODMANSEY (Analyst, 1936, 61, 23—26).—The composition,

pharmacology, transport, and storage of the waters are discussed. E. C. S.

**Analysis of water from Torrente Iungari, Calabria.** B. RICCA and P. MEDURI (Annali Chim. Appl., 1935, 25, 571—586).—Chemical, physico-chemical, and bacteriological data are given and the therapeutic val. of the  $H_2O$  is discussed. F. O. H.

**Chemical and biological aspects of Orbetello lagoon water.** I, II. C. M. MALDURA (Atti R. Accad. Lincei, 1935, [vi], 22, 64—68, 140—145).—I. Data for annual variations in temp., salinity, and oxygenation are given and discussed.

II. Data for variations in temp., salinity,  $p_H$ , alkalinity, and content of  $Cl^-$ ,  $SO_4^{--}$ ,  $O_2$ ,  $NH_4^+$ ,  $NO_2^-$ , and  $NO_3^-$ -N, P, and Si are tabulated. F. O. H.

**Hydrogen-ion concentration and temperature of surface waters of several seas.** R. C. MILLER (Proc. V Pacific Sci. Congr., 1934, 3, 2111—2113).—The  $p_H$  varied from 8.23 to 8.03. CH. ABS. (e)

**Determination and quantity of boron in sea-water.** M. W. HARDING and E. G. MOBERG (Proc. V Pacific Sci. Congr., 1934, 3, 2093—2095).—The B in sea-water is titrated in presence of mannitol. The content was 4.3—4.8 mg. of B per kg. of sea-water. CH. ABS. (e)

**Probable rôle of boron in the buffer mechanism of sea-water.** R. REVELLE and E. G. MOBERG (Proc. V Pacific Sci. Congr., 1933, 3, 2147—2151).—The modification of the buffer relations of sea-water by borates is discussed. CH. ABS. (e)

**Simultaneous change in chemical composition of sea-water and *Mytilus crassitesta*, Lischke, influenced by season.** K. HAYASHI (Proc. V Pacific Sci. Congr., 1934, 3, 2069—2071).—The correlation between changes in the composition of sea-

for Cs 8521 and 8944 Å. The mineral is mixed with NaCl and evaporated in the C arc. Saturation of the arc with Na ions secures evaporation under comparable conditions. Comparison is made with known Cs and Rb contents, or with Ba and Li. In agreement with the authors' views and the large ionic radius of Cs and Rb, Cs and Rb are enriched relatively to Ca and Na in magmatic rocks and sedimentary rocks. J. S. A.

The pair chalcostibite-emplectite, and the agreement between dimensions of unit cells and the crystallographic parameters. M. H. UNGEMACH (Bull. Soc. franç. Min., 1934, 57, 186—207; Chem. Zentr., 1935, i, 2657).—Agreement with X-ray and crystallographic data for emplectite is obtained by a choice of new co-ordinate axes for chalcostibite. J. S. A.

Determination of the specific volume of fused masses at temperatures up to 1400°. M. P. VOLAROVITSCH and A. A. LEONTJEVA (Z. anorg. Chem., 1935, 225, 327—332).—By a dilatometric method, the sp. vol. of the rocks diorite, basalt, and diabase, and the salts  $K_2SiO_3$ ,  $NaBO_2$ , and  $K_2B_4O_7$ , in the fused state, has been determined at different temp. and the expansion coeff. calc. M. S. B.

Distribution of useful metals in the earth's crust. I. NODDACK and W. NODDACK (Angew. Chem., 1936, 49, 1—5).—A discussion. E. S. H.

Determination of activity of rocks with the tube counter. J. N. HUMMEL (Nach. Ges. Wiss. Göttingen, 1935, [ii], 1, 73—81; Chem. Zentr.,

1935, i, 2643—2644).—The Geiger counter is applied to the determination of the radioactivity of rocks. Separation of the effects of the Th and U families is possible only under (under-ground) conditions of screening from cosmic radiation. J. S. A.

Radioactivity of rocks in the Far East and its influence on forests. L. L. LAGUNOV (Bull. Far East. Branch Acad. Sci. U.S.S.R., 1934, No. 9, 105—109).—Increase in radioactivity of soil increases self-seeding, growth, and the no. of trees per unit area. CH. ABS. (c)

Enelectrite, a new mineral found in chemawinite. T. L. WALKER (Univ. Toronto Studies, Geol. Ser., 1934, No. 36, 11—12).—The mineral (hydrocarbon?) forms colourless, lath-shaped monoclinic crystals. CH. ABS. (c)

Chemawinite or Canadian amber. T. L. WALKER (Univ. Toronto Studies, Geol. Ser., 1934, No. 36, 5—10).—Cedarite and chemawinite are identical. Physical properties are recorded. Analysis gave C 81.40, H, 10.70, O 7.23, N 0.02, ash 0.65%. CH. ABS. (c)

Distribution of sulphur in Illinois coals and its geological implications. G. H. CADY (Ill. State Geol. Survey, Rept. Invest., 1935, No. 35, 23—41).—Data are discussed. CH. ABS. (c)

Influence of structural irregularities on the chemical character of No. 6 coal in Franklin and Williamson counties, Illinois. E. T. BENSON and G. H. CADY (Ill. State Geol. Survey, Rept. Invest., 1935, No. 35, 5—22). CH. ABS. (c)

## Organic Chemistry.

Tautomerism. B. NILSSEN (Tidsskr. Kjemi, 1935, 15, 145—150).—A review. M. H. M. A.

Hydrogenation of unsaturated compounds. N. K. JURASCHEVSKI (J. Gen. Chem. Russ., 1935, 5, 1098—1107).—Addition of  $H_2$  (Pd on Ni) to the second double linking of geraniol and linaloyl acetate commences before complete saturation of the first, whilst in limonene (I) the two processes proceed simultaneously. The following pairs of substituted ethylenes behave similarly to (I): stilbene-benzoyl-eugenol (II), allyl alcohol (III)— $CHPh:CH \cdot CO_2Na$  (IV); in the pairs (IV)—pulegone (V), fumaric acid (VI)—(V), (V)— $CHMe:CMe_2$ , (III)—(VI), (III)—(IV), (IV)—(I),  $CHPh:CH \cdot CO_2Me$  (VII)—(IV), and (VII)— $CHPh:CH \cdot CO_2H$  the second component is hydrogenated after complete or almost complete saturation of the first. The pair (II)—(IV) occupies an intermediate position. R. T.

Determination of butadiene by condensation with quinones. A. B. DOLGOPLOSK (Sintet. Kautschuk, 1934, No. 2, 29—31).—The rectified butadiene was bubbled through a solution of benzoquinone in PhOH at 120°. The condensation product is 1:4:5:8-tetrahydroanthraquinol. The method is applicable in presence of other olefines,  $Et_2O$ , and MeCHO. CH. ABS. (c)

Polymerisation products of normal ( $\Delta^2$ ) pentene at high temperature. H. I. WATERMAN, J. J. LEENDERTSE, and J. DE HULSTER (J. Inst. Petroleum Tech., 1935, 21, 952—958).—The polymerised product obtained from  $\Delta^2$ -pentene by treatment with  $AlCl_3$  at 0° did not undergo any appreciable change by heating at 200° (a) in presence of a Ni catalyst in  $N_2$ , or (b) in presence of  $H_2$  without a catalyst; hence with Ni and  $H_2$  it is probable that the mol. structure remains unaltered. At 300°, however, depolymerisation occurs under conditions (a) and (b). Rapid hydrogenation (high-pressure  $H_2$ ; Ni) protects the product from destruction, the product being similar to that obtained at 200° under the same conditions. At 435° an unsaturated and cyclic liquid product (with increased no. of rings) was obtained under conditions (a), whereas under (b) considerable destruction was also observed, but the total no. of rings had not appreciably changed. Under conditions (a) and (b) the higher-mol. fraction contained more rings per mol. than the raw material. C. C.

Reaction between sulphur dioxide and olefines. III. Higher olefines. Limitations of the reaction. L. L. RYDEN and C. S. MARVEL (J. Amer. Chem. Soc., 1935, 57, 2311—2314; cf. A., 1935, 1349).—*iso*- $C_4H_8$ ,  $\Delta^2$ - and  $\Delta^3$ -pentene,  $\Delta^2$ -nonene,  $\gamma$ -cyclohexylpropene, and 3-methylcyclohexene give

alcoholic polysulphones, m.p. (block) 340°, 290—300° (215—220° in a tube), 340°, >300°, 330°, and 270°, respectively, but further substitution on the ethylenic linking hinders addition. Mol. wt. determination by means of the Cl content of the  $\text{CH}_2\text{Cl}\cdot\text{CO}$  and  $\text{CCl}_3\cdot\text{CO}$  derivatives is inaccurate owing to difficulties of purification and low Cl content; mol. wts. are about 100,000—200,000. The N content of the anilide of propylidenepolysulphone indicates a mol. wt. of about 50,000. Undecenyl alcohol and  $\Delta^a$ -heptinene give polysulphones, darkens at 330° ( $\text{CH}_2\text{Cl}\cdot\text{CO}$  derivative) and m.p. 160—169°, respectively. R. S. C.

$\alpha\gamma$ -Disubstituted allene.  $\Delta^{8\gamma}$ -Hexadiene. H. VAN RISSSEGHEM (Bull. Soc. chim. Belg., 1935, 44, 593—596).—Hexane- $\gamma\delta$ -diol with  $\text{PBr}_3$  affords the  $\gamma\delta$ -dibromide and  $\gamma$ -bromo- $\Delta^\gamma$ -hexene, b.p. 49.0—49.2°/26 mm., which with KOH in  $\text{CH}_2\text{Ph}\cdot\text{OH}$  gives  $\Delta^{8\gamma}$ -hexadiene, b.p. 67.75—68.25°/760 mm.

J. L. D.

Chloroform-*d* (deuteriochloroform). F. W. BREUER (J. Amer. Chem. Soc., 1935, 57, 2236—2237).— $\text{CCl}_3\cdot\text{CHO}$  and  $\text{D}_2\text{O}$  give the deuterate (I), which with NaOD gives deuteriochloroform, m.p. —64.69° to —64.15°, b.p. 0.5° > that of  $\text{CHCl}_3$ . Physical data are given. (I) and NaOD are less sol. in  $\text{D}_2\text{O}$  than are  $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$  and NaOH, respectively, in  $\text{H}_2\text{O}$ . R. S. C.

Synthesis of  $\alpha\beta$ -dichlorobutadiene, and its polymerisation. A. L. KLEBANSKI, A. S. VOLKENSCHTEIN, and A. P. ORLOVA (J. Gen. Chem. Russ., 1935, 5, 1255—1267).— $\text{CH}_2\text{:CH}\cdot\text{C}\cdot\text{CH}$ , b.p. 55—57°, obtained in 57% yield by shaking  $\text{CH}_2\text{:CH}\cdot\text{C}\cdot\text{CH}$  with aq. NaOCl for 10 hr. at room temp., yields  $\alpha\beta$ -dichloro- $\Delta^{\alpha\gamma}$ -butadiene (I), b.p. 60—65°/105 mm., when shaken with  $\text{CuCl}+\text{NH}_4\text{Cl}$  in 50% HCl (16 hr., room temp.); the structure of (I) is established by treating it with  $\text{O}_3$ , when  $\text{CHCl}\cdot\text{CCl}\cdot\text{CO}_2\text{H}$  is obtained. (I) polymerises spontaneously at room temp., to yield a gelatinous product, sol. in org. solvents; the velocity of polymerisation is intermediate between that of chloroprene and chlorobutadiene, and increases with rising temp. and intensity of illumination. An ebonite-like product is obtained by hot-pressing the mixture (I) 5, MgO 1, ZnO 0.25, neozone 0.1, and colophony 0.25 pts.

R. T.

Initial formation of methyl alcohol in the oxidation of methane. W. A. BONE (Nature, 1935, 136, 910).—Small amounts of MeOH (0.13%) and  $\text{CH}_2\text{O}$  (0.03%) have been detected in the suddenly-cooled products of the explosion of a  $5\text{CH}_4+2\text{O}_2$  mixture at an initial pressure of approx. 50 atm. L. S. T.

Presence of active *sec.*-butyl alcohol in fermentation propyl alcohols. Qualitative and quantitative analysis by Raman spectra. G. DUPONT and R. DULOU (Bull. Soc. chim., 1935, [v], 2, 2156—2163).—Samples of supposedly pure fermentation PrOH are shown by Raman spectra to contain up to 19% of *l-sec.*-BuOH. R. S. C.

South American drugs. I. Bixol. II. *Cana-  
valia obtusifolia*.—See this vol., 123.

Application of the xanthic reaction to the dehydration of di-tertiary  $\alpha$ -glycols. V. A. FOMIN (J. Gen. Chem. Russ., 1935, 5, 1192—1194).— $\text{OH}\cdot\text{CMe}_2\cdot\text{CMe}_2\cdot\text{OK}$  in xylene and  $\text{CS}_2$  (100°; 4 hr.), followed by addition of MeI and further heating (100°; 6 hr.), yield the substance  $\begin{matrix} \text{CMe}\cdot\text{O} \\ \text{CMe}\cdot\text{O} \end{matrix} > \text{CS}$ , m.p. 156°, converted into pinacolin,  $\text{H}_2\text{S}$ , and  $\text{CO}_2$  by heating with  $\text{H}_2\text{SO}_4$ . R. T.

Reaction of ethylene oxide with acetylenic Grignard reagents. J. P. DANEHY, R. R. VOGT, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1935, 57, 2327).—The Grignard reagent from 2 mols. of  $\Delta^a$ -heptinene (I) with  $(\text{CH}_2)_2\text{O}$  gives  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ , (I), and  $\Delta^\gamma$ -heptinene- $\alpha$ -ol. The reagents from  $\Delta^a$ -hexinene and  $\text{CH}\cdot\text{CPh}$  react similarly. R. S. C.

Acetylene polymerides and their derivatives. XXIII. Preparation and polymerisation of oxy-prenes [ $\beta$ -alkoxybutadienes]. H. B. DYKSTRA (J. Amer. Chem. Soc., 1935, 57, 2255—2259; cf. A., 1935, 1480).—Me  $\beta$ -alkoxyethyl ketones and alkyl orthoformates give  $\alpha\gamma\gamma$ -trialkoxybutanes (I), which at >130° afford  $\beta$ -alkoxybutadienes (termed oxy-prenes). At lower temp. with acid catalysts unsaturated ketals (II),  $\text{CH}_2\text{:CH}\cdot\text{CMe}(\text{OR})_2$ , with basic catalysts  $\alpha\gamma$ -dialkoxy- $\Delta^\beta$ -butenes (III), are formed. Below the dissociation temp. (II) and (III) add alcohols, phenols, and thiophenols to give (I) and its S derivatives, mixed oxy-prenes being thus obtainable. Oxy-prenes alone polymerise very slightly in several months; in ultra-violet light at room temp. ethoxyprene ( $\beta$ -ethoxybutadiene) (IV) gives in 7 days 20% of rubbery polymeride (VI) only; at 100° (daylight) in 6 days 15% of polymerisation [1 part of liquid, largely dimeric polymeride and 3 of (VI)] occurs, at 130° 100% [equal parts of liquid and (VI)] in 2 weeks; certain catalysts, notably I and HCN, rapidly produce liquid polymerides of low mol. wt., metal halides and AcOH produce resins;  $\text{SnCl}_4$  acts explosively. (VI) is plastic and sol. in EtOAc and  $\text{C}_6\text{H}_6$ , but lacks the resilience of rubber; with hot dil. HCl it gives a polymeride,  $(\text{C}_4\text{H}_6\text{O})_x$ . Structures are established by reactions given below, but some doubt attaches to those of (III). The following are described.  $\alpha\gamma\gamma$ -Tri-methoxy-, b.p. 61—63°/20 mm., -ethoxy- (VII), b.p. 75°/9 mm., and -n-butoxy-n-butane, b.p. 120°/3 mm. Me vinyl ketone  $\text{Me}_2$ , b.p. 98—100°,  $\text{Et}_2$  (VIII), b.p. 69°/100 mm.,  $\text{Bu}^a_2$ , b.p. 79—80°/8 mm., and  $\text{Ph}_2$  ketal, b.p. 81°/2 mm.  $\alpha\gamma$ -Di-ethoxy- (IX), b.p. 101°/100 mm., and -butoxy- $\Delta^\beta$ -butene, b.p. 91—93°/4 mm.  $\beta$ -Methoxy-, b.p. 75°, and -n-butoxy-butadiene, b.p. 65°/54 mm., and (IV), b.p. 96.5°, called methoxyprene etc. (IV) and EtOH at 100 or 130° give (VII), and with  $(\cdot\text{CH}_2\cdot\text{OH})_2$  at 110° gives a substance ( $\beta$ - $\beta'$ -hydroxyethoxybutadiene or  $\text{CH}_2\text{:CH}\cdot\text{CMe}\begin{matrix} \text{O}\cdot\text{CH}_2 \\ \text{O}\cdot\text{CH}_2 \end{matrix}$ ), b.p. 56°/100 mm.; PhOH and PhSH add on at room temp. (IV) and naphthoquinone give a product, oxidised to 2-ethoxyanthraquinone, m.p. 136° (lit. 135°). With  $\text{H}_2$ -PtO<sub>2</sub>-EtOH (IV) is only partly hydrogenated, yielding  $\beta$ -ethoxy- $\Delta^a$ - or - $\Delta^\beta$ -butene or a mixture thereof. With dil. HCl (IV) and (VIII) give  $\text{CH}_2\text{:CH}\cdot\text{COMe}$ . (VIII) and  $\text{H}_2$ -PtO<sub>2</sub> give 40% of  $\text{CMeEt}(\text{OEt})_2$ . (IX) with dil.

HCl gives  $\text{OEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe}$  and with  $\text{KMnO}_4$ ,  $\text{AcOH}$  and  $\text{EtOAc}$ . Physical data are given.

R. S. C.

**Ester condensation and keten acetals.** F. ADICKES and M. MEISTER (Ber., 1935, 68, [B], 2191—2205).—Contrary to Scheibler (cf. A., 1926, 711; 1927, 338, 1051; 1929, 1296, etc.), no intermediate products are known between the ether enolates, which probably play a part in the reaction, and the enolates of the reaction products. A definite "primary reaction product" does not exist, and theories based thereon and on its fission to keten  $\text{Et}_2$  acetal are devoid of experimental foundation. The distillate from Scheibler's "primary product" consists of  $\text{EtOH}$ , the "acetal" reaction of which depends on the presence of small and varying amounts of  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ . Treatment of the "primary product" in  $\text{Et}_2\text{O}$  with  $\text{CO}_2$  shows it to be mainly a mixture of  $\text{NaOEt}$  and  $\text{ONa}\cdot\text{CMe}\cdot\text{CH}\cdot\text{COEt}$ ; a substance  $\text{ONa}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et} + \text{EtOH}$  or  $\text{EtOAc} + \text{NaOEt}$  is not present. Similar observations apply to the condensation of  $\text{PhCHO}$  with  $\text{EtOAc}$ . Repetition of Scheibler's condensation of  $\text{CHPhK}\cdot\text{CO}_2\text{Et}$  with  $\text{BzCl}$  or  $\text{ClCO}_2\text{Et}$  shows that the supposed *o*-benzoylphenylketen acetal is *Et*  $\beta$ -benzoyloxy- $\alpha\beta$ -diphenylacrylate (I), m.p. 103°, the constitution of which is established by analysis, determination of  $\text{OEt}$ , hydrolysis by  $\text{KOH}-\text{EtOH}$  to  $\text{BzOH}$  (2 mols.) and  $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$  (1 mol.), and by conc.  $\text{H}_2\text{SO}_4$  alone or in presence of  $\text{AcOH}$  to  $\text{BzOH}$  (1 mol.) and  $\text{CHPhBz}\cdot\text{CO}_2\text{Et}$  (1 mol.). (I) is converted by  $\text{NHPh}\cdot\text{NH}_2$  into benzphenylhydrazide and 1:3:4-triphenylpyrazol-5-one, m.p. 204—205°. Hydrogenation ( $\text{PtO}_2$ ) of (I) leads to *Et*  $\beta$ -benzoyloxy- $\alpha\beta$ -diphenylpropionate (II), m.p. 170°, also obtained by use of  $\text{Al}-\text{Hg}$  in moist  $\text{Et}_2\text{O}$  and hydrolysed by  $\text{KOH}-\text{EtOH}$  to  $\text{BzOH}$  and phenylcinnamic acid, m.p. 171°. (I) is obtained synthetically by addition of  $\text{BzCl}$  to the enolate from  $\text{CHPhBz}\cdot\text{COEt}$  and powdered  $\text{K}$  or  $\text{NaNH}_2$  in  $\text{Et}_2\text{O}$ , whilst (II) is readily prepared from  $\text{BzCl}$  and  $\text{OH}\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{CO}_2\text{Et}$  in  $\text{C}_5\text{H}_5\text{N}$ . When heated above its m.p., (I) is converted into a second (?) polymorphic variety, m.p. 112°. A third, obviously stereoisomeric form, m.p. 105°, which cannot be isomerised by heat, is not hydrogenated in presence of  $\text{Pt}$  and only incompletely reduced by  $\text{Al}$  in moist  $\text{Et}_2\text{O}$ , is obtained from  $\text{CHPhBz}\cdot\text{CO}_2\text{Et}$  and  $\text{BzCl}$  in  $\text{CHCl}_3-\text{C}_5\text{H}_5\text{N}$ ; it is almost quantitatively hydrolysed by conc.  $\text{H}_2\text{SO}_4$  to  $\text{BzOH}$  and  $\text{CHPhBz}\cdot\text{CO}_2\text{Et}$ . *Et*  $\alpha\beta$ -dibromo- $\alpha\beta$ -diphenylpropionate, m.p. 81—82°, is incidentally described. Scheibler's pyrolytic product is identified as 4:6-diketo-5-benzoyl-2:3:5-triphenyl-5:6-dihydropyran (III), m.p. 200—201°, converted by conc.  $\text{H}_2\text{SO}_4$  into 4:6-diketo-2:3:5-triphenyl-5:6-dihydropyran, m.p. 236° (*K* salt), which gives (III) with  $\text{BzCl}$  in  $\text{C}_5\text{H}_5\text{N}$  and is transformed by  $\text{AcCl}$  in  $\text{CHCl}_3-\text{C}_5\text{H}_5\text{N}$  into 4:6-diketo-5-acetyl-2:3:5-triphenyl-5:6-dihydropyran (IV), m.p. 182°. (III) or (IV) is transformed by conc.  $\text{NH}_3$  at 160° into 4:6-dihydroxy-2:3:5-triphenylpyridine, m.p. 288—289° (*K* salt; *Ac}\_2* derivative, m.p. 143—144°). The product of the action of  $\text{ClCO}_2\text{Et}$  on  $\text{CHPhK}\cdot\text{CO}_2\text{Et}$  (Scheibler's *o*-carbethoxyphenylketen acetal) is identified as  $\text{CHPh}(\text{CO}_2\text{Et})_2$  mixed with  $\text{CPh}(\text{CO}_2\text{Et})_3$ ; the product decolorises

$\text{KMnO}_4-\text{Na}_2\text{CO}_3$ , which is not suitable for the identification of keten acetals.

H. W.

**Isotopic exchange reactions of organic compounds. I. Intermolecular nature of three-carbon tautomerism.** D. J. G. IVES and H. N. RYDON (J.C.S., 1935, 1735—1742).—The partition of *D* and *H* between butyric (I), crotonic (II), and vinylacetic (III) acids and dil.  $\text{D}_2\text{O}$  at 100° in presence of 1.05 mol. of  $\text{NaOH}$  is studied using a new method of isotopic analysis depending on *d* determinations accurate to 1 p.p.m. As (III) shows appreciable isotopic interchange with the solvent, whilst (I) and (II) do not, it is concluded that purely intramol. mechanisms for this type of three-C tautomerism are unacceptable.

F. N. W.

**Configurative relationships of phenylmethyl- and methylhexyl-acetic acids. Correlation of the configurations of  $\alpha$ -hydroxy-acids with those of disubstituted acetic acids containing a methyl group.** P. A. LEVENE and S. A. HARRIS (J. Biol. Chem., 1935, 112, 195—208).—Correlation is established in the series,  $\text{CHMeRR}'$ , in which  $\text{R}=\text{Et}$  or  $\text{CO}_2\text{H}$  and  $\text{R}'=\text{Ph}$ ,  $\text{CH}_2\text{Ph}$ ,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2$ ,  $\text{C}_6\text{H}_{13}$ ,  $\text{C}_7\text{H}_{15}$ ,  $\text{C}_6\text{H}_{11}$ ,  $\text{C}_6\text{H}_{11}\cdot\text{CH}_2$ , or  $\text{C}_6\text{H}_{11}[\text{CH}_2]_2$ . Speculations are given concerning correlation of the series,  $\text{OH}\cdot\text{CHR}\cdot\text{CO}_2\text{H}$  and  $\text{OH}\cdot\text{CHRR}'$ , with those,  $\text{CHMeR}\cdot\text{CO}_2\text{H}$  and  $\text{CHMeRR}'$ , respectively ( $\text{R}$  and  $\text{R}'=\text{alkyl}$ , aryl, and aralkyl).  $\text{CHMeEt}\cdot\text{CO}_2\text{Et}$ ,  $[\alpha]_D^{25} -7.11^\circ$ , and  $\text{MgBr}\cdot[\text{CH}_2]_5\cdot\text{MgBr}$  give 60% of  $\eta$ -methyl- $\Delta^2$ -nonen- $\zeta$ -ol (dibromide, b.p. 161°/4 mm.) and 40% of 1-sec.-butylcyclohexan-1-ol, which on distillation gives  $\text{H}_2\text{O}$  and 1-1-sec.-butyl- $\Delta^1$ -cyclohexene, b.p. 172—174°,  $[\alpha]_D^{20} -4.06^\circ$ , hydrogenated ( $\text{PtO}_2$ ) in abs.  $\text{EtOH}$  to *d*-sec.-butylcyclohexane, b.p. 176—178°,  $[\alpha]_D^{20} +0.59^\circ$ .  $\text{C}_5\text{H}_{11}\cdot\text{MgBr}$  (from  $\text{C}_5\text{H}_{11}\text{Br}$ ,  $[\alpha]_D^{25} +2.40^\circ$ ) and  $\text{C}_6\text{H}_{13}\cdot\text{CHO}$  give  $\gamma$ -methylundecan- $\epsilon$ -ol, b.p. 70—75°/0.1 mm.,  $[\alpha]_D^{25} +3.54^\circ$ , converted into the iodide, b.p. 88°/1 mm.,  $[\alpha]_D^{25} +5.85^\circ$ , and thence (Raney Ni) into  $\gamma$ -methylundecane, b.p. 94°/15 mm.,  $[\alpha]_D^{25} +3.87^\circ$ .

R. S. C.

**Acetylenes. II. Pharmacological properties of the acetylenic linking.** G. B. BACHMAN (J. Amer. Chem. Soc., 1935, 57, 2167—2168; cf. A., 1935, 193).— $\beta$ -*NEt}\_2\cdot\text{C}\_2\text{H}\_4 octoate, b.p. 162—164°/20 mm.,  $\Delta^2$ -octenoate, b.p. 171—173°/20 mm., and  $\Delta^2$ -octinenoate, b.p. 150—152°/7 mm., *NEt}\_2\cdot[\text{CH}\_2]\_3 octoate, b.p. 178—181°/20 mm.,  $\Delta^2$ -octenoate, b.p. 183—186°/20 mm., and  $\Delta^2$ -octinenoate, b.p. 164—166°/7 mm., and *NBu}\_2\cdot[\text{CH}\_2]\_3 octoate, b.p. 212—215°/20 mm.,  $\Delta^2$ -octenoate, b.p. 217—220°/20 mm., and  $\Delta^2$ -octinenoate, b.p. 193—195°/7 mm., are prepared.  $\Delta^2$ -Octenoyl chloride (prep. by  $\text{SOCl}_2$ ) has b.p. 109—111°/30 mm. Physical data are given. The effectiveness of aliphatic novocaine analogues as local anaesthetics is, within limits,  $\propto$  the mol. wt. of the alcoholic component and inversely  $\propto$  the degree of unsaturation of the acid.***

R. S. C.

**Direct esterification of higher fatty acids with glycerol and with ethylene glycol.** T. P. HILDITCH and J. G. RIGG (J.C.S., 1935, 1774—1778).—A mixture of mono- (I) and di-glycerides in which the latter predominate is obtained by the interaction of higher fatty acids and excess (10:1) of glycerol (II) at 140—

160° and reduced pressure. The yield of (I) [ $\alpha$ -monolaurin (100%), -palmitin (93%), -stearin (82%), -olein (95%)] is greatly increased by using an inert solvent (PhOH), and camphor- $\beta$ -sulphonic acid (III) (about 0.1%) as catalyst. Increase in the time or temp. of reaction or in the amount of (III) increases the total yield, but lowers the yield of (I), whilst a preponderance of (II) favours the formation of (I). Identical results, but higher yields, are obtained by using  $(\cdot\text{CH}_2\cdot\text{OH})_2$  in place of (II). F. N. W.

Seeds of *Allanblackia klainei*.—See this vol., 258.

Crystalline substance from oil of *Lachnophyllum gossypinum*, Bge.—See this vol., 259.

Destructive distillation of calcium oleate and undecenoate. G. BREUER and K. WEINMANN (Monatsh., 1935, 67, 42—50).—Ca oleate at 130—170°/15 mm. gives oleones, m.p. 58.5°, and liquid (*oxime* of the latter, an oil), and a little *hydroxyheptadecyl heptadecenyl ketone*, m.p. 60.5°, which with  $\text{H}_2\text{SO}_4$  give *di-(hydroxyheptadecyl) ketones*, m.p. 89°, 90°, and 86°, respectively (possibly identical). Ca undecenoate at 90—120°/20 mm. gives *didecyl ketone*, m.p. 51°.

R. S. C.

Elaidinisation of oleic acid and *cis-trans*-isomerism. S. H. BERTRAM (Chem. Weekblad, 1936, 33, 3—5).—0.03—0.1% of Se at 150—200° is a most powerful catalyst for elaidinising unsaturated oils and fatty acids. Unlike other catalysts, it is very mild in its action and produces no by-products. Elaidinised castor oil is dimorphous, m.p. 47.5° and 55.4°, and has the same  $[\alpha]$  as the original oil. Elaidinisation of oleic acid is a balanced reaction irrespective of the catalyst used, the equilibrium mixture containing 2 mols. of elaidic and 1 mol. of oleic acid. The results are in accordance with the supposition that oleic acid has a *trans*-configuration. S. C.

Polymerisation of fatty oils. XI. Hydrogenation of polymerised ethyl linoleate. A. STEGER and J. VAN LOON (Fettchem. Umschau, 1935, 42, 217—219; cf. A., 1935, 1482).—Vac.-distilled Et linoleate (I) (prepared from tetrabromolinoleic acid pptd. from the fatty acids of safflower oil) was polymerised by heating at 290° in an atm. of  $\text{CO}_2$  for 15 hr.; the product was saponified, the unsaponifiable matter removed, and the fatty acids were recovered and converted into Et esters, which were examined by fractional distillation and hydrogenation of the principal fractions over Pd-C at 170°/50 atm. and over colloidal Pd in EtOH solution at room temp. at 1 atm. The analyses of the hydrogenated fractions indicate that the polymerised ester contained [in addition to unchanged (I)] low-mol. decomp. products, small amounts ( $\approx 10\%$ ) of a cyclic ester which could not be reduced by  $\text{H}_2$ , high-mol. compounds formed by the combination of several mols. of linoleate and/or decomp. products (also unreducible to stearic acid or its ester), and  $\approx 5\%$  of a conjugated linoleic acid (II); the presence of (II) was confirmed quantitatively by a study (L. N. J. VAN DER HULST) of the ultra-violet absorption spectrum of the polymerised (I). E. L.

Separation of physeteric acid from sardine and pilot-whale oils. Y. TOYAMA and T. TSUCHIYA (J.

Soc. Chem. Ind. Japan, 1935, 38, 680—684B).—Physeteric acid has been isolated from sardine and pilot-whale (body) oils, and is shown by oxidation to be the  $\Delta^8$ -tetradecenoic acid.  $\Delta^6$ -Tetradecenoic acid was not isolated. H. G. M.

Highly unsaturated acids in sardine oil. IX. Constitution of docosahexaenoic acid,  $\text{C}_{22}\text{H}_{32}\text{O}_2$ .

X. Separation of highly unsaturated  $\text{C}_{24}$  acids.

XI. Constitution of nisinic acid,  $\text{C}_{24}\text{H}_{36}\text{O}_2$ , in sardine oil. Y. TOYAMA and T. TSUCHIYA (Bull. Chem. Soc. Japan, 1935, 10, 539—543, 543—547, 547—551).—IX. Ozonolysis of amyl docosahexaenoate (A., 1935, 1482) (containing a little amyl clupanodionate) affords MeCHO, AcOH,  $\text{CO}_2$ ,  $(\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$ , and its amyl H ester. Docosahexaenoic acid is therefore either  $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot[\text{CH}\cdot\text{CH}\cdot\text{CH}_2]_2\cdot(\text{CH}\cdot\text{CH}\cdot[\text{CH}_2]_2)_3\cdot\text{CO}_2\text{H}$ , or  $\text{CHMe}\cdot\text{CH}\cdot[\text{CH}_2\cdot\text{CH}\cdot\text{CH}]_4\cdot[\text{CH}_2]_2\cdot\text{CH}\cdot\text{CH}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$ .

X. Separation of the  $\text{C}_{24}$  unsaturated acids (obtained by hydrolysis of the Me ester residues of high b.p.) by the Na salt-COME<sub>2</sub> method (*loc. cit.*), re-esterification and fractionation of the Me esters up to b.p. 215°/2 mm., and hydrolysis and refractionation as Na salts affords nisinic acid (I) (A., 1934, 1381) as the only pure product, but the presence of less saturated acids  $\text{C}_{24}\text{H}_{38}\text{O}_2$  and  $\text{C}_{24}\text{H}_{40}\text{O}_2$  was indicated.

XI. Ozonolysis of the amyl ester of (I) affords EtCHO, EtCO<sub>2</sub>H, MeCHO, and AcOH [as secondary products from  $\text{CH}_2(\text{CO}_2\text{H})_2$ ,  $\text{CO}_2$ ,  $(\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$  and its amyl H ester. On the basis of these results the structure  $\text{CHEt}\cdot\text{CH}\cdot[\text{CH}_2\cdot\text{CH}\cdot\text{CH}]_3\cdot\{[\text{CH}_2]_2\cdot\text{CH}\cdot\text{CH}\}_2\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$  is suggested for (I). J. W. B.

Hydrogenation of fish oil. V. Formation of an unsaturated fatty acid of the linolenic series in the hydrogenation of methyl clupanodionate. M. TAKANO (J. Soc. Chem. Ind. Japan, 1935, 38, 652—653B).—Me clupanodionate, b.p. 206—208°/0.8 mm., prepared from the acids obtained from sardine oil, when hydrogenated (Ni) affords a product which contains acids of the linoleic and linolenic series. The existence of two isomerides, one giving a tetra- and the other a hexa-thiocyanate, of the linolenic series is suggested. H. G. M.

Catalytic hydrogenation of acetone compounds of  $\alpha$ -hydroxy-acids. H. ÔEDA (Bull. Chem. Soc. Japan, 1935, 10, 531—539).—Reduction of the  $\text{CMe}_2$ :

derivatives of  $\alpha$ -OH-acids,  $\text{CMe}_2\begin{matrix} \text{O}\cdot\text{CHR} \\ \diagdown \\ \text{O}\cdot\text{CO} \end{matrix}$ , with  $\text{H}_2$

and a CuO-BaO-Cr<sub>2</sub>O<sub>3</sub> catalyst at 240—260°/100—120 atm. effects cleavage at both O linkings to give both alcohols and glycols. Thus the *isopropylidene* derivative of *dl*-lactic acid gives Pr <sup>$\beta$</sup> OH (I) ( *$\alpha$ -naphthylurethane*, m.p. 104—105°) and OH·CHMe·CH<sub>2</sub>·OH (bisphenylurethane, m.p. 143—144°); that of *l*-leucic acid gives (I), CH<sub>2</sub>Bu <sup>$\beta$</sup> ·CH<sub>2</sub>·OH, and an active *isohexylene glycol*, OH·CHBu <sup>$\beta$</sup> ·CH<sub>2</sub>·OH, b.p. 111—113.5°/15 mm. (*bisphenylurethane*, m.p. 115—116°); that of *dl*-mandelic acid gives (I), CH<sub>2</sub>Ph·CH<sub>2</sub>·OH (*phenylurethane*, m.p. 78—79°), and an aromatic hydrocarbon containing PhEt; and that of *l*- $\alpha$ -hydroxy- $\beta$ -phenylpropionic acid affords (I), CH<sub>2</sub>Ph·CH<sub>2</sub>·CH<sub>2</sub>·OH (*phenylurethane*, m.p. 45—46°), active CH<sub>2</sub>Ph·CHMe·OH (*phenylurethane*, m.p. 88—89°), and CH<sub>2</sub>Ph·CH(OH)·CH<sub>2</sub>·OH [*bisphenylurethane*,

obtained in two interconvertible forms *A*, m.p. 108—109° (cryst.), and *B*, m.p. 132—133° (amorphous)].

J. W. B.

**Action of hydrogen peroxide on simple carbon compounds. III. Glycollic acid.** H. S. FRY and K. L. MILSTEAD (J. Amer. Chem. Soc., 1935, 57, 2269—2272; cf. A., 1931, 819).—The  $\text{HCO}_2\text{H}$ ,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{O}_2$ , and unattacked  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (I) formed when (I) reacts with acidified  $\text{H}_2\text{O}_2$  give the following percentages of the reactions occurring, the figures recorded being those obtained with 0.5 and 4 mols. of  $\text{H}_2\text{O}_2$ , respectively: (a) 6.3—37%: (I)  $\rightarrow \text{H}_2\text{O} + \text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{O}_2\text{H} \rightarrow \text{H}_2\text{O} + \text{CHO}\cdot\text{CO}_2\text{H} \rightarrow \text{HCO}_2\text{H} + \text{CO}_2 + \text{H}_2\text{O}$ ; (b) 1.84—12.9%: (I)  $\rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O} + \text{CO}_2$ ;  $2\text{CH}_2\text{O} \rightarrow 2\text{HCO}_2\text{H} + \text{H}_2$ ; (c) 23.2—39.9%:  $\text{HCO}_2\text{H} \rightarrow 2\text{H}_2\text{O} + \text{CO}_2$ .

R. S. C.

**Anhydrous glyoxylic acid.** A. TALVITIE (Suomen Kem., 1935, 8, B, 32).—Evaporation of a dil. aq. solution of  $\text{CHO}\cdot\text{CO}_2\text{H}$  over  $\text{H}_2\text{SO}_4$  at room temp./vac., extraction of the residual syrup with dry  $\text{Et}_2\text{O}$  (removes  $\text{CaC}_2\text{O}_4$ ), and re-evaporation of the  $\text{Et}_2\text{O}$  extract over  $\text{H}_2\text{SO}_4$  at room temp./< 1 mm. affords the anhyd. acid.

J. W. B.

**Application of the indophenine test to the detection of polycarboxylic acids.** J. V. SANCHEZ (Farm. moderna, 1935, 46, 58—63).—The aq. solution of the free acid is neutralised with  $\text{Na}_2\text{CO}_3$  (phenolphthalein), and a drop of the solution is evaporated to dryness in a small tube. The residue is heated (120°) and mixed with powdered  $\text{P}_2\text{S}_5$ . A solution of isatin in conc.  $\text{H}_2\text{SO}_4$  is added, and the mixture heated until fusion begins and S sublimes. A green or blue colour indicates the presence of succinic (I), pyrotartaric (II), tartaric, fumaric, maleic, or citric acid. Oxidation with acid  $\text{KMnO}_4$  oxidises all except (I) and (II), which may be detected separately. Glutaric, adipic, suberic, azelaic, and sebacic acids interfere and may be removed with  $\text{Pb}(\text{OAc})_2$ .

CH. ABS. (p)

**Detection of oxalate ions.** N. A. TANANAEV and A. A. BUDKEVITSCH (Z. anal. Chem., 1935, 103, 353—355).—To the test solution, acidified aq.  $\text{K}_2\text{Cr}_2\text{O}_7$  is added, followed by indigotin (I). In presence of  $\text{C}_2\text{O}_4^{2-}$  ( $\approx 10^{-4}N$ ), decolorisation occurs, due to the induced mutual oxidation of  $\text{C}_2\text{O}_4^{2-}$  and (I).  $\text{S}^{2-}$ ,  $\text{SO}_3^{2-}$ , and  $\text{S}_2\text{O}_3^{2-}$  must first be removed by boiling with  $\text{H}_2\text{SO}_4$ .  $\text{C}_2\text{O}_4^{2-}$  may alternatively be pptd. as  $\text{CaC}_2\text{O}_4$ , which is dissolved in  $\text{H}_2\text{SO}_4$  and detected by the decolorisation of 0.01N- $\text{KMnO}_4$ .

J. S. A.

**Potentiometric determination of oxalates with silver nitrate.** P. SPACU (Z. anal. Chem., 1935, 103, 272—274).— $\text{C}_2\text{O}_4^{2-}$  may be titrated potentiometrically with  $\text{AgNO}_3$  in 60% aq. EtOH.

J. S. A.

**Optical activity. IV. Racemisation of the optically active oxalates.** C. H. JOHNSON. V. Racemisation of the strychnine salts of *d*- and *l*-chromioxalate in the crystalline state. C. H. JOHNSON and A. MEAD. VI. Racemisation of potassium chromioxalate in aqueous solution. The accelerating influence of ions. N. W. D. BEESE and C. H. JOHNSON (Trans. Faraday Soc., 1935, 31, 1612—1621, 1621—1632, 1632—1642; cf. A., 1933, 114, 581, 585).—IV. The optical activity

and racemisation of compounds of the type  $\text{M}_3[\text{M}^{\text{III}}(\text{C}_2\text{O}_4)_3]$  are discussed. The experimental evidence accepted as supporting the theory of secondary ionisation in racemisation is untrustworthy and based on a misconception, since if ionisation were responsible for loss of rotatory power it could not be determined by ordinary chemical methods for compounds racemising at measurable rates. The racemisation of chromi- and cobalti-oxalates in the cryst. state suggests that intramol. rearrangement may occur in solution as well as in the crystals. The racemisation of these compounds is greatly accelerated by presence of  $\text{H}_2\text{O}$ .

V. The velocity of racemisation of tristrychnine *d*- and *l*-chromioxalates at 47.7—100° has been studied. The loss of rotatory power occurs principally after dehydration. The mechanism of the intramol. rearrangement is discussed.

VI.  $(\text{C}_2\text{O}_4)^{2-}$  does not affect the rate of racemisation of  $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$ , this being in accord either with the racemisation being a measure of the rate of ionisation, or with racemisation not involving ionisation. Loss of optical activity is accelerated by positive ions, the more so the higher is the valency of the ions. The results indicate that the  $\text{Hg}^{\text{I}}$  ion is  $\text{Hg}_2^{2+}$ . The effects of adding  $\text{CaCl}_2$ ,  $\text{MnCl}_2$ , and  $\text{CuCl}_2$  have been studied in detail.

J. W. S.

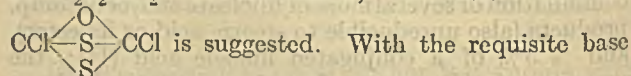
**Oxalates and formates in organic fluids.** M. PITTARELLI (Minerva Med., 1935, 1, 428—429).—Mg powder converts  $\text{H}_2\text{C}_2\text{O}_4$  into  $\text{CHO}\cdot\text{CO}_2\text{H}$ , and  $\text{HCO}_2\text{H}$  into  $\text{CH}_2\text{O}$ . On adding  $\text{NHPH}\cdot\text{NH}_2$  and *p*- $\text{NH}_2\text{-C}_6\text{H}_4\text{-OH}$ , and making alkaline with  $\text{NaOH}$ , the Pittarelli test is obtained. The red-violet colour is extractable with amyl alcohol. If Mg salts are present, a blue-violet lake is formed. CH. ABS. (e)

**Complex formation with malonates.**—See this vol., 160.

**Hydrogenation of aldonic  $\delta$ - and  $\gamma$ -lactones and of aldoses.** J. W. E. GLATTFIELD and G. W. SCHIMPF (J. Amer. Chem. Soc., 1935, 57, 2204—2208).—The best yields of aldoses by hydrogenation of aldonic lactones are obtained in 0.2M aq. solution with moderate amounts of catalyst and rapid agitation.  $\gamma$ -Lactones give more alcohol than do  $\delta$ -lactones. Aldoses give 63—80% of alcohols.

R. S. C.

**Dimeride of thiocarbonyl chloride and its derivatives, chloro-oxysulphide,  $\text{C}_2\text{S}_2\text{OCl}_2$ , and a new chlorosulphide,  $\text{C}_2\text{S}_3\text{Cl}_2$ .** M. DELÉPINE, L. LABRO, and F. LANGE (Bull. Soc. chim., 1935, [v], 2, 1969—1980).—The structure of  $\text{C}_2\text{S}_3\text{Cl}_4$  (I) is discussed (cf. A., 1933, 487). By the action of EtOH on (I) the compound, probably  $\text{S}(\text{CS}\cdot\text{Cl})_2$ , m.p. 58—59°, is obtained. The prep. and properties of  $\text{C}_2\text{S}_2\text{OCl}_2$  are described, and the structure



is suggested. With the requisite base it affords the following thiuram oxides:  $\text{Me}_4$ , m.p. 79°;  $(\text{CH}_2\text{Ph})_4$ , m.p. 100—101°;  $\text{Ph}_2\text{Me}_2$ , m.p. 116°;  $\text{Ph}_2\text{Et}_2$ , m.p. 147.5—148°; *di*-*o*-tolyl dimethyl-, m.p. 93—94°; *diphenyl dibenzyl*-, m.p. 128.5—129.5°; *di*-*o*-anisyl dimethyl-, m.p. 158°. O. J. W.

Catalytic action of monoses on the form-aldehyde condensation. III. Intermediate products of the reaction. A. KUSIN (Ber., 1935, 68, [B], 2169—2173; cf. A., 1935, 733, 1224).—Attempts to isolate the intermediate products of the catalysis of the  $\text{CH}_2\text{O}$  condensation are unsuccessful when glucose or fructose is used as accelerator, but succeed if benzoin (I), which behaves analogously, is employed. The mechanism,  $\text{OH}\cdot\text{CR}\cdot\text{CR}\cdot\text{OH} + \text{CH}_2(\text{OH})_2 \rightarrow \text{OH}\cdot\text{CH}_2\cdot\text{CR}(\text{OH})\cdot\text{CR}(\text{OH})_2 \rightarrow \text{OH}\cdot\text{CH}\cdot\text{CR}\cdot\text{CO}\cdot\text{R}$  (II);  $(\text{II}) + \text{CH}_2(\text{OH})_2 \rightarrow \text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CR}(\text{OH})\cdot\text{CO}\cdot\text{R} + \text{H}_2\text{O} \rightarrow \text{OH}\cdot\text{CHR}\cdot\text{CO}\cdot\text{R} + \text{OH}\cdot\text{CH}\cdot\text{CH}(\text{OH})_2$  (III);  $(\text{III}) - \text{H}_2\text{O} \rightarrow \text{OH}\cdot\text{CH}\cdot\text{CH}\cdot\text{OH}$  (IV);  $(\text{IV}) + \text{CH}_2(\text{OH})_2 \rightarrow \text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})_2$  etc., is suggested. (I) and  $\text{CH}_2\text{O}$  with  $\text{Ca}(\text{OH})_2$  in  $\text{H}_2\text{O}-\text{MeOH}-\text{EtOH}$  at  $37-40^\circ$  afford *benzoylphenylhydroxymethylcarbinol* (V), m.p.  $85.5^\circ$ , also obtained from (I),  $\text{CH}_2\text{O}$ , and  $\text{NaOH}$  in  $\text{EtOH}$ , which contains 2 OH (Zerevitinov) and with  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$  gives the compound  $\text{C}_{21}\text{H}_{18}\text{O}_4\text{N}_3$ , m.p.  $166.5^\circ$ . In 50%  $\text{EtOH}$  (V) gives a feeble fuchsin- $\text{H}_2\text{SO}_3$  reaction, and immediately reduces Fehling's solution (to Cu),  $\text{Ag}_2\text{O}-\text{NH}_3$ , and dichlorophenol-indophenol in alkaline but not in acid solution. (V) exactly resembles (I) in accelerating the  $\text{CH}_2\text{O}$  condensation with formation of sugar-like products; it is converted into (I) during the change.

H. W.

Thermal decomposition of certain gaseous organic compounds. M. W. TRAVERS (Nature, 1935, 136, 909—910).—Processes involved in the thermal decomp. of  $\text{MeCHO}$  and  $(\text{CH}_2)_2\text{O}$  are further discussed (cf. A., 1935, 708). Additional experiments support the view that the reactions depend on the surface of the system and involve a chain mechanism.

L. S. T.

Volumetric determination of carbonyl compounds. II. Determination of acetaldehyde by the hydrogen sulphite method. S. HÄRNEL (Svensk Kem. Tidskr., 1935, 47, 275—285; cf. A., 1935, 1390).—The direct determination of  $\text{MeCHO}$  by  $\text{I}-\text{HSO}_3'$  gives more reproducible results than the indirect method. The formation of acetals in aq. alcoholic solutions has been studied, and methods for the determination of free and total  $\text{MeCHO}$  in such solutions are given. For the reaction  $\text{CHMe}(\text{OEt})_2 + \text{H}_2\text{O} \rightleftharpoons \text{CHMe}(\text{OH})\cdot\text{OEt} + \text{EtOH}$ ,  $K = 0.94$ .

M. H. M. A.

$\beta$ -Chloropropaldehyde and its derivatives. A. KIRRMANN, M. GOUDARD, and M. CHAHIDZADEH (Bull. Soc. chim., 1935, [v], 2, 2143—2152).—The halogen of  $\beta$ -halogenopropaldehydes is very labile, but elimination of  $\text{HCl}$  often takes precedence over exchange reactions.  $\text{CH}_2\cdot\text{CH}\cdot\text{CHO}$  (I) and dry  $\text{HCl}$  at  $-10^\circ$  give  $\beta$ -chloropropaldehyde (II), b.p.  $130-131^\circ$  ( $\text{NaHSO}_3$  compound, from which it cannot be recovered), the  $\text{Me}_2$  acetal, b.p.  $51^\circ/19$  mm., of which with  $\text{HCl}$  gives  $\alpha\gamma$ -dichloro- $\alpha$ -methoxypropane (III), b.p.  $55^\circ/19$  mm.  $\beta$ -Bromopropaldehyde ( $\text{NaHSO}_3$  compound, from which it cannot be recovered) could not be obtained pure, but yielded a mixture of  $\beta$ -bromo- (IV), b.p.  $58-60^\circ/17$  mm., and  $\beta$ -methoxypropaldehyde  $\text{Me}_2$  acetal, b.p.  $45-46^\circ/17$  mm.,  $146^\circ/760$  mm., and  $\alpha\gamma$ -dibromo- $\alpha$ -methoxypropane, b.p.  $75^\circ/16$  mm. (II) with  $\text{NaOAc}$  or  $\text{NaOEt}$  loses  $\text{HCl}$  to re-form (I), but with  $\text{Ac}_2\text{O}$  gives the diacetate, m.p.  $43^\circ$ ,

$\alpha$ -chloroallyl acetate, and the trimeride, m.p.  $36^\circ$ . (IV) loses  $\text{HBr}$  with  $\text{NaOAc}$ ,  $\text{NaOMe}$ , or  $\text{Ag}_2\text{O}$ , but with  $\text{NHEt}_2$  in hot  $\text{COMe}_2$  gives  $\beta$ -dimethylamino-propaldehyde  $\text{Me}_2$  acetal, b.p.  $85^\circ/16$  mm.  $\beta$ -Cyano-propaldehyde  $\text{Me}_2$  acetal, b.p.  $93^\circ/17$  mm., with  $\text{MgMeBr}$  gives  $\alpha$ -chloroallyl acetate, b.p.  $85^\circ/16$  mm. (IV) does not react with  $\text{MgMeBr}$ , but (III) gives  $\alpha$ -chloro- $\gamma$ -methoxy- $n$ -butane, b.p.  $125^\circ$ , and with  $\text{MgPhBr}$  affords  $\alpha$ -chloro- $\gamma$ -methoxy- $\gamma$ -phenylpropane (V), b.p.  $113-114^\circ/16$  mm. (III) and  $\text{AlCl}_3$  in  $\text{C}_6\text{H}_6$  give  $\alpha$ -methoxy- $\alpha\gamma$ -diphenylpropane, m.p.  $34^\circ$ , also obtained in traces similarly from (V). (III) does not react readily with  $\text{Mg}$  in hot  $\text{Et}_2\text{O}$  or  $\text{Bu}_2\text{O}$ . R. S. C.

Phytochemical reduction of lactaldehyde. E. OCHIAI and K. MIYAKI (Biochem. Z., 1935, 282, 293—296).—The production of optically inactive propylene glycol using a Japanese bottom yeast is described.

P. W. C.

Constitution of dimeric keten. W. R. ANGUS, A. H. LECKIE, C. G. LE FÈVRE, R. J. W. LE FÈVRE, and A. WASSERMANN (J.C.S., 1935, 1751—1755).—The dipole moment ( $3.15$  at  $25^\circ$  in  $\text{C}_6\text{H}_6$ ;  $3.30$  in  $\text{CCl}_4$ ), mol. refraction, and heat of combustion ( $447.1$  kg.-cal. per mol. in the liquid and  $456 \pm 2$  kg.-cal. per mol. in the gaseous state) of dimeric keten favour the view that it exists predominately in the keto-enol form. Dissolution has little effect on the Raman spectrum, and therefore presumably on the constitution.

F. N. W.

Preparation of acyloins of high mol. wt. V. L. HANSLEY (J. Amer. Chem. Soc., 1935, 57, 2303—2305).—The appropriate ester and  $\text{Na}$  (2 atoms) in hot  $\text{PhMe}$  or xylene give  $80-95\%$  yields of the acyloins,  $\text{R}\cdot\text{CO}\cdot\text{CHR}\cdot\text{OH}$ , in which  $\text{R} = \text{C}_8\text{H}_{17}$ , m.p.  $45^\circ$ ,  $\text{C}_9\text{H}_{19}$ , m.p.  $51-62^\circ$  (osazone, m.p.  $79-80^\circ$ ),  $\text{C}_{11}\text{H}_{23}$  (I), m.p.  $61-62^\circ$  (osazone, m.p.  $61-63^\circ$ ),  $\text{C}_{13}\text{H}_{27}$ , m.p.  $71-72^\circ$  (osazone, m.p.  $44-46^\circ$ ),  $\text{C}_{15}\text{H}_{31}$ , m.p.  $77-78^\circ$ , and  $\text{C}_{17}\text{H}_{35}$ , m.p.  $82-83^\circ$ ; those in which  $\text{R} = \text{Me}$ ,  $\text{Pr}^a$ , m.p.  $-10^\circ$  (osazone, m.p.  $140-141^\circ$ ), and  $\text{C}_5\text{H}_{11}$ , m.p.  $9^\circ$  (osazone, m.p.  $119-120^\circ$ ), are best prepared in  $\text{Bu}^a_2\text{O}$  or  $\text{Bu}^b_2\text{O}$ . Oxidation of (I) gives *di-n-undecyl ketone*, m.p.  $71-72.5^\circ$ . Hydrogenation (Pt at room temp or Ni at  $125-150^\circ$ ) affords the glycols,  $(\text{OH}\cdot\text{CHR}\cdot)_2$ , in which  $\text{R} = \text{C}_{17}\text{H}_{35}$ , m.p.  $123-124^\circ$  (diacetate),  $\text{C}_{13}\text{H}_{27}$ , m.p.  $124^\circ$  (diacetate),  $\text{C}_{11}\text{H}_{23}$ , m.p.  $125-126^\circ$  (diacetate),  $\text{C}_7\text{H}_{15}$ , m.p.  $129-130^\circ$  (diacetate),  $\text{C}_5\text{H}_{11}$ , m.p.  $135-136^\circ$ , and  $\text{Pr}$ , m.p.  $123-124^\circ$ . R. S. C.

Tetrose sugars. I. Crystalline triacetate of *d*-threose from the degradation of strontium xylonate with hydrogen peroxide. Nomenclature in the tetrose group. II. Degradation of *d*-xylose by Wohl's method. Rotation of *d*-threose. R. C. HOCKETT (J. Amer. Chem. Soc., 1935, 57, 2260—2264, 2265—2268).—I. By electrolytic oxidation xylose yields *Sr d*-xylonate,  $+5\text{H}_2\text{O}$ ,  $[\alpha]_D^{20} +13.2^\circ$  in  $\text{H}_2\text{O}$ , oxidised by  $\text{Fe}_2(\text{SO}_4)_3-\text{Ba}(\text{OAc})_2$  to *d*-threose triacetate, m.p.  $117-118^\circ$  (corr.),  $[\alpha]_D^{20} +35.55^\circ$  in  $\text{CHCl}_3$ , which by  $\text{NaOMe}$  at  $<0^\circ$  yields solutions of *d*-threose (I),  $[\alpha]_D^{20} -12.3^\circ$  in  $\text{H}_2\text{O}$ . Errors in nomenclature, due to overlooking Fischer's error in calling *d*-xylose *l*-xylose, are corr. The name erythritol should be confined to the inactive alcohol, the active tetrityls being named *d*- and *l*-threitol.

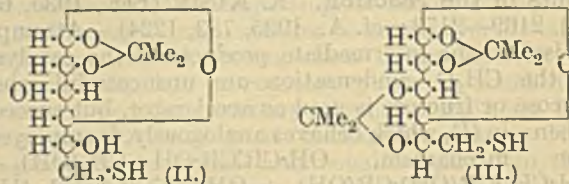
II. *d*-Xylose oxime (syrupy mixture) with  $\text{Ac}_2\text{O}$  (dropwise) in dioxan gives tetra-acetyl-*d*-xylo-nitrile, m.p. 81—82° (corr.),  $[\alpha]_D^{20} + 50.3^\circ$  in  $\text{CHCl}_3$ , which with conc. aq.  $\text{NH}_3$  yields diacetamido-*d*-threose (I), m.p. 165—167° (corr.),  $[\alpha]_D^{20} - 10.86^\circ$  in  $\text{H}_2\text{O}$  (triacetate, m.p. 179—180°,  $[\alpha]_D^{20} + 74.2^\circ$  in  $\text{CHCl}_3$ ), which gives (I) with  $[\alpha]$  as stated. R. S. C.

Detosylation [deacylation] of isopropylidene-*l*-methylrhamnose-4- and -5-*p*-toluenesulphonates. P. A. LEVENE and J. COMPTON (J. Amer. Chem. Soc., 1935, 57, 2306—2316).—The high-boiling fraction obtained on alkaline hydrolysis of isopropylidene-*l*-methylrhamnoside 5-*p*-toluenesulphonate (I) is isopropylidene-*l*-methylrhamnopyranoside (II), derived from pyranose present in (I) (cf. Muskat, A., 1935, 199). The following data appear new. (I), m.p. 82—83°,  $[\alpha]_D^{20} - 13.6^\circ$  in MeOH. isoPropylidene-*l*-methylpyranoside 4-*p*-toluenesulphonate, m.p. 61—62°,  $[\alpha]_D^{24} + 21.94^\circ$  in MeOH. (II), b.p. 84—85°/0.3 mm.,  $[\alpha]_D^{25} - 21.3^\circ$  in MeOH. The ring structure of the *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2$  derivatives is proved by their relative rates of hydrolysis. R. S. C.

Carbohydrates and furfuraldehyde. II. Reactions with  $\beta$ -methylglucoside and glucose; preparation of  $\beta$ -methylglucoside 2 : 3-diacetate. H. BREDERECK (Ber., 1935, 68, [B], 2299—2302; cf. A., 1935, 847).—Furfuraldehyde (I) containing a little  $\text{HNO}_3$  (*d* 1.20) and anhyd. glucose at 170—175° yield a non-cryst. product which when treated with  $\text{Ac}_2\text{O}$  and anhyd.  $\text{NaOAc}$  at 100° affords  $\beta$ -4 : 6-furfurylidene-glucose 1 : 2 : 3-triacetate (II), m.p. 203—204°,  $[\alpha]_D^{25} - 46.6^\circ$  in  $\text{CHCl}_3$ , in modest yield. The constitution of (II) is established by elimination of (I) and transformation of the product into non-cryst.  $\beta$ -6-triphenylmethylglucose 1 : 2 : 3-triacetate, converted by  $\text{Ac}_2\text{O}$  in  $\text{C}_5\text{H}_5\text{N}$  into  $\beta$ -6-triphenylmethylglucose 1 : 2 : 3 : 4-tetra-acetate, m.p. 165—166°,  $[\alpha]_D^{25} + 48.3^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ . Similarly (I) and  $\beta$ -methylglucoside at 170—175° yield 4 : 6-furfurylidene- $\beta$ -methylglucoside, m.p. 160—162°,  $[\alpha]_D^{25} - 97.2^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ , transformed by  $\text{Ac}_2\text{O}$  in  $\text{C}_5\text{H}_5\text{N}$  into 4 : 6-furfurylidene- $\beta$ -methylglucoside 2 : 3-diacetate, m.p. 205—207°,  $[\alpha]_D^{25} - 85.1^\circ$  in  $\text{CHCl}_3$ , which is converted by  $\text{HCl}$ -EtOH at 60° into  $\beta$ -methylglucoside 2 : 3-diacetate, m.p. 109—111°,  $[\alpha]_D^{25} - 51.8^\circ$  in  $\text{CHCl}_3$ , whence  $\beta$ -methylglucoside 2 : 3-diacetate 4 : 6-dibenzoate, m.p. 167—168°,  $[\alpha]_D^{25} - 11.8^\circ$  in  $\text{CHCl}_3$ . 4 : 6-Furfurylidene- $\alpha$ -methylmannoside and  $\text{PhCHO}$  do not react when heated in  $\text{CO}_2$ ; when shaken in presence of  $\text{ZnCl}_2$  they yield dibenzylidene- $\alpha$ -methylmannoside. H. W.

Syntheses with 5 : 6-anhydroisopropylidene-glucose. I. 6-Thiol-*d*-glucose, *d*-glucomethylglucose-6-sulphonic acid, and 6-acyl derivatives of isopropylidene-glucose. H. OHLE and W. MERTENS [with, in part, M. ANDRÉE and E. EULER] (Ber., 1935, 68, [B], 2176—2187).—The action of  $\text{H}_2\text{S}$  on an aq. solution of  $\text{Ba}(\text{OH})_2$  and 5 : 6-anhydroisopropylidene-glucose (I) at 0° rapidly affords isopropylidene-6-thiogluucose (II), m.p. 96—97°, b.p. 200—220°/high vac.,  $[\alpha]_D^{21} - 18.2^\circ$  in  $\text{CHCl}_3$ ,  $[\alpha]_D^{20} - 14.35^\circ$  in  $\text{H}_2\text{O}$ ,  $[\alpha]_D^{20} - 11.87^\circ$  in  $\text{COMe}_2$  (triacetate, m.p. 69°,  $[\alpha]_D^{20} + 44.15^\circ$  in  $\text{CHCl}_3$ ). The position of SH in (II) is

established, since (I) is transformed by  $\text{COMe}_2$  containing conc.  $\text{H}_2\text{SO}_4$  at 20° into diisopropylidene-6-



thiogluucose (III), b.p. 120° (bath)/0.06 mm., m.p. 74°,  $[\alpha]_D^{20} + 16.67^\circ$  in  $\text{CHCl}_3$ , which contains a free SH and with  $\text{HgCl}_2$  gives a white ppt. similar to but not identical with that yielded by (II). S is retained so firmly in (II) and (III) that it cannot be removed without fundamental alteration of the mol. The acidity of SH is slight; the alkali mercaptides are extensively hydrolysed in  $\text{H}_2\text{O}$ , and a marked tendency to autoxidation is absent. 6-Thiogluucose could not be obtained cryst.; it gives ill-defined products with  $\text{NHPh}\cdot\text{NH}_2$ . Acetylation in  $\text{C}_5\text{H}_5\text{N}$  gives a mixture of penta-acetates from which 6-thio- $\beta$ -glucose penta-acetate, m.p. 123°,  $[\alpha]_D^{20} - 14.5^\circ$  in  $\text{CHCl}_3$ , is isolated in small amount; the mixture does not give a cryst. product with  $\text{HBr}$ -AcOH or  $\text{TiCl}_4$ . (II),  $\text{NaHCO}_3$ , and I afford 1 : 2-1' : 2'-diisopropylidenedi-*d*-glucosyl 6 : 6'-disulphide, m.p. 127°,  $[\alpha]_D^{20} - 7.1^\circ$  in  $\text{CHCl}_3$  (tetra-acetate, m.p. 121°), which is hydrolysed to non-cryst. di-*d*-glucosyl 6 : 6'-disulphide, the non-homogeneous octa-acetate of which is transformed by  $\text{HBr}$ -AcOH into  $\alpha'$ -hexa-acetyldi-*d*-glucosyl 6 : 6'-disulphide 1 : 1'-dibromohydrin, m.p. 160°,  $[\alpha]_D^{20} + 193.2^\circ$  in  $\text{CHCl}_3$ . (I) condenses with (II) in boiling  $\text{C}_5\text{H}_5\text{N}$  containing  $\text{C}_5\text{H}_5\text{N}$  giving 1 : 2-1' : 2'-diisopropylidenedi-*d*-glucosyl 6 : 6'-sulphide, m.p. 125—126°,  $[\alpha]_D^{20} + 9.3^\circ$  in  $\text{CHCl}_3$  (tetra-acetate, m.p. 122°); non-cryst. di-*d*-glucosyl 6 : 6'-sulphide, its non-homogeneous octa-acetate and  $\alpha'$ -hexa-acetyldi-*d*-glucosyl 6 : 6'-sulphide 1 : 1'-dibromohydrin, m.p. 175°,  $[\alpha]_D^{20} + 231.1^\circ$  in  $\text{CHCl}_3$ , are described. Exhaustive oxidation of (II) with  $\text{Br}$ - $\text{NaHCO}_3$  or preferably with alkaline  $\text{KMnO}_4$  leads to *d*-glucomethylglucose-6-sulphonic acid (*K* salt,  $[\alpha]_D^{20} + 59.5^\circ$  to  $+38.1^\circ$  in  $\text{H}_2\text{O}$ ; *K* salt of  $\text{Ac}_4$  derivative,  $[\alpha]_D^{20} + 65.9^\circ$  in  $\text{H}_2\text{O}$ ) best characterised as the phenylhydrazine salt of the phenylosazone, m.p. 168—170°,  $[\alpha]_D^{20} - 66.6^\circ$  to  $-39.2^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ . Addition of H halide to (I) is not possible in  $\text{H}_2\text{O}$  on account of the readier hydrolysis, and is complicated in  $\text{C}_5\text{H}_5\text{N}$  by the formation of quaternary salts. The adducts are, however, readily isolated in modest yield when acetylation occurs simultaneously, and thus are obtained diacetylisopropylidene-glucose 6-chlorohydrin, m.p. 129°,  $[\alpha]_D \pm 0^\circ$  in  $\text{CHCl}_3$ , the corresponding bromohydrin, m.p. 115°,  $[\alpha]_D^{20} - 8.49^\circ$  in  $\text{CHCl}_3$ , and iodohydrin, m.p. 74—75°,  $[\alpha]_D^{20} - 22^\circ$  in  $\text{CHCl}_3$ , in each of which the halogen is very firmly retained. Addition of carboxylic acid occurs when a few drops of  $\text{C}_5\text{H}_5\text{N}$  are added to a mixture of the components at 140°, the acid residue occupying position 6. Sulphonic acids are not added similarly. (I) and  $\text{MgMeI}$  could not be caused to react. H. W.

Improved preparation of diisopropylidene-glucose. D. J. BELL (J.C.S., 1935, 1874—1875).—Diisopropylidene-glucose (72% yield) is obtained



by the interaction of glucose and  $\text{COMe}_2$  in presence of 4% of  $\text{H}_2\text{SO}_4$  during 5 hr. F. N. W.

**Fructose anhydride from the leaves of the barley plant.**—See this vol., 258.

**Advantageous preparation of isoglucosamine ; catalytic hydrogenation of osazones.** K. MAURER and B. SCHLEDT (Ber., 1935, 68, [B], 2187—2191).—Hydrogenation of glucosazone in  $\text{AcOH-EtOH-H}_2\text{O}$  containing Pd acetate at room temp./3 atm. readily yields 1-aminofructose (isoglucosamine) acetate (I), m.p.  $137^\circ$ ,  $[\alpha]_D^{20} -63.7^\circ$  in  $\text{H}_2\text{O}$  (corresponding oxalate,  $[\alpha]_D^{20} -58.5^\circ$  in  $\text{H}_2\text{O}$ , and sparingly sol. *reineckate*). Treatment of (I) with  $\text{NH}_2\text{Et}$  in  $\text{MeOH}$  rapidly affords 2 : 5-ditetrahydroxybutylpyrazine, m.p.  $236^\circ$ ,  $[\alpha]_D^{20} -79.60^\circ$  in  $\text{H}_2\text{O}$  (identical with fructosepyrazine from fructose and  $\text{NH}_3$ ), which with  $\text{NaOAc}$  and boiling  $\text{Ac}_2\text{O}$  gives the *octa-acetate*, m.p.  $176^\circ$ ,  $[\alpha]_D^{20} -6.22^\circ$  in  $\text{CHCl}_3$ . Glucosazone *tetra-acetate* has m.p.  $116^\circ$ ,  $[\alpha]_D^{20} -57.22^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ . Similar hydrogenation of acetophenoneketazine leads to *s-di- $\alpha$ -phenylethylhydrazine (hydrochloride)*, m.p.  $174^\circ$ ; *sulphate*, m.p.  $236^\circ$ ; *reineckate*, transformed by  $\text{NPh}_2\text{C}=\text{O}$  into 4-phenyl-1 : 2-di- $\alpha$ -phenylethylsemicarbazide. H. W.

**Crystalline *d*- $\alpha$ -galaheptose and its derivatives.** R. M. HANN, (MISS) A. T. MERRILL, and C. S. HUDSON (J. Amer. Chem. Soc., 1935, 57, 2100—2103).—*d*- $\alpha$ -Galaheptose (I) closely resembles the configuratively related mannose in chemical and physical properties. The prep. of *d*- $\alpha$ -galahepton-*amide* and -*lactone*, *d*- $\alpha$ -galaheptonic acid (optical behaviour recorded; Na salt, + $\text{H}_2\text{O}$ ,  $[\alpha]_D^{20} +9.7^\circ$  in  $\text{H}_2\text{O}$ ), and (I) is improved. The following derivatives of (I) are prepared:  $\beta$ -*Me*, *cryst.*,  $[\alpha]_D^{20} -70.2^\circ$  in  $\text{H}_2\text{O}$  (*penta-acetate*, m.p.  $108^\circ$ ),  $[\alpha]_D^{20} -20.4^\circ$  in  $\text{CHCl}_3$ , and  $\beta$ -*Et d*- $\alpha$ -galaheptoside, m.p.  $138^\circ$ ,  $[\alpha]_D^{20} -65.4^\circ$  in  $\text{H}_2\text{O}$  (*penta-acetate*, m.p.  $92^\circ$ ),  $[\alpha]_D^{20} -24.9^\circ$  in  $\text{CHCl}_3$ ); *benzylthiol* derivative, m.p.  $191^\circ$ ,  $[\alpha]_D^{20} +30.3^\circ$  in  $\text{C}_5\text{H}_5\text{N}$  (*hexa-acetate*, m.p.  $120^\circ$ ),  $[\alpha]_D^{20} -10.6^\circ$  in  $\text{CHCl}_3$ , and *benzoate*, m.p.  $129^\circ$ ,  $[\alpha]_D^{20} -48.1^\circ$  in  $\text{CHCl}_3$ . M.p. are corr. R. S. C.

**Caramelisation of sucrose.** A. JOSZT and S. MOLINSKI (Biochem. Z., 1935, 282, 269—276).—By heating sucrose in vac. (3—5 mm.) up to 10% wt. loss at a bath temp. just above the m.p. of sucrose ( $187.5-189.5^\circ$ ), no gaseous but only liquid substances separated, consisting largely of  $\text{H}_2\text{O}$  and 20% of dry substance which is chiefly  $\omega$ -hydroxymethylfurfuraldehyde. P. W. C.

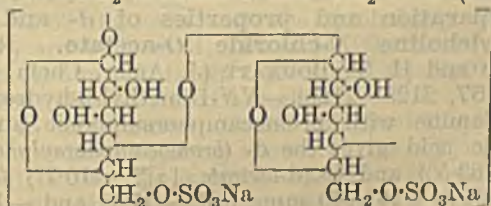
**Syntheses in the sugar series. II. Derivatives of cellobiose.** J. BRISKO and H. ZAK (Monatsh., 1935, 67, 111—117; cf. A., 1930, 583).—Heptaacetylcellobiosidyl bromide with the appropriate Ag salt in dry xylene gives the *thiocyanate*, m.p.  $201^\circ$ ,  $[\alpha]_D^{19} -7.48^\circ$  in  $\text{EtOAc}$ , *phthalimide*, m.p.  $141-142^\circ$ , and *theophyllide*, m.p.  $174^\circ$  after sintering at  $165^\circ$ ,  $[\alpha]_D^{19} +14.1^\circ$  in  $\text{EtOAc}$ , all unstable in  $\text{H}_2\text{O}$ ; the cyanide and theobromide could not be obtained. 1-*Menthylcellobioside hepta-acetate*, m.p.  $163-165^\circ$ ,  $[\alpha]_D^{18} -11.2^\circ$  in  $\text{EtOAc}$ , was prepared, but the *d*-bornyl, vanillyl, and thymyl glucosides are unobtainable.  $[\alpha]$  are for white light. R. S. C.

**Polysaccharides synthesised by micro-organisms. II. Molecular structure of varianose produced from glucose by *Penicillium varians*,**

G. SMITH. W. N. HAWORTH, H. RAISTRICK, and M. STACEY (Biochem. J., 1935, 29, 2668—2678).—The mould grown in Czapek-Dox medium at  $24^\circ$  containing glucose yields a polysaccharide, *varianose* (I),  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ ,  $[\alpha]_D^{20} +15^\circ$  in  $\text{H}_2\text{O}$ , reducing Fehling's solution slightly and giving no colour with I. Hydrolysis with  $\text{HCl}$  affords galactose. The  $(\text{Ac}_3)_n$  derivative,  $[\alpha]_D^{20} +30.0^\circ$  in  $\text{CHCl}_3$ ,  $+38.2^\circ$  in  $\text{COMe}_2$ , is homogeneous. Complete methylation of (I) or its acetate gives the  $(\text{Me}_3)_n$  derivative, m.p.  $90-100^\circ$ ,  $[\alpha]_D^{20} +20^\circ$  in  $\text{CHCl}_3$ ,  $+23^\circ$  in  $\text{C}_6\text{H}_6$ ,  $[\alpha]_D^{20} +15^\circ$  in  $\text{H}_2\text{O}$ , hydrolysed ( $\text{MeOH-HCl}$ ) to 2 : 3 : 4 : 6-tetramethylmethylglucopyranoside [14% ; corresponding with a chain of 8 hexose members of mol. wt. 1300 for (I)] and trimethylmethylgalactoside (70%) which hydrolyses to a trimethylgalactose (II). (II) is oxidised by Br to a trimethyl- $\gamma$ -galactonolactone (III), m.p.  $99^\circ$  (amide, m.p.  $135^\circ$ ), and methylated by  $\text{MeI}$  to tetramethylmethylgalactoside, b.p.  $95/0.05$  mm., hydrolysed to a mixture of the pyranose (isolated as anilide, m.p.  $198^\circ$ ) and furanose forms of tetramethylgalactose. This indicates (III) to be the 2 : 3 : 6-isomerid (cf. A., 1932, 1113). Methylation of (I) also yields a trimethylmethylhexoside, hydrolysed to a trimethylhexose (IV), oxidised by Br to a trimethylhexono- $\gamma$ -lactone, b.p.  $110-115/0.04$  mm. (*Me* derivative; *phenylhydrazide*, m.p.  $175^\circ$ ), which on further oxidation ( $\text{HNO}_3$ ) and treatment with  $\text{NH}_3$  affords oxamide and *d*-dimethoxysuccinamide. Methylation of (IV) yields a tetramethylmethylhexoside, b.p.  $90-95/0.03$  mm., hydrolysis and subsequent oxidation of which affords a tetramethylhexonolactone (*phenylhydrazide*, m.p.  $172^\circ$ ). (IV) appears to be a derivative of either *d*-idose or *l*-altrose. Hence (I) is a chain of 6—8  $\beta$ -galactopyranose units with a glucopyranose unit at one end of the chain and a unit of either *l*-altrose or *d*-idose at the reducing end. F. O. H.

**Structure of deoxyriboside of thymus-nucleic acid.** K. MAKINO (Biochem. Z., 1935, 282, 263—264).—The author's earlier result (A., 1935, 772) according to which deoxyribosenucleoside from ox intestine must possess a pyran structure, since it gives a positive  $\text{H}_3\text{BO}_3$  test, is now negated in view of the fact that the pure nucleosides (hypoxanthine-, guanine-, and thymine-deoxyribosides) all give negative  $\text{H}_3\text{BO}_3$  reactions. P. W. C.

**Structure of [the mono]sodium sulphate ester of galactan from *Iridaea laminarioides* (Rhodophyceae).** W. Z. HASSID (J. Amer. Chem. Soc., 1935, 57, 2046—2050).—This ester (I) is probably as shown. It gives a  $\text{Ac}_2$  derivative and  $\text{Me}_2$  ether (II),  $[\alpha]_D^{20}$



+ $17.2^\circ$  in  $\text{CHCl}_3$ , is hydrolysed by hot 0.5N- $\text{H}_2\text{SO}_4$  or 5% aq.  $\text{Ba}(\text{OH})_2$  to a galactan,  $[\alpha]_D^{20} +82.2^\circ$  in  $\text{H}_2\text{O}$ , the  $\text{Me}_3$  ether,  $[\alpha]_D^{20} +32.4^\circ$  in  $\text{H}_2\text{O}$ , of which with hot 2N- $\text{HCl}$  gives a trimethylgalactose (III), b.p.  $94/0.1$  mm. (III) does not give an osazone and,

when oxidised successively by Br and HNO<sub>3</sub> and then esterified, gives *Me<sub>2</sub> arabodimethoxyglutarate*, b.p. 115°/0.1 mm. Hydrolysis of (II) by 2% H<sub>2</sub>SO<sub>4</sub> affords a reducing monosaccharide, which with HCl-MeOH affords a *methyl-dimethylgalactoside*,  $[\alpha]_D^{20} +97.2^\circ$  in H<sub>2</sub>O. When titrated, (I) behaves as the salt of a strong acid. Its mol. wt. is determined in H<sub>2</sub>O.

R. S. C.

**Specific polysaccharide from the bacillus Calmette-Guerin (BCG).**—See this vol., 248.

**Constitution of starch and mode of action of starch-splitting enzymes.** W. ZIESE (Z. Spiritus-ind., 1936, 59, 3—4).— $\beta$ -Diacetase has no action on PO<sub>4</sub>-free hydroxyethylstarch (I), whilst the action of  $\alpha$ -diacetases is restricted to the production of non-reducing derivatives of high mol. wt. The latter fact, together with viscosity measurements during the hydrolysis of (I) by  $\alpha$ -diacetases, indicates that other factors besides principal valency are concerned in the constitution of (I). Further, the distinctions between the dextrinising and saccharifying actions of diacetase are thus emphasised.

I. A. P.

**Importance of Svedberg's ultracentrifuge for the determination of the mol. wt. of cellulose.** M. ULMANN (Cellulosechem., 1935, 16, 114—118).—A lecture.

R. S. C.

**Preparation and properties of double chlorides and bromides of bivalent nickel and of organic bases.** J. AMIEL (Compt. rend., 1935, 201, 1198—1200).—The following compounds, for which a co-ordination structure cannot yet be assigned, are prepared by evaporating conc. solutions of the mixed Ni and org. halides: *NiCl<sub>2</sub>.NH<sub>3</sub>MeCl*; *NiCl<sub>2</sub>.NH<sub>3</sub>EtCl*; *NiCl<sub>2</sub>.NH<sub>3</sub>Pr<sup>n</sup>Cl*; *2NiCl<sub>2</sub>.(CH<sub>2</sub>.NH<sub>3</sub>Cl)<sub>2</sub>*, anhyd. or +6H<sub>2</sub>O; *NiCl<sub>2</sub>.C<sub>4</sub>H<sub>9</sub>N.HCl*; *NiCl<sub>2</sub>.C<sub>5</sub>H<sub>10</sub>N.HCl*; *2NiCl<sub>2</sub>.C<sub>4</sub>H<sub>8</sub>(NH<sub>2</sub>Cl)<sub>2</sub>*, anhyd. or +6H<sub>2</sub>O; *NiCl<sub>2</sub>.C<sub>9</sub>H<sub>7</sub>N.HCl*; *NiBr<sub>2</sub>.NH<sub>3</sub>MeBr*; *NiBr<sub>2</sub>.NH<sub>3</sub>EtBr*; *NiBr<sub>2</sub>.NH<sub>3</sub>Pr<sup>n</sup>Br*; *2NiBr<sub>2</sub>.(CH<sub>2</sub>.NH<sub>3</sub>Br)<sub>2</sub>*; *NiBr<sub>2</sub>.C<sub>5</sub>H<sub>5</sub>N.HBr*; *NiBr<sub>2</sub>.C<sub>9</sub>H<sub>7</sub>N.HBr*; *2NiBr<sub>2</sub>.C<sub>4</sub>H<sub>8</sub>(NH<sub>2</sub>Br)<sub>2</sub>*, anhyd. or +6H<sub>2</sub>O; *NiBr<sub>2</sub>.C<sub>9</sub>H<sub>7</sub>N.HBr*. When heated the above decompose without melting. In solution the only Ni ions detected are Ni<sup>++</sup>.

E. W. W.

**Preparation of ethyleneimine from ethanolamine.** H. WENKER (J. Amer. Chem. Soc., 1935, 57, 2328).—(CH<sub>2</sub>)<sub>2</sub>NH, b.p. 55—56.5°, is readily prepared by heating OH.C<sub>2</sub>H<sub>4</sub>.NH<sub>2</sub>.H<sub>2</sub>SO<sub>4</sub> at 250° and boiling the resulting NH<sub>2</sub>.C<sub>2</sub>H<sub>4</sub>.SO<sub>3</sub>H with 40% aq. NaOH.

R. S. C.

**Preparation and properties of d- and l- $\beta$ -methylcholine N-chloride O-acetate.** R. T. MAJOR and H. T. BOUNATT (J. Amer. Chem. Soc., 1935, 57, 2125—2126).—*NN*-Dimethyl- $\beta$ -hydroxy-*n*-propylamine with bromocamphorsulphonic and *d*-tartaric acid gives the *d*-(*bromocamphorsulphonate*,  $[\alpha]_D^{25} +83.5^\circ$ ) and *l*-(*d-tartrate*,  $[\alpha]_D^{25} -10.7^\circ$ ) forms, b.p. 124.5—126°/770 mm.,  $[\alpha]_D^{25} +17.1^\circ$  and  $-14.8^\circ$ , respectively, which lead to the *d*- and *l*-forms of  $\beta$ -*methylcholine*, m.p. 165—167°,  $[\alpha] +38.8^\circ$ ,  $-38.2^\circ$  (*iodide*, m.p. 176.5—177.5°,  $[\alpha] \pm 24.7^\circ$ ), and  $\beta$ -*methylcholine N-chloride O-acetate*, m.p. 201—202°,  $[\alpha] +41.9^\circ$ ,  $-41.3^\circ$ .

R. S. C.

**Hydrogenation of carbon dioxide. Correction of the reported synthesis of urethanes.** M. W. FARLOW and H. ADKINS (J. Amer. Chem. Soc., 1935, 57, 2222—2223).—CO<sub>2</sub> and H<sub>2</sub> in presence of amines and Raney Ni at 80—150° or brass at 250° gives HCO<sub>2</sub>H (as amine formate) and HCO-derivatives (of primary bases). In presence of brass *s*-di-( $\beta$ -phenylethyl)- and *s*-di-*n*-amyl-carbamide, m.p. 88°, are also obtained. The following are incidentally described. *N-Formyl-n-amylamine*, b.p. 124—125°/10 mm., and  $\beta$ -phenylethylamine, b.p. 180—181°/14 mm.; *formates* of CH<sub>2</sub>Ph.CH<sub>2</sub>.NH<sub>2</sub>, m.p. 128—129° (decomp.), 4-hydroxy-2 : 2 : 6 : 6-tetramethylpiperidine, m.p. 207° (decomp.), and  $\alpha$ -phenylpropyl- $\beta$ -amine, m.p. 160° (decomp.). The so-called pentamethyleneurethanes previously recorded (cf. A., 1935, 70) are const.-boiling mixtures of formylpiperidine (HgCl<sub>2</sub> compound, m.p. 147—148°) and ROH.

R. S. C.

**Multivalent amino-acids and polypeptides.** V. Cystinecyamidene. J. P. GREENSTEIN (J. Biol. Chem., 1935, 112, 35—38; cf. A., 1935, 1203).—Di- $\alpha$ -guanidinopropionic acid  $\gamma$ -disulphide and conc. HCl give the *dianhydride*, decomp. >240° (*dihydrochloride*, m.p. 150°; *monopicrate*, m.p. 188°), readily hydrolysed by NaOH at both C:S and C:N linkings to give AcCO<sub>2</sub>H.

R. S. C.

**Isolation of homocysteine. Its conversion into a thiolactone.** B. RIEGEL and V. DU VIGNEAUD (J. Biol. Chem., 1935, 112, 149—154).—*S*-Benzoyl-homocysteine and Na-NH<sub>3</sub> give an 80% yield of *homocysteine* (I), m.p. 232—233° (corr.) (photomicrograph), converted by acid into the *thiolactone* [*hydrochloride*, m.p. 200—201° (corr.); hydriodide, also obtained similarly from methionine]. Lactonisation occurs as follows: with hot 0.1*N*-, 20%, and cold conc. HCl 50% in 3 hr., 100% in a few min., and 50% in 5 min. (100% in 1 hr.), respectively; with conc. H<sub>2</sub>SO<sub>4</sub> with much oxidation hot, but little cold; with *N*- or 6*N*-H<sub>2</sub>SO<sub>4</sub> mainly ring-closure.

R. S. C.

**Carbon monoxide-ferroglutathione.** F. KUBOWITZ (Biochem. Z., 1935, 282, 277—281).—The ability of Fe to enable glutathione (I) to absorb CO as does ferrocysteine depends on the concn. of (I). Ferroglutathione (II) itself dissociates. Using a const. concn. of Fe<sup>++</sup> salt and increasing the amount of (I), the amount of (II) and of CO absorbed increase until finally the Fe becomes saturated with (I) and 2CO are fixed per atom of Fe. CO-(II) is split by visible light into (II)+CO.

P. W. C.

**Formation of amides from nitriles by the action of hydrogen peroxide.** L. McMASTER and C. R. NOLLER (J. Indian Chem. Soc., 1935, 12, 652—653).—Conditions are given for obtaining max. yields of amide from 13 nitriles by H<sub>2</sub>O<sub>2</sub>.

R. S. C.

**Micro-determination of carbamide in very dilute solutions.** K. W. HOU (Bull. Nat. Acad. Peiping, 1932, 3, No. 5, 7 pp.).—Pptn. with xanthhydrol gives results, of approx. 2% accuracy, with solutions containing 10—100 mg. of CO(NH<sub>2</sub>)<sub>2</sub> per litre.

CH. ABS. (p)

**Explosion in the preparation of guanidine nitrate from ammonium thiocyanate.** C. SCHÖPF and H. KLAPPROTH (Angew. Chem., 1936, 49, 23).—

Gockel's method of prep. (A., 1935, 1111) may lead to an explosion, the cause of which has not been traced.

E. S. H.

[Explosion in the preparation of guanidine nitrate from ammonium thiocyanate.] H. GOCKEL (Angew. Chem., 1936, 49, 23; cf. preceding abstract).—The explosion is probably due to decomp. of  $\text{NH}_4\text{NO}_3$ .

E. S. H.

Separation of guanidine and methylguanidine by naphthalene-2-sulphonic acid. W. C. HESS and M. X. SULLIVAN (J. Amer. Chem. Soc., 1935, 57, 2331—2332).—2-Naphthalenesulphonyl guanidine, m.p. 204—206°, and -methylguanidine, m.p. 101—102°, are prepared. The bases can be separated by these derivatives, since the former is obtained preferentially with a limited amount of alkali.

R. S. C.

Second synthesis of *d*-glutamine. H. NIENBURG (Ber., 1935, 68, [B], 2232—2234).—*d*-Glutamic acid is converted into the Et  $\gamma$ -ester, the carbobenzyloxy-derivative of which is transformed by liquid  $\text{NH}_3$  at 15—20° into *N*-carbobenzyloxy-*d*-glutamine, hydrogenated (Pd-AcOH-EtOH) to *d*-glutamine, m.p. 184—185°,  $[\alpha]_D + 8.3^\circ$  in  $\text{H}_2\text{O}$ .

H. W.

Formation of hydrocyanic acid from organic compounds in the presence of ammoniacal copper sulphite. J. PARROD (Compt. rend., 1935, 201, 993—995; cf. A., 1935, 1109).—Besides *d*-fructose, other sugars and allied compounds yield HCN at 58—62°. Lactose, maltose, and rhamnose give HCN only at higher temp. (80—85°). Yields of about 20 mols. of HCN per 100 C atoms in the compound have been obtained. CO and  $\text{CH}_2\text{O}$  do not yield HCN.

F. A. A.

Photolytic and thermal decomposition products of azomethane. Thermal reaction rates in quartz at 260—290°. L. J. HEIDT and G. S. FORBES (J. Amer. Chem. Soc., 1935, 57, 2331).—Pressure changes during the decomp. of azomethane at -183° to 30° and for the thermal reaction at 300° in  $\text{SiO}_2$  indicate decomp. to  $\text{N}_2$  and much  $\text{CH}_4$ . The 10° temp. coeff. for 260—290° is 2.9 and is but little affected by the presence of Hg.

R. S. C.

Compounds of the type  $\text{BCl}_{3-n}(\text{OR})_n$ . III. Preparation of  $\text{BCl}_2\text{OMe}$  and  $\text{BCl}(\text{OMe})_2$  from boron trichloride and methyl borate. E. WIBERG and H. SMEDSRUD (Z. anorg. Chem., 1935, 225, 204—208; cf. A., 1935, 459).—Improved methods of preparing  $\text{BCl}_2\text{OMe}$  and  $\text{BCl}(\text{OMe})_2$  are described.

F. L. U.

Preparation of magnesium dialkyl compounds from Grignard reagents. A. C. COPE (J. Amer. Chem. Soc., 1935, 57, 2238—2240).—The extent of disproportionation,  $2\text{MgRX} \rightleftharpoons \text{MgR}_2 + \text{MgX}_2$ , in  $\text{Et}_2\text{O}$  is  $>$  in  $\text{Bu}_2\text{O}$ , and is raised by rise in temp. The mobility of the equilibrium is shown by gradual dissolution of the  $\text{MgPh}_2$  pptd. by dioxan. Dioxan ppts.  $\text{MgCl}_2$  etherate from  $\text{MgMeI}$  solutions.

R. S. C.

Constitution of platinum compounds with thioethers. K. A. JENSEN (Z. anorg. Chem., 1935, 225, 115—141).—Contrary to the inferences of Drew and others (cf. A., 1935, 100), there is no structural difference between the  $\alpha$ - (I) and  $\beta$ - (II) -isomerides

of the type  $[\text{PtCl}_2(\text{Et}_2\text{S})_2]$ . The marked difference in the electrical conductivities of (I) and (II) in  $\text{H}_2\text{O}$  or MeOH is due to the change  $[\text{PtCl}_2(\text{Et}_2\text{S})_2] + 2\text{H}_2\text{O} \rightarrow [\text{Pt}(\text{H}_2\text{O})_2(\text{Et}_2\text{S})_2]^{++} + 2\text{Cl}^-$  (or similarly with MeOH) occurring rapidly with (II) and slowly with (I). Only two isomerides of this type exist, and "super-numerary isomerides" reported by various workers are shown to have been mixtures. Mol. wt. determinations show that compounds from equimol. proportions of  $\text{PtCl}_2$  and  $\text{R}_2\text{S}$  have the formula  $\text{Pt}_2(\text{R}_2\text{S})_2\text{Cl}_4$ .

F. L. U.

Complex metallic salts. III.—See this vol., 140.

1-Benzyl- $\Delta^1$ -cyclohexene and benzylidene-cyclohexane. K. VON AUWERS (Ber., 1935, 68, [B], 2174—2175; cf. A., 1915, i, 789).—A reply to Prévost *et al.*, (A., 1934, 649).

H. W.

Monodeuterobenzene. N. MORITA and T. TITANI (Bull. Chem. Soc. Japan, 1935, 10, 557—558).—PhD (97% pure) is obtained by distillation of  $\text{Ca}(\text{OBz})_2$  with  $\text{Ca}(\text{OD})_2$  at 300°.

J. W. B.

Preparation of partly deuterated benzenes. I. H. P. WELDON and C. L. WILSON (Nature, 1936, 137, 70).—1 : 3 : 5-Trideuterobenzene, m.p. 6.1°, has been prepared [(?) from trimesic acid] by decarboxylation with  $\text{Ca}(\text{OD})_2$ .

L. S. T.

Mechanism of aromatic side-chain reactions with special reference to the polar effects of substituents. IV. Mechanism of quaternary salt formation. V. Polar effects of alkyl groups. J. W. BAKER and W. S. NATHAN. VI. Effects of *p*-alkyl substituents on prototropy in the methyleneazomethine system. J. W. BAKER, W. S. NATHAN, and C. W. SHOPPEE (J.C.S., 1935, 1840—1844, 1844—1847, 1847—1849; cf. A., 1935, 710).—IV. Data for the velocity of interaction of the following benzyl bromides with  $\text{C}_5\text{H}_5\text{N}$  (I) in dry  $\text{COMe}_2$  show that the alkyl substituents increase the reaction velocity, and that with a single *p*-alkyl substituent, the velocity decreases in the order  $\text{Me} > \text{Et} > \text{Pr}^\beta > \text{Bu}^\gamma$ : *p*-Me-, b.p. 84°/0.8 mm., m.p. 14.5—15.2°; -*Pr* $^\beta$ -, b.p. 75°/0.4 mm., 2 : 4-*Me* $_2$ -, b.p. 79°/1.2 mm., m.p. 15° [all obtained from the corresponding chlorides, prepared by Sommelet's method (A., 1914, i, 156), by refluxing with aq.- $\text{COMe}_2$  solution of NaBr]; *p*-*Bu* $^\gamma$ -, b.p. 99°/0.3 mm., m.p. 15.1° (prep. by direct bromination of *p*- $\text{C}_6\text{H}_4\text{MeBu}^\gamma$ ), and 2 : 4-dinitrobenzyl bromide (II), m.p. 46.4° (modified prep.) [with (I) yields 2 : 4-dinitrobenzylpyridinium bromide, m.p. 196° (decomp.)]. The energy of activation of the reaction is 12.2—12.57 kg.-cal. and the probability factors ( $\times 10^6$ ) are 0.75—2.61. Data for the reaction between (I) and (II) in aq.  $\text{COMe}_2$  and aq. EtOH, and between (II) and EtOH are given.

V. An explanation of the unexpected order of electron release capacity shown by the alkyl groups studied in Part IV is given, based on the tentative supposition that when Me is attached to a conjugated system the duplet of electrons forming the C-H linking in this group are appreciably less localised (and hence more easily released) than those in a similarly placed C-C linking.

VI. In the azomethine system (A)  $p$ - $C_6H_4R \cdot CH=N \cdot CH_2Ph \rightleftharpoons$  (B)  $p$ - $C_6H_4R \cdot CH_2 \cdot N:CHPh$  the following order of mobility is obtained:  $p$ -Bu<sup>γ</sup> >  $p$ -Pr<sup>β</sup> >  $p$ -Me, whilst the % of form (A) at equilibrium are Me 45.0, Pr<sup>β</sup> 56.0, Bu<sup>γ</sup> 60.0. From these sequences it is inferred that the type of electron release by Me outlined in Part V is permanent (mesomeric). The Schiff's bases: *benzylidene-p-tert.-butyl-*, b.p. 155—157°/0.4 mm.; *p-tert.-butylbenzylidene-*, b.p. 161°/0.5 mm., and *p-isopropylbenzylidene-benzylamine*, b.p. 155°/0.5 mm., are obtained directly from the aldehyde and amine by Shoppee's method (A., 1931, 834). *p-tert.-Butyl-* (*p-nitrophenylhydrazone*, m.p. 214°) and *p-isopropyl-benzaldehyde* (*p-nitrophenylhydrazone*, m.p. 190°) are prepared by oxidation [boiling aq.  $Cu(NO_3)_2$  in  $CO_2$ ; 24 hr.] of the corresponding benzyl bromide and chloride, respectively. *p-tert.-Butylbenzylamine*, b.p. 124°/16 mm. [carbamido-derivative, m.p. 137°; *picrate*, m.p. 270° (decomp.)], is obtained by the action of  $N_2H_4 \cdot H_2O$  on *phthalop-tert.-butylbenzylamine*, m.p. 103°, which results from the interaction of K phthalimide and *tert.-butylbenzyl bromide* (180°; 2–3 hr.). F. N. W.

#### Derivatives of *p*-fluorobenzenesulphonic acid.

R. M. HANN (J. Amer. Chem. Soc., 1935, 57, 2166—2167).— $PhF$ ,  $HCl$ ,  $SO_2$ , and  $AlCl_3$  in  $CS_2$  give *Na p-fluorobenzenesulphinate*,  $+2H_2O$ , *cryst.*, which leads to the *benzyl-ψ-thiocarbamide salt*, m.p. 161°, and the corresponding *sulphonate*, m.p. 166°, *p-C\_6H\_4F CH\_2Bz*, m.p. 151°, and *p-NO\_2 \cdot C\_6H\_4 \cdot CH\_2 sulphone*, m.p. 185°, *p-fluorophenylsulphonyl-acetic acid*, m.p. 110—111° [*benzyl-ψ-thiocarbamide salt*, m.p. 144° (decomp.)]; *p-C\_6H\_4Br \cdot CO \cdot CH\_2 ester*, m.p. 126°, and *-acetone*, m.p. 66°, and *s-di-p-fluorophenylsulphonylacetone*, m.p. 144°. All are ineffective against pneumococcal infections. M.p. are *corr.* R. S. C.

**Ullmann reaction.** H. C. YUAN and M. TSAO (J. Chinese Chem. Soc., 1935, 3, 358—364).—*3-Bromo-4-iodo-5-nitrotoluene* (I), m.p. 82—83° (prepared by boiling diazotised 3-bromo-5-nitro-*p*-toluidine with KI), when heated with Cu-bronze at 230—250° in the absence of solvent yields 3-bromo-5-nitrotoluene (II), but when boiled in  $PhNO_2$  with Cu-bronze affords 2 : 2'-*dibromo-4 : 4'-dimethyl-6 : 6'-dinitrodiphenyl*, m.p. 195—196°. The formation of (II) is considered to be due to the catalytic dehydrogenation by Cu of a part of (I) and the replacement of I in the remainder by the H thus formed. 3 : 5 : 6 : 1- $C_6H_2Cl_2I \cdot NO_2$  when heated with Cu-bronze, with or without  $PhNO_2$ , yields only 2 : 2' : 4 : 4'-*tetrachloro-6 : 6'-dinitrodiphenyl*, m.p. 128—129°; no 3 : 5 : 1- $C_6H_3Cl_2 \cdot NO_2$  was isolated. It is considered therefore that in (I) it is mainly the Me which is dehydrogenated. H. G. M.

**Butylcymenes and their nitro-derivatives.** H. BARBIER (Rev. Marques Parfum. Savonn., 1934, 12, 325—327; Chem. Zentr., 1935, i, 2350; cf. A., 1932, 729).—Condensation ( $AlCl_3$ ) of  $Pr^βCl$  and *p-tert.-butyltoluene* (I) or (with  $H_2SO_4$ ) of  $Pr^βOH$  and (I) yields (?) *isopropyl-4-tert.-butyltoluene*, b.p. 230°, which on nitration affords a *dinitro-4-tert.-butyltoluene*, m.p. 96°. (?) *isoPropyl-3-tert.-butyltoluene*, b.p. 235°, and the corresponding ( $NO_2$ )<sub>2</sub>-derivative, m.p. 172°, are obtained similarly. Condensation

( $H_2SO_4$ ) of  $PhPr^β$  and  $Bu^γOH$  affords (?) *isopropyl-* (?) *tert.-butylbenzene*, b.p. 221°, which, with  $CH_3O$  and  $HCl$ , yields an *isopropyl-tert.-butylbenzyl chloride*, b.p. 98°/2 mm., converted, through the Mg compound, into a *tert.-butylcymene*, b.p. 236°, which yields a liquid ( $NO_2$ )<sub>2</sub>-compound. H. N. R.

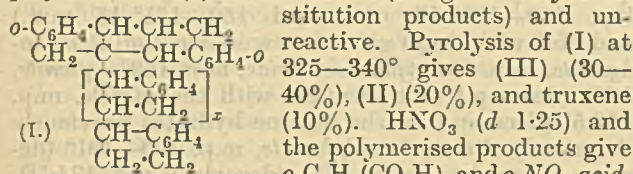
**s-Tetradiphenylvinylethane**, a tetra-substituted ethane hydrocarbon which decomposes into radicals. G. WITTIG and B. OBERMANN (Ber., 1935, 68, [B], 2214—2218).— $ααεε$ -Tetraphenylpentane- $αε$ -diol is converted by boiling  $AcOH$  containing a little conc.  $H_2SO_4$  into  $ααεε$ -tetraphenyl- $Δ^{αε}$ -*pentadiene* (I), m.p. 76—77° (in absence of mineral acid the product is 2 : 2 : 6 : 6-tetraphenylpentamethylene oxide, m.p. 176—177°), transformed by successive treatment with  $LiPh$  and  $C_2Me_4Br_2$  into  $ααββ$ -tetra- $β$ - $β'$ -*diphenylvinylethane* (II), m.p. 169—171.5° (slight decomp.), more conveniently obtained by dehydrogenating (I) with  $PhNO$ ,  $KMnO_4$ , or  $SeO_2$ . An unsymmetrical structure for (II) involving a conjugated system is excluded, since it does not react with maleicanhydride, behaves sluggishly towards  $KMnO_4$  and  $NaOH$  in  $COMe_2$ , and is converted by  $O_3$  or  $CrO_3$  in boiling  $AcOH$  mainly into  $COPh_2$ . When heated in boiling xylene or  $PhOMe$  (II) affords a yellowish-green solution the colour of which disappears on cooling. The instability of the ethane bridge is demonstrated by the reduction of (II) with P and HI in boiling  $AcOH$  to  $ααεε$ -tetraphenylethane. H. W.

#### Bromine derivatives of indene and indane.

H. D. PORTER and C. M. SUTER (J. Amer. Chem. Soc., 1935, 57, 2022—2026).—Many of Jacobi's results (A., 1931, 354) are incorrect. 2-Bromo-1-hydroxyindane (I) (prep. from crude indane-containing oil) at 155—160°, with  $PhBr$  at 156°, or best, with  $P_2O_5$  in hot  $CCl_4$ , gives 2-bromoindene (II), m.p. 38—39°, b.p. 125—127°/3 mm. This with hot  $NaOEt$  gives indan-2-one (III), but does not react with hot 2*N*- $NaOH$  or  $HCO_2K \cdot MeOH$ . (II) yields (Grignard) a little indene-2-carboxylic acid only. With  $HBr \cdot AcOH$  (II) gives an oil, hydrolysed to (I) by aq.  $COMe_2$ ; with  $Br$  in  $CCl_4$  it gives 1 : 2 : 3-*tribromoindene* (IV), an oil, oxidised by  $KMnO_4$  to  $o$ - $C_6H_4(CO_2H)_2$ , and hydrolysed by  $CaCO_3$  in aq.  $COMe_2$  to an oily *dibromoindenol*. (I) and 47%  $HBr$  at 100° give indene dibromide (V), which at 200—210° alone or, better, in tetrahydronaphthalene gives (III). (V) with  $C_5H_5N$  in  $EtOH$  or  $CaCl_2$  and  $Na_2CO_3$  in aq.  $EtOH$  gives 38% of 2-bromo-1-ethoxyindane, b.p. 147—148°/19 mm., converted by  $NaNH_2$  in liquid  $NH_3$  or by hot 18%  $H_2SO_4$  into indan-1-one (VI), by  $Br \cdot CCl_4$  into (IV) and 2 : 2-dibromoindan-1-one. *trans*-1 : 2-Dihydroxyindane [improved prep. from (I); 60% yield; gives also a *substance*, m.p. > 235°] with 10%  $H_2SO_4$  gives 71% of (III). (I) and 7%  $H_2SO_4$  give (VI) in 80.6% yield. R. S. C.

**Polymerisation. I. Formation, properties, and constitution of polyindenes, in particular of "tri-indene."** J. RISI and D. GAUVIN (Canad. J. Res., 1935, 13, 228—255).—"Tri-indene" (I) is shown to be a mixture of polymerides by fractional crystallisation. It is formed with a small amount of a *substance* (II),  $C_{27}H_{18}$ , m.p. 214°, by polymerisation of indene (III). Unsaturated di-indene (2-1'-hydrind-

enylindene; modified prep. in 73% yield) at 215° gives 60% of truxene, m.p. 116°, and a mixture of polymerides. (I) is saturated (Br gives only substitution products) and unreactive. Pyrolysis of (I) at 325—340° gives (III) (30—40%), (II) (20%), and truxene (10%). HNO<sub>3</sub> (*d* 1.25) and the polymerised products give *o*-C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)<sub>2</sub> and a *NO*<sub>2</sub>-acid, m.p. 160—165°, the amount of the latter increasing with the degree of polymerisation of the substance oxidised. (I) is probably as annexed. Polystyrenes are probably CHPh<math>\begin{matrix} \text{CH}\_2 \\ \text{CH}\_2 \end{matrix}>\text{CPh}[\text{CH}\_2\cdot\text{CHPh}]\_x\cdot\text{CH}\_2\cdot\text{CH}\_2\text{Ph} and caoutchouc is probably



the latter thus resembling many natural polyterpenes. R. S. C.

Sulphonation of naphthalene. II. Mechanism of the monosulphonation. R. LANTZ (Bull. Soc. chim., 1935, [v], 2, 2092—2108; cf. A., 1935, 1116).—The rates of sulphonation of C<sub>10</sub>H<sub>8</sub>, of hydrolysis of 1- and 2-C<sub>10</sub>H<sub>7</sub>·SO<sub>3</sub>H, and of transformation of one acid into the other are determined in sealed tubes at 60—180° in presence of 45—94% H<sub>2</sub>SO<sub>4</sub>. Hydrolysis of the 1-acid is about 50 times as fast as that of the 2-acid and is increased to a greater extent by rise in temp. and/or concn. of H<sub>2</sub>SO<sub>4</sub>. No 2-acid is formed from 1-acid by H<sub>2</sub>SO<sub>4</sub>, which, although strong enough to effect hydrolysis, is too weak to cause sulphonation. The relative amounts of 1- and 2-acid formed are independent of the concn. of the H<sub>2</sub>SO<sub>4</sub>. Only 2—4% of sulphones are formed at 140° with 45—70% H<sub>2</sub>SO<sub>4</sub> in 39 hr. and none in 2 hr. Increase in the amount of 2-acid at high temp. is due to the more rapid hydrolysis of the 1-acid. R. S. C.

Asymmetric syntheses. IV. Action of optically active nitrates on 2-bromofluorene. J. T. THURSTON and R. L. SHRINER (J. Amer. Chem. Soc., 1935, 57, 2163—2166; cf. A., 1934, 76).—2-Bromofluorene (from fluorene, Br, and a trace of I in hot C<sub>6</sub>H<sub>6</sub>), m.p. 113°, *d*- or *l*-octan-β-ol nitrate, and KOEt in EtOH—Et<sub>2</sub>O give the *K* salts (I), [α]<sub>D</sub><sup>25</sup> +4.48°, -1.71° in dry EtOH, of 2-bromo-9-nitrofluorene (II), which with air give KNO<sub>2</sub> and 2-bromofluorenone, m.p. 196° (lit. 194—195°), with dil. AcOH give the *ac*-form (III), m.p. 132°, of (II) [converted in hot EtOH into the normal form (IV), m.p. 170°], with Br in EtOH yields 2 : 9-dibromo-9-nitrofluorene, m.p. 139°, [α]<sub>D</sub><sup>0</sup>°, and leads by way of the *Ag* salt to 2-bromo-9-nitrofluorene *O*-*Me* ether (V), m.p. 72—80°, readily decomposed to CH<sub>2</sub>O and 2-bromofluorenone oxime (VI). (I), (III), (IV), (V), and (VI) absorb 0.9, 0.5, 0, 0.49—0.53, and 0.51 mol. of Br, respectively. R. S. C.

Dissociable anthracene oxides: influence of mesonaphthyl groups. A. WILLEMART (Compt. rend., 1935, 201, 1201—1202).—9 : 10-Dihydroxy-9 : 10-di-β-naphthyl-dihydroanthracene is converted by KI in AcOH into 9 : 10-di-β-naphthylanthracene, m.p. 378—379°. Both this and the di-α-naphthyl compound, in solutions exposed to sunlight in presence of

air, yield *photo-oxides*, which when heated at 180—200° lose O<sub>2</sub> and regenerate the hydrocarbons.

E. W. W.

Dissociable organic oxides. Diphenyldi-*p*-bromophenyldibromorubene and its dissociable oxide. C. DUFRAISSE and H. ROCHER (Bull. Soc. chim., 1935, [v], 2, 2235—2240).—(*p*-C<sub>6</sub>H<sub>4</sub>Br)<sub>2</sub>CO and CPh:C-MgBr give *γ*-phenyl-*αα*-di-*p*-bromophenyl-Δ<sup>β</sup>-propinen-*α-cl* (I), m.p. 170—171°, which yields an unstable chloride, m.p. 122—123°, converted at 115°/vac. in quinoline into diphenyldi-*p*-bromophenyldibromorubene, m.p. 309—310°, yellow and garnet-red forms (absorption spectra given). In Et<sub>2</sub>O—C<sub>6</sub>H<sub>6</sub> in light this gives a *cryst. oxide*, which at 195—220° rapidly dissociates (45—58% of O<sub>2</sub> liberated). (I) (*Me ether*, m.p. 103°) with H<sub>2</sub>SO<sub>4</sub>—EtOH gives *Ph ββ*-di-*p*-bromophenylvinyl ketone, m.p. 112—113°. R. S. C.

Cholanthrene and related hydrocarbons. L. F. FIESER and A. M. SELIGMAN (J. Amer. Chem. Soc., 1935, 57, 2174—2176).—4-Bromohydrindone, m.p. 97°, prepared in 70% yield from β-*o*-bromophenylpropionic acid (best obtained from *o*-C<sub>6</sub>H<sub>4</sub>BrMe), gives (Clemmensen) a 77% yield of 4-bromohydrindene, b.p. 118°/18 mm., the Grignard reagent (I) of which with α-C<sub>10</sub>H<sub>7</sub>·COCl gives 4-*α*-naphthoylhydrindene, an oil (50% yield), pyrolysed at 400—405° to cholanthrene (34%), m.p. 173—173.5° (corr.) [*picrate*, m.p. 169—170° (corr.)]. (I) and β-C<sub>10</sub>H<sub>7</sub>·COCl give 4-β-naphthoylhydrindene, m.p. 68—69°, and thence 5 : 10-dimethylene-1 : 2-benzanthracene, m.p. 176.5—177° (corr.) [*picrate*, m.p. 158—159° (corr.)]. Fluorenone-1-carboxylic acid (modified prep. from 7 : 8-benzacenaphthene; 48% yield), m.p. 191—193°, and 4% Na—Hg and H<sub>2</sub>O give 83% of fluorene-1-carboxylic acid, m.p. 245°, the Grignard reagent (II) from the chloride of which with 1-C<sub>10</sub>H<sub>7</sub>Br in C<sub>6</sub>H<sub>6</sub>—Et<sub>2</sub>O gives 56% of 1-*α*-naphthoylfluorene (III), m.p. 113—114°, giving at 415° in N<sub>2</sub> 60% of 15 : 16-benzdehydrocholanthrene (IV), m.p. 181—181.3° (*picrate*, m.p.



174.5—175.5° (corr.)]. (II), C<sub>10</sub>H<sub>8</sub>, and AlCl<sub>3</sub> in C<sub>6</sub>H<sub>6</sub>Cl<sub>4</sub> give mainly 1-β-naphthoylfluorene, m.p. 159—162°, yielding 7 : 8-benz-1 : 2 : 1' : 2'-naphthacene (V), m.p. 178—179° (corr.) [*picrate*, m.p. 181—182° (corr.)]; in CS<sub>2</sub>, however, much (III) is formed. R. S. C.

Amides of benzene-sulphinic [ and -sulphinic] acid. L. C. RAIFORD and S. E. HAZLET (J. Amer. Chem. Soc., 1935, 57, 2172—2174).—The following are prepared, the yields varying greatly. *Benzenesulphinic-o*, m.p. 107—108°, -*m*-, m.p. 106°, and -*p*-chloro-anilide, m.p. 155.5°, -*o*-, m.p. 108—110°, -*m*-, 112—114°, and -*p*-bromoanilide, m.p. 150.5°, -*o*-, m.p. 124—125°, -*m*-, m.p. 102—103°, and -*p*-toluidide, m.p. 100—101°, -*o*-, m.p. 108—113°, -*m*-, 133—134°, and -*p*-anisidide, m.p. 131°, -*p*-carboethoxyanilide, m.p. 114—115°, -4-nitro-*o*-toluidide, m.p. 133°, -β-naphth-

*alide*, m.p. 143—144°, *-benzylamide*, m.p. 100—104°, *-4'-diphenylamide*, m.p. 165·5°, *-4-chlorodiphenyl-2'-*, m.p. 206°, and *-4'-amide*, m.p. 165—166°; *benzenesulphon-o-*, m.p. 130—131°, and *-m-bromoanilide*, m.p. 117·5—118·5°, *-o-toluidide*, m.p. 122—123° (lit. 124—125°), *-m-anisidide*, m.p. 82·5—83·5°, *-p-carboethoxyanilide*, m.p. 183·5—184°, *-4-nitro-o-toluidide*, m.p. 175—176° (lit. 172°), *-4'-diphenylamide*, m.p. 147—148°, *-4-chlorodiphenyl-2'-*, m.p. 136—138°, and *-4'-amide*, m.p. 145—145·5°. R. S. C.

**Phenylthiocarbamides. Triad N·C·S. I. Aniline thiocyanate.** K. KRALL and R. D. GUPTA. **II. Action of hydrolytic agents on phenylthiocarbamide.** **III. Action of nitrous acid on phenylthiocarbamide.** S. MEHTA and H. KRALL (J. Indian Chem. Soc., 1935, 12, 629—634, 635—639, 640—646).—I. *NH<sub>2</sub>Ph, HCNS*, best obtained from *NH<sub>2</sub>Ph* and *HCNS* in *Et<sub>2</sub>O*, at above 85° rapidly gives *NHPh·CS·NH<sub>2</sub>* (I) with evolution of heat. Yields never exceed 80—83%, suggesting an equilibrium, but the reverse change cannot be realised. (I) is best obtained (80%) from dry *NH<sub>2</sub>Ph, HCl* and *KCNS* at 110° (1 hr.).

II. At high  $p_H$  (I) hydrolyses in *H<sub>2</sub>O* mainly to *H<sub>2</sub>S* and *NHPh·CN*, at low  $p_H$  mainly to *NH<sub>3</sub>* and *PhNCS*, with minor amounts of hydrolysis to *HCNS* and *NH<sub>2</sub>Ph*. The last reaction predominates at about  $p_H$  7. This indicates dynamic isomerism.

III. With aq. *NaNO<sub>2</sub>-HCl* (I) reacts mainly thus:  $2(I) + 4HNO_2 \rightarrow C_{14}H_{12}N_4S$  (A., 1889, 872) +  $4NO + 4H_2O + S$ , but with aq. *NaNO<sub>2</sub>-AcOH* mainly thus:  $(I) + HNO_2 \rightarrow PhNCS + N_2 + H_2O$ . Traces of *PhNC* are also formed. R. S. C.

**Organic reagent for cadmium.**—See this vol., 179.

**Mechanism of amination by sodamide. Preparation of substituted amidines.** A. KIRSSANOV and J. IVASTCHENKO (Bull. Soc. chim., 1935, [v], 2, 2109—2124).—As anticipated from their containing a C·N group (cf. *C<sub>2</sub>H<sub>5</sub>N*), arylideneamines react with *NaNH<sub>2</sub>* in hot *PhMe*. *CHPh·NHPh* (I) affords *NH<sub>2</sub>Ph* (12%), *phenylbenzamidine* (II) (19·6%), *NHPh·CH<sub>2</sub>Ph* (III) [14·9%; Ac derivative, m.p. 56—57° (lit. an oil)], and 2 : 4 : 5-triphenylglyoxaline (IV) (12·8%), the probable mechanism being:  $(I) \rightarrow NH_2·CHPh·NPhNa \rightarrow NaH + NH_2·CPh·NPh$  (V)  $\rightarrow NHNa·CPh·NPh$  (VI) +  $H_2$ ;  $(I) + H_2 \rightarrow (III)$ ;  $(V) + NaNH_2 \rightarrow (VI) + NH_3$ ;  $3(I) + 2NH_3 \rightarrow 3NH_2Ph + 2 : 4 : 5$ -triphenyl-4 : 5-dihydroglyoxaline  $\rightarrow$  (IV). *CHPh·N·C<sub>6</sub>H<sub>4</sub>Me-p* affords *p-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub>* (22·6%), *p-tolylbenzamidine* (22·6%), *p-C<sub>6</sub>H<sub>4</sub>Me·NH·CH<sub>2</sub>Ph* (20·6%), m.p. 19—20° (lit. an oil; NO-derivative, m.p. 45·5—48·5°), and the glyoxaline derivative (12·3%). Piperonylideneaniline gives 13% of the amidine, m.p. 138—139°, and a little piperonylaniline, m.p. 78—79°. This is the best way of preparing benzamidines. R. S. C.

**Preparation and geometrical isomerism of asymmetric quaternary ammonium salts and betaine hydrates derived therefrom.** (MME.) M. GUAISNET-PILAUD (Ann. Chim., 1935, [xi], 4, 365—448).—The geometrical isomerism of the betaine hydrates previously described (A., 1930, 1563;

1933, 387, 948, 1004; 1934, 763) depends on the order of introduction of the hydrocarbon radicals. The quaternary iodide from *NPhEt·CH<sub>2</sub>·CO<sub>2</sub>Me* (*Et* ester, b.p. 149—150°/13 mm. and 150—151°/15 mm.) and *MeI* with *Ag<sub>2</sub>O* gives a new stable betaine monohydrate, m.p. 104° {*platinichloride*, m.p. 169°; *picrate*, 186° (decomp.) (not identical with the *picrate*, m.p. 158·5° [decomp.], of the betaine hydrates previously described), *d-camphorsulphonate*, m.p. 190—191° (decomp.); *oxalate*, m.p. 173° (decomp.) and 134·5°}. Similarly the quaternary iodide from *Et phenylpropylaminoacetate*, b.p. 161—162°/14 mm. (from *NHPhMe* with *CH<sub>2</sub>I·CO<sub>2</sub>Et* or *CH<sub>2</sub>Cl·CO<sub>2</sub>Et*), yields a stable betaine monohydrate, m.p. 108° {*picrate*, m.p. 189° (decomp.) [not identical with the *picrate*, m.p. 127° (decomp.)], of the betaine hydrates previously described, of which the following new derivatives are described: *platinichloride*, m.p. 198° (decomp.); *oxalate*, m.p. 208°; *d-camphorsulphonate*, m.p. 227—227·5° (decomp.)}. Similarly the quaternary iodide from *CH<sub>2</sub>I·CO<sub>2</sub>Et* and *p-C<sub>6</sub>H<sub>4</sub>Me·NEt<sub>2</sub>* gives a single betaine hydrate, *cryst.* (*oxalate*, m.p. 138—139°). The following were also prepared from the appropriate bases and iodides: *NPhMe<sub>2</sub>EtI*, m.p. 134° (decomp.); *p-C<sub>6</sub>H<sub>4</sub>Me·NEt<sub>2</sub>I*, m.p. 156·5°. *NHMePr picrate* has m.p. 105·5—106°. F. R. G.

**Decomposition of *p*-iodoaniline.** F. B. DAINS, R. Q. BREWSTER, and J. A. DAVIS (J. Amer. Chem. Soc., 1935, 57, 2326—2327).—Purified *p-C<sub>6</sub>H<sub>4</sub>I·NH<sub>2</sub>* in a glass-stoppered bottle in diffused light after 3 years had decomposed giving traces of *I* and *NH<sub>2</sub>Ph* and much 2 : 4-*C<sub>6</sub>H<sub>3</sub>I<sub>2</sub>·NH<sub>2</sub>*. R. S. C.

**Identification of carboxylic acids as salts of benzylamine and  $\alpha$ -phenylethylamine.** C. A. BUEHLER, L. CARSON, and R. EDDES (J. Amer. Chem. Soc., 1935, 57, 2181—2182).—The following *CH<sub>2</sub>Ph·NH<sub>2</sub>* and *CHMePh·NH<sub>2</sub>* salts, respectively, are prepared. Formate, m.p. 95—97°, 97·8—98·8°, acetate, m.p. 96·3—97·1°, 92·1—92·5°, propionate, m.p. 46·7—47·5°, b.p. 120—121°/42 mm., *n*-butyrate, b.p. 109—110°/15 mm., 125°/37 mm., *n*-valerate, m.p. 51·7—52·7°, —, chloro-, m.p. 119·9—120·9°, 94·7—95·5°, and trichloro-acetate, m.p. 120·3—121·3°, —, phenylacetate, m.p. 122—122·6°, 115·6—116·4°, *o*-toluate, m.p. 145·4—146·4°, 113·3—113·7°, cinnamate, m.p. 135·9—136·3°, 144·5—145·1°, benzoate, m.p. 127·2—128·4°, 140·6—141·2°, *o*-, m.p. 112—113·2°, 111—111·6°, *m*-, m.p. 135·9—136·5°, 168·9—169·4°, and *p*-amino-, m.p. 197·6—198·6°, 185·6—186·4°, *m*-bromo-, m.p. 160·6—161·2°, 148·9—149·7°, *o*-, m.p. 150·5—151·5°, 130·9—131·9°, *m*-, m.p. 149·2—149·8°, 144·7—145·3°, and *p*-chloro-, m.p. 160·3—161·3°, 152·3—153·3°, *m*-, m.p. 188·2—189·6°, 137·2—138·4°, and *p*-hydroxy-, m.p. 216·2—217·2°, 199·3—199·9°, *o*-, m.p. 121·5—122·3°, 158·7—159·1°, *m*-, m.p. 113·1—114·1°, 131·4—131·8°, and *p*-methoxy-, m.p. 144·8—145·6°, 132·8—133·4°, *o*-, m.p. 143·9—145·7°, 129·5—130·1°, *m*-, m.p. 174·9—175·5°, 170·7—171·1°, and *p*-nitrobenzoate, m.p. 197·3—198·9°, 195·8—196·8°, and salicylate, m.p. 94·3—95·5°, 102·1—102·9°. The low-melting salts can be distilled in vac. The aliphatic salts are hygroscopic. M.p. are corr.

R. S. C.

**Organic sulphur-nitrogen linking. VIII.** E. RIESZ (Monatsh., 1935, 67, 51—62; cf. A., 1928, 748; 1931, 1295).—The product obtained from 4'-chloro-2'-nitrophenylthiol-*p*-dimethylaminoanilide (I) and  $K_2Cr_2O_7$  is 4'-chloro-2'-nitrophenyl-*p*-benzoquinonethioliminedimethylimmonium dichromate. (I) and  $PbO_2$  in  $Et_2O$  or  $CHCl_3$  give a green solution, which slowly oxidises, contains 1 H less than (I) (quinol titration), and is fairly stable at  $-60^\circ$ . The green solution is considered to contain a free radical. Complete reduction of this green solution with quinol gives a mixture containing 4 : 4'-dichloro-2 : 2'-dinitrodiphenyl disulphide, also obtained by I with a substance,  $C_8H_{10}N_2I_2$  (*p*-di-iodoaminodimethyl-aniline or *p*-benzoquinoneiodoiminedimethylimmonium iodide). Formulæ are discussed for the product, m.p.  $260-270^\circ$  (decomp.), about  $C_{48}H_{20-28}O_{12}N_{10}S_6Cl_6$ , obtained from *s*-di-4'-chloro-2'-nitrophenylthiol-*p*-phenylenediamine and  $CrO_3$ . R. S. C.

**Molecular compounds of benzidine with certain phenols and acids.** K. HRYNAKOWSKI, H. STASZEWSKI, and M. SZMYTÓWNA (Rocz. Chem., 1935, 15, 391—399).—The m.-p. diagrams suggest compounds of 1 mol. of benzidine with 2 of resorcinol, m.p.  $137^\circ$ , with 2 of salicylic acid, m.p.  $156^\circ$ , with 1 of quinol, m.p.  $130^\circ$ , with 3 of  $BzOH$ , m.p.  $108^\circ$ , and with 1 of  $\alpha$ -, m.p.  $97^\circ$ , and  $\beta$ -naphthol, m.p.  $178^\circ$ . The composition of the eutectic mixture can be predicted by Kordes' formula only when one of the components is present in large excess. R. T.

**as-Diphenylhydrazine (supercooling of the liquid and mol. form).** D. VORLÄNDER and C. BITTINS (Ber., 1935, 68, [B], 2269—2276).—The ease with which liquid  $NPh_2 \cdot NH_2$  can be supercooled is not due to the presence of impurities, but is a consequence of its mol. dissymmetry. Examination of its derivatives shows that the relationships between supercooling and constitution are not simple. Treatment of  $NPh_2 \cdot NH_2$  with  $CH_2Br \cdot CO_2Et$  in boiling  $EtOH$  or of  $NPh_2 \cdot NH_2 \cdot HCl$  and  $NaOEt$  with  $CH_2Br \cdot CO_2Na$  followed by hydrolysis of the ester with  $NaOH$  yields *Na as-diphenylhydrazinoacetate* (I),  $NPh_2 \cdot NH \cdot CH_2 \cdot CO_2Na$ , anhyd., decomp.  $180-185^\circ$  (+ $5H_2O$ ), m.p. about  $80^\circ$  (corresponding *Pb*,  $Hg^{II}$ , *Mg*, *Ca*, *Sr*, *Zn*, *Cd*, *Al*, and *K* salts). The free acid (hydrochloride) gives a moss-green solution in conc.  $H_2SO_4$  at  $15-20^\circ$ , whereas non-oxidising acids ( $PhSO_3H$ ;  $p-C_6H_4Me \cdot SO_3H$ ) give no colour.  $HClO_4$  gives a colourless salt. With  $PbO_2$  in  $AcOH$  it gives an immediate dark red and subsequently a comparatively stable reddish-violet colour. *N-Acetyl-as-diphenylhydrazinoacetic acid*, m.p.  $185^\circ$  (corr.  $+2^\circ$ ), from (I) and  $Ac_2O$  at about  $95^\circ$ , is converted by  $HNO_3$  (d 1.4) in  $AcOH$  at  $15-20^\circ$  into a  $(NO_2)_2$ -derivative, m.p. about  $210^\circ$  (decomp.). *as-Diphenylhydrazinoacet-as-diphenylhydrazide*, m.p.  $214^\circ$  (decomp.) after softening [hydrochloride; *Ac* derivative, m.p.  $229^\circ$  (corr.)], and non-cryst.  $\alpha$ -*diphenylhydrazino- $\beta$ - $\beta$ -diacetic acid* are obtained as by-products in the prep. of (I) under different conditions.  $NPh_2 \cdot NHAc$  and sodio-*p*-nitrophenylnitrosoamine afford  $\alpha$ -*acetyl- $\beta$ -phenyl- $\beta$ -p-nitrobenzeneazophenylhydrazine*, m.p.  $246^\circ$  (corr.);  $\alpha$ -*acetyl- $\beta$ -phenyl- $\beta$ -p-nitrobenzeneazophenylhydrazinoacetic acid* is described. H. W.

**Ammonium character of tetra-arylhidrazines. II. Ammonium character of tetra(dimethylaminophenyl)hydrazine.** E. WEITZ and L. MÜLLER (Ber., 1935, 68, [B], 2306—2312; cf. A., 1927, 658).—The action of  $ClO_2$  on tetra-(*p*-dimethylaminophenyl)hydrazine (I) gives a green product which is difficult to purify. (I) and tritolylammonium perchlorate in  $PhBr$  afford the perchlorate of Bindschedler's green,  $NMe_2 \cdot C_6H_4 \cdot N : C_6H_4 \cdot NMe_2 \cdot ClO_4$  (obtained also from the chloride and  $NaClO_4$ ), and identified by its absorption spectrum and titration with di-*N*-ethylcollidinium (II)  $[C_5H_2Me_2 \cdot NEt]_2$ , of which 2 equivs. are required, and the resulting yellow solution, when shaken with  $H_2O$  gives tetramethyldiaminodiphenylnitrosoamine, m.p.  $155^\circ$  (decomp.). The change is explained by dissociation of (I) into the free radicals and reaction of the latter in the valency-tautomeric form. By use of a deficiency of Cl or Br, (I) can be transformed into the chloride or bromide of Bindschedler's green, but the analogous use of I leads to a (?) periodide,  $RI + RI(I_2)$ , identical with the "hydriodide" of Drew *et al.* (A., 1933, 516), which has not the constitution assigned by the latter authors. Reduction of the salts with (II) leads to (I); the change can also be effected with Zn dust or  $Na-Hg$  in  $C_5H_5N$  or  $COMe_2$ , but the product has not yet been isolated in substance. During the reduction of the salts or of the more readily available  $ZnCl_2$  or  $ZnBr_2$  compounds, particularly with Zn dust in  $C_5H_5N$ , intermediate dark blue solutions are formed, from which by addition of  $Et_2O$  the substance  $[N(C_6H_4 \cdot NMe_2)_2]_2Cl, ZnCl_2$  and the analogous bromide are pptd. The corresponding iodide decomposed during its prep. 1 mol. of the blue salts requires 0.5 mol. of (II), and (I) is identified in the reddish-yellow solutions in the usual manner. H. W.

**Diazo-compounds. VI. Action of dilute solutions of alkalis on diazonium salts.** G. ODDO and INDOVINA (Gazzetta, 1935, 65, 939—993).—Earlier work is reviewed. Velocity of decomp. of diazo-compounds from chloro-, bromo-, iodo-, and nitroanilines, and aminophenols (*o*-, *m*-, and *p*- in each case), *o*- and *p*-anisidine, *m*-aminobenzaldehyde, *o*-, *m*-, and *p*-aminobenzoic acids, and their *Et* esters, in presence of 0.4, 0.8, and 1.6%  $NaOH$  at room temp. (from  $11^\circ$  to  $26^\circ$ ) is measured by  $N_2$  evolved, resin pptd., and stable diazotates and isodiazotates remaining; the results are tabulated and discussed. Increased  $[NaOH]$  normally increases stability, but accelerates decomp. of the esters. Diazotates derived from *o*- and *p*-nitroaniline are stable; those from *m*- and *p*-aminobenzoic acid are stable in presence of 1.2%  $NaOH$ ; those from *m*-iodo- and *m*-nitro-aniline decompose rapidly. Partial transformation into isodiazotates is normal, except where  $\cdot OH$  or  $\cdot CO_2H$  is the substituent. Decomp. graphs correspond approx. with unimol. reactions. The slow decomp. of isodiazotates is also studied. The industrial application of the decomp. tables is suggested. E. W. W.

**Reaction of titanium tetrachloride with phenol.**—See this vol., 173.

**Halogenation of phenolsulphonic acids in nitrobenzene.** R. C. HUSTON and A. H. NELEY (J. Amer. Chem. Soc., 1935, 57, 2176—2178).— $PhOH$  is

sulphonated and the product dissolved in  $\text{PhNO}_2$ , treated successively with oleum at  $< 10^\circ$  and Br in  $\text{PhNO}_2$ , and hydrolysed with steam at  $200^\circ$ . There are formed 10.4—46.5% of  $o\text{-C}_6\text{H}_4\text{Br}\cdot\text{OH}$  (I), 72.7—9.5% of  $2:6\text{-C}_6\text{H}_3\text{Br}_2\cdot\text{OH}$  (II), and a little  $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{OH}$ , the proportion of (I) and (II) depending on the amount of  $\text{H}_2\text{SO}_4$  used in the sulphonation. Similar procedure leads to 17—72% of  $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{OH}$ , and 70.3—24% of  $2:6\text{-C}_6\text{H}_3\text{Cl}_2\cdot\text{OH}$ , 3-bromo-*o*-cresol, b.p.  $206\text{--}207^\circ/740$  mm. (60%) and 3:5-dibromo-*o*-cresol (13%), 3-chloro- (30%), and 3:5-dichloro-*o*-cresol (12%), 2-bromo-*m*-cresol, m.p.  $61\text{--}62^\circ$  (7—40%), with ? some 4-Br- and 0—8% of 6-Br-compound, m.p.  $58\text{--}59.5^\circ$  (*p*-toluenesulphonate, m.p.  $112\text{--}113^\circ$ ), and 0—23% of 2:4-dibromo-*m*-cresol, m.p.  $36.5\text{--}37.5^\circ$  (*p*-toluenesulphonate, m.p.  $131\text{--}132^\circ$ ), and 2-chloro-, 2:6-, m.p.  $58\text{--}59^\circ$ , b.p.  $75\text{--}80^\circ/4$  mm.,  $235\text{--}236^\circ/745$  mm., and 2:4-dichloro-*m*-cresol, b.p.  $80\text{--}85^\circ/4$  mm.,  $239.5\text{--}240.5^\circ/745$  mm. The structures of the cresol derivatives are proved by their prep. also from nitrocresols and/or their chlorination to substances prepared from nitrocresols.

R. S. C.

**Pyrolysis of allyl-*p*-phenetidine.** F. L. CARNAHAN (J. Amer. Chem. Soc., 1935, 57, 2210—2211).—*N*-Allyl-*p*-phenetidine (prep. by  $\text{C}_3\text{H}_5\text{Br}$ , b.p.  $134.5^\circ/10$  mm.,  $265^\circ$  (decomp.)/ $745$  mm. ( $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2$  derivative, m.p.  $81^\circ$ , also obtained from *p*-toluenesulphon-*p*-phenetidine and  $\text{C}_3\text{H}_5\text{Br}$  in *N*-KOH), when refluxed, gives *p*-OEt- $\text{C}_6\text{H}_4\cdot\text{NH}_2$  (0.465 mol.),  $\text{C}_3\text{H}_6$  (0.4 mol.), and resin (equiv. to 0.447 mol.), but no  $\text{H}_2$  or quinoline derivative, probably by the following steps:  $\text{NHR}\cdot\text{C}_6\text{H}_5$  (I)  $\rightarrow$   $\text{NHR}\cdot\text{C}_3\text{H}_5$ ; (I) +  $2\text{NHR}\cdot\text{C}_6\text{H}_5 \rightarrow 2\text{NH}_2\text{R} + \text{NR}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2$  (II); (I) +  $2\text{C}_3\text{H}_5 \rightarrow$  (II) +  $2\text{C}_3\text{H}_6$ ; (II)  $\rightarrow$  resin.

R. S. C.

**Acetylation of dulcin (*p*-phenetylcarbamide).** C. ALBERTI (Gazzetta, 1935, 65, 922—925).—*p*-Phenetylcarbamide (I) with  $\text{AcCl}\text{-C}_5\text{H}_5\text{N}$  yields the Ac derivative (II);  $\text{Ac}_2\text{O}\text{-NaOH}$  gives only a small quantity of (II), phenacetin (III) and  $\text{NH}_2\text{Ac}$  being formed.  $\text{AcOH}$  also decomposes (I), but yields, with (III), di-*p*-phenetylcarbamide and  $\text{NH}_4$  salts. Mechanisms are suggested (cf. A., 1928, 485).

E. W. W.

**Pyrolysis of *p*-phenetylcarbamide and of acetyl-*p*-phenetylcarbamide.** C. ALBERTI (Gazzetta, 1935, 65, 926—929).—*p*-Phenetylcarbamide (I) and its Ac derivative (II) are decomposed at about  $250^\circ$  to give di-*p*-phenetylcarbamide, with, from (I),  $\text{NH}_3$  and some  $\text{HNCO}$ , and, from (II),  $\text{CO}_2$ ,  $\text{NH}_2\text{Ac}$ ,  $\text{MeCN}$ , and some  $\text{NH}_3$ .

E. W. W.

**Derivatives of diphenyl ether.** L. C. RAIFORD and J. C. ZIMMERMANN (Amer. J. Pharm., 1935, 107, 472—475; cf. A., 1926, 1242; 1930, 767).—The product obtained by nitration of 2':4'-dibromo-4-nitrodiphenyl ether is 2':4'-dibromo-2:4:5'-trinitrodiphenyl ether, which, with piperidine (I), gives 2:4-dinitrophenylpiperidine and 2:4-dibromo-5-nitrophenol. (I) also reacts with other substituted diphenyl ethers giving substituted phenols.

W. McC.

**Preparation of [alkyl]aminoisopropylidene-pyrocatechols.** J. DRUEY (Bull. Soc. chim., 1935, [v], 2, 2261—2263).—Addition of  $\text{P}_2\text{O}_5$  to  $o\text{-C}_6\text{H}_3(\text{OH})_2$  in  $\text{CH}_2\text{Cl}\cdot\text{COMe}$  gives a 40—45% yield of the chloroiso-

propylidene derivative, b.p.  $104\text{--}105^\circ/13$  mm. ( $\text{NO}_2$ -derivative, m.p.  $80\text{--}81^\circ$ ), the Cl of which is inactive, but with the appropriate base in  $\text{C}_6\text{H}_6$  at  $180^\circ$  gives slowly poor yields of dimethylamino-, b.p.  $115\text{--}117^\circ/22$  mm. [hydrochloride, m.p.  $217\text{--}218^\circ$  (decomp.)], diethylamino-, b.p.  $123\text{--}125^\circ/20$  mm. (hydrochloride, an oil), and piperidino-isopropylidene-pyrocatechol, b.p.  $150\text{--}151^\circ/17$  mm. [hydrochloride, m.p.  $224\text{--}225^\circ$  (decomp.)].

R. S. C.

**Syntheses of pharmacologically important amines. XI. Preparation of arylethylamines and arylethanolamines by catalytic reduction.** K. KINDLER, W. PESCHKE, and E. BRANDT (Ber., 1935, 68, [B], 2241—2245).—The interference of intermediate products in the smooth reduction of ketoximes and cyanohydrins to amines is avoided by the gradual addition of a solution of the substance to be reduced to the catalyst charged with H. In the prep. of primary amines, conc.  $\text{H}_2\text{SO}_4$  is added. The following examples are cited:  $\text{CPhMe}\cdot\text{N}\cdot\text{OH}$  to  $\text{CHPhMe}\cdot\text{NH}_2$  (yield 83%); *p*-methylacetophenone-oxime to  $\alpha\text{-p-tolylethylamine}$  (80% yield) [hydrochloride, m.p.  $167\text{--}168^\circ$ ]; *p*-methoxyacetophenone-oxime to  $\alpha\text{-p-anisylethylamine}$  (yield 70%); 3:4-dimethoxybenzaldehyde cyanohydrin to  $\beta\text{-hydroxy-}\beta\text{-3:4-dimethoxyphenylethylamine}$  (yield 47%) and  $\beta\text{-3:4-dimethoxyphenylethylamine}$  (yield 18%); 3:4-diethoxybenzaldehyde cyanohydrin to  $\beta\text{-hydroxy-}\beta\text{-3:4-diethoxyphenylethylamine}$ , m.p.  $93^\circ$  (picrate, m.p.  $171^\circ$ ), and  $\beta\text{-3:4-diethoxyphenylethylamine}$ ; 3-methoxy-4-ethoxybenzaldehyde cyanohydrin to  $\beta\text{-hydroxy-}\beta\text{-3-methoxy-4-ethoxyphenylethylamine}$ , m.p.  $110^\circ$  (picrate, m.p.  $161^\circ$ ); hydrochloride, m.p.  $176^\circ$ ), and  $\beta\text{-3-methoxy-4-ethoxyphenylethylamine}$ , b.p.  $155^\circ/10$  mm. (picrate, m.p.  $182^\circ$ ).

H. W.

**Preparation of resorcinol methyl ether. Correction.** B. B. DEY (J. Indian Chem. Soc., 1935, 12, 685—686).—Details given for the prep. of this ether (A., 1935, 211) are corr.

R. S. C.

**M.p. of resorcinol.** N. A. VALJASCHKO and M. M. SCHTSCHERBAK (Ukrain. Chem. J., 1935, 10, 305—310).—The f.p. is  $109.8^\circ$  and the m.p.  $110.2^\circ$ .

R. T.

**Alkyl ethers of  $\beta\beta$ -di-*p*-hydroxyphenylpropane. I. Dialkyl ethers.** G. R. YOHE and J. F. VITCHA (J. Amer. Chem. Soc., 1935, 57, 2259—2260).—An excess of  $\text{CMe}_2(\text{C}_6\text{H}_4\cdot\text{OH})_2$  with alkyl sulphates in aq.  $\text{NaOH}$  or  $\text{KOH}$  gives mono- and di-alkyl ethers; the  $\text{Me}_2$ , m.p.  $59\text{--}61.5^\circ$ , b.p.  $190^\circ/5$  mm.,  $\text{Et}_2$ , m.p.  $49\text{--}50^\circ$ ,  $\text{Pr}^n_2$ , b.p.  $200\text{--}202^\circ/3$  mm.,  $\text{Bu}^n_2$ , m.p.  $20^\circ$ , b.p.  $212\text{--}213^\circ/3$  mm., and di-*n*-amyl ether, m.p.  $34.5\text{--}35.5^\circ$ , b.p.  $225\text{--}230^\circ/3$  mm., are described.  $n\text{-C}_8\text{H}_{17}\cdot\text{OH}$  and  $\text{SOCl}_2$  are kept for 1 week and neutralised with  $\text{NaOH}$ , and the resulting mixture is then used for alkylation.

R. S. C.

**Production of dihydroxydihydroanthracene from anthracene.**—See this vol., 234.

**Molecular rearrangement of *N*-thiolanilides. II.** M. L. MOORE and T. B. JOHNSON (J. Amer. Chem. Soc., 1935, 57, 2234—2236; cf. A., 1935, 1359).—With hot  $\text{KOH}\text{-EtOH}$  *N*-thiolanilides give *o*-thiolodiphenylamines, possibly by way of *o*-aminodiphenyl sulphides. *N*-*o*-Nitrophenylthiol-anilide, -*o*-



and *p*-toluidide thus give *o*-nitro-*o'*-thiol-, *2'*-thiol-5'-methyl-, and *2'*-thiol-3'-methyl-diphenylamine (Na salts, which with MeI-EtOH give the *Me* ethers, m.p. 98°, 94°, and 84—85°), respectively. R. S. C.

**Spatial configurations of 1:2-dialkylcyclopentan-1-ols.** G. CHIURDOGLU (Bull. Soc. chim. Belg., 1935, 44, 527—550).—2-Methylcyclopentanone (cf. A., 1926, 1238) [*phenylhydrazone*, decomp. at 60°; Et 2-methylcyclopentanonecarboxylate (*phenylhydrazone*, decomp. at 68°)] is converted into 1:2-dimethylcyclopentan-1-ol, which when fractionally distilled yields *trans*- and *cis*-isomerides, m.p. 27.3° and 28.9°, respectively. The former is the more quickly converted into 1:2-dimethyl- $\Delta^1$ -cyclopentene by 85% HCO<sub>2</sub>H, and is the more rapidly reduced (H<sub>2</sub>-Pt), and has OH and H in *trans*-positions (cf. A., 1931, 954; 1932, 844). *trans*-Isomerides with different pairs of 1:2-substituents are reduced (H<sub>2</sub>-Pt) at the same rate as are the *cis*-, and suffer no change in configuration prior to reduction. Reduction of either isomeride gives mainly a *trans*-product. A mechanism is suggested to explain these reactions. J. L. D.

**Addition of chloroform and bromoform to *p*-chlorobenzaldehyde.** J. W. HOWARD (J. Amer. Chem. Soc., 1935, 57, 2317—2318).—*p*-C<sub>6</sub>H<sub>4</sub>Cl-CHO, CHCl<sub>3</sub>, and KOH give *p*-chlorophenyltrichloromethylcarbinol, b.p. 187—188°/26 mm. (*acetate*, m.p. 120—121°; *propionate*, m.p. 71—72°; *benzoate*, m.p. 128—129°). *p*-Chlorophenyltribromomethylcarbinol, m.p. 90—91°, is similarly obtained. R. S. C.

**Chemical study of the functions of ephedrine.**  
I. New method for its determination. J. A. SANCHEZ (J. Pharm. Chim., 1935, [viii], 22, 489—496).—The formation from ephedrine of BzOH by alkaline oxidation, PhCHO and an amine by the action of KMnO<sub>4</sub> or NaOCl, and nitrosoephedrine by the action of NaNO<sub>2</sub> and HCl, the reactions of the diazo-compound, and the products of pyrogenic decomp. are described. Ephedrine reacts with NaOH and I giving CHI<sub>3</sub>, and a method of determination based on this sensitive reaction is proposed. E. H. S.

**Phenanthrene series. IX. Amino-alcohols derived from 1:2:3:4-tetrahydrophenanthrene.** E. MOSETTIG and A. BURGER (J. Amer. Chem. Soc., 1935, 57, 2189—2192; cf. A., 1935, 973).—Some phenanthrene derivatives carrying a basic and OH group in one reduced ring have analgesic action comparable with that of codeine. 2-Bromo-1-keto-1:2:3:4-tetrahydrophenanthrene (I), m.p. 84—85° [by bromination of the 1-CO-compound (II) in dry Et<sub>2</sub>O containing a little HCl], with the appropriate base affords 2-dimethylamino- [hydrochloride, m.p. 219—220 (decomp.)], 2-diethylamino- (III) (hydrochloride, m.p. 156° after sintering at 138°), 2-piperidino-, m.p. 138—140° [hydrochloride, m.p. 236—238° (decomp.)], and 2-1':2':3':4'-tetrahydroisoquinolino-1-keto-1:2:3:4-tetrahydrophenanthrene [hydrochloride, m.p. 226—227° (decomp.)], hydrogenated (PtO<sub>2</sub>) in MeOH to 2-dimethylamino-, m.p. 105—108° after sintering at 95°, sublimes at 90°/high vac. [hydrochloride, m.p. 223—224° (decomp.)]; Bz derivative, m.p. 179—181° (decomp.)], 2-diethylamino-, m.p. 70—72° after softening at 60°, b.p. 90°/high vac. [hydro-

chloride, m.p. 221—223° (decomp.); 3:5-C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>2</sub>CO derivative, m.p. 209—211° (decomp.)], 2-piperidino-, m.p. 121—126°, sublimes at 105°/high vac. [hydrochloride, m.p. 259° (decomp.)], and 2-1':2':3':4'-tetrahydroisoquinolino-1-hydroxy-1:2:3:4-tetrahydrophenanthrene, m.p. 155—156° [hydrochloride, m.p. 227° (decomp.)]. As by-products to (III) are obtained 1-hydroxyphenanthrene (IV), m.p. 153°, and an additive 1:1-compound (V), m.p. 119°, of (IV) and (I). (IV) is also obtained from (I) and NPhEt<sub>2</sub> or (II) and Se at 295°. (V) with hot KOH-EtOH gives (I) and (IV), from which it is obtained by crystallisation of the 1:1 mixture, and with semicarbazide gives the semicarbazone of (I). 3-Bromo-4-keto-1:2:3:4-tetrahydrophenanthrene (VI), m.p. 104—105°, leads similarly to (a) 3-dimethylamino- [hydrochloride, m.p. 208—210° (decomp.)], 3-diethylamino- [hydrochloride, m.p. 184—185° (decomp.)]; picrate, m.p. 173—174° (decomp.)], 3-piperidino- [hydrochloride, m.p. 248—250° (decomp.)], and 3-1':2':3':4'-tetrahydroisoquinolino-4-keto-1:2:3:4-tetrahydrophenanthrene [hydrochloride, m.p. 164—166° (decomp.)]; perchlorate, m.p. 210° (decomp.)], (b) 3-dimethylamino- [hydrochloride, m.p. 230° (decomp.)]; Bz derivative, m.p. 89—90° (hydrochloride, m.p. 177—178°)], 3-diethylamino- [hydrochloride, m.p. 239.5—240° (decomp.)]; picrate, m.p. 206—208° (decomp.)]; Bz derivative [picrate, m.p. 173—174° (decomp.)]; 3:5-C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>2</sub>CO derivative, m.p. 216—217.5°, 3-piperidino- [hydrochloride, m.p. 246—247° (decomp.)]; Bz derivative [hydrochloride, m.p. 181—182° (decomp.)], and 3-1':2':3':4'-tetrahydroisoquinolino-4-hydroxy-1:2:3:4-tetrahydrophenanthrene [hydrochloride, m.p. 230—231° (decomp.)], (c) 4-hydroxyphenanthrene, m.p. 113°, and the 1:1 additive compound thereof with (VI), m.p. 107°. M.p. are corr. R. S. C.

**Adrenal cortex. I. Fractionation of hormone concentrates. II. Isolation of physiologically inactive crystalline compounds from active extracts.**—See this vol., 115.

**Auxochromes and resonance.** C. R. BURY (J. Amer. Chem. Soc., 1935, 57, 2115—2117).—The theory that dyes owe their colour to resonance and that the function of auxochromes is to render resonance possible is applied to various classes of dyes.

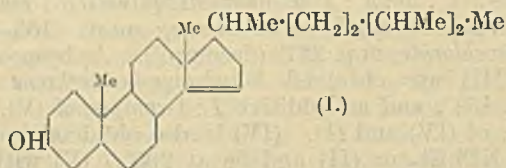
R. S. C.

**Carotenoid origin of cholesterol.** W. M. D. BRYANT (Chem. and Ind., 1935, 1082—1083).—Arguments are presented in favour of the carotenoid origin of sterols and related compounds. Sterols containing "extra" Me and Et groups may arise by degradation of more highly cyclised carotenoids.

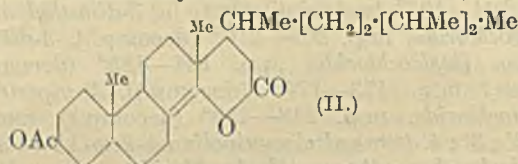
R. S. C.

**Constitution of  $\beta$ -ergosterol.** F. LAUCH (Z. physiol. Chem., 1935, 237, 236—246).—Ozonisation of  $\alpha$ -ergostenyl acetate suspended in AcOH and reductive fission of the ozonides yields at least two isomeric dehydroergosterols, m.p. (indef.) 132°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -56.1° in CHCl<sub>3</sub>, and m.p. 114—116°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -81.0° in CHCl<sub>3</sub>, respectively. O<sub>3</sub> functions therefore as a dehydrogenating agent, and its action affords no evidence of the position of the double linking in  $\alpha$ -ergosterol. Similar ozonisation of  $\beta$ -ergostenyl acetate

affords the keto-alcohol,  $C_{16}H_{26}O_2$ , and its acetate (I) described by Achtermann (A., 1934, 1000) and an aldehyde containing 12 C (*semicarbazone*,  $C_{13}H_{25}ON_2$ , m.p. 125–131°). Since dehydrogenation of (I) by



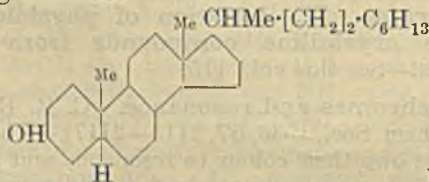
Se at 320° yields 2-methylphenanthrene, the above constitution is established for  $\beta$ -ergosterol. This view is confirmed by the isolation from the acidic products of ozonolysis of an *enol-lactone* (II), m.p.



144°,  $[\alpha]_D^{25} +92.5^\circ$  in  $CHCl_3$ , which is insol. in cold alkali and is transformed with some difficulty by boiling KOH–MeOH followed by acid into the corresponding non-cryst. acid, transformed by  $CH_2N_2$  into the Me ester,  $C_{29}H_{50}O_4$ , m.p. (indef.) 51°,  $[\alpha]_D^{25} -24.6^\circ$  in  $CHCl_3$  (acetate,  $C_{31}H_{52}O_5$ , m.p. 124°,  $[\alpha]_D^{25} +14.3^\circ$  in  $CHCl_3$ ). H. W.

Sexual hormones and related substances.

VI. Degradation of acetylepidihydrocinchol to  $\beta$ -3-hydroxynorallocholanolic acid or to 3-hydroxynorallocholanolic acid. W. DIRSCHERL (Z. physiol. Chem., 1935, 237, 268–272).—Dihydrocinchol acetate has been oxidised to  $\beta$ -3-hydroxynorallocholanolic acid and epidihydrocinchol acetate to 3-hydroxynorallocholanolic acid. Dihydrocinchol has therefore the following structure.

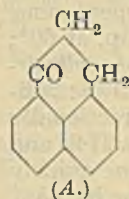


Action of hydrogen sulphide on acid chlorides.

VI. Hydrogen sulphide and 3:4-dimethylbenzoyl chloride. L. SZFERL and L. OZIEBŁO (Rocz. Chem., 1935, 15, 408–413).—1:2:4- $C_6H_3Me_2Br$  and Mg yield a Grignard compound, converted by  $CO_2$  into 3:4-dimethylbenzoic acid, the chloride of which, when treated with  $H_2S$  in boiling xylene, yields chiefly *di*-3:4-dimethylbenzoyl sulphide (I), m.p. 119–120°, together with some disulphide, m.p. 127–128°. (I) is converted by EtOH– $NH_3$  into 3:4-dimethylbenzamide, m.p. 111–113.5°, and  $NH_4$  3:4-dimethylthiobenzoate. R. T.

Preparation of  $\beta$ -1-naphthylpropionic,  $\beta$ -2-naphthylpropionic, and  $\beta$ -2-tetrahydronaphthylpropionic acids. Synthesis of dihydrophenalene and 5:6-tetrahydrobenzindan-1-one. G. DARZENS and A. LÉVY (Compt. rend., 1935, 201, 902–904).—1-Naphthylmethyl- and 2-tetrahydronaphthyl-

methyl-malonic esters (cf. A., 1935, 975) when hydrolysed and decarboxylated at 175–195° afford  $\beta$ -1-naphthylpropionic, m.p. 156° [amide, m.p. 133°; Me ester, b.p. 162°/2 mm.; chloride (I), m.p. 26°] (cf. A., 1922, i, 740), and  $\beta$ -2-tetrahydronaphthylpropionic acid, m.p. 127° [amide, m.p. 133°; Me ester, b.p. 183°/15 mm.; chloride (II), b.p. 162°/2 mm.], respectively; the Me ester of the latter with S or Se gives  $\beta$ -2-naphthylpropionic acid. (I) in  $PhNO_2$  containing  $AlCl_3$  gives 7:8-dihydrophenal-9-one (*perinaphthindanone*) (A, annexed). Similarly, (II) affords 5:6-tetrahydrobenzindan-1-one, m.p. 47° (oxime, m.p. 224°), which when oxidised ( $HNO_3$ ) gives 1:2:4:5- $C_6H_2(CO_2H)_4$ .



J. L. D.

Apparent cases of liquid-crystal formation in *p*-alkoxybenzoic acids. B. JONES (J.C.S., 1935, 1874).—The following acids, prepared by interaction of *p*-OH- $C_6H_4$ - $CO_2H$  (1 mol.) and the alkyl iodide (2 mol.) in presence of NaOH (1 mol.; 1 hr.; 100°), show liquid crystal formation (the recorded temp. are the transition point and the true m.p.): *p*-*n*-amyloxy- (122°, 148°); *n*-hexyloxy- (105°, 150°); *n*-heptyloxy- (91°, 145°); *n*-octyloxy- (100°, 145°); *cetyloxy-benzoic acid* (99°, 131°). The corresponding *m*-series does not show this formation. F. N. W.

Condensation of phenylglyoxyanilide with acetone, ethyl phenylacetate, and ethyl malonate. J. V. SCUDI and H. G. LINDWALL (J. Amer. Chem. Soc., 1935, 57, 2302–2303).— $NHPh$ -COBz (I),  $COMe_2$ , and 5 drops of  $NH_2Et_2$  at room temp. give  $\alpha$ -hydroxy- $\gamma$ -keto- $\alpha$ -phenyl-*n*-valerianilide, m.p. 137–138° [*phenylhydrazone*, m.p. 174–175° (decomp.); decomposed by hot aq. alkali into the starting products], which with more (I) gives  $\alpha\alpha'$ -dihydroxy- $\gamma$ -keto- $\alpha\alpha'$ -diphenylpimeldianilide, m.p. 171–172°.  $CH_2Ph$ - $CO_2Et$  (I), and a little  $NH_2Et_2$  give slowly diphenylmaleinanil, m.p. 178–179°, reduced by  $Na_2S_2O_4$  to  $\alpha\alpha'$ -diphenylsuccinanil.  $CH_2(CO_2Et)_2$  and (I) give *Et* $\beta$ -carbonanilido- $\beta$ -phenylpropane- $\alpha\alpha\gamma\gamma$ -tetracarboxylate, m.p. 107–108°, which, when distilled/25 mm., affords EtOH,  $CH_2(CO_2Et)_2$ , and  $\alpha$ -carbethoxyphenylmaleinanilide, m.p. 111°, reduced ( $Na_2S_2O_4$ ) to  $\alpha$ -carbethoxy- $\alpha'$ -phenylsuccinanil, m.p. 104–105°, which with conc. HCl gives phenylsuccinanil. R. S. C.

Walden inversion reactions of the *p*-toluenesulphonic and *p*-toluenesulphonic esters of ethyl *d*- $\beta$ -hydroxy- $\beta$ -phenylpropionate. J. KENYON, H. PHILLIPS, and G. R. SHUTT (J.C.S., 1935, 1663–1668).—*dl*- $\beta$ -Hydroxy- $\beta$ -phenylpropionic acid may be resolved through the brucine salt (cf. J.C.S., 1910, 97, 121). The *d*-acid with EtOH–HCl yields the Et *d*-(+)-ester (I), which with EtI,  $Ag_2O$ , and anhyd.  $Et_2O$  yields Et *d*-(+)- $\beta$ -ethoxy- $\beta$ -phenylpropionate (II), b.p. 85–86°/0.1 mm.,  $\alpha_{441}^{17} +7.59^\circ$ , but with  $K-Et_2O$  gives chiefly  $CHPh$ : $CH$ : $CO_2Et$ . (I) when heated with  $Ac_2O$  or anhyd.  $HCO_2H$  affords, respectively, the corresponding *d*-(+)- $\beta$ -acetoxy- and *d*-(+)- $\beta$ -formoxy-derivatives, also obtained when Et *d*-(+)- $\beta$ -*p*-toluenesulphinoxy- $\beta$ -phenylpropionate (III),  $\alpha_{5461}^{17} +3.77^\circ$  [an undistillable oil prepared from (I), *p*-toluenesulphonyl chloride, and  $C_5H_5N$ ], is heated respectively with  $AcOH$ - $Ac_2O$  and anhyd.  $HCO_2H$ .

(III) when treated with  $\text{Cl}_2\text{-CHCl}_3$ ,  $\text{Cl}_2\text{-H}_2\text{O}$ ,  $\text{ICl}$ , or  $\text{HOCl}$  gives *Et l(-)- $\beta$ -chloro- $\beta$ -phenylpropionate* (IV); with  $\text{HOCl}$  some *Et l(-)- $\beta$ -hydroxy- $\beta$ -phenylpropionate* (V) was also formed. Similarly, (III) with  $\text{Br-CHCl}_3$  yields *Et l(-)- $\beta$ -bromo- $\beta$ -phenylpropionate*, b.p.  $82\text{--}84^\circ / < 0.1 \text{ mm.}$ ,  $\alpha_{\text{D}}^{17} -1.43^\circ$ ; with  $\text{Br-H}_2\text{O}$  some (V) was also formed. (III) with  $\text{CNCl}$  in light petroleum yields *Et l(-)- $\beta$ -cyano- $\beta$ -phenylpropionate*, b.p.  $78\text{--}79^\circ / < 0.1 \text{ mm.}$ ,  $\alpha_{\text{D}}^{17} -0.53^\circ$ . (III) when treated with  $\text{HNO}_2$  (in a freezing mixture) yields (V), and when refluxed in  $\text{EtOH}$  with  $\text{N}_2$  yields *Et l(-)- $\beta$ -ethoxy- $\beta$ -phenylpropionate*, but with  $\text{EtOH-K}_2\text{CO}_3\text{-N}_2$  yields mainly optically pure (I), no trace of the  $\text{OEt}$ -derivative being obtained. (III) when refluxed in  $\text{N}_2$  with  $\text{LiCl}$ ,  $\text{K}_2\text{CO}_3$ , and  $\text{EtOH}$  yields (II). (III) is oxidised by  $\text{H}_2\text{O}_2$  to *Et d(+)- $\beta$ -p-toluensulphonoxy- $\beta$ -phenylpropionate* (VI), which when refluxed with  $\text{K}_2\text{CO}_3\text{-EtOH}$  affords (V), but with  $\text{K}_2\text{CO}_3$ ,  $\text{LiCl}$ , and  $\text{EtOH}$  yields (II). (II) is also obtained when (IV) is refluxed with  $\text{K}_2\text{CO}_3\text{-EtOH}$ . (VI) with  $\text{AcOH}$  affords *Et l(-)- $\beta$ -acetoxy- $\beta$ -phenylpropionate*, also obtained together with some *Et (-)- $\beta$ -chloro- $\beta$ -phenylpropionate* (VII) from (VI),  $\text{Ac}_2\text{O}$ , and  $\text{LiCl}$ . (I) when treated in  $\text{Et}_2\text{O}$  with  $\text{PCl}_5$ ,  $\text{PCl}_5\text{-C}_5\text{H}_5\text{N}$ ,  $\text{PCl}_3$ ,  $\text{PCl}_3\text{-C}_5\text{H}_5\text{N}$ , or  $\text{SOCl}_2\text{-C}_5\text{H}_5\text{N}$  yields (VII), but with  $\text{SOCl}_2$  alone yields *Et (+)- $\beta$ -chloro- $\beta$ -phenylpropionate* (cf. A., 1930, 598; 1931, 480). (I) with  $\text{PBr}_3$  or  $\text{PBr}_3\text{-C}_5\text{H}_5\text{N}$  yields *Et (-)- $\beta$ -bromo- $\beta$ -phenylpropionate*. Reasons are given for the relative configurations ascribed to the various products obtained from (I). H. G. M.

**4-Hydroxy-3-phenylbenzoic acid.** K. H. SLOTTA and A. E. NOLD (Ber., 1935, 68, [B], 2226—2231).—Treatment of *K 2-hydroxy-3-phenylbenzoate* with  $\text{CO}_2$  under pressure at  $220\text{--}230^\circ$  does not cause migration of  $\text{CO}_2\text{K}$ . When similarly treated *o-C}\_6\text{H}\_4\text{Ph-OH}* acquires  $2 \text{ CO}_2\text{H}$ . Treatment of *o-C}\_6\text{H}\_4\text{Ph-OH}* with anhyd.  $\text{HCN}$  and  $\text{AlCl}_3$  in  $\text{C}_6\text{H}_6$  gives an aldehyde, m.p.  $69\text{--}71.3^\circ$  (*p-nitrophenylhydrazone*, m.p.  $229^\circ$ ), scarcely oxidised by  $\text{KMnO}_4$ ,  $\text{KOBz}$ , or  $\text{H}_2\text{O}_2$ , but converted by molten  $\text{KOH}$  into *2-hydroxy-3-phenylbenzoic acid*. [ $3:4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CHO}$  is oxidised by  $\text{H}_2\text{O}_2$  in alkaline solution much more readily than  $3:4\text{-C}_6\text{H}_3(\text{OMe})_2\text{CHO}$  or  $3:4\text{-C}_6\text{H}_3(\text{OEt})_2\text{CHO}$ ]. Oxidation of *4-acetyl-2-phenylphenol* with  $\text{CaOCl}_2$  gives amorphous, smearable products. *o-C}\_6\text{H}\_4\text{Ph-OH}* is transformed by  $\text{NaOH}$  and  $\text{Me}_2\text{SO}_4$  into *o-phenylanisole*, b.p.  $146\text{--}149^\circ / 11 \text{ mm.}$ , which with  $\text{AlCl}_3$  and  $\text{AcCl}$  in  $\text{CS}_2$  affords *4-acetyl-2-phenylanisole*, m.p.  $91.5\text{--}92^\circ$ , in 92% yield. The latter compound is oxidised by  $\text{CaOCl}_2$  to *4-methoxy-3-phenylbenzoic acid*, m.p.  $217.5\text{--}218^\circ$ , demethylated by  $\text{HBr}$  ( $d$  1.49) in boiling  $\text{AcOH}$  to *4-hydroxy-3-phenylbenzoic acid*, m.p.  $148\text{--}149^\circ$  after softening at  $142^\circ$ . *Me*, m.p.  $91\text{--}92^\circ$ , and *Et*, m.p.  $62\text{--}63^\circ$ , *4-methoxy-3-phenylbenzoate* and *Et*, m.p.  $112\text{--}114^\circ$ , and *Pr*<sup>a</sup>, m.p.  $92\text{--}93^\circ$ , or m.p.  $104^\circ$ , *4-hydroxy-3-phenylbenzoate* are described.

H. W.

**Diaryls and their derivatives. VI. Oxidation of  $\beta$ -naphthol-3-carboxylic acid. VII. Oxidation of 2-hydroxyanthracene.** I. S. JOFFE (J. Gen. Chem. Russ., 1935, 5, 1205—1209, 1210—1212).—VI [with I. Z. SMOLJANITZKAJA].  $\beta$ -Naphthol-3-carboxylic acid (I) in boiling  $\text{H}_2\text{O}$  or aq.  $\text{NaOH}$  and excess

of  $\text{FeCl}_3$  yield chiefly *2:2'-dihydroxy-1:1'-dinaphthyl-3:3'-dicarboxylic acid* (II), together with some *1-chloro- $\beta$ -naphthol-3-carboxylic acid*, which is the chief product when the reaction mixture is acid. (I) and  $\text{CuO}$  in  $\text{PhNO}_2$  ( $210\text{--}220^\circ$ ; 6 hr.) yield (II), which is converted into *dinaphthylene dioxide* by more prolonged treatment with  $\text{CuO}$  at  $300^\circ$ . (II) is not further oxidised by  $\text{FeCl}_3$ . The  $\text{Pb}$  salt of (II) undergoes a perylene condensation when heated with  $\text{AlCl}_3$  ( $160^\circ$ ; 1 hr.) to yield an acid orange dye, probably *1:12-dihydroxyperylene-2-carboxylic acid*, m.p.  $> 330^\circ$ , converted into the *quinone* by  $\text{CrO}_3$ , and into perylene by distillation from  $\text{Zn}$  dust.

VII. *2-Hydroxyanthracene* in boiling  $\text{AcOH}$  and conc. aq.  $\text{FeCl}_3$  yield *2-hydroxy-1:1':9:2'-dianthriline oxide* (*Ac* derivative, m.p.  $247\text{--}250^\circ$ ), converted at  $> 200^\circ$  into an unidentified product (probably the dioxide). R. T.

**Preparation of  $\beta$ -naphthol-3-carboxylic acid.** P. P. KARPUCHIN and I. E. CHUSID (Ukrain. Chem. J., 1935, 10, 375—391).—At  $< 110^\circ$   $\beta\text{-C}_{10}\text{H}_7\text{ONa}$  and  $\text{CO}_2$  yield  $\text{C}_{10}\text{H}_7\text{O}\cdot\text{CO}_2\text{Na}$ , which at  $< 180^\circ$  is transformed into  $\beta$ -naphthol-1-carboxylic acid (I), converted into the *2:3-isomeride* (II) at  $180\text{--}225^\circ$ . (II) can be obtained in good yield, and of high purity, by adding aq.  $\text{NaOH}$  to  $\beta\text{-C}_{10}\text{H}_7\text{OH}$  (III), drying at  $< \text{atm.}$  pressure at  $\approx 200^\circ$ , and treating the product with  $\text{CO}_2$  at  $225\text{--}260^\circ / 2\text{--}50 \text{ atm.}$  Methods involving esters of (I) as intermediates, or involving carboxylation in liquid media in presence of excess of (III), do not give as good results as the above. R. T.

**Condensation of aldehydes with malonic acid in presence of organic bases. IV. Piperonal.** T. A. VAHIDY and K. C. PANDYA (Proc. Indian Acad. Sci., 1935, 2, A, 402—405).—The condensation of piperonal (I) with  $\text{CH}_2(\text{CO}_2\text{H})_2$  (II) in presence of any of 19 different bases gives varying yields of piperonylacrylic acid, new m.p.  $242^\circ$ , also obtained from (I) and (II) alone, heated at  $100^\circ$  for 18 hr. E. W. W.

**Preparation of isovalerylsalicylic acid.** J. MILIOTIS (Bull. Soc. chim., 1935, [v], 2, 2134—2135).—This acid (prep. by  $\text{Bu}^t\text{COCl}$ ) has m.p.  $95^\circ$  (cf. A., 1911, i, 53; 1928, 1005). R. S. C.

**Action of selenium on acid anhydrides.** W. THIELE and G. TRAUTMANN (Ber., 1935, 68, [B], 2245—2247).—In connexion with the production of *2:3-C}\_{10}\text{H}\_6\text{Me}\_2* by dehydrogenation of vitamin-maleic anhydride adducts it is shown that *1-C}\_{10}\text{H}\_7\text{Me}* is formed by the action of  $\text{Se}$  on *1:8-C}\_{10}\text{H}\_6(\text{CO})\_2\text{O}* at  $320\text{--}330^\circ$  in presence of cholesterol or from *1:8-C}\_{10}\text{H}\_6(\text{CO})\_2\text{O}* in absence of a  $\text{H}$  donor. Similarly, *2:3-C}\_{10}\text{H}\_6(\text{CO})\_2\text{O}* in presence of *p-cyclohexylphenol* yields *2:3-C}\_{10}\text{H}\_6\text{Me}\_2*. H. W.

**Synthesis of phenanthrene and hydrophenanthrene derivatives. II. Hydrocarbon synthesis.** L. F. FIESER and E. B. HERSHBERG (J. Amer. Chem. Soc., 1935, 57, 2192—2196; cf. A., 1935, 1358).—*3:4-Dihydronaphthalene-1:2-dicarboxylic anhydride* (I), *1:2-dihydrophenanthrene-3:4-dicarboxylic anhydride*, and the *3:4-dihydro-1:2-anhydride* analogue of the latter add dienes slowly but smoothly; the acids derived from the product obtained from (I) have the expected properties; decarboxylation is

difficult and leads to mixed hydrophenanthrenes from which phenanthrene and its derivatives are readily obtained. (I) and  $(\text{CH}_2\cdot\text{CMe})_2$  at  $100^\circ$  (20–25 hr.) give 2:3-dimethyl-1:4:9:10:11:12-hexahydrophenanthrene-11:12-dicarboxylic anhydride (II), forms, m.p.  $75\text{--}76^\circ$  (unstable) and  $95\text{--}96^\circ$ , b.p.  $175\text{--}185^\circ/1$  mm., respectively, hydrolysed by hot 6*N*-KOH to the corresponding acid (III), m.p.  $176\text{--}177^\circ$  with loss of  $\text{H}_2\text{O}$ , or by hot KOH-MeOH to the *H Me* ester (IV), m.p.  $157\text{--}159^\circ$  with loss of MeOH; (III) or (IV) with  $\text{CH}_2\text{N}_2$  gives the  $\text{Me}_2$  ester, m.p.  $93\text{--}94^\circ$ , which is resistant to hydrolysis and with 50% KOH gives (III). Hydrogenation ( $\text{PtO}_2$ ) of (II) in AcOH gives 2:3-dimethyl-1:2:3:4:9:10:11:12-octahydrophenanthrene-11:12-dicarboxylic anhydride, m.p.  $117\text{--}118^\circ$ , hydrolysed to the acid (V),  $+0\cdot5\text{C}_6\text{H}_6$ , m.p.  $183\text{--}184^\circ$ . (III) or (V) with Se undergo reversal of the Diels-Alder reaction and S leads to a S-containing compound, m.p.  $73\text{--}74^\circ$ . (III) or (IV) with KOH at  $325\text{--}350^\circ$  and then at  $400\text{--}420^\circ$  gives much  $\text{H}_2$ - and a mixture of (?)  $\text{H}_4$ - and  $\text{H}_8$ -hydrocarbons; the  $\text{K}_2$  salt of (III) gives CO and a similar mixture; these mixtures with Se give 2:3-dimethylphenanthrene, m.p.  $79\text{--}80^\circ$  [picrate, m.p.  $146\text{--}147^\circ$ ; styphnate, m.p.  $147\text{--}148^\circ$ ; quinone, m.p.  $237\cdot5\text{--}238\cdot5^\circ$  (quinoxaline derivative, m.p.  $208\text{--}209^\circ$ ); cf. lit.; oxidised to pyromellitic acid]. (I) and  $(\text{CH}_2\cdot\text{CH})_2$  give 1:4:9:10:11:12-hexahydrophenanthrene-11:12-dicarboxylic anhydride, m.p.  $83\cdot5\text{--}84^\circ$ , b.p.  $160\text{--}170^\circ/1$  mm., converted by KOH into a hexahydrophenanthrene, b.p.  $179\text{--}180^\circ/23$  mm. (no picrate), which with Se gives 86% of phenanthrene. Similarly are obtained in dioxan 4:5-dimethyl-1:2:3:6:15:16-hexahydrochrysene-15:16-dicarboxylic anhydride, m.p.  $196\text{--}196\cdot5^\circ$ , 1:4:9:10:11:12-hexahydro-5:6-benzphenanthrene-11:12-dicarboxylic anhydride, m.p.  $161\cdot5\text{--}162^\circ$ , and 2:3-dimethyl-1:4:9:10:11:12-hexahydro-5:6-benzphenanthrene-11:12-dicarboxylic anhydride, m.p.  $128\text{--}128\cdot5^\circ$ . R. S. C.

**Derivatives of diphenyl ether. II. Monoaldehydes.** G. LOCK and F. H. KEMPTER (Monatsh., 1935, 67, 24–35; cf. A., 1930, 767).—*p*- $\text{OPh}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  (amide, m.p.  $130^\circ$ ) with  $\text{PCl}_5$  or  $\text{SOCl}_2$  gives, after distillation, xanthone, but the crude chloride, prep. by  $\text{SOCl}_2$ , when hydrogenated, affords *o*-phenoxybenzaldehyde (I), b.p.  $172\text{--}174^\circ$  (phenylhydrazone, m.p.  $147^\circ$ ; anil, m.p.  $66\text{--}67^\circ$ ), which is also obtained from *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  by reduction and diazotisation of the crude unstable  $\text{NH}_2$ -aldehyde; with  $\text{Ag}_2\text{O}$  (I) gives the acid and with 50% KOH at  $60^\circ$  also *o*-phenoxybenzyl alcohol, an oil. *m*-Phenoxybenzaldehyde, b.p.  $175\text{--}176^\circ/11$  mm., m.p.  $13\text{--}14^\circ$  (NaHSO<sub>3</sub> compound; phenylhydrazone, m.p.  $102^\circ$ ; oxime, m.p.  $45\text{--}46^\circ$ ; semicarbazone, m.p.  $217^\circ$ ; anil, m.p.  $58^\circ$ ), is obtained by  $\text{HCl}\text{--}\text{SnCl}_2\text{--}\text{Et}_2\text{O}$ -reduction of the nitrile, b.p.  $179\text{--}180^\circ/13$  mm. (prep. from the  $\text{NO}_2$ -compound), and by hydrogenation of *m*-phenoxybenzoyl chloride, b.p.  $174\text{--}175^\circ/12$  mm. (corresponding amide, m.p.  $127^\circ$ ), and is converted by boiling 50% aq. KOH into *m*-phenoxybenzyl alcohol, m.p.  $71^\circ$ , and *m*-phenoxybenzyl cinnamic acid, m.p.  $115^\circ$ . *p*-Phenoxybenzaldehyde, m.p.  $24\cdot5\text{--}25^\circ$ , b.p.  $185^\circ/14$  mm. (anil, m.p.  $48\text{--}49^\circ$ ),

is obtained by hydrogenation of the acid chloride and leads to *p*-phenoxybenzyl alcohol, m.p.  $53^\circ$ , and *p*-phenoxybenzyl cinnamic acid, m.p.  $155^\circ$ . Temp. are corr. R. S. C.

**Pharmacology of phenanthrene derivatives.** V.—See this vol., 106.

**Action of oxidising agents on cyclobutylamine.** N. J. DEMJANOV and Z. I. SCHUJKINA (J. Gen. Chem. Russ., 1935, 5, 1213–1225).—*cyclo*Butylamine (I) is oxidised by  $\text{CrO}_3$ ,  $\text{CrO}_3\text{--H}_2\text{SO}_4$ ,  $\text{KMnO}_4$ , and  $\text{O}_2\text{--O}_3$  to cyclobutanone (II), by the stages: (I)  $\rightarrow$  *cyclo*butylhydroxylamine  $\rightarrow$  (II) ketoxime  $\rightarrow$  (II)+ $\text{NH}_2\text{OH}$ ; (II)  $\rightarrow$  succinic acid (III);  $\text{NH}_2\text{OH} \rightarrow \text{HNO}_2$ . In presence of atm.  $\text{O}_2$  and Cu, or of  $\text{O}_3$  and osmic anhydride (IV) the process consists of (I)  $\rightarrow$  (II)+ $\text{NH}_3$ ; (II)  $\rightarrow$  (III). The highest yields of (II) (25%) are obtained using (IV) (12 hr. at room temp.). R. T.

**Multiplanar cyclohexane rings.** R. D. DESAI and R. F. HUNTER (Nature, 1935, 136, 953–954; A., 1935, 1495).—In a further examination of the Sachse-Mohr hypothesis the condensation of the cyanohydrins of the methylcyclohexanones with arylamines has been investigated. The formation of two, but never  $>$  two, isomeric cyanoarylamino-methylcyclohexanes has been observed in certain cases. L. S. T.

**Reduction of oximes.** (MLLE.) A. WOHL (Bull. Soc. chim., 1935, [v], 2, 2135–2140).—Hydrogenation ( $\text{PtO}_2$ ) of  $\text{CHPh}\cdot\text{NOH}$  in 95% EtOH gives  $\text{NH}(\text{CH}_2\text{Ph})_2$  (absorption spectrum given), but ketoximes [ $\text{CPhMe}\cdot\text{N}\cdot\text{OH}$  (I) and  $\text{CMe}_2\text{Bu}\cdot\text{CPh}\cdot\text{N}\cdot\text{OH}$  (II)] are unaffected. (I) and (II) are not reduced by  $\text{CaCl}_2\text{--Zn}$  in hot EtOH. With Al-Hg in moist  $\text{Et}_2\text{O}$  (I) gives  $\text{CHPhMe}\cdot\text{OH}$ , but (II) is unaffected owing to its isooxime structure. R. S. C.

**Chemistry and spectroscopy of oxime acetates.** (MLLE.) A. WOHL (Bull. Soc. chim., 1935, [v], 2, 2140–2143).—The absorption spectra of oximes and their acetates are very similar. With Al-Hg  $\text{CPhMe}\cdot\text{N}\cdot\text{OAc}$  gives  $\text{CHPhMe}\cdot\text{OH}$  and  $\text{CHPhMe}\cdot\text{OAc}$ , m.p.  $75^\circ$  (lit.  $65^\circ$ ), but *Ph*  $\alpha$ -dimethylbutyl ketoxime acetate, b.p.  $172\text{--}173^\circ/17$  mm., is not affected owing to its isooxime structure. R. S. C.

**Reaction of ketens with Grignard reagents.** C. D. HURD, R. N. JONES, and F. H. BLUNCK (J. Amer. Chem. Soc., 1935, 57, 2033–2036).—The ester groups of  $\text{CO}_2\text{Et}\cdot\text{CET}\cdot\text{CO}$  (I) and  $\text{CO}_2\text{Et}\cdot\text{CET}\cdot\left\langle\begin{array}{c} \text{CO} \\ \text{CO} \end{array}\right\rangle\text{CET}\cdot\text{CO}_2\text{Et}$  (II) do not react with  $\text{MgEtBr}$  or  $\text{MgPhBr}$ .  $\text{CHEt}(\text{CO}_2\text{Et})_2$  (prep. in 62% yield by EtBr or 80–88% yield by  $\text{Et}_2\text{SO}_4$ ) with  $\text{P}_2\text{O}_5$  at  $180\text{--}200^\circ$  gives 23% of (I), b.p.  $45\text{--}55^\circ/11\text{--}12$  mm., stable at  $-78^\circ$ , and a little  $\text{Pr}\cdot\text{CO}_2\text{H}$ . (I) reacts with  $\text{NH}_2\text{Ph}$ , but not with  $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$  in  $\text{C}_6\text{H}_6$ . (I) and  $\text{MgPhBr}$  (1 mol.) give, after hydrolysis,  $\text{CHBzEt}\cdot\text{CO}_2\text{Et}$  (III), but with 3 mols. of  $\text{MgPhBr}$  affords also some *Ph*  $\alpha$ -benzhydrylidenepropyl ketone (IV), m.p.  $126\text{--}127^\circ$  (with  $\text{O}_3$  gives  $\text{COPh}_2$ ,  $\text{BzOH}$ , and  $\text{EtCO}_2\text{H}$ ), probably arising thus: (I)  $\rightarrow \text{CO}_2\text{Et}\cdot\text{CET}\cdot\text{CPh}\cdot\text{OMgBr} + \text{MgPhBr} \rightarrow \text{CBzEt}\cdot\text{CPh}\cdot\text{OMgBr} \rightarrow (+\text{MgPhBr} + \text{H}_2\text{O})$  (IV). (II) and  $\text{MgPhBr}$  lead to (III). (I) and  $\text{MgEtBr}$  (1 mol.) give a product, hydrolysed to  $\text{COEt}\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$  (V)

and pyrolysed at 200—300° to EtBr and an unsaturated substance, b.p. 100—110°. (III) and MgEtBr give (V). R. S. C.

**Attempted resolution of oximes.** (MILLER.) A. WOHL (Bull. Soc. chim., 1935, [v], 2, 2163—2168).—CPhEt·N·ONa, CH<sub>2</sub>Cl·CO<sub>2</sub>H, and NaOAc in EtOH give *propiofenoneoxime O-glycollic acid ether*, m.p. 58°, which resembles the parent oxime in absorption. CMe<sub>2</sub>Bu·CPh·N·OH (I) gives similarly *Ph αα-dimethylbutyl ketoxime O-glycollic acid ether*, m.p. 70°, which, since it resembles (I) in absorption, has the *isooxime* structure, but could, nevertheless, not be resolved by alkaloids or moulds; the *brucine* salt has  $[\alpha]_D^{20} +15^\circ$ . (I) with NaOEt and CMe<sub>2</sub>Br·CO<sub>2</sub>Na in EtOH gives an ether, m.p. 135°, and in a second experiment an (?) isomeric ether, m.p. 79°. R. S. C.

**Ketones obtained by condensation of acetyl chloride with saturated hydrocarbons in presence of aluminium chloride.** C. D. NENTZESCU and G. G. VANTU (Bull. Soc. chim., 1935, [v], 2, 2209—2219).—cycloHexane (I), AcCl, and excess of AlCl<sub>3</sub> give only 2-acetyl-1-methylcyclopentane (II), but with less AlCl<sub>3</sub> some 2-acetyl-1-methyl-Δ<sup>1</sup>-cyclopentene (III) is also formed by the following steps: (I) ⇌ methylcyclopentane → 1-methyl-Δ<sup>1</sup>-cyclopentene → 1-chloro-2-acetyl-1-methylcyclopentane → HCl

+ (III) or  $\xrightarrow{+2H}$  HCl + (II). 1-Methylcyclopentane-2-carboxyl chloride (IV) gives by the Br-azide method 2-methylcyclopentanone and a little 1-methyl-Δ<sup>1</sup>-cyclopentene-2-carboxylic acid. (II) gives (Clemmensen) a mixture of 78.7% of *trans*- and 21.3% of *cis*-1-methyl-2-ethylcyclopentane, b.p. 121°/753 mm. 1-Methyl-2-α-hydroxyethylcyclopentane is dehydrated by the xanthate method to 2-ethylidene-1-methylcyclopentane, b.p. 123—124°, but H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> or KHSO<sub>4</sub> gives a mixture thereof with a little 1:3-dimethyl-Δ<sup>1</sup>-cyclohexene. (II) and PhCHO give 2-cinnamoyl-1-methylcyclopentane, b.p. 153°/4 mm. (*dibromide*, m.p. 107°). *Et* 1-methylcyclopentane-2-carboxylate, b.p. 179—180°, and Na-EtOH give 1-methylcyclopentyl-2-carbinol, b.p. 171—172°/758 mm., and thence the *bromide*, b.p. 65°/14 mm., 1:2-dimethylcyclopentane, b.p. 93—94°, and β-1-methylcyclopentyl-2-propionic acid, b.p. 147—148°/15 mm. (*chloride*, b.p. 98°/15 mm.; *amide*, m.p. 93°). Hydrogenation of (IV) gives 1-methylcyclopentane-2-aldehyde, b.p. 148—150° (*semicarbazone*, m.p. 121.5°). Physical data are given. R. S. C.

**Benzophenones from carboxylic acids.** H. P. NEWTON and P. H. GROGGINS (Ind. Eng. Chem., 1935, 27, 1397—1399; cf. A., 1935, 214).—Boiling PhCl (3—6 mols.) with *p*-C<sub>6</sub>H<sub>4</sub>Cl·CO<sub>2</sub>H (1 mol.) and AlCl<sub>3</sub> gives 4:4'-dichlorobenzophenone (>80%) and the 2:4'-isomeride. 4-Chloro- (82%), 4-chloro-4'-methyl- (81%), and 3:4-dichloro-benzophenone (79%) are prepared similarly. *p*-C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)<sub>2</sub> with PhCl and AlCl<sub>3</sub> at 175—180° gives 3:4-dichloro-4'-(3':4'-dichlorobenzoyl)benzophenone, m.p. 253° (*oxime*, m.p. 210°; *anilide*, m.p. 288°). Cu increases the yield of 4:4'-diaminobenzophenone (prepared from the Cl-compound and NH<sub>3</sub>) to a greater extent at 180° than at 200°; at the higher temp. the extent of non-catalytic amination increases greatly. KClO<sub>4</sub> sometimes exerts a beneficial effect. In the absence of

catalysts, 4'-chloro-4-aminobenzophenone is the main product. 4'-Amino-4-methylbenzophenone is prepared from the Cl-compound. J. L. D.

**Reversibility of the Friedel-Crafts condensation. Hydrogenation phenomena.** L. L. ALEXANDER, A. L. JACOBY, and R. C. FUSON (J. Amer. Chem. Soc., 1935, 57, 2208—2209).—In presence of AlCl<sub>3</sub> the reaction, C<sub>6</sub>H<sub>4</sub>X·CH:CHR (R=CO·R or Ph) + C<sub>6</sub>H<sub>6</sub> → (+2H) 2C<sub>6</sub>H<sub>5</sub>X + CH<sub>2</sub>Ph·CH<sub>2</sub>R, occurs, but the origin of the 2H is unknown. Thus Ph ββ-di-*p*-chlorophenylvinyl ketone and Ph ββ-diphenylvinyl ketone both give Ph ββ-diphenylethyl ketone, the latter perhaps by simple hydrogenation; similarly, ββ-diphenylvinyl Bu' ketone adds H<sub>2</sub>. β-*p*-Chlorophenylcinnamic acid, m.p. 168°, with C<sub>6</sub>H<sub>6</sub> and AlCl<sub>3</sub> gives ββ-diphenylpropionic acid; *pp'*-dichlorostilbene, (CH<sub>2</sub>Ph)<sub>2</sub>; stilbene, (CH<sub>2</sub>Ph)<sub>2</sub>; *p*-bromostilbene, (CH<sub>2</sub>Ph)<sub>2</sub>. *p*-C<sub>6</sub>H<sub>4</sub>Cl·COPh gives (Reformatsky) *Et* β-hydroxy-β-phenyl-β-*p*-chlorophenylpropionate, m.p. 79—80.5°, hydrolysed to the acid, m.p. 188.5—189° (decomp.), which with Ac<sub>2</sub>O-NaOAc yields (II). R. S. C.

**Chemistry and physiology of the androsterone group.** K. TSCHERNING (Angew. Chem., 1936, 49, 11—16).—A summary.

**Estrogenic activity of 1-keto-1:2:3:4-tetrahydrophenanthrene.** A. BUTENANDT and G. SCHRAMM (Ber., 1935, 68, [B], 2303; cf. this vol., 76).—The physiological activity of 1-keto-1:2:3:4-tetrahydrophenanthrene is confirmed (cf. Cook *et al.*, A., 1933, 323). H. W.

**Anhydrobismethone (bithon).** N. J. TOIVONEN, T. FJÄDER, and A. HEIKEL (Suomen Kem., 1935, 8, B, 32—33).—When boiled in aq. solution containing 0.2—0.5 mol. of NaOH and NH<sub>4</sub>Cl dimedon (I) (1:1-dimethylcyclohexane-3:5-dione) gives a condensation product, "bithon" (II), m.p. 155—157°, probably 4-(5'-keto-3':3'-dimethylcyclohexylidene)-1:1-dimethylcyclohexane-3:5-dione (*Ag* and *Cu* salts). (II) is also obtained by boiling a C<sub>6</sub>H<sub>6</sub> solution of (I) with K, or by heating (I) at 150—170°. Prolonged boiling of (II) in aq. solution partly reconverts it into (I). J. W. B.

**Self-condensation of acetylacetone.** A. HEIKEL (Suomen Kem., 1935, 8, B, 33—34).—When boiled with very dil. aq. NaOH, CH<sub>2</sub>Ac<sub>2</sub> affords 4-acetyl-*m*-5-xyleneol (von Auwers, A., 1915, i, 145; 1916, i, 34). A mechanism is suggested. J. W. B.

**Dimesityl diketones and their derivatives. II. Isomerism of βε-dibromo-αζ-dimesityl-αζ-hexanedione.** T. Y. KAO and Y. J. LO (J. Chinese Chem. Soc., 1935, 3, 355—357).—αζ-Dimesityl-αζ-hexanedione, m.p. 105—107° (lit. 102—103°), prepared from adipyl chloride and mesitylene, with Br affords two forms of βε-dibromo-αζ-dimesityl-αζ-hexanedione, m.p. 203—204° and 151—152°, respectively. The former is the chief product, and is also obtained when the latter is heated to 155°. H. G. M.

**Attempted preparation of vanilloylformic acid.** W. E. BARCH (J. Amer. Chem. Soc., 1935, 57, 2330).—Contrary to Mottern (A., 1934, 1354) this acid is not obtained from apocyanin (I), PhNO<sub>2</sub>, and alkali,

a result confirmed by other workers. (I) is best obtained by a low-temp. Fries isomerisation. R. S. C.

**Action of the Grignard reagent on fuchsones.** P. L. JULIAN and W. J. GIST (J. Amer. Chem. Soc., 1935, 57, 2030—2033).—1:6-Addition of MgMeI to fuchsones (I) is confirmed by methylation ( $\text{Me}_2\text{SO}_4\text{-NaOH}$ ) of the product to  $\alpha$ -diphenyl- $\alpha$ -p-anisylethane, m.p. 77°, also prepared from *p*-OMe- $\text{C}_6\text{H}_4\text{-CPh}_2\text{Cl}$  and MgMeI (3 mols.). 4-Benzoyl-1-naphthyl Me ether and MgPhBr give diphenyl-4-methoxynaphthyl-1-carbinol, m.p. 162°, converted by  $\text{SOCl}_2$  (not HCl in  $\text{Et}_2\text{O}$ ) into the chloride, m.p. 151°, which at 180—200° yields naphthafuchsones (II), m.p. 83°. 1:6-Addition of MgMeI to (II) occurs, but only in small amount; the product,  $\alpha$ -diphenyl- $\alpha$ -4-methoxynaphthyl-1-ethane, b.p. 220—230° (bath)/0.1 mm., m.p. 144°, is also obtained from OMe- $\text{C}_{10}\text{H}_6\text{-CPh}_2\text{Cl}$  and MgMeI. Anthrafuchsones (III) reacts with MgMeI, however, by 1:2-addition to give 10-benzhydrylidene-9-methyl-9:10-dihydroanthranol, m.p. 223°, oxidised by  $\text{CrO}_3$  to  $\text{COPh}_2$  and anthraquinone. Little or no 1:6-addition occurs with MgPhBr, (I) and (II) giving gums, whilst (III) yields 9-phenyl-10-benzhydrylidene-9:10-dihydroanthranol (IV), converted by HCl- $\text{Et}_2\text{O}$  into 9-chloro-9-phenyl-10-benzhydrylidene-9:10-dihydroanthracene, m.p. 220° (decomp. from 185°), reconverted into (IV) by moist  $\text{CaCO}_3$  in  $\text{COMe}_2$  and giving with Ag in  $\text{C}_6\text{H}_6$  followed by air an oily peroxide. The corresponding 9-Br-compound, m.p. 165°, differs from a Br-derivative (V), m.p. 143°, prepared from (?) 9-phenyl-10-benzhydrylanthracene (A., 1930, 903). Hydrolysis of (V) does not give (IV). R. S. C.

**Vat dyes of the benzanthrone series.** XIII, XIV, 6:6'- and 8:8'-Derivatives of isoviolanthrone. T. MAKI and Y. NAGAI (J. Soc. Chem. Ind. Japan, 1935, 38, 560—564B, 564—567B; cf. A., 1935, 1499).—XIII, 6:13-Dichlorobenzanthrone (I) when heated with KOH-PhOH-EtOH at 143° (1 hr.) yields chiefly 6:6'-dichloroisoviolanthrone (II) and a compound, insol. in alkaline  $\text{Na}_2\text{S}_2\text{O}_4$  and converted by hot conc.  $\text{H}_2\text{SO}_4$  into a vat dye (cf. B., 1934, 752); provisional structures are proposed for the two last-mentioned compounds. Some alkali- and AcOH-sol. products are also formed. (II), when heated repeatedly with KOH-MeOH at 180° (7 hr.), is converted into 6:6'-dimethoxyisoviolanthrone, whilst with KOH-PhOH at 200° it yields 6:6'-dihydroxyisoviolanthrone (*di-p*-nitrobenzoyl derivative). These compounds form vats with  $\text{Na}_2\text{S}_2\text{O}_4\text{-EtOH-H}_2\text{O}$  at 80°, and dye cotton various shades of blue.

XIV, 8:13-Dichlorobenzanthrone (III) with KOH-PhOH-EtOH at 143° (1 hr.) yields 8:8'-dihydroxyisoviolanthrone (*di-p*-nitrobenzoyl derivative; converted into Me<sub>2</sub> ether when boiled with  $\text{PhNO}_2\text{-Me}_2\text{SO}_4\text{-NaOH}$ ) and a "B-dyestuff" (cf. *loc. cit.*), sol. in alkaline  $\text{Na}_2\text{S}_2\text{O}_4$ , and converted by hot conc.  $\text{H}_2\text{SO}_4$  into a dark grey-violet vat dye. The Cl at position 8 is much more labile than at 6. The 8:8'-substitution has little bathochromic effect; the derivatives form vats more readily than the 6:6'-derivatives, and dye cotton violet. H. G. M.

**Grignard reagent of pinene hydrochloride.** Action of phthalic anhydride. R. BOUSSET (Bull.

Soc. chim., 1935, [v], 2, 2182—2187).—Pinene hydrochloride, m.p. 125—126°, under  $\text{H}_2$  gives a Grignard reagent, which with *o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$  (1 mol.) yields *d*-2-*o*-carboxybenzoylcamphane, m.p. 154°, with small amounts of another acid, m.p. 337° (rapid heating; sublimes if slowly heated), *d*-bornylene, and *dl*-camphane. R. S. C.

**Simultaneous formation of two diastereoisomeric alcohols in the action of organomagnesium derivatives on active camphenyl ketones.** M. TIFFENEAU, J. LÉVY, and E. DITZ (Bull. Soc. chim., 1935, [v], 2, 1855—1866; cf. A., 1931, 848).—Campholenamide with MgEtX and MgPhX yields respectively camphenyl ketone (I), b.p. 77°/2 mm.,  $[\alpha]_{\text{D}}^{19} + 27.5^\circ$ ,  $[\alpha]_{\text{D}}^{19} + 30.6^\circ$  (semicarbazone, m.p. 162°; oxime, b.p. 145°/14 mm.), and Ph camphenyl ketone (II), b.p. 121°/2 mm.,  $[\alpha]_{\text{D}}^{19} + 34.1^\circ$ ,  $[\alpha]_{\text{D}}^{20} + 38.6^\circ$  (semicarbazone, m.p. 167°; oxido-derivative, m.p. 64—65°,  $[\alpha]_{\text{D}}^{19} + 27.8^\circ$ ,  $[\alpha]_{\text{D}}^{19} + 31.0^\circ$ ) (cf. *loc. cit.*). (I) and MgPhX gives an oil which with  $\text{BzO}_2\text{H}$  yields mainly  $\alpha$ -oxidocamphenylphenylethylcarbinol, m.p. 98°,  $[\alpha]_{\text{D}}^{19} - 42.7^\circ$ ,  $[\alpha]_{\text{D}}^{19} - 51.7^\circ$ , and some of the  $\beta$ -isomeride, m.p. 133.5—134°,  $[\alpha]_{\text{D}}^{20} + 15.0^\circ$ ,  $[\alpha]_{\text{D}}^{20} + 17.5^\circ$  (cf. *loc. cit.*). By similar methods (II) and MgEtX give the same two products (with slightly higher  $[\alpha]$ ), the relative amounts being inverted. These results show that a  $\beta$ -asymmetric C with respect to the CO causes the double linking of the CO to react partly unsymmetrically. H. G. M.

**Camphor series.** I. D. C. SEN (J. Indian Chem. Soc., 1935, 12, 647—652).—*dl*- or *l*-Camphor, HCl, and  $\text{H}_2\text{S}$  in dry EtOH at 0° give 50% of *dl*-thiocamphor (I), m.p. 145°, but *d*-camphor gives *l*-thiocamphor, m.p. 146°,  $[\alpha]_{\text{D}}^{20} - 12^\circ$  in EtOH; (I) gives nearly quantitatively camphoroxime and the semicarbazone and phenylhydrazone, and with Zn-HCl-EtOH yields thioborneol, m.p. 120° (lit. 65°), converted by I into dibornyl disulphide, m.p. 198° (lit. 178°). R. S. C.

**6-Hydroxycamphor.** K. MIYAKE and M. WATANABE (Proc. Imp. Acad. Tokyo, 1935, 11, 322—323; cf. A., 1935, 754).—4-Carboxymethyl-2:3:3-trimethylcyclopentan-1-one at 280—300° affords 6-hydroxycamphor, m.p. 194—195° [dioxime, m.p. 241—242° (decomp.); disemicarbazone, m.p. 228°], which is hydrolysed to the original acid; its semicarbazone is reduced to camphane. J. L. D.

**Synthesis of "ketonopinone."** P. C. GUHA and K. GANAPATHI (Current Sci., 1935, 4, 312—313).—Mepinonate (cf. A., 1935, 975) with  $\text{CMe}_2$   $\begin{matrix} \text{CH-CO} \\ \text{CH}_2 \text{ CH}_2 \\ \text{CH-CO} \end{matrix}$  Na in PhMe or NaOMe in MeOH gives ketonopinone, m.p. 104° (*Cu* derivative, sinters 238°), which is (*A*), since with  $\text{Ba(OH)}_2$  it gives pinonic acid. F. R. G.

**Sulphur compounds of terpenes.** VI. Action of gold chloride on  $\text{C}_{10}\text{H}_{18}\text{S}$  ( $\geq \text{C}\cdot\text{S}\cdot\text{C} \leq$  type). VII. Action of gold chloride on  $\text{C}_{10}\text{H}_{18}\text{S}$  ( $\geq \text{C}\cdot\text{S}\cdot\text{C} \leq$  type) at higher temperature. VIII. Action of gold chloride on thioborneol and thiocamphor. IX. Action of gold chloride on various terpene sulphur compounds. A. NAKATSUCHI (J. Soc. Chem. Ind., Japan, 1935, 38, 511—512B, 512—513B, 617B, 617—618B).—VI.  $\text{C}_{10}\text{H}_{18}\text{S}$  (I) (cf. A., 1932,

1038) and  $\text{AuCl}_3\text{-H}_2\text{O}$  at  $30^\circ$  yield  $\text{C}_{10}\text{H}_{18}\text{S}\cdot\text{AuCl}_3$  (II), which on keeping with (I) and  $\text{H}_2\text{O}$  yields  $\text{C}_{10}\text{H}_{18}\text{S}\cdot\text{AuCl}$  (III),  $\text{C}_{10}\text{H}_{18}\text{SO}$ , and  $\text{HCl}$ . In the presence of excess of (I), the reaction between (I) and (II) is pseudo-minomol. (II) in  $\text{CHCl}_3$  at  $50^\circ$  is partly reduced to Au by limonene,  $\text{PhNO}_2$ , and amyl alcohol, but not by (I).

VII. (II) when heated at  $116\text{--}120^\circ$  (sealed vessel; 30 min.) is reduced to Au, but when (I) is present, the amount of Au formed is diminished. Similarly the amount of Au obtained when (III) is heated at  $120^\circ$  (sealed; 5 hr.) with  $\text{H}_2\text{O}$  is diminished by addition of (I), but is increased at  $109\text{--}111^\circ$  if colophony, ester gum, and ethylcellulose, but not organo-sulphur compounds, are also added. (III) with excess of (I) is stable at  $100^\circ$ , but at  $120^\circ$  decomposes rapidly giving Au and  $\text{Cl}_2$ . (I) and  $\text{AuCl}_3\text{-H}_2\text{O}$ , and (I) and (II) at  $110^\circ$  yield a compound, decomp.  $166^\circ$ , which contains 71.35% Au and 8.11% S.

VIII. A white Au compound,  $\text{C}_{10}\text{H}_{17}\text{SAu}$ , obtained from thioborneol, has m.p.  $194\text{--}195^\circ$ , decomp.  $206^\circ$ . Thiocamphor gives rise to a greenish-black amorphous compound, and a compound, m.p.  $179\text{--}180^\circ$  (decomp.).

IX. Similarly the S compound from  $\Delta^3$ -*p*-menthene (cf. A., 1933, 830) and  $\text{AuCl}_3\text{-H}_2\text{O}$  yield a Au compound,  $\text{C}_{10}\text{H}_{17}\text{SAu}$ , m.p.  $92^\circ$ , decomp.  $171^\circ$ , whilst the S compound from  $\Delta^{8(9)}$ -*p*-menthene and  $\text{AuCl}_3\text{-H}_2\text{O}$  yield a Au compound, decomp.  $169.5\text{--}171^\circ$ . The Au compounds obtained from the S compounds of  $\alpha$ -phellandrene, linaloolene, and linalyl acetate decompose at  $158\text{--}163^\circ$ ,  $161^\circ$ , and  $192\text{--}193^\circ$ , respectively. Most of the above Au compounds are sol. in certain org. solvents.

H. G. M.

Diterpene, "sciadopitene," from leaf- and wood-oil of *Sciadopitys verticillata*, S. and Z. I. Properties. K. NISHIDA and H. UOTA (J. Agric. Chem. Soc. Japan, 1935, 11, 489-494).—Fractional distillation/1-2 mm. affords approx. 5% of a diterpene, *sciadopitene*,  $\text{C}_{20}\text{H}_{32}$ , m.p.  $95\text{--}96^\circ$ ,  $[\alpha]_{\text{D}}^{20} +11.06^\circ$  in  $\text{CHCl}_3$  [nitrosochloride, decomp.  $127\text{--}128^\circ$ ; nitrosate,  $\text{C}_{20}\text{H}_{32}\text{O}_4\text{N}_2$ , decomp.  $126\text{--}127^\circ$ ; monohydrochloride, m.p.  $106^\circ$  (decomp.), which with  $\text{KOAc-EtOH}$  yields the isomeride, *isosciadopitene*, m.p.  $106\text{--}107^\circ$ , also prepared (m.p.  $108\text{--}109^\circ$ ) by isomerisation of the diterpene with  $\text{H}_2\text{SO}_4$ , but not  $\text{HCO}_2\text{H}$ ]. F. O. H.

Number of primary dicyclic terpene alcohols. R. BOUSSER (Bull. Soc. chim., 1935, [v], 2, 2187).—Myrtenol is not the first of these alcohols, as claimed by Dupont *et al.* (A., 1935, 624; cf. A., 1930, 1591; 1935, 219).

R. S. C.

Balata resin. I. Crystalline constituents of Surinum sheet balata resin. Y. TANAKA, T. KUWATA, and T. SUZUKI (J. Soc. Chem. Ind. Japan, 1935, 38, 504-505b).—The cryst. constituents of the resin are the acetates of three triterpene alcohols,  $\beta$ -amyrin (*Bz* derivative, m.p.  $229\text{--}230^\circ$ ), *isolupeol* (*Bz* derivative, m.p.  $269\text{--}270^\circ$ ), and *balatol* (*Ac*, m.p.  $100\text{--}101^\circ$ , and *Bz* derivative, m.p.  $121\text{--}121.5^\circ$ ).

H. G. M.

Constitution of matairesinol. L. H. BRIGGS, D. A. PEAK, and J. L. D. WOOLLOXALL (J. Proc. Roy. Soc. New South Wales, 1935, 69, 61-67).—Contrary to Easterfield (J.C.S., 1910, 97, 1028), matairesinol (I) [*Bz*<sub>4</sub>-derivative, m.p.  $169\text{--}169.5^\circ$ ; *Ac*<sub>2</sub> (lit., *Ac*<sub>1</sub>)

derivative, m.p.  $110^\circ$ ] is  $\text{C}_{20}\text{H}_{32}\text{O}_6$ , isomeric with pinoresinol (lit.,  $\text{C}_{19}\text{H}_{20}\text{O}_6$ ). With  $\text{Me}_2\text{SO}_4$  in  $\text{NaOH}$  it affords a *Me*<sub>2</sub> derivative (II), m.p.  $126.5\text{--}127^\circ$ , hydrolysed ( $\text{NaOH}$ ) to *dimethylmatairesinolic acid*, m.p.  $80\text{--}84^\circ$ , which indicates the persistence of the lactone ring in the former derivative, and of two phenolic groups. (I) is not reduced by  $\text{Pd-H}_2$ , but with  $\text{KMnO}_4$  in  $\text{NaOH}$  at  $100^\circ$  affords veratric acid in  $> 50\%$  yield, which shows that two veratryl residues are present, and as no veratroylformic acid is obtained (cf. A., 1929, 1064), the aromatic nuclei must be linked through  $\text{-CH}_2\text{-}$ . The formula  $\begin{matrix} \text{R}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2 \\ \text{R}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CO} \end{matrix} > \text{O}$  [ $\text{R}=4:3\text{-C}_6\text{H}_3(\text{OH})\cdot\text{OMe}$ ] is proposed on chemical and phytochemical evidence.

J. L. D.

Pigment of ebony wood. E. WEDEKIND (Ber., 1935, 68, [B], 2363-2366).—West African ebony sawdust is freed from lignin by treatment with dioxan containing 3-5% of conc.  $\text{HCl}$  at  $100^\circ$  and the residue after being washed with dioxan and  $\text{COMe}_2$  is shaken with 72%  $\text{H}_2\text{SO}_4$  or treated with superconc.  $\text{HCl}$  at  $0^\circ$  to remove cellulose. The black, amorphous residue contains small amounts of adsorbed lignin, which are removed by  $\text{PhOH}$ . The composition of the black pigment (I), which is insol. in all org. and inorg. media, corresponds closely with the formula  $\text{C}_9\text{H}_6\text{O}_3$ . Alkali hydroxides partly dissolve (I) to colloidal solutions. Fusion with  $\text{KOH}$  does not lead to recognisable products. Powerful oxidising agents, particularly  $\text{NaOCl}$ , cause decomp., but no defined product could be isolated. The possible relationship of (I) to lignin  $\text{C}_9\text{H}_{12}\text{O}_3$  (Freudenberg's min. empirical formula) is examined by dehydrogenating the lignin extracted by dioxan from ebony wood with S at  $180\text{--}200^\circ$ , whereby  $\text{H}_2\text{S}$  is only very slowly evolved, giving a black, amorphous, completely insol., non-homogeneous product containing somewhat less C and somewhat more H than (I) and also 0.92% of S. A closely similar product is obtained from beechwood (dioxan) lignin. Dehydrogenation with Sc is impossible, since the requisite high temp. induces decomp. of (I). Similar treatment of the wood of *Eucalyptus marginata* gives a red-brown pigment the H content of which is  $<$  that of lignin. H. W.

Hydrolysis of pine and beech wood. K. STORCH (Ber., 1935, 68, [B], 2367-2374).—Treatment of pine wood with 64%  $\text{H}_2\text{SO}_4$  at  $15\text{--}20^\circ$  during 3-48 hr. shows the presence of 28-30% of lignin; when hydrolysis of the cellulose has proceeded so far that the solution remains clear when diluted, it is immaterial whether or not the mixture is diluted with  $\text{H}_2\text{O}$  previous to filtration. Under similar conditions red beech wood appears to contain about 12% of lignin when the mixture is directly filtered and about 24% when it is diluted (and boiled) previously to filtration. After 16 hr. the lignin retains the fibrous structure of the wood; that from pine contains C 65.0, H 5.4, *OMe* 14.9%, whereas that from beech has C 63.0, H 5.6, and *OMe* 19.2%. Pine lignin retains 84% of the *OMe* in wood; the filtrate contains about 5% as  $\text{MeOH}$  and the remaining 11% is present in sol. org. compounds. In the beech residue (12% of wood) only 37% of the total *OMe* is retained. The matter pptd. by dilution contains 39% of the

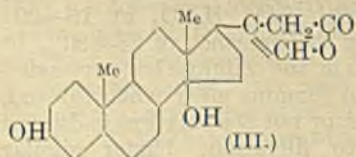
OMe whereas  $\approx 9\%$  is present as MeOH and the remaining  $15\%$  in OMe-compounds. Hilpert's view that beech lignin is a product of the action of conc. acid on the carbohydrates of wood is difficult to reconcile with the fibrous structure of insol. beech lignin. The beech lignin sol. in acid is sol. also in NaOH,  $C_5H_5N$ , and  $COMe_2-H_2O$  and retains this property after intense desiccation. Pine-wood ( $H_2SO_4$ ) lignin is not appreciably sol. in NaOH. Similar behaviour is shown by the woods. Beech wood is dissolved by  $5\%$  NaOH to the extent of  $28\%$  and  $35\%$  at room temp. and  $100^\circ$ , respectively, and the treatment does not cause enrichment of the residue in lignin. It is therefore probable that the sol. and insol. lignin components of beech are in some manner (possibly anatomically) separated from one another. The insol. component has the same composition when isolated after 16 or 48 hr. treatment; after complete hydrolysis, the sol. portion closely resembles it in elementary composition and OMe content. H. W.

**Sapinic acids from various species of pine and spruce.** T. HASSELSTROM and M. T. BOGERT (J. Amer. Chem. Soc., 1935, 57, 2118—2121).—These are shown by hydrogenation and isomerisation to be a mixture of *l*- (I) and *d*-pimaric acid. Since (I) belongs to the abietic class, it is renamed *l*-sapietic acid.

R. S. C.

**An acid ester contained in the root of official valerian.** E. CIONGA (Compt. rend., 1935, 201, 1152—1154).—From industrial residues, an acid (I),  $C_{10}H_{18}O_4$ , b.p.  $120-122^\circ/0.6$  mm.,  $[\alpha]_D^{20} +4.83^\circ$ , has been separated, yielding on hydrolysis  $Bu^tCO_2H$  and *d*- $\alpha$ -hydroxy- $\beta$ -methylbutyric acid, b.p.  $124-125^\circ/13$  mm., m.p.  $66.5-67.5^\circ$ ,  $[\alpha]_D^{21} -1.56^\circ$  in  $H_2O$ . (I) is therefore  $Bu^tCO_2O \cdot CHPr^t \cdot CO_2H$ . W. O. K.

**Vegetable heart poisons. VII. Constitution of uzarigenin.** R. TSCHESCHE and K. BOHLE [with, in part, P. T. P. SAH] (Ber., 1935, 68, [B], 2252—2256).—Fresh analyses of anhydrouzarigenin (I) [obtained by Windaus *et al.* (A., 1930, 1024) from *Gomphocarpus* root] and its derivatives ( $\alpha$ -benzoate, m.p.  $261-262^\circ$ ) shows it to be a monoanhydro-compound,  $C_{23}H_{32}O_3$ . This view is in harmony with the observed absence of conjugation in the  $\alpha$ - or  $\beta$ -compound or in  $\alpha$ -anhydrouzarigenone, m.p.  $255^\circ$  [oxime, m.p.  $283-285^\circ$  (decomp.); semicarbazone, decomp.  $266-268^\circ$ ], and with the catalytic



absorption of  $2H_2$ . Uzarin (II) is therefore  $C_{35}H_{51}O_{14} \cdot 2H_2O$ . (I) is pptd. by digitonin and hence contains OH attached to C-3. Since (II) is converted by the successive action of KOH-MeOH and AcOH into isouzarin,  $C_{35}H_{51}O_{14} \cdot 3H_2O$ , m.p.  $240^\circ$  (decomp.),  $[\alpha]_D^{21} -6.7^\circ$  in MeOH, the *tert*-OH is very probably united to C-14 and uzarigenin is (III). (I) is also obtained from uzaren, the second *Gomphocarpus* glucoside. H. W.

**Manchurian kaoliang (*Andropogon sorghum*, Brot.).**—See this vol., 124.

**Carotenoids of purple bacteria.**—See this vol., 259.

**New type of plant lipochrome.**—See this vol., 259.

**Carotenoids from the anthers of *Litium tigrinum*: antheraxanthin.**—See this vol., 259.

**Antineuritic vitamin.**—See this vol., 253.

**Oxidation-reduction during dehydration of furyl alcohols.** R. PAUL (Bull. Soc. chim., 1935, [v], 2, 2220—2227).—Partly already reviewed (A., 1935, 867). 2- $\alpha$ -Hydroxypropylfuran at  $400^\circ$  gives 2- $\Delta^{\alpha}$ -propenylfuran, b.p.  $132-133^\circ/756$  mm., and 2-propionylfuran. 2- $\alpha$ -Hydroxy-*n*-butylfuran gives 2- $\Delta^{\alpha}$ -*n*-butenyl-, b.p.  $59-60^\circ/24$  mm., 2-*n*-butyl-, b.p.  $48-49^\circ/24$  mm., and 2-*n*-butylfuryl-furan, b.p.  $92-94^\circ/18$  mm. (semicarbazone, m.p.  $182^\circ$ ). 2-Alkylenfurans are stable under  $N_2$  in presence of a trace of quinol. R. S. C.

**$\delta$ -Diketones and 1:4-pyrans.** A. P. DE CARVALHO (Ann. Chim., 1935, [xi], 4, 449—522).—PhCOMe with  $CO(p-C_6H_4Br)_2$  or  $COPH_2$  in  $Et_2O$  yields  $\alpha\epsilon$ -diphenyl- $\gamma\gamma$ -di-*p*-bromophenyl-, m.p.  $195-196^\circ$ , or  $\alpha\gamma\gamma\epsilon$ -tetraphenyl-penta- $\alpha\epsilon$ -dione (I), m.p.  $182-183^\circ$  ( $\beta\delta$ - $Br_2$ -derivative, m.p.  $133-134^\circ$ ); dioxime, m.p.  $191-192^\circ$ ; diphenylhydrazone, m.p.  $184.5-185.5^\circ$ ).  $\alpha\alpha\epsilon\epsilon$ -Tetrachloro- $\alpha\gamma\gamma\epsilon$ -tetraphenylpentane has m.p.  $159-160^\circ$ . The dione with the appropriate Grignard reagent gives  $\alpha\alpha\gamma\gamma\epsilon\epsilon$ -hexaphenylpentane-(II), m.p.  $193-194^\circ$ ,  $\alpha\gamma\gamma\epsilon$ -tetraphenyl- $\alpha\epsilon$ -diethylpentane-, m.p.  $189-190^\circ$  (alcoholate, m.p.  $130^\circ$ ), and  $\alpha\gamma\gamma\epsilon$ -tetraphenyl- $\alpha\epsilon$ -dimethylpentane- $\alpha\epsilon$ -diol, m.p.  $166-167^\circ$ . When heated at  $200^\circ$  it gives  $\alpha$ -benzoyl- $\beta\beta$ -diphenylethylene; with  $CrO_3$  it gives BzOH and  $CHPh_2 \cdot CO_2H$ , with  $P_2O_5$  in boiling xylene gives 2:4:4:6-tetraphenyl-1:4-pyran, m.p.  $157-158^\circ$  (3:5- $Br_2$ -derivative, m.p.  $215-216^\circ$ ), and with  $NH_4OAc$  in AcOH yields 2:4:4:6-tetraphenyl-1:4-dihydropyridine, m.p.  $235-236^\circ$ . With deficiency of the above Grignard reagent there are formed 2:4:4:6-tetraphenyl-2-ethyl-dihydropyran, m.p.  $167-168^\circ$  (5- $Br$ -derivative, m.p.  $112-113^\circ$ ), and 2:2:4:4:6:6-hexaphenyltetrahydropyran (3:5- $Br_2$ -derivative, m.p.  $177-178^\circ$ ), also obtained by dehydration of (II). Hydrogenation ( $PtO_2$ ) of (I) gives 2:4:4:6-tetraphenyltetrahydropyran (III), m.p.  $145-146^\circ$ . PhCHO and (I) give 3:5-dibenzoyl-2:4:4:6-tetraphenyltetrahydropyran (IV), m.p.  $178-179^\circ$ . The phototropy of (I), (III), and (IV) is discussed. F. R. G.

**Dibenzofuran. [Diphenylene oxide.] VII. Derivatives of tetrahydrodibenzofuran.** H. GILMAN, E. W. SMITH, and L. C. CHENEY (J. Amer. Chem. Soc., 1935, 57, 2095—2099; cf. A., 1935, 985).—With 1:2:3:4-tetrahydrodibenzofuran (I) the Friedel-Crafts reaction, sulphonation, and nitration involve the 7- and metalation the 8-position. (I) gives the 7- $NO_2$ -derivative (II), m.p.  $124-125^\circ$ , giving with Br 2-nitrodibenzofuran and on reduction 7-amino-1:2:3:4-tetrahydrodibenzofuran (III) (Ac derivative, m.p.  $146^\circ$ ). (I) with  $Ac_2O-SnCl_4$  in  $C_6H_6$  gives the 7-Ac derivative (IV), m.p.  $66-67^\circ$ , b.p.  $210^\circ/15$  mm. [and a little dibenzofuran (V)], oxidised by NaOI to 1:2:3:4-tetrahydrodibenzofuran-7-carboxylic acid, m.p.  $247-248^\circ$  (Me ester, m.p.  $72.5-$



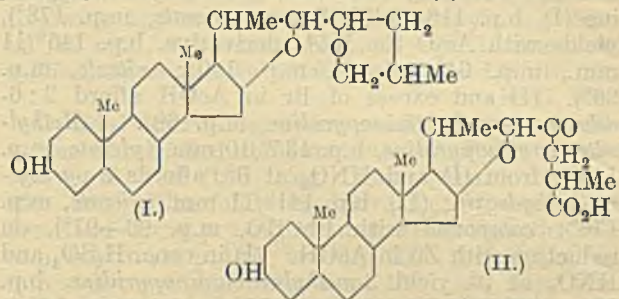
73.5°), giving dibenzfuran-2-carboxylic acid with Br. (I) and  $\text{ClSO}_3\text{H}$  in  $\text{CCl}_4$  at 10° yield the 7-sulphonic acid (Ba salt), the amide, m.p. 207.5—208.5°, of which with Br affords dibenzfuran-2-sulphonamide, m.p. 241—242°, which was synthesised (diazo-reaction;  $\text{Cu-SO}_2$ ) from 2-aminodibenzfuran by way of the sulphonyl chloride, m.p. 148.5°. (I) with  $\text{LiPh}$  or, less well,  $p\text{-C}_6\text{H}_4\text{MeLi}$  or  $\text{LiBu}^a$  gives a product which with  $\text{CO}_2$  affords 1:2:3:4-tetrahydrodibenzfuran-8-carboxylic acid, m.p. 197°, dehydrogenated by Br to dibenzfuran-1-carboxylic acid. The latter acid with  $\text{Na-EtOH}$  gives 1:2:3:4-tetrahydrodibenzfuran-1-carboxylic acid, m.p. 168°. The structure of 8-methoxy-1:2:3:4-tetrahydrodibenzfuran is confirmed by dehydrogenation by S at 275° to 1-methoxydibenzfuran. The "dihydrodibenzfuran" of Hönigschmidt (A., 1901, i, 700) was impure (V). Hexahydrodibenzfuran (von Braun, A., 1923, i, 103) may exist, but the so-called  $\text{H}_6$ -derivatives are really (II), (III), and (IV), and it gives a picrate, m.p. 97°, whence (I) is formed by distillation in steam. Hydrogenation of (V) in presence of noble metals at moderate temp. and pressure gives only decahydrodibenzfuran, b.p. 258—259°/740 mm., 108—110°/7 mm. R. S. C.

**Amino-alcohols from dibenzfuran [diphenylene oxide].** E. MOSETTIG and R. A. ROBINSON (J. Amer. Chem. Soc., 1935, 57, 2186—2189).—2- $\beta$ -Amino- $\alpha$ -hydroxyethylidibenzfuran (I) and certain *N*-derivatives thereof have no morphine-like pharmacological action on the cat; they are more analgesic and toxic than similar phenanthrene derivatives. 2-Acetyldibenzfuran (II) and Br in dry  $\text{Et}_2\text{O}$  at 0° give 55% of 2- $\alpha$ -bromoacetyldibenzfuran, m.p. 105—106° [with  $\text{NaOCl}$  gives dibenzfuran-2-carboxylic acid (III), which with the appropriate amine in  $\text{Et}_2\text{O}$  affords 2-dimethyl-, m.p. 82—83° (hydrochloride,  $+\text{H}_2\text{O}$ , m.p. 212—235°), -diethyl-, an oil (hydrochloride, m.p. 200—212°), -piperidino-, sinters at 97—98° (hydrochloride, m.p. 255—265°), ?-methyl- (IV) (hydrochloride, m.p. 225—250°), and -ethyl-aminoacetyldibenzfuran, unstable, m.p. 65—75° [hydrochloride, m.p. 254—256° (decomp.); 30% yield; some (III) also obtained]. (IV) (30% yield) is accompanied by some (III) and di(dibenzfuran-2-carbonylmethyl)methylamine (hydrochloride, m.p. 235—245°). Hydrogenation of 2-oximinoacetyldibenzfuran gives 64% of 2-aminoacetyldibenzfuran, decomp. from 171° [hydrochloride, m.p. 245—255° (decomp.)]. Hydrogenation of the keto-base or its hydrochloride affords 2- $\beta$ -dimethyl-, m.p. 88—89° (hydrochloride, m.p. 173—174°; *O*-benzoate, m.p. 99—100°), -diethyl-, m.p. 75—76° (hydrochloride, m.p. 157—159°), -piperidino-, m.p. 116.5—117.5° (hydrochloride, m.p. 250—251°; *O*-benzoate, m.p. 119°), and -ethyl-amino- $\alpha$ -hydroxyethylidibenzfuran, m.p. 99.5—101° (hydrochloride, m.p. 219—219.5°), and (I), m.p. 132° [hydrochloride, m.p. 261° (decomp.)]. (II) affords 2- $\alpha$ -hydroxyethylidibenzfuran, m.p. 63—64°. The Friedel-Crafts reaction in  $\text{PhNO}_2$  affords 2-propionylidibenzfuran, m.p. 101.5—102.5° (semicarbazone, m.p. 184—186°), oxidised to (II) by  $\text{NaOCl}$ . M.p. are corr. R. S. C.

**Constitution of calycopterin.** H. S. MAHAL and K. VENKATARAMAN (Current Sci., 1935, 4, 311—

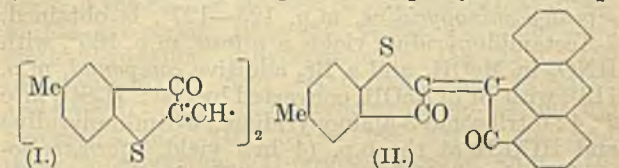
312).—Calycopterin (cf. Ratnagiriswaran, A., 1935, 246) is shown to be 6:4'-dihydroxy-3:5:7:8-tetramethoxyflavone, since with  $\text{AlCl}_3$  it yields either 5:6:4'-trihydroxy-3:7:8-trimethoxy- or 3:5:6:4'-tetrahydroxy-7:8-dimethoxy-flavone. F. R. G.

**Saponins of the cyclopentanohydrophenanthrene group. III. Constitution of Digitalis saponins.** R. TSCHESCHE and A. HAGEDORN (Ber., 1935, 68, [B], 2247—2252; cf. A., 1935, 1126).—Reduction of cholestan-4-one with Na and boiling  $\text{EtOH}$  affords cholestan-4-ol, m.p. 189°,  $[\alpha]_{\text{D}}^{25} +3.9^\circ$  in  $\text{CHCl}_3$ , whereas hydrogenation (Adams-Shriner) yields epicholestan-4-ol, m.p. 132°,  $[\alpha]_{\text{D}}^{25} +29.0^\circ$  in  $\text{CHCl}_3$ . Neither substance is pptd by digitonin. It is therefore established that OH in tigogenin (I) is attached to C-3 and that its steric position is probably the same as in cholesterol. (I) has therefore



the structure shown. The acid  $\text{C}_{27}\text{H}_{42}\text{O}_5$  obtained by drastic oxidation of tigogenin acetate (*loc. cit.*) gives an *Et* ester, m.p. 134°, which contains 1 active H (Zerevitinov), does not yield an oxime or semicarbazone, and is not hydrogenated catalytically. It is formulated as in (II). H. W.

**Indigoid dyes.** S. K. GUHA (J. Indian Chem. Soc., 1935, 12, 659—664).—2-Hydroxy-4-methylthionaphthen, the appropriate aldehyde, and  $\text{HCl}$  in hot  $\text{EtOH}$  give 1-*p*-, m.p. 264°, and -*m*-nitro-, m.p. 233°, -*p*-chloro-, m.p. 178°, -*p*-methoxy-, m.p. 157°, -*p*-, m.p. 252°, and -*m*-hydroxy-, m.p. 200°, -4'-hydroxy-3'-methoxy-, m.p. 194°, and -3':4'-dihydroxy-benzylidene-, m.p. 248°, 1-*p*-tolylidene-, m.p.



159°, 1-piperonylidene-, m.p. 231°, 1-cinnamylidene-, m.p. 184°, and 1-benzylidene-2-keto-1:2-dihydrothionaphthen, m.p. 147°, and the compound (I), m.p. >300°. Aceanthracenequinone affords the compound (II), m.p. >310°. R. S. C.

**Chemical investigation of the liana "Efiri."** IV.—See this vol., 259.

**Syntheses of 1:2-dimethyl- and 2-methylpyrrolidine-5-carboxylic acid.** K. WINTERFELD and H. E. RÖNSBERG (Arch. Pharm., 1936, 274, 40—47).— $\delta$ -Hexolactone (prep. from  $\text{CH}_2\text{I-CH}_2\text{-CO}_2\text{H}$ ) and  $\text{HBr}$  at 100° give  $\delta$ -bromohectic acid, which leads, by way of the chloride, to *Et*  $\alpha$ -dibromohexoate, b.p. 136°/11 mm. With 25%  $\text{NH}_3\text{-MeOH}$  at 110—

120° this gives 2-methylpyrrolidine-5-carboxylamide, m.p. 193°, hydrolysed by conc. HCl at 100° to the corresponding acid, m.p. 207° (Cu salt, +2H<sub>2</sub>O, m.p. 228°; reineckate, decomp. 159°; Et ester platinchloride, m.p. 130°; with PhNCO gives the anhydride, m.p. 130°, of the 1-NPh-CO-derivative). NH<sub>2</sub>Me affords similarly 1:2-dimethylpyrrolidine-5-carboxylic acid, m.p. about 123—125° (Cu salt, +2H<sub>2</sub>O; reineckate, decomp. 156°). Neither acid is identical with the product from dehydrosparteine methoacetate.

R. S. C.

**Alkali bromo-salts and bromo-pyridine derivatives of rhodium.**—See this vol., 175.

**3-Aminopyridine. II. Methyl derivatives, and acetamido- and formamido-pyridine.** E. PŁAŻEK, A. MARCINKÓW, and C. STAMMER (Rocz. Chem., 1935, 15, 365—377).—3-Methylaminopyridine (I), b.p. 118—120°/12 mm. (picrate, m.p. 178°), yields with Ac<sub>2</sub>O the N-Ac derivative, b.p. 145°/11 mm., m.p. 64° (picrate, m.p. 150°; nitrate, m.p. 96°). (I) and excess of Br in AcOH afford 2:6-dibromo-3-methylaminopyridine, m.p. 69°. 3-Methyl-nitrosoaminopyridine, b.p. 135°/10 mm. (picrate, m.p. 136°), from (I) and HNO<sub>2</sub> at 0°, affords 3-pyridyl-methylhydrazine (II), b.p. 141°/11 mm. (picrate, m.p. 176°; compound with PhCHO, m.p. 96—97°), on reduction with Zn in AcOH. (I) in conc. H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> at 0° yield 3-methylnitroaminopyridine, b.p. 124—125°/1.2 mm., m.p. 54—55° (picrate, m.p. 141°), reduced to (II) by Zn in AcOH, and converted by conc. H<sub>2</sub>SO<sub>4</sub> at 0—5° into 2-nitro-3-methylaminopyridine (III), m.p. 110°, together with 6-nitro-3-methylaminopyridine, m.p. 188°. 2-Amino-3-methylaminopyridine, m.p. 124° (picrate, m.p. 234°), is prepared by reduction of (III) with SnCl<sub>2</sub>, or from (I) and NaNH<sub>2</sub> in cymene (205—210°; 4—5 hr.), and 6-amino-3-methylaminopyridine, m.p. 70° (picrate, m.p. 228°), is obtained from 3-bromo-6-aminopyridine and NH<sub>2</sub>Me (110—115°; 20 hr.). Br and 3-dimethylaminopyridine in MeOH give a mixture of 2:6(?)-dibromo-, b.p. 113—115°/0.5 mm., and (?)-bromo-3-dimethylaminopyridine, m.p. 64—66° (picrate, m.p. 192—194°), whilst with HNO<sub>3</sub> in Ac<sub>2</sub>O trinitro-3-dimethylaminopyridine, m.p. 125—127°, is obtained. 3-Acetamidopyridine yields a nitrate, m.p. 165°, with HNO<sub>3</sub> in MeOH, and a Br<sub>2</sub> additive compound, m.p. 118°, with Br in AcOH, converted by conc. H<sub>2</sub>SO<sub>4</sub> into 2:4:6-tribromo-3-aminopyridine. 3-Aminopyridine and HCO<sub>2</sub>H at the b.p. (4 hr.) yield 3-formamidopyridine, b.p. 200°/25 mm., m.p. 96° (nitrate, m.p. 158°; Br<sub>2</sub> additive compound, m.p. 92°).

R. T.

**Pyridine series. II.** U. BASU and B. BANERJEE (J. Indian Chem. Soc., 1935, 12, 665—671).—The syntheses previously described (A., 1935, 1250) are generalised. NH<sub>2</sub>·CMe·CH·COMe with COPh·CH·CH·OH (I), *p*-C<sub>6</sub>H<sub>4</sub>Me·CO·CH·CH·OH, or COEt·CMe·CH·OH in Et<sub>2</sub>O gives 3-acetyl-6-phenyl-, m.p. 90° (hydrochloride, m.p. 143—144°; picrate, m.p. 166°; semicarbazone, m.p. 212°; oxime, m.p. 106°), and *p*-tolyl-2-methylpyridine, m.p. 78° (hydrochloride, m.p. 150—151°; picrate, m.p. 163—164°; semicarbazone, m.p. 207°; oxime, m.p. 127°), and 3-acetyl-2:5-dimethyl-6-ethylpyridine, m.p. 60° (picrate, m.p. 118°; semicarbazone, m.p. 201°; oxime, m.p.

128°), respectively. NH<sub>2</sub>·CMe·CH·COPh affords similarly in EtOH or Et<sub>2</sub>O—EtOH 3-benzoyl-6-phenyl-, m.p. 77° (picrate, m.p. 196°; no semicarbazone), and *p*-tolyl-2-methylpyridine, m.p. 84°.

NH<sub>2</sub>·CMe·CH·CO<sub>2</sub>Et with (I) in Et<sub>2</sub>O gives Et 2:5-dimethyl-6-ethylpyridine-3-carboxylate, b.p. 145°/10 mm. (picrate, m.p. 120°), hydrolysed by KOH to the corresponding acid, m.p. 193—194° (decomp.), which, when heated/vac. with soda-lime, affords 2:5-dimethyl-6-ethylpyridine, b.p. 181—182°/756 mm. (picrate, m.p. 127°). 6-Phenyl-, b.p. 285—287° (picrate, m.p. 180°), and 6-*p*-tolyl-2:5-dimethylpyridine, b.p. 291—292° (picrate, m.p. 146°), and 2:5:6-trimethylpyridine, b.p. 176—178°, are similarly obtained.

R. S. C.

**Indole series. VI. Synthesis of [1:3-dimethylketo]tryptophan.** 3-Alkylation of oxindoles. P. L. JULIAN, J. PIKL, and F. E. WANTZ (J. Amer. Chem. Soc., 1935, 57, 2026—2029; cf. A., 1935, 765).—1:3-Dimethyloxindole, NaOEt, and CH<sub>2</sub>Br·CH(OEt)<sub>2</sub> in hot EtOH give a good yield of 1:3-dimethyl-3-β-dimethoxyethylloxindole, b.p. 182.5—183.5°/11 mm., hydrolysed by cold 5% HCl to 1:3-dimethyloxindolyl-3-acetaldehyde, b.p. 177—178°/12 mm., which by the Strecker synthesis affords the cyanohydrin, m.p. 142°, and β-1:3-dimethyloxindolyl-3-alanine (1:3-dimethylketotryptophan), m.p. 188° (decomp.), which above the m.p. in vac. loses CO<sub>2</sub> to give the base. Oxindole (2 active H) and 1-methyloxindole, however, with bromoacetals give only tars. CH<sub>2</sub>Cl·COCl and *p*-OEt·C<sub>6</sub>H<sub>4</sub>·NHMe yield 5-ethoxy-, m.p. 92°, and 1-hydroxy-5-methyl-oxindole. Oxindoles condense with esters in presence of NaOEt·EtOH. Thus are obtained 3-formyl-, -acetyl-, m.p. 109°, -carbethoxy-, m.p. 67°, and -dimethylaminoacetyl-1-methyloxindole, m.p. 219°, 3-acetyl-1:3-dimethyl-, (I), m.p. 79°, and 3-dimethylaminoacetyl-5-ethoxy-1-methyl-oxindole, m.p. 196°, and 3-formyl-2-methoxy-1-methylindole; CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub> gives also the bi-, m.p. 67°, and ter-mol., m.p. 225°, condensation products. Hydrogenation (PtO<sub>2</sub>; 1.5 atm.) of the acyl derivatives in EtOH at room temp. or, in some cases, AcOH at 50° gives the alkyl derivatives, viz.: 1:3-dimethyl-, 1-methyl-3-ethyl-, m.p. 169° (Br<sub>2</sub>-derivative), and -3-β-dimethylaminoethyl-oxindole, b.p. 185°/16 mm. (picrate, m.p. 168°), 5-ethoxy-1-methyl-3-β-dimethylaminoethylloxindole, b.p. 221°/17 mm. (picrate, m.p. 157°), β-1-methyloxindolyl-3-propionic acid, b.p. 160°/1 mm., and 2-methoxy-1-methylindolyl-3-carbinol, m.p. 62° (readily hydrolysed to 1-methyloxindolyl-3-carbinol). (I), which has no enolisable H, resists hydrogenation.

R. S. C.

**Synthesis of derivatives of indole which contain sulphur.** H. WUYTS and (ILLE.) A. LACOURT (Bull. Soc. chim. Belg., 1935, 44, 587—592).—The *S*-Me derivative of β-phenylthioacet-α-phenyl-α-methylhydrazide (cf. A., 1933, 498) with warm MeOH—10% HCl (gas) gives 2-methylthiol-3-phenyl-N-methylindole, m.p. 96°, which loses 1 Me with HI at 120° and another at a high temp. The *S*-Me derivative of β-*o*-thiotolu-α-*o*-tolylhydrazine gives no indole because the hydrazine is substituted solely by aromatic groups. The *S*-Me derivative, m.p. 59°, of β-*m*-tolylthioacet-α-phenyl-α-methylhydrazide, m.p. 91°, with

MeOH-10% HCl affords 2-methylthiol-3-m-tolyl-N-methylindole, an oil (*picrate*, m.p. 84°), from which 2 Me are removed by energetic demethylation.  $\beta$ -Phenylthioacet- $\alpha$ -phenyl- $\alpha$ -methylhydrazide, m.p. 82°, affords 2-thion-3-phenyl-N-methyl-2:3-dihydroindole, m.p. 57° (*picrate*, m.p. 141°), insol. in alkali.  $\beta$ -Phenylthioacet- $\alpha$ -phenylhydrazide affords no indole, but is hydrolysed. J. L. D.

**Action of sodium methoxide on ethyl isatin-N-acetate.** N. I. PUTCHIN (J. Gen. Chem. Russ., 1935, 5, 1176—1184).—Et isatin-N-acetate and NaOMe in MeOH (75—80°; 2—3 hr.) give first the compound,  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}(\text{ONa})(\text{OMe})_2$ , decomp. 230°, and then either (8 hr.; 75—80°) 3:4-diketol-1:2:3:4-tetrahydroquinoline-2-carboxylic acid (I) (*Na*, *Ag*<sub>1</sub>, and *Ag*<sub>2</sub> salts; *Et*<sub>2</sub> derivative, m.p. 119—120°) or (80—100°) *o*-glycinobenzoylformic acid,  $\text{CO}_2\text{H}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ . (I) is reduced (HI) to 1:2:3:4-tetrahydroquinoline-2-carboxylic acid. R. T.

**Reactions of mixed aromatic ketones with disubstituted thiocarbamides containing different aryl radicals.** K. DZIEWOŃSKI, L. GIZLER, and J. MOSZEW (Rocz. Chem., 1935, 15, 400—407).—Diarylthiocarbamides and substituted ketones yield quinoline derivatives when fused together; the reaction consists of three stages, viz., conversion of diarylthiocarbamide into amine and thiocarbimide, condensation of the former with the ketone to yield an anil, and condensation of the anil with the latter to yield a substituted quinoline. COPhMe (I) and *as*-phenyl-*p*-tolylthiocarbamide (5 hr. at 180—210°, then 30 min. at 270°), or acetophenone-*p*-tolil and PhNCS (2 hr. at 210—220°, then 30 min. at 270°) afford 4-anilino-2-phenyl-6-methylquinoline, m.p. 161° (*hydrochloride*, m.p. 171°; *picrate*, m.p. 210°; 4-N-NO-, m.p. 137—138°; 4-N-Ac-, m.p. 142°; 4-N-MeI-, m.p. 235°; 4-N-Me derivative, m.p. 167°), converted into 4-hydroxy-2-phenyl-6-methylquinoline by EtOH-KOH (200°; 4 hr.). *as*-Phenyl- $\beta$ -naphthylthiocarbamide (II) and (I) (4 hr. at 180°, then 30 min. at 280°) give 4- $\beta$ -naphthylamino-2-phenyl-5:6-benzoquinoline, m.p. 202—203° [*hydrochloride*, m.p. 286—287°; *picrate*, m.p. 260—261°; *methiodide*, m.p. 293—294°; 4-N-NO-, m.p. 250—251° (decomp.)]; 4-N-Ac derivative, m.p. 172—173°], yielding 4-hydroxy-2-phenyl-5:6-benzoquinoline with EtOH-KOH (200°; 4 hr.). (II) and *p*-tolyl Me ketone (5 hr. at 180—260°, then 30 min. at 290°) yield 4- $\beta$ -naphthylamino-2-*p*-tolyl-5:6-benzoquinoline, m.p. 226° [*hydrochloride*, m.p. 195°; *picrate*, m.p. 297° (decomp.)]; 4-N-NO-derivative, m.p. 195° (decomp.)], giving 4-hydroxy-2-*p*-tolyl-5:6-benzoquinoline, m.p. 314—315°, with EtOH-KOH (200°; 4 hr.). R. T.

**Fries-Rosenmund rearrangement of N-acetylcarbazole.** E. MEITZNER (J. Amer. Chem. Soc., 1935, 57, 2327—2328).—N-Acetylcarbazole with  $\text{AlCl}_3$  in  $\text{PhNO}_2$  gives 50—60% of 3- and some 1-acetylcarbazole, m.p. 136° (*oxime*, m.p. 179—180°; with molten KOH gives the 1-carboxylic acid), also obtained with tars from carbazole, AcCl, and  $\text{AlCl}_3$  in  $\text{PhNO}_2$ .  $\text{AlCl}_3$  alone is unsatisfactory. R. S. C.

**Some amino-alcohol esters of acridine-5-carboxylic acid.** B. SANDAHL and C. F. WEIDER

(Bull. Soc. chim., 1935, [v], 2, 2008—2016).—The following esters of acridine-5-carboxylic acid (I) were prepared by heating the *hydrochloride*, m.p. 215—216° (decomp.), of the acid chloride of (I) with the appropriate alcohol in  $\text{C}_6\text{H}_6$ . They are feebly anaesthetic, but not antiseptic.  $\beta$ -Aminoethyl, m.p. 238—240° (decomp.) [*monohydrochloride*, m.p. 238—240° (decomp.)];  $\beta$ -dimethylaminoethyl [*mono*-, m.p. 189—190° (decomp.), and *di-hydrochloride*, m.p. 172—173° (decomp.)];  $\beta$ -diethylaminoethyl [*mono*-, m.p. 179—180° (decomp.), and *di-hydrochloride*, m.p. 179—180° (decomp.)];  $\beta$ -dipropylaminoethyl [*mono*-, m.p. 177—178° (decomp.), and *di-hydrochloride*, m.p. 177—178° (decomp.)];  $\beta$ -diisobutylaminoethyl [*mono*-, m.p. 178—180° (decomp.), and *di-hydrochloride*, m.p. 168—169° (decomp.)];  $\beta$ -diisooamylaminoethyl [*mono*-, m.p. 130—146°, and *di-hydrochloride*, m.p. 167—168° (decomp.)]. The following appear to be new:  $\beta$ -dipropyl-, b.p. 90—92°/22 mm.,  $\beta$ -diisobutyl-, b.p. 96—98°/15 mm., and  $\beta$ -diisooamyl-aminoethyl alcohol, b.p. 126—128°/15 mm. H. G. M.

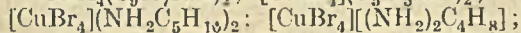
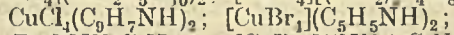
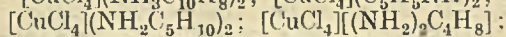
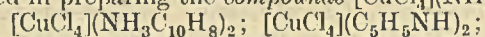
**Optical crystallographic study of some derivatives of barbital and luminal.** M. E. HULTQUIST and C. F. POE (Ind. Eng. Chem. [Anal.], 1935, 7, 398—399).—The following derivatives of veronal are described: *o*-, m.p. 140°, *m*-, m.p. 91°, *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CH}_2$ -, m.p. 146°, *o*-, m.p. 127°, *m*-, m.p. 102°, *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}_2$ -, m.p. 142°, *p*- $\text{C}_6\text{H}_4\text{I}\cdot\text{CH}_2$ -, m.p. 122°, *m*-, m.p. 159°, *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2$ -, m.p. 192°, *PhCO}\cdot\text{CH}\_2-, m.p. 191°, *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{CH}_2$ -, m.p. 191.5°. The following derivatives of 5-phenyl-5-ethylbarbituric acid are described: *o*-, m.p. 116°, *m*-, m.p. 130°, *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CH}_2$ -, m.p. 117°, *m*-, m.p. 111°, *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}_2$ -, two forms, m.p. 111° and 113°, *p*- $\text{C}_6\text{H}_4\text{I}\cdot\text{CH}_2$ -, m.p. 127—128°, *m*-, m.p. 149.5°, *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2$ -, m.p. 182.5°, *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{CH}_2$ -, m.p. 164°.  $n_a, n_b, n_c$ , crystallographic data, and block m.p. are recorded. F. R. G.*

**4(5)-Amino-5(4)-methylglyoxaline.** R. WEIDENHAGEN and R. HERRMANN (Ber., 1935, 68, [B], 2205—2209).—Reduction of 4(5)-nitro-5(4)-methylglyoxaline by cold  $\text{SnCl}_2$  and conc. HCl and evaporation of the Sn-free solution in vac. causes little fission of the glyoxaline ring and yields 4(5)-amino-5(4)-methylglyoxaline dihydrochloride (I), m.p. 186° (decomp.), in 67% yield. (I) is transformed by NaOAc and PhCHO into 4(5)-benzylideneamino-5(4)-methylglyoxaline, m.p. 216°, by NaOAc, EtOH, and  $\text{Ac}_2\text{O}$  into 4(5)-acetamido-5(4)-methylglyoxaline, m.p. 216°, by  $\text{BzCl}$  (1 and 2 mols., respectively) in  $\text{C}_5\text{H}_5\text{N}$  into 4(5)-benzamido-, m.p. 262°, and 4(5)-benzamido-1-benzoyl-, m.p. 170°, -5(4)-methylglyoxaline, and by KOAc and PhNCO in  $\text{H}_2\text{O}$  into phenyl-5(4)-methylglyoxalinylicarbamide, m.p. 283°. H. W.

**Glyoxalinecarboxylic esters.** W. JOHN (Ber., 1935, 68, [B], 2283—2291).—Contrary to Oddo *et al.* (A., 1928, 1331) the product of the action of Mg glyoxalyl bromide (I) on  $\text{ClCO}_2\text{Et}$  is *Et glyoxaline-1-carboxylate* (II), b.p. 100°/16 mm. (*picrate*, m.p. 124°), the constitution of which follows from its ready conversion by dil. acid into glyoxaline. Similarly Mg 5-methylglyoxalyl bromide and  $\text{ClCO}_2\text{Et}$  afford *Et 5-methylglyoxaline-1-carboxylate* (III), b.p.

118—119°/21 mm. (*picrate*, m.p. 148—149°; *nitrate*, m.p. 116—117°), readily hydrolysed to 5-methylglyoxaline. The discrepancy in the m.p. of the *picrates* obtained by Oddo and the author respectively suggests the possibility of an isomerisation of (I) or (II) during the experiments. (I) appears unchanged when heated at 200° and yields the same product with  $\text{ClCO}_2\text{Et}$  as under normal conditions. (II) is very rapidly transformed at 250—260° into 1-ethylglyoxaline, b.p. 110°/16 mm. (*picrate*, m.p. 170°), identical with the product derived from glyoxaline and  $\text{EtBr}$ . Similarly, but less smoothly, (III) is converted into 5-methyl-1-ethylglyoxaline (*picrate*, m.p. 140°) mixed with 5-methylglyoxaline. Gradual addition of  $\text{NH}_3$  to  $\text{AcCHO}$  and  $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$  in  $\text{EtOH}$  leads to 2-styryl-5-methylglyoxaline (V), m.p. 235° [*nitrate*, m.p. 168° (decomp.); *picrate*, m.p. 248° (decomp.)], and small amounts of 2-phenyl-5-methylglyoxaline. Oxidation of (V) by  $\text{KMnO}_4$  in  $\text{CO}_2$  affords 5-methylglyoxaline-2-carboxylic acid, m.p. 175° (decomp.) (*Et* ester and its *nitrate*, m.p. 124°), decarboxylated when heated above its m.p. to 5-methylglyoxaline (*picrate*, m.p. 159—160°). Oxidation of (V) with  $\text{CrO}_3$  gives  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}_2$ . H. W.

**Organic cupric tetrachlorides and tetrabromides.** J. AMIEL (*Compt. rend.*, 1935, 201, 964—966; cf. A., 1935, 312).—The previous method was applied in preparing the compounds  $[\text{CuCl}_4](\text{NH}_3\text{Ph})_2$ ;



$[\text{CuBr}_4](\text{C}_9\text{H}_7\text{NH})_2$ . The Cl and Br compounds were yellow and black, respectively. The piperazine (I) compounds formed dihydrates. With a large excess of halide of (I), or of Cu halide, respectively, the compounds  $\text{CuX}_2\cdot 2\text{X}_2[(\text{NH}_2)_2\text{C}_4\text{H}_8]\cdot 4\text{H}_2\text{O}$  and  $[\text{CuX}_3]_2[(\text{NH}_2)_2\text{C}_4\text{H}_8]$  were formed (X=Cl or Br).

H. J. E.

**Organic sulphur compounds. III. Action of hydrogen cyanide, ammonia, and hydrogen sulphide on  $\alpha$ - $\beta$ -unsaturated ketones.** K. ABE (*Sci. Rep. Tokyo Bunrika Daigaku*, 1935, 3, 17—27).—Treatment of mesityl oxide with  $\text{EtOH}\text{-HCN}$  (from KCN and  $\text{AcOH}$ ) followed by  $\text{NH}_3$  and  $\text{H}_2\text{S}$  affords  $\alpha$ -amino- $\alpha$ -methylpyrroterebic thionamide, m.p. 220°; similarly, benzylideneacetone (I) affords a mixture of  $\alpha$ -amino- $\beta$ -benzylidene- $\alpha$ -methylpropionic thionamide, m.p. 165—166°, and 2:5-dithioketo-3:6-distyryl-3:6-dimethylpiperazine, m.p. 172—173°. Under the same conditions furfurylideneacetone (II) gives  $\alpha$ -amino- $\beta$ -furfurylidene- $\alpha$ -methylpropionic thionamide, m.p. 190—191°. (I) with the same reagents but using  $\text{NaCN}+\text{NH}_4\text{Cl}$  as source of HCN affords diplo-benzylidenedithioacetone. Phenylacetonitrile was not obtained from (I) and HCN, and (II), under the same conditions, gave a substance, sinters at 210°, m.p. > 210°. P. G. C.

**Pyrimidines. CXLVIII. Action of chlorine on mercaptopyrimidines.** J. M. SPRAGUE and T. B. JOHNSON (*J. Amer. Chem. Soc.*, 1935, 57, 2252—2255).—Four known 4-chloro-2-ethylthiolpyrimidines are prepared from the corresponding 4-CO-compounds by  $\text{POCl}_3$ . The 4-Cl-

compounds and  $\text{NaOEt}\text{-EtOH}$  at room temp. give 2-ethylthiol-4-ethoxy-, b.p. 123—124°/11 mm., and 4-ethoxy-5-methyl-, b.p. 135—136°/12 mm., and 5-bromo-2-ethylthiol-4-ethoxy-pyrimidine, b.p. 140°/6 mm. 4-Chloro-2-ethylthiol-5-carbethoxypyrimidine is unstable to  $\text{NaOEt}$  in  $\text{EtOH}$ , but in hot  $\text{C}_6\text{H}_6$  gives the 4-*OEt*-compound (I), b.p. 175°/18 mm. 2:4-Diethylthiol- (II), b.p. 135—137°/6 mm., and 2:4-diethylthiol-5-methyl-pyrimidine (III), b.p. 158—161°/11 mm., are obtained from the 2:4- $\text{Cl}_2$ -compounds and  $\text{NaEtS}$  in  $\text{PhMe}$ . 2-Ethylthiolpyrimidines with  $\text{Cl}_2$  in  $\text{H}_2\text{O}$  at < 20° give 2- $\text{EtSO}_2$ -derivatives. Thus are obtained (a) 2-ethylsulphonyl-4-ethoxy-, b.p. 183—185°/4 mm., and 4-ethoxy-5-methyl-, m.p. 67—68°, (b) 4-chloro-2-ethylsulphonyl-5-methyl-, m.p. 67.5—68°, and 5-carbethoxy- (IV), m.p. 72.5—73.5°, (c) 4-chloro-, m.p. 57—58°, and 4-chloro-5-bromo-2-ethylsulphonyl-, m.p. 81—82°, (d) 5-bromo-2-ethylsulphonyl-4-ethoxy-, m.p. 89.5—90.5°, 4-amino-2-ethylsulphonyl-5-carbethoxy- (prepared in  $\text{HCl}$  at 0°), m.p. 143.5—144.5°, and 2:4-diethylsulphonyl-pyrimidine, m.p. 87—88°. At < 5° (I) gives 60% of (IV) and 15—20% of 2:4-dichloro-5-carbethoxypyrimidine (V), m.p. 36—37°, but at 30—40° 7% of (IV), 69—75% of (V), and 47—75% of  $\text{EtSO}_2\text{Cl}$ ; (V) is probably formed by way of the 2-sulphoxide. (II) and (III) give amorphous products. The structure of the  $\text{EtSO}_2$ -compounds is proved by hydrolysis by 20%  $\text{HCl}$  to the diketopyrimidines,  $\text{SO}_2$ , and a little  $\text{EtSO}_3\text{H}$  (probably formed from  $\text{EtSO}_2\text{H}$  produced as a primary product of hydrolysis). R. S. C.

**Complex dipyrindyl salts of nickel and copper.**—See this vol., 175.

**3:3'-Dipyridyl derivatives.** W. BRYDOWNA and W. WISZNIIEWSKI (*Rocz. Chem.*, 1935, 15, 378—382).—The Ag salt of 3:3'-dipyridyl-2:2'-dicarboxylic acid (I) and  $\text{EtI}$  or  $\text{MeI}$  in  $\text{C}_6\text{H}_6$  (at the b.p.; 2-5 hr.) yield the *Et*<sub>2</sub>, m.p. 82—84°, and *Me*<sub>2</sub>, m.p. 153—153.5°, esters of (I), which with  $\text{EtOH}\text{-NH}_3$  (8 hr.; 135—145°) afford the diamide, m.p. 268.5—270° (decomp.) of (I), converted by the Hofmann reaction into 2:2'-diamino-3:3'-dipyridyl, m.p. 181—182.5°, together with some 2-amino-3:3'-dipyridyl-2'-carboxylic acid lactam, m.p. 366—368° (decomp.). The chloride, m.p. 147—150°, of (I) is prepared from (I) and  $\text{SO}_2\text{Cl}_2$ . R. T.

**Reactions between indoles and Schiff's bases.** M. PASSERINI and F. ALBANI (*Gazzetta*, 1935, 65, 933—938).—The product from indole and  $\text{NPh}\cdot\text{CHPh}$  (A., 1933, 615) is converted by boiling 20%  $\text{HCl}$  into a substance (I),  $\text{C}_{30}\text{H}_{22}\text{N}_2$ , m.p. > 350°, regarded as  $\text{C}_6\text{H}_4\cdot\text{C}\cdot\text{CHPh}\cdot\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{NH}$ ,  $\text{NH}\cdot\text{C}\cdot\text{CHPh}\cdot\text{C}\cdot\text{NH}$ . Indole and  $\text{NPh}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$  yield anisyl-di-indolylmethane, m.p. 180°, converted by boiling  $\text{HCl}$  into a substance,  $\text{C}_{32}\text{H}_{26}\text{O}_2\text{N}_2$ , m.p. > 350°, similar to (I). Phenyl-di- $\alpha$ -methylindolylmethane is unchanged by  $\text{HCl}$ . E. W. W.

**Pyrrolidine derivatives. II. Ring enlargement from the indolizidine to the norlupanine series.** E. OCHIAI, K. TSUDA, and J. YOKOYAMA (*Ber.*, 1935, 68, [B], 2291—2298; cf. A., 1934, 901).—Pyrrole is converted by the successive action of K and  $\text{Bu}^n\text{Br}$  in boiling  $\text{C}_6\text{H}_6$  into 1-n-butylpyrrole,

catalytically hydrogenated (PtO<sub>2</sub> in AcOH) to 1-n-butylpyrrolidine, b.p. 88°/63 mm. (picrate, m.p. 124·5°; methiodide, m.p. 183°; platinichloride, m.p. 122·5°). The corresponding bromocyanide, b.p. 120°/0·01 mm., is converted by KCN in boiling EtOH-H<sub>2</sub>O into ω-cyanobutylbutylamine cyanide (I) CN·[CH<sub>2</sub>]<sub>4</sub>·NBu<sup>α</sup>·CN, b.p. 167°/1 mm., and ω-butylamino-n-valeronitrile (II), b.p. 125°/9 mm. (hydrochloride, m.p. 211°). (I) or (II) with conc. HCl at 150° gives ω-butylamino-n-valeric acid hydrochloride, m.p. 124·5°; the corresponding acid, m.p. 112·5°, when heated at 150° gives 1-n-butylpiperid-2-one (III), b.p. 120°/5 mm. (platinichloride, m.p. 150—151°), also obtained by oxidising butylpyridinium bromide with K<sub>3</sub>Fe(CN)<sub>6</sub> in alkaline solution and catalytic reduction (PtO<sub>2</sub>) of the pyridone.

2-Methylindolizidine bromocyanide (*loc. cit.*) is converted by KCN into 2-γ-cyano-β-methylpropylpiperidine cyanide, b.p. 159°/0·003 mm., hydrolysed by conc. HCl to γ-2-piperidyl-β-methylbutyric acid hydrochloride, m.p. 145°, converted by successive treatment with Ag<sub>2</sub>CO<sub>3</sub> and heating at 150° into 3-methyl-α-norlupinone (IV), b.p. 107°/2 mm. (platinichloride, decomp. 175°). Similarly, indolizidine is transformed successively into 2-γ-cyanopropylpiperidine cyanide, b.p. 175°/0·12 mm., γ-2-piperidylbutyric acid hydrochloride, m.p. 188—189°, and α-norlupinone, b.p. 105°/3 mm. (hydrochloride, m.p. 146—147°). Reduction of (III) cannot be effected by HCl and Zn-Hg, electrolytically at a Pb cathode, or by Na and boiling C<sub>5</sub>H<sub>11</sub>·OH; with MgMeI it yields 1-n-butyl-α-pipecoleine, b.p. 85—90°/11 mm. (hydriodide, m.p. 166·5°), hydrogenated (PtO<sub>2</sub> in AcOH) to 1-n-butyl-α-pipecoline, b.p. 115—120°/60 mm. (hydrochloride, m.p. 177·5°; picrate, m.p. 116°; perchlorate, m.p. 127·5°; aurichloride, m.p. 114°; methiodide, m.p. 224°; hydrobromide, m.p. 203°; hydriodide, m.p. 193°), also obtained from butylpicolinium bromide. Similar treatment of (IV) gives Δ<sup>1</sup>-1 : 3-dimethylnorlupinene, b.p. 115°/22 mm. (hydriodide, decomp. 237°), reduced (PtO<sub>2</sub>) to 1 : 3-dimethylnorlupinane, b.p. 127°/69 mm., (hydrochloride, decomp. 280°; perchlorate, decomp. 228°; picrate, m.p. 142·5°; methiodide, m.p. 168°). H. W.

Reaction of αβ-diketonic acids with o-phenylenediamine. H. OHLE and W. GROSS (Ber., 1935, 68, [B], 2262—2269; cf. A., 1934, 634).—Et<sub>2</sub> mesoxalate (I) and o-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> in EtOH or EtOH-H<sub>2</sub>O afford Et 2-hydroxyquinoxaline-3-carboxylate (II), m.p. 175°, hydrolysed to 2-hydroxyquinoxaline-3-carboxylic acid (III), m.p. 265° (decomp.). With a larger proportion of o-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> in boiling AcOH-EtOH-H<sub>2</sub>O (I) gives 2-hydroxyquinoxaline-3-carboxy-2'-aminoanilide, m.p. about 350° after becoming yellow at 250° and subliming at about 300°, is obtained, which is not readily hydrolysed by boiling dil. acid or alkali, is not attacked by Ac<sub>2</sub>O in C<sub>5</sub>H<sub>5</sub>N at 40°, but is transformed by boiling Ac<sub>2</sub>O into the Ac<sub>2</sub> derivative, m.p. 225°, relatively readily hydrolysed to (III). Since it is indifferent towards CH<sub>2</sub>N<sub>2</sub>, it probably has a spiran structure at room temp., and the open form when heated. (II) reacts readily with CH<sub>2</sub>N<sub>2</sub> in CHCl<sub>3</sub> giving Et 2-keto-1-methyl-1 : 2-dihydroquinoxaline-3-carboxylate, m.p. 125—126°, hydrolysed to the corre-

sponding acid, m.p. 173°, from which Me is not appreciably removed under the conditions of Zeisel's determination. Even with an excess of o-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>, αβ-diketobutyric esters give 2-methylquinoxaline-3-carboxylic esters. Me<sub>2</sub> dihydroxymaleate is transformed by the successive action of benzoquinone in boiling MeOH and o-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> into Me<sub>2</sub> quinoxaline-2 : 3-dicarboxylate, m.p. 325°. Hydroxytetronic acid when similarly treated yields the o-aminoanil of 2-hydroxy-1 : 2-dihydroquinoxaline 3-hydroxymethyl ketone (IV),  $\begin{matrix} \text{NH}\cdot\text{CO} \\ | \\ \text{C}_6\text{H}_4\cdot\text{N} \end{matrix} \gg \text{C}\cdot\text{C}(\text{CH}_2\cdot\text{OH})\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , m.p.

167·5—168·5°, in which the presence of NH<sub>2</sub> is established by the formation of a monohydrochloride, by diazotisation and coupling with β-C<sub>10</sub>H<sub>7</sub>·OH, by condensation with COMe<sub>2</sub> to the compound,  $\begin{matrix} \text{NH}\cdot\text{CO} \\ | \\ \text{C}_6\text{H}_4\cdot\text{N} \end{matrix} \gg \text{C}\cdot\text{C}(\text{CH}_2\cdot\text{OH})\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{CMe}_2$ , m.p. 184·5—186°, and by the formation of a Ac<sub>3</sub> derivative, m.p. 182° (with small amounts of a Ac<sub>2</sub> compound, m.p. 212—213°), converted by cautious hydrolysis into the N-Ac compound, m.p. 233·5°, and by Ag<sub>2</sub>O and MeI into the substance

$\begin{matrix} \text{N}\cdot\text{C}(\text{OMe}) \\ | \\ \text{C}_6\text{H}_4\cdot\text{N} \end{matrix} \gg \text{C}\cdot\text{C}(\text{CH}_2\cdot\text{OMe})\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ , m.p. 136·5—137·5°. In contrast to the derivative C<sub>18</sub>H<sub>18</sub>O<sub>4</sub>N<sub>4</sub> from isoascorbic acid (*loc. cit.*), (IV) does not yield o-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> when boiled with dil. acid, although extensive decomp. occurs. H. W.

Oxidation of uric acid.—See this vol., 233.

Reaction between aminoantipyrine and phenylhydrazine. M. PASSERINI and M. RIDI (Gazzetta, 1935, 65, 930—933; cf. A., 1935, 501).—Pyrimidone and NPh·NH<sub>2</sub> at 180—190° give 4-benzeneazo-1-phenyl-3-methyl-5-pyrazolone (I), with bis-(1-phenyl-3-methylpyrazol-5-on-4-yl), also obtained from (I) and NPh·NH<sub>2</sub>. Aminoantipyrine and p-tolylhydrazine yield 4-p-tolueneazo-1-p-tolyl-3-methyl-5-pyrazolone. E. W. W.

Occurrence of decomposition products of chlorophyll. III. Isolation of pyrroporphyrin from ox bile. P. ROTHMUND (J. Amer. Chem. Soc., 1935, 57, 2179—2180; cf. A., 1935, 110).—Fractional extraction of ox bile pigments from Et<sub>2</sub>O by HCl gives a trace of coproporphyrin by 0·5% HCl, pyrroporphyrin by 3% HCl, phylloerythrin by 10% HCl, traces of other pigments by 15 and 20% HCl, but no phyllo- or rhodo-porphyrin. R. S. C.

Susceptibility of complex porphyrin-nickel salts. F. HAUROWITZ and W. KLEMM (Ber., 1935, 68, [B], 2312—2313).—Re-examination of the Ni salt of dimethylmesoporphyrin confirms its diamagnetic properties (Klemm, A., 1935, 1311), whereas the behaviour of Ni-tetramethylhæmatoporphyrin ester (Haurowitz, A., 1935, 1384) varies, probably owing to non-uniformity. H. W.

Spectrophotometric studies. II—V.—See this vol., 221.

Alcoholic ammonia as a reagent in the nitrostilbene series. D. E. WORRALL (J. Amer. Chem. Soc., 1935, 57, 2299—2301).—α-Nitrostilbene (I) and NH<sub>3</sub>-EtOH give PhCHO, much 3 : 4 : 5-triphenylisooxazoline oxide (II), and some dibenzoylphenyl-

*methaneoxime* ( $\alpha$ -oximino- $\gamma$ -keto- $\alpha\beta\gamma$ -triphenylpropane) (III), m.p. 152—153°; the same products are formed from (I) and  $\text{CH}_2\text{Ph}\cdot\text{NO}_2$  or from the latter and  $\text{PhCHO}$  with  $\text{NH}_3\text{-EtOH}$ . (III) gives (II) immediately with hot  $\text{HCl}$  or alkali and slowly above the m.p. The intermediate formation of some (III) in the prep. of (II) by more strongly alkaline reagents (cf. Heim, A., 1911, i, 717) is thus proved. In abs.  $\text{EtOH-NH}_3$  some  $\alpha$ -nitro- $\beta$ -benzylideneaminodibenzyl, m.p. 137—138°, is also formed. Similarly are obtained 3:5-diphenyl-4-p-bromophenyl-, m.p. 172—173°, -4-anisyl-, m.p. 145—146°, and -4-piperonyl-, m.p. 165—166°, 3:4-diphenyl-5-p-bromophenyl-, m.p. 213—215° (decomp.), 3-phenyl-4:5-di-p-bromophenyl-, m.p. 160—161°, and 5-p-bromophenyl-4-piperonyl-isooxazoline oxide, m.p. 192—193°; 3:5-diphenyl-4-p-bromophenyl-, m.p. 182—183°, -4-piperonyl-, m.p. 227—228°, -4-ochlorophenyl-, m.p. 127—128°, 3-phenyl-4:5-di-p-bromophenyl-, m.p. 179—180°, 5-p-bromophenyl-4-anisyl-, m.p. 188—189°, and 5-p-bromophenyl-4-piperonyl-isooxazole, m.p. 204—205°;  $\alpha$ -nitro- $\beta$ -o-chlorobenzylideneamino- $\alpha$ -phenyl- $\beta$ -o-chlorophenylethane, m.p. 144—145°. R. S. C.

**Synthesis and pharmacological study of some derivatives of aminomethyl-dihydro-oxazine which exhibit an adrenaline-like action.** (MLLE.) G. BENOIT and D. BOVET (J. Pharm. Chim., 1935, [viii], 22, 544—548).—*o*- $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$  with  $\text{C}_3\text{H}_5\text{Br}$  in  $\text{COMe}_2$  containing  $\text{K}_2\text{CO}_3$  affords the *O*-allyl ether, the  $\text{Br}_2$ -derivative of which is hydrolysed ( $\text{HCl}$ ) to the  $\beta\gamma$ -dibromoallyl ether (*hydrochloride*, m.p. 171°) of *o*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ . The latter is cyclised with  $\text{K}_2\text{CO}_3$  in  $\text{COMe}_2$  in  $\text{N}_2$  and then reacts with  $\text{NHEt}_2$  to give 3-diethylaminomethyl-2:3-dihydro-oxazine, m.p. 130° (*dihydrochloride*, m.p. 188°). 2-Diethylaminomethyl-, b.p. 195°/23 mm. (*dihydrochloride*, m.p. 190—192°), and 2-piperidinomethyl-2:3-dihydro-oxazine, b.p. 170—175°/1.5 mm., are prepared from *o*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$  with diethyl- $\beta\gamma$ -dibromopropylamine, b.p. 105—110°/769 mm. [from  $\text{C}_3\text{H}_5\text{Br}$  and  $\text{NHEt}_2$ , followed by bromination] and 1- $\beta\gamma$ -dibromopropylpiperidine, b.p. 147—152°/753 mm. [from  $\text{C}_3\text{H}_5\text{Br}$  and piperidine, followed by bromination], respectively. The pharmacological effects are described. J. L. D.

**Synthesis of phenylated benzoxazoles and [their] derivatives.** V. J. MIKESKA and M. T. BOGERT (J. Amer. Chem. Soc., 1935, 57, 2121—2124).—The prep. of *o*- and *p*- $\text{C}_6\text{H}_4\text{Ph}\cdot\text{OH}$  and  $\text{Ph}_2\text{SO}_2$  from commercial  $\text{PhOH}$  residues is described. 3-Nitro-4-hydroxydiphenyl (I) (*p*-toluenesulphonate, m.p. 114.8°) with conc.  $\text{H}_2\text{SO}_4$  at 70° gives a sulphonic acid (*Ba* salt). 3-Amino-4-hydroxydiphenyl with  $\text{BzCl}$  gives 1:4-diphenyl-, m.p. 132.8°, and with *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$  at 210° 4-phenyl-1-*p*-nitrophenylbenzoxazole (II), m.p. 288.8° (with a little 3-*p*-nitrobenzamido-4-hydroxydiphenyl, m.p. 249.3°). (II) or the *p*-nitrobenzoate, m.p. 169°, of (I) with  $\text{SnCl}_2\text{-HCl-AcOH}$  gives 4-phenyl-1-*p*-aminophenylbenzoxazole, m.p. 174.2°, which with 60% oleum gives (?) 6-sulpho-4-phenyl-1-4'-amino-(?) 3'-sulphophenylbenzoxazole and with  $\text{NaNO}_2$  in conc.  $\text{HCl}$  4-phenyl-1-(*p*-benzenediazonium chloride)benzoxazole, m.p. 270°. The  $\text{Na}$  salt of 3:5-dinitro-2-hydroxydiphenyl and  $\text{BzCl}$  in  $\text{COMe}_2$  gives the benzoate, m.p. 119.5°, reduced to

4-amino-2:6-diphenylbenzoxazole, m.p. 220.8° (*sulphonic acid*,  $+\text{H}_2\text{O}$ , decomp.  $> 375^\circ$ ). M.p. are corr. R. S. C.

**Crystalline by-product, obtained in the large-scale extraction of theelin and theelol.** A. W. DOX, W. G. BYWATER, and F. H. TENDICK (J. Biol. Chem., 1935, 112, 425—430).—Human pregnancy urine contains a non- $\alpha$ -sterogenic, acidic substance,  $\text{C}_{21}\text{H}_{23}\text{O}_3\text{N}_4$ , decomp. 360° [3 active H; *Et* ester or ether, m.p. 277—278° (decomp. from 275°)], stable to 25%  $\text{KOH}$  and hot conc. acid, oxidised by  $\text{CrO}_3\text{-AcOH}$  to an acid,  $\text{C}_{18}\text{H}_{18}\text{O}_7\text{N}_2$ , decomp. 253—269°, and giving a pyrrole pine-splinter reaction and a red solution in conc.  $\text{H}_2\text{SO}_4$  (green fluorescence when heated), but no protein,  $\text{NH}_2$ -acid, or purine reactions. R. S. C.

**Unsaturation and tautomeric mobility of heterocyclic compounds. VI. Mobility of 5-substituted 1-hydroxybenzthiazoles, and the ultra-violet absorption of mobile and static derivatives of 1-hydroxybenzthiazole.** R. F. HUNTER and E. R. PARKEN. VII. Selenazole derivatives. C. HASAN and R. F. HUNTER (J.C.S., 1935, 1755—1761, 1762—1766).—VI. 1-Hydroxy-5-methylbenzthiazole (I), m.p. 168—169° (*Ac* derivative, m.p. 109°; *Ag* salt; *Na* salt, decomp. 260—261°), obtained by hydrolysis of the 1-*OEt*-compound, m.p. 35—36°, which is prepared from *p*-tolylthiourethane, is methylated ( $\text{Me}_2\text{SO}_4$ ) to 1-keto-2:5-dimethyl-1:2-dihydrobenzthiazole, m.p. 76—77°, also obtained by heating the corresponding 1-nitrosoimino-compound, explodes 144° (from the methosulphate of 1-amino-5-methylbenzthiazole and  $\text{NaNO}_2$ ). 1-Methoxy-5-methylbenzthiazole, m.p. 32—33°, obtained from *Me p*-tolylthioncarbamate, m.p. 79—80°, is not present in the methylation product of (I). (I) is brominated to 4(or 6)-bromo-1-hydroxy-5-methylbenzthiazole, m.p. 239—240°, methylated to 4(or 6)-bromo-1-keto-2:5-dimethyl-1:2-dihydrobenzthiazole (II), m.p. 145°. *o*-Bromo-*p*-tolylthiourethane, m.p. 32—33°, gives 3-bromo-1-ethoxy-5-methylbenzthiazole, m.p. 36—37°, hydrolysed to the 1-*OH*-compound, m.p. 209°, which is methylated to 3-bromo-1-keto-2:5-dimethyl-1:2-dihydrobenzthiazole, m.p. 116°, not identical with (II). 2-Bromo-*p*-tolylthiocarbimide, m.p. 44—45°, forms 2-bromo-*p*-tolylthiourethane, m.p. 106°, which yields 4(or 6)-bromo-1-ethoxy-5-methylbenzthiazole, m.p. 50—51°, hydrolysed to the 1-*OH*-compound.

A similar series of reactions leads to the following: *p*-phenylthiourethane, m.p. 93—94°; 1:5-diethoxy-, m.p. 54°, 1-hydroxy-5-ethoxy-, m.p. 147°, and 1-keto-5-ethoxy-2-methyl-1:2-dihydrobenzthiazole, m.p. 85°; *Me p*-phenylthioncarbamate, m.p. 68—69°, 1-methoxy-5-ethoxybenzthiazole, m.p. 75—76°, *p*-iodophenylthiourethane, m.p. 106—107°, 5-iodo-1-ethoxy-, m.p. 76—77°, and -hydroxybenzthiazole, m.p. 225—226°, 5-iodo-1-keto-, m.p. 135°, and 5-iodo-1-nitrosoimino-2-methyl-1:2-dihydrobenzthiazole, explodes 160°; *Me p*-bromophenylthioncarbamate, m.p. 99—100°, 5-bromo-1-methoxybenzthiazole, m.p. 82—83°; *Me* phenylthioncarbamate, m.p. 93°, oxidised to 1-methoxybenzthiazole, m.p. 88—89°; 5-bromo-1-hydroxybenzthiazole is methylated to 5-bromo-1-keto-2-methyl-1:2-dihydrobenzthiazole; 5-chloro-1-ethoxy-, m.p. 60—61°,

and *-hydroxy-benzthiazole*, m.p. 204°, *5-chloro-1-keto-*, m.p. 112°, and *5-chloro-1-nitrosoimino-2-methyl-1:2-dihydrobenzthiazole*, explodes 138—139°; and *5-nitro-1-nitrosoimino-*, explodes 152°, is converted into *5-nitro-1-keto-2-methyl-1:2-dihydrobenzthiazole*, m.p. 162—163°, also obtained by methylation of *5-nitro-1-hydroxybenzthiazole*, m.p. 251°. Absorption spectra of (I) indicate that it has the structure  $C_6H_4Me \begin{array}{c} \diagup S \\ \diagdown N(H) \end{array} CO$ .

VII. *1-Aminobenzselenazole* (III), m.p. 142°, is methylated to *1-imino-2-methyl-1:2-dihydrobenzselenzazole*, m.p. 104°, converted into the *1-nitrosoimino*-compound, explodes 142—144°. *s-Phenylmethylselenocarbamide*, m.p. 11°, with Br gives *1-methylaminobenzselenazole*, m.p. 140°. (III) is acetylated to *1-acetamidobenzselenazole*, m.p. 190°. Acetylation of phenylselenocarbamide gives *s-acetylphenylselenocarbamide*, m.p. 195°. Diphenylselenocarbamide is cyclised to *1-anilinobenzselenazole*, m.p. 170° (*picrate*, m.p. 245°), methylated to *1-phenylmethylaminobenzselenazole*, isolated as the *picrate*, m.p. 200°, and *1-anilo-2-methyl-1:2-dihydrobenzselenzazole* (*picrate*, m.p. 172°). *Bis-o-aminophenyl diselenide* and  $ClCO_2Et$  yield *bis-o-urethanophenyl diselenide*, m.p. 110°, reduced (Sn-HCl) to *1-hydroxybenzselenzazole*, m.p. 140°, which is methylated to *1-keto-2-methyl-1:2-dihydrobenzselenzazole*, m.p. 60°, also obtained from the nitrosoimino-compound. *1-Thiolbenzselenzazole*, m.p. 159°, obtained by condensation of nascent *o-aminoselenophenol* with  $CS_2$ , is methylated to a compound, which differs from the corresponding *1-thio-2-methyl-1:2-dihydrobenzselenzazole*, m.p. 80°.

*1-Amino- $\alpha$ -naphthaselenazole*, m.p. 252° (*Ac* derivative, m.p. 250°), with NaOH gives *bis-2-amino- $\alpha$ -naphthyl diselenide*, decomp. about 120°, which with NaHS and  $CS_2$  in  $H_2S$  yields *1-thiol- $\alpha$ -naphthaselenazole*, m.p. 228°. *s-Phenyl- $\beta$ -naphthylselenocarbamide*, m.p. 174°, is cyclised to *1-anilino- $\alpha$ -naphthaselenazole*, m.p. 210°. F. R. S.

**Metallic salts of thiolbenzthiazole.** G. SPACU and M. KURAŠ (J. pr. Chem., 1935, [ii], 144, 106—114).—Treatment of hot aq.  $CuSO_4$  with thiolbenzthiazole (I) in EtOH affords the salt  $(C_7H_4NS)_2Cu$ , which is internally complex, since it does not add  $NH_3$ ,  $C_5H_5N$ , or  $(CH_2NH_2)_2$ ; it can be used for the determination of (I). Analogous *Bi*, *Pb*, *Cd*, *Ni*, *Hg*\*, *Tl*\*, and *Au*\*\* salts are described; (I) is recommended for the determination of these metals with the exception of  $Hg^*$ . The compounds  $C_7H_4NS_2Pb(OH)$ ,  $(C_7H_4NS_2)_2[Cd(NH_3)_2] \cdot H_2O$ ,  $(C_7H_4NS_2)_3Co_2(OH)$ , and  $(C_7H_4NS_2)_3Zn_2(OH)$  are described. H. W.

**Thiochrome from vitamin-B<sub>1</sub> (antineurin).** G. BARGER, F. BERGEL, and A. R. TODD (Ber., 1935, 68, [B], 2257—2262; cf. A., 1935, 1286).—Details are given of the oxidation of antineurin (I) by  $K_3Fe(CN)_6$  to thiochrome (II),  $C_{12}H_{14}ON_4S$ , identical with that obtained by Kuhn *et al.* (A., 1935, 1026) from yeast. The reaction does not consist in a simple dehydrogenation of (I). Unlike (I), (II) does not appear to contain a quaternary N.  $NH_2$  attached to the pyrimidine ring in (I) appears involved in the production of (II), since (I) quantitatively affords  $NH_4Cl$  when treated with conc. HCl at 100°, whereas

(II) (hydrochloride, m.p. 217—221° after slow decomp. at 200°) is largely unchanged. The structure  $CH_3N:C:N:C:S \cdot C \cdot CH_2 \cdot CH_2 \cdot OH$  is suggested for (II).  $N \cdot CEt \cdot C \cdot N \cdot CMe$  H. W.

**Thiochrome.** R. KUHN and H. VETTER (Ber., 1935, 68, [B], 2375—2385).—The conversion of vitamin B (I) into thiochrome (II),  $N \cdot CMe \cdot C \cdot N \cdot CMe$  proceeds readily in presence of NaOH but not of  $Na_2CO_3$ ; among redox indicators, only porphyrin (III) gives satisfactory results.  $N \cdot CMe \cdot C \cdot NCl \cdot CMe \cdot C \cdot [CH_2]_2 \cdot OH$   $\xrightarrow{NaOH}$   $N \cdot CMe \cdot C \cdot NH_2 \cdot CH \cdot S$  (I)  $\begin{array}{c} \diagup N \cdot CMe \\ \diagdown CH(OH) \cdot S \end{array} \cdot [CH_2]_2 \cdot OH$  (III.)

At  $p_H$  13 this can be replaced by  $K_3Fe(CN)_6$  or mol.  $O_2$ , the action of the latter being, however, dependent on the presence of suitable catalysts. The product is identical with that obtained from yeast or by Barger *et al.* (preceding abstract). Since  $K_3Fe(CN)_6$  is active in presence of NaOH, but not of  $Na_2CO_3$ , the preliminary stage of the reaction consists in the transformation of (I) into the  $\psi$ -base (IV). Titration of (IV) with (III) causes the removal of 2 H corresponding with the difference in empirical formula between (IV) and (II). The no. of *C-Me* groups remains unchanged, since drastic oxidation of (I) and (II) by  $CrO_3$  gives harmonising yields of AcOH. The mode of union of S is unchanged, since (I) and (II) evolve  $H_2S$  when heated with NaOH. The  $NH_2$  and CH of (I) are lost during the formation of the pigment, since (II) does not evolve  $N_2$  when treated with  $HNO_2$  (van Slyke) and does not couple with diazotised *p-NH\_2 \cdot C\_6H\_4 \cdot SO\_3H* in presence of  $CH_2O$ . The correspondingly altered basic dissociation const. of (II) corresponds with the dependence of its fluorescence on  $p_H$ . The  $NH_2$  is involved in the formation of a new ring, since only conjugated systems with cyclic arrangement show a brightness of fluorescence comparable with that of (II), which is therefore formulated as in (II). (II) appears devoid of physiological activity. H. W.

**Condensation of  $\omega$ -bromoacetophenone with 3-phenyl-1-o-aminophenylthiocarbamide.** T. N. GHOSH (Current Sci., 1935, 4, 312).—The hydrobromide, m.p. 223° (decomp.), described by Pathak (A., 1935, 1386) is not the same as the heptathiodiazine, m.p. 230° (decomp.), obtained by the author (A., 1931, 854). F. R. G.

**Alkaloids obtained from jaborandi leaves; synthesis of pilocarpidine.** N. A. PREOBRAŠENSKI, A. M. POLJAKOVA, and V. A. PREOBRAŠENSKI (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 267—269).—*d*-Pilopic acid is converted by  $SOCl_2$  into the *chloroanhydride*, which with  $CH_2N_2$  affords *d-pilopyl diazomethyl ketone*, m.p. 106—108°; in  $H_2O$  the latter is converted by  $Na_2S_2O_4$  and  $Ag_2O$  into *d-homopilopic acid* (I). This synthesis is confirmed by conversion of (I) into *d-homopilopyl chloromethyl ketone* (A., 1933, 1311) identical with material prepared from natural (I). P. G. C.

**Peganine. VIII. Derivatives of peganine and its ring homologues.** E. SPATH and N.

PLATZER (Ber., 1935, 68, [B], 2221—2226).—Pyrrolidone and isatoic anhydride (I) at 120—180° afford  $\Delta^9$ -pegen-8-one, m.p. 110—111°, reduced at a Pb electrode to 1-*o*-aminobenzylpyrrolidine. Condensation of *o*-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>Cl with Me  $\delta$ -amino-*n*-valerate [obtained from piperidone (II)] yields 1-*o*-nitrobenzylpiperidone, m.p. 117°, reduced by Zn dust and 20% AcOH to 1-*o*-aminobenzylpiperidone, m.p. 92.5—93.5°, which is dehydrated by POCl<sub>3</sub> to the base (III), *o*-C<sub>6</sub>H<sub>4</sub> $\left\langle \begin{array}{l} \text{CH}_2 \cdot \text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \text{N} = \text{C} \cdot \text{CH}_2 \cdot \text{CH}_2 \end{array} \right.$ , m.p. 82—83° (corresponding H<sub>2</sub>-derivative, m.p. 71—72°). Alternatively (I) is condensed with (II) to piperidino-4-ketodihydroquinazoline, C<sub>6</sub>H<sub>4</sub> $\left\langle \begin{array}{l} \text{CO} \cdot \text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \text{N} = \text{C} \cdot \text{CH}_2 \cdot \text{CH}_2 \end{array} \right.$ , m.p. 99—100°, reduced by Zn and acid to (III). H. W.

Lupin alkaloids. VIII. G. R. CLEMO, W. MCG. MORGAN, and R. RAPER (J.C.S., 1935, 1743—1745).—*Et* pyridyl-2- $\beta$ -propionate, b.p. 95°/1 mm. (*picrolonate*, m.p. 141°, *picrate*, m.p. 84°), with CH<sub>2</sub>Br·CO<sub>2</sub>Et gives *Et* pyridinium-1-acetate-2- $\beta$ -propionate bromide, m.p. 159°, reduced to *Et* piperidyl-1-acetate-2- $\beta$ -propionate, b.p. 138—140°/1 mm. Ring-closure of this ester gives 3-keto-octahydropyridocoline, b.p. 74—76°/1 mm. (*picrate*, m.p. 185°), which with Zn-Hg-HCl yields octahydropyridocoline-A, identical with norlupinane, confirming the structure previously assigned. *Et* pyridyl-2-acetate, b.p. 134—135°/21 mm. (*picrate*, m.p. 136—137°), is reduced to the piperidyl ester, b.p. 105°/14 mm. (*picrate*, m.p. 125°), which with CHBrMe·CO<sub>2</sub>Et forms *Et* piperidyl-2-acetate-1- $\alpha$ -propionate, b.p. 135—140°/1 mm., cyclised to 3-keto-2-methyloctahydropyrrocoline, b.p. 67—69°/1 mm. (*picrate*, m.p. 162°). The ketone with Zn-Hg-HCl yields 3-hydroxy-2-methyloctahydropyrrocoline, b.p. 100—105°/16 mm. (*picrate*, m.p. 159°; *picrolonate*, m.p. 181°), and with N<sub>2</sub>H<sub>4</sub> followed by Na gives 2-methyloctahydropyrrocoline, b.p. 32—35°/1 mm. (*picrate*, m.p. 197°; *picrolonate*, m.p. 208°).

F. R. S.

Lupin alkaloids. X. Degradation of dehydrosparteine methoacetate by oxidation. K. WINTERFELD and H. E. RÖNSBERG (Arch. Pharm., 1935, 273, 521—532).—The CrO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> oxidation product of dehydrosparteine methoacetate (A., 1930, 1300) yields the platinumchloride, m.p. 250°, of a substance which is not C<sub>7</sub>H<sub>13</sub>O<sub>2</sub>N, as thought by Winterfeld and Ipsen (*loc. cit.*), but the acid C<sub>15</sub>H<sub>26</sub>O<sub>4</sub>N<sub>2</sub> (I), [ $\alpha$ ]<sub>D</sub><sup>18</sup> -38.2° in H<sub>2</sub>O (*aurichloride*, m.p. 205°). (I) is decarboxylated to a resinous substance; with CH<sub>2</sub>N<sub>2</sub>, (I) loses H<sub>2</sub>O and forms the Me ester, C<sub>16</sub>H<sub>26</sub>O<sub>3</sub>N<sub>2</sub>, which with Pd-CaCO<sub>3</sub> absorbs 1 H<sub>2</sub>. A second CrO<sub>3</sub> oxidation product forms a Cu salt, and a *reineckate*, m.p. 186°; it is decarboxylated, and with MeOH-HCl yields two esters, b.p. 136°/15 mm. and 155—160°/1 mm., respectively. It consists of a mixture of the acid, C<sub>14</sub>H<sub>24</sub>O<sub>4</sub>N<sub>2</sub>, with a similar substance. Methylpyrrolidonecarboxylic acid is absent. E. W. W.

Lupin alkaloids. XI. Oxidative degradation of  $\alpha$ -didehydrosparteine. K. WINTERFELD and H. E. RÖNSBERG (Arch. Pharm., 1936, 274, 48—60).— $\alpha$ -Didehydrosparteine (I) with CrO<sub>3</sub> gives only NH<sub>2</sub>·[CH<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>H and CO<sub>2</sub> (8 mols.), indicating that one ethylenic linking is in position 4 : 5. (I) gives an

unstable Bz derivative, indicating that the second ethylenic linking is  $\alpha\beta$  to the second N and attached to a *tert*-C. (I) and KMnO<sub>4</sub> in dil. H<sub>2</sub>SO<sub>4</sub> give (·CH<sub>2</sub>·CO<sub>2</sub>H)<sub>2</sub>, which must have come from ring IV and thus favours the symmetrical formula for sparteine. R. S. C.

Solanidine t. I. H. DIETERLE and H. ROCHELMAYER (Arch. Pharm., 1935, 273, 532—539).—Solaniidine (I) is hydrogenated in AcOH to dihydrosolanidine, m.p. 219—220°. Action of MeI on (I) for 24 hr. at 125° yields not solanidine methiodide (II) (cf. Schaffnit, Diss., Frankfurt, 1932), but solanthrine, C<sub>27</sub>H<sub>41</sub>N, also obtained by heating (II) at 325°. Se at 320° converts (I) into phenanthrene, chrysene, and another hydrocarbon, with pyridine and other bases. E. W. W.

Solanthrine. II. H. DIETERLE and H. ROCHELMAYER (Arch. Pharm., 1935, 273, 539—540).—Dihydrosolanthrine (I) (A., 1933, 171) is identical with solanidine (*ibid.*, 290), but not with dihydrosolanidene (II) (*ibid.*, 1061); both (I) and (II) are, however, hydrogenated to tetrahydrosolanthrine (*ibid.*, 729). Thus (I) and (II) are isomerides differing in the position of a double linking. E. W. W.

[Attempted synthesis of] ergot alkaloids. Synthesis of 4-carbolinecarboxylic acids. W. A. JACOBS and L. C. CRAIG (Science, 1935, 82, 421—422).—Condensation of tryptophan with CH<sub>2</sub>O, MeCHO, paralal, and PhCHO gives 3 : 4 : 5 : 6-tetrahydro-4-carboline-5-carboxylic acid, the 3-Me, m.p. 295° (decomp.), 3- $\beta$ -hydroxypropyl-, m.p. 261°, and 3-Ph derivative, m.p. 223—226°, respectively. Crotonaldehyde gives an amorphous substance. Using *N*-methyltryptophan instead of tryptophan in the condensations, PhCHO gives 3-phenyl-4-methyltetrahydro-4-carboline-5-carboxylic acid, m.p. 199—201° (decomp.). These substances, however, and those obtained by direct methylation, do not give the colour reaction with *p*-NMe<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CHO characteristic of lysergic acid and its derivatives. L. S. T.

Strychnine and brucine. XXXV. Hofmann degradation of dihydrobrucidine. O. ACHMATOWICZ, (Miss) P. LEWI, and R. ROBINSON (J.C.S., 1935, 1685—1694).—N(b)-Methyl-dihydrobrucidininium carbonate and N(a)N(b)-dimethyl-dihydrobrucidininium dicarbonate (+16H<sub>2</sub>O), m.p. 190—192° (decomp.), undergo thermal decomp., the dicarbonate giving more satisfactory results; the products are N(b)-methyl-dihydrobrucidine-a (I) (methyl- $\psi$ -dihydrobrucidine, m.p. 221—222°) and -b (II), dihydrobrucidine, and hydroxymethyltetrahydrobrucidine (III), m.p. 169°. (I) and MeI at low temp. yield N(b)-methyl-dedihydrobrucidine-a dimethiodide (+4H<sub>2</sub>O), m.p. 284—286° (decomp.) [dimethochloride (+3H<sub>2</sub>O), decomp. 296—298°], and at high temp. form allo-N(b)-methyl-dihydrobrucidine-a dimethiodide (+3H<sub>2</sub>O), m.p. 245—246° [dimethochloride (+4H<sub>2</sub>O, 3MeOH), m.p. 202—204° (decomp.)]. The *allo*-dimethochloride and NaOMe give dimethyldebrucidine, m.p. 155—156°. (I) absorbs 2H (Pd-C) to give (NaI) N(b)-methyl-dihydrobrucidininium-d (+2H<sub>2</sub>O), m.p. 317—318° (decomp.) [chloride (+3H<sub>2</sub>O), m.p. 304—306° (decomp.)], and -c iodide (+2.5H<sub>2</sub>O), m.p. 304—306° (decomp.) [chloride (+3H<sub>2</sub>O), m.p. 233—235°]. (III) with



Ac<sub>2</sub>O-NaOAc gives *acetoxymethyltetrahydrobrucidine*, m.p. 258—260° (decomp.), is methylated (Me<sub>2</sub>SO<sub>4</sub>-NaI) to methoxymethyltetrahydrobrucidine methiodide, and with hot aq. H<sub>2</sub>SO<sub>4</sub> leads to methylidihydrobrucidinium H sulphate. (II) is isolated as the *methiodide* (+CHCl<sub>3</sub>), decomp. 242—244° (+2MeOH), m.p. 80—82°, decomp. 242—244°, converted into the *methochloride*, m.p. 165—170°, solidifies 175—180°, decomp. 245—248°, from which the base is obtained. The constitution of the compounds is discussed.

F. R. S.

**Strychnos alkaloids. LXXXVIII. Transformation of dihydrobrucine into three isomerides and preparation of isodihydrostrychnine.** H. LEUCHS and A. DORNOW (Ber., 1935, 68, [B], 2234—2241).—Treatment of dihydrobrucine with NaOMe affords a mixture of *isodihydrobrucine* III, m.p. 235—245°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +28.8° in abs. EtOH, which gives a very sparingly sol. *perchlorate*, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +13° in H<sub>2</sub>O, a *methiodide*, decomp. 310° after darkening at 280°, [ $\alpha$ ]<sub>D</sub><sup>15</sup> +41.7° in 90% AcOH, and an *acetate* (*perchlorate*, softens at 240°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -18° in H<sub>2</sub>O), and *isodihydrobrucine* I (I), C<sub>22</sub>H<sub>28</sub>O<sub>4</sub>N<sub>2</sub>, m.p. 225—235°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -165° in abs. EtOH, -195° in CHCl<sub>3</sub> [identical with the so-called dihydrobrucine hydrate of Wieland *et al.* (A., 1930, 1455)], which affords a *sulphate*, m.p. > 290°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -223° in H<sub>2</sub>O, a *perchlorate*, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -231° in H<sub>2</sub>O, a *methiodide*, decomp. 310° after softening at 280—300° (vac.), and an *acetate* [*perchlorate*, m.p. 240—260° (decomp.), [ $\alpha$ ]<sub>D</sub><sup>20</sup> -133° in H<sub>2</sub>O]. In addition, small amounts of *isodihydrobrucine* II, m.p. 215—216° (vac.), [ $\alpha$ ]<sub>D</sub><sup>20</sup> -10.2° in CHCl<sub>3</sub>, +4.3° in abs. EtOH, are occasionally produced; this becomes the main product when less drastic conditions of isomerisation are used. It gives a *perchlorate*, m.p. 215—230°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +24° in H<sub>2</sub>O, *methiodide*, m.p. 208—218° (sealed tube), [ $\alpha$ ]<sub>D</sub><sup>15</sup> +17.2° in 90% AcOH, and *acetate*, m.p. 103—105° (*perchlorate*, m.p. 138—143°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +12° in H<sub>2</sub>O). It is not hydrogenated in presence of PtO<sub>2</sub> and AcOH and is isomerised to (I) by NaOMe. The presence of the *isostrychnine* type is established for all isomerides, and isomerism is caused by new, asymmetric C atoms. Treatment of dihydrostrychnine with NaOMe leads to *isodihydrostrychnine* (II), m.p. 249—250°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +6.5° in CHCl<sub>3</sub>, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +23° in abs. EtOH, but other isomerides do not appear to be formed. (II) gives a *perchlorate*, m.p. 258—260° (decomp.), [ $\alpha$ ]<sub>D</sub><sup>20</sup> +37° in H<sub>2</sub>O, *methiodide*, m.p. about 318° (decomp.), and an *acetate*, m.p. 202° [*perchlorate*, m.p. 260° (decomp.), [ $\alpha$ ]<sub>D</sub><sup>20</sup> +25° in H<sub>2</sub>O]. It is hydrogenated (PtO<sub>2</sub>-dil. AcOH) to the base C<sub>21</sub>H<sub>26</sub>O<sub>2</sub>N<sub>2</sub>, m.p. 228°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -4.02° in CHCl<sub>3</sub> [*perchlorate*, m.p. about 141° (decomp.), [ $\alpha$ ]<sub>D</sub><sup>20</sup> -14.3° in H<sub>2</sub>O].

Dihydrobrucine methiodide separates from hot H<sub>2</sub>O with 1 mol. of H<sub>2</sub>O and has m.p. 245° or m.p. 255—258° (vac.). From MeOH it gives crystals +0.5MeOH, m.p. 290—295° (decomp.). The anhyd. salt has m.p. 290—295° (decomp.). H. W.

**Alkaloids of Papaver types. II. Alkaloids of P. floribundum.** R. KONOVALOVA, S. YUNUSOV, and A. OREKHOV (Ber., 1935, 68, [B], 2277—2282; cf. this vol., 88).—The air-dried foliage of *P. floribundum* is moistened with 10% NH<sub>3</sub> and percolated

with C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> and the mixture of alkaloids thus obtained (0.36% yield) is separated into phenolic (I) and non-phenolic (II) bases. Crystallisation of (I) from EtOH affords *floripavine* (III), C<sub>19</sub>H<sub>21</sub>O<sub>4</sub>N, m.p. 200—201°, [ $\alpha$ ]<sub>D</sub> +90.5° in CHCl<sub>3</sub> (*hydrochloride*, m.p. 235—236°; *picrate*, m.p. 223—224°; *methiodide*, m.p. 220—221°), which contains 1 OH and 2 OMe. Treatment of the mother-liquors from (III) with H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> in EtOH gives *arnepavine*. (II), when preserved, deposits crystals which are transformed into the corresponding hydrochlorides; these after repeated crystallisation from H<sub>2</sub>O and subsequent treatment with NH<sub>3</sub> yield *floripavidine* (IV), C<sub>21</sub>H<sub>29</sub>O<sub>5</sub>N, m.p. 241—242°, [ $\alpha$ ]<sub>D</sub> -156.25° in MeOH (*hydrochloride*, m.p. 209—210°; *hydriodide*; *methiodide*, m.p. 228—230°), which contains CH<sub>2</sub>O<sub>2</sub>: but not ·OH (Zerevitinov). The mother-liquors from (IV) afford *floribundine* (V), C<sub>18</sub>H<sub>19</sub>O<sub>3</sub>N, m.p. 193—195°, [ $\alpha$ ]<sub>D</sub> -204.28° in CHCl<sub>3</sub> (*tartrate*, m.p. 181—183°; *methiodide*, m.p. 178—180°), which contains ·OH, ·OMe, and ·NMe. The mother-liquors from (V) give small amounts of "base V," m.p. 200—203°.

H. W.

**Deoxymorphine-C, deoxycodine-C, and their hydrogenated derivatives.**—See this vol., 107.

**Percaine.**—See this vol., 240.

**Alkaloids of Hanfangchi. II. Hanfangchin B.** C. F. HSÜ [with, in part, G. H. WANG and T. W. LU] (J. Chinese Chem. Soc., 1935, 3, 365—371; cf. A., 1935, 1257).—Hanfangchin B, C<sub>36</sub>H<sub>40</sub>O<sub>6</sub>N<sub>2</sub>, m.p. 241—242°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +272.4° in CHCl<sub>3</sub> (COMe<sub>2</sub> compound, m.p. 134—136°; *picrate*, m.p. 186°; *aurichloride*, m.p. 172°; *methiodide*, m.p. 252°; *platinichloride*, m.p. 260°; *phosphate*, m.p. 215°; forms an Ac derivative with Ac<sub>2</sub>O at 150—160°), was isolated by extracting the evaporated alcoholic mother-liquors from the prep. of hanfangchin A (*loc. cit.*) with C<sub>6</sub>H<sub>6</sub> and then crystallising from COMe<sub>2</sub>. It contains 2 double linkings, 3 OMe, and 1 NMe, but no phenolic OH, N·NO, C·O, O<sub>2</sub>CH<sub>2</sub>, ester, or lactone groups. Intra-peritoneal injection of the *hydrochloride* into the albino rat has no characteristic effect (minimal lethal dose, 250 mg. per kg. body-wt.). No alkaloids were found in Mofangchi or Kwangfangchi. H. G. M.

**Sulpharsphenamine. New method of preparation.** W. J. C. DYKE and H. KING (J.C.S., 1935, 1745—1747).—Na<sub>2</sub> 3:3'-diamino-4:4'-dihydroxyarsenobenzene-*NN'*-dimethylenesulphite, prepared from salvarsan and Na formaldehydebisulphite, with aq. CH<sub>2</sub>O followed by NaHSO<sub>3</sub> in CO<sub>2</sub> gives sulpharsphenamine; it is not essential to isolate the Na<sub>2</sub> salt. The mono-*N*-methylenesulphite of 4-nitro-2-aminophenol with CH<sub>2</sub>O followed by NaHSO<sub>3</sub> affords Na<sub>2</sub> 5-nitro-2-hydroxyanilino-*NN*-dimethylenesulphite. F. R. S.

**Arsenicals containing the furan nucleus. II. Action of chlorine. Substituted furan arsenicals.** W. G. LOWE and C. S. HAMILTON (J. Amer. Chem. Soc., 1935, 57, 2314—2317; cf. A., 1935, 997).—Furyldichloroarsine, difurylchloroarsine (I), trifurylarsine, or 2-chlorofuran with Cl<sub>2</sub> in CHCl<sub>3</sub> give 2-chlorofuran tetrachloride, an oil, which loses HCl with KOH-EtOH, dil. HNO<sub>3</sub>-EtOH, or AgNO<sub>3</sub>-HNO<sub>3</sub>-

EtOH. Crude (I) and  $\text{Cl}_2\text{-CHCl}_3$  give also some *difurylarsinic acid*, m.p.  $138^\circ$ , and *trifurylarsine dichloride*, m.p.  $132^\circ$ . 5-Chloro-2-chloromercurifuran, m.p.  $181^\circ$ , and  $\text{AsCl}_3$  in  $\text{C}_6\text{H}_6$  give *tri-5-chlorofurylarsine*, m.p.  $63^\circ$ . *Tri-5-bromofurylarsine*, m.p.  $106^\circ$ , is similarly prepared. These compounds do not readily react with  $\text{HgCl}_2$ . R. S. C.

**Constitution of some additive compounds of tertiary phosphines.** W. C. DAVIES and (in part) W. P. WALTERS (J.C.S., 1935, 1786—1792).—The stability of  $\text{CS}_2$  compounds of phosphines is determined by measuring the total dissociation pressure of the compound; the stability of  $\text{PPhMe}_2\text{CS}_2$  is taken as 1 and that of any other compound obtained by comparing the temp. at which the dissociation pressure of the latter and of the standard become 50 mm. The m.p. of the additive compounds of  $\text{PRMe}_2$  and  $\text{PREt}_2$  run parallel, with one exception, to the stabilities in the two groups. The factors which affect stability are nuclear substituents in *p*- and *o*-positions and the change from aryl-dimethyl- to -diethyl-phosphine. The formulæ of the compounds are discussed. The following have been prepared: *triethylphosphine-p-tolyl-*, m.p.  $88\text{--}90^\circ$ , and *-p-nitrophenyl-thiocarbimide*, m.p.  $97^\circ$ , *triethylphosphine-p-benzoquinone*, m.p. about  $180^\circ$ , *tri-n-butyl-*, m.p.  $180\text{--}190^\circ$ , and *p-tolyldimethyl-phosphine-p-benzoquinone*, m.p. above  $250^\circ$ . F. R. S.

**Derivatives of allyl ethers of phenols having mercury substituted in the nucleus.** A. N. NESMEJANOV and R. K. SCHATZKAJA (J. Gen. Chem. Russ., 1935, 5, 1268—1272).—*o*-OH $\cdot\text{C}_6\text{H}_4\cdot\text{HgCl}$  in boiling  $\text{COMe}_2$  and  $\text{RBr}$  ( $\text{R}=\text{CH}_2\text{CH}_2\text{CH}_2$ ) (7 hr.) yield the ether *o*-OR $\cdot\text{C}_6\text{H}_4\cdot\text{HgCl}$  (I), m.p.  $89^\circ$ , whilst when RCl is taken in place of RBr the product is (*o*-OR $\cdot\text{C}_6\text{H}_4$ ) $_2\text{Hg}$ , m.p.  $59\cdot5\text{--}60\cdot5^\circ$ , into which (I) is converted by the action of  $\text{Na}_2\text{SnO}_2$ . With  $\text{C}_5\text{H}_5\text{N}$  in place of  $\text{COMe}_2$  in the above reaction (at  $-10^\circ$ ) the sole product is  $2\text{C}_5\text{H}_5\text{N}\cdot 2\text{RBr}\cdot\text{HgBr}_2$ , m.p.  $120\cdot5\text{--}121\cdot5^\circ$ . PhOR in aq. AcOH, HgO, and NaCl (at the b.p.) yield the *p*-isomeride of (I), m.p.  $101\text{--}101\cdot5^\circ$ , converted by  $\text{Na}_2\text{SnO}_2$  into (*p*-OR $\cdot\text{C}_6\text{H}_4$ ) $_2\text{Hg}$ , m.p.  $108\cdot5\text{--}110^\circ$ . The compound OR $\cdot\text{C}_{10}\text{H}_6\cdot\text{HgCl}$ , m.p.  $161\text{--}162^\circ$ , is obtained from  $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$  in AcOH, HgO, and NaCl, as above. R. T.

**Arylation of mercuri-organic hydroxides by means of organic derivatives of tin, antimony, and boron.** R. C. FREIDLINA, A. A. KOTSCHESKOV, and A. N. NESMEJANOV (J. Gen. Chem. Russ., 1935, 5, 1171—1175).—The following compounds of the type  $\text{HgRR}'$  have been prepared by the general reaction  $\text{RHgX} + \text{R}'_m\text{MX}_n \rightarrow \text{HgRR}' + \text{R}'_{m-1}\text{MX}_{n+1}$  ( $\text{M}=\text{Sn}$ ,  $\text{Sb}$ , or  $\text{B}$ ;  $\text{X}=\text{halogen}$  or  $\text{OH}$ ):  $\text{R}=\text{Me}$ ,  $\text{R}'=\alpha\text{-C}_{10}\text{H}_7$ , m.p.  $80\text{--}82^\circ$ , from  $\text{RHgI}$  and  $\text{R}'_2\text{SnCl}_2$ , in EtOH-NaOH at the b.p.;  $\text{R}=\text{Ph}$ ,  $\text{R}'=m$ , m.p.  $113\text{--}116^\circ$ , or *p*- $\text{C}_6\text{H}_4\cdot\text{NO}_2$ , sintering at  $144\text{--}145^\circ$ , from *m*- or *p*- $\text{R}'\text{HgCl}$  and  $\text{R}_2\text{SnCl}_2$ , as above;  $\text{R}=\text{p-C}_6\text{H}_4\text{Cl}$ ,  $\text{R}'=\text{CH}_2\text{Ph}$ , m.p.  $104\text{--}108^\circ$ , from  $\text{R}'\text{HgCl}$  and  $\text{RSbO}$ . R. T.

***o*- and *p*-Tolylstannic acids.** K. A. KOTSCHESKOV and M. M. NADJ (J. Gen. Chem. Russ., 1935, 5, 1158—1167).— $\text{R}_2\text{SnCl}_2$  (I) ( $\text{R}'=o$ ,  $\text{R}=\text{p-C}_6\text{H}_4\text{Me}$ ) and  $\text{HgCl}_2$  in EtOH yield  $\text{RHgCl}$ , whilst in presence

of alkali the product is  $\text{HgR}_2$ .  $\text{RSnCl}_3$ , b.p.  $157^\circ/23$  mm. (1 : 2 compound with  $\text{C}_6\text{H}_5\text{N}$ ), prepared from  $\text{SnCl}_4$  and  $\text{SnR}_4$ , or from (I) and  $\text{SnCl}_4$ , is converted into *p-tolylstannic acid*, decomp. at  $295^\circ$ , by aq. KOH at room temp.  $\text{R}'_2\text{SnCl}_2$ , m.p.  $49\text{--}50^\circ$ , obtained from  $\text{SnCl}_4$  and  $\text{SnR}'_4$ , yields  $\text{R}'\text{SnCl}_3$ , b.p.  $157\text{--}158^\circ/20$  mm., with  $\text{SnCl}_4$ , and is converted into  $(\text{R}'\text{SnS})_2\text{S}$  by  $\text{H}_2\text{S}$ , and into *o-tolylstannic acid* (II) by KOH. (II) is oxidised by  $\text{K}_3\text{Fe}(\text{CN})_6$  at room temp. to yield PhMe,  $\text{R}'\text{CN}$ , and  $\text{H}_2\text{SnO}_3$ . R. T.

**Separation of diketopiperazines and amino-acids in protein hydrolysates by ionophoresis.** II. V. S. BALABUCHA-POZKOVA, N. I. GAVRILOV, and A. M. RIKALEVA (Biochem. Z., 1935, 283, 62—70).—Mixtures of anhydrides and  $\text{NH}_2$ -acids are quantitatively separated by electrophoresis of the cathode fluid 3 or 4 times. In protein hydrolysates, the anhydride fraction can also be removed by electrophoresis, the cathodic fluid only retaining traces of anhydride. Hg, Ag, or Pb but not Ni is usable as cathode; the c.d. at the cathode should be  $>10\text{--}13$  milliamp. per sq. cm. cathode surface and the liquid in cathode and anode chambers should be feebly acidified with 0.1N- $\text{H}_2\text{SO}_4$  beforehand. With protracted electrophoresis, loss of N occurs. P. W. C.

**Derivatives of keratin.** D. R. GODDARD and L. MICHAELIS (J. Biol. Chem., 1935, 112, 361—371).—Keratin (I) (keratin reduced by  $\text{SNa}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$ ) with  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{Et}$ ,  $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$ ,  $\text{CH}_2\text{I}\cdot\text{CO}\cdot\text{NH}_2$ , and  $\text{CH}_2\text{I}\cdot\text{CH}_2\cdot\text{OH}$  gives *S-derivatives*, differing from (I) in solubility and isoelectric point, and digestible by pepsin or trypsin. The product from  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{Et}$  is fractionally pptd. by  $(\text{NH}_4)_2\text{SO}_4$ , indicating non-homogeneity of (I). The substance formed by re-oxidation of (I) is called metakeratin. *N*-Derivatives are not formed by the above procedure. R. S. C.

**Formation of thio-derivatives of proteins using carbon disulphide.** M. LOISELEUR (Compt. rend., 1935, 201, 966—968).— $\text{CS}_2$  and casein in 0.1N-NaOH at  $40\text{--}45^\circ$  give after pptn. by acid a red-orange product, which decomposes on drying and probably has  $\text{CS}_2\text{K}$  groups attached to protein- $\text{NH}_2$ . F. A. A.

**Acid autoclaving of blood-albumin.**—See this vol., 222.

**Direct simultaneous micro-determination of carbon, hydrogen, and oxygen.** II. Analysis of pure compounds containing carbon, hydrogen, oxygen, and sulphur. III. Analysis of pure compounds containing carbon, hydrogen, oxygen, and nitrogen. W. R. KIRNER (Ind. Eng. Chem. [Anal.], 1935, 7, 363—365, 366—368; cf. A., 1934, 1239).—II.  $\text{Ph}_2\text{SO}_2$  and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Ph}$  analysed by the method previously described give vals. for S accurate to  $0\cdot4\pm 0\cdot1\%$ .

III. The ratio of  $\text{NO}_2$  and  $\text{N}_2$  is determined in micro-combustions by the same method for various compounds containing N. F. R. G.

**[Determination of] chlorine in organic compounds.** I. Rapid lamp method. W. N. MALLSOFF (Ind. Eng. Chem. [Anal.], 1935, 7, 428).—Cl can be determined accurately by the lamp method (cf. Kennedy, B., 1928, 539). F. R. G.

Action of perchloric acid on iodine and iodine derivatives.—See this vol., 177.

Semi-micro-Kjeldahl determination of nitro- and azo-nitrogen. R. A. HARTE (Ind. Eng. Chem. [Anal.], 1935, 7, 432—433).—A modification of the method of Elek *et al.* (A., 1926, 632). F. R. G.

Micro-determination of protein-nitrogen in the presence of ammonium salts. A. ROCHE and F. MARQUET (Bull. Soc. Chim. biol., 1935, 17, 1630—1632).—The protein is pptd. with tannin in aq. AcOH and N determined in the ppt. A. L.

Determination of protein-nitrogen. H. W. GERRITZ and J. L. ST. JOHN (Ind. Eng. Chem. [Anal.], 1935, 7, 380—383).—0.8 of the sulphates in the Kjeldahl-Gunning-Arnold method are replaced by phosphate, giving a reduction of digestion time to 10—25 min. F. R. G.

Determination of selenium in organic matter. K. T. WILLIAMS and H. W. LAKIN (Ind. Eng. Chem. [Anal.], 1935, 7, 409—410).—Modification of the method of Robinson *et al.* (B., 1934, 798) results in a saving of 4—6 hr. in the time of digestion. F. R. G.

Determination of the nitrogen of the nitro-groups of cyclotrimethylenetrinitroamine ( $T_1$ ). E. VERNAZZA (Chim. e l'Ind., 1935, 17, 685—687).—0.02—0.05 g. of the substance is treated with 10 c.c. of  $H_2SO_4$  and 0.3—0.4 g. of  $KMnO_4$  for 10 min. at room temp. and then at  $100^\circ$  until no more gas is evolved (about 20 min.). When cool, 1—3 drops of a saturated solution of I in  $H_2SO_4$ , followed by 0.1—0.2 c.c. of glacial  $HCO_2H$ , are added and the mixture is heated at  $100^\circ$  until colourless (1 min.). The excess of  $KMnO_4$  is thus reduced to  $Mn^{++}$  and the N of the  $NO_2$  groups is converted quantitatively into  $NO_2 \cdot SO_3H$ , which is determined by adding an excess of standard  $KMnO_4$ , followed by an excess of standard  $FeSO_4$ , and titrating with  $KMnO_4$ . D. R. D.

"Glacial acetic acid" method of determination of amino- or other basic groups in amino-acids etc. L. J. HARRIS (Biochem. J., 1935, 29, 2820—2829).—The considerable "blank" correction in the aq. titration of basic groups in  $NH_2$ -acids, polypeptides, etc. is obviated by using glacial AcOH as solvent,  $HClO_4$  in glacial AcOH as titrant, and brilliant-cresyl-blue as indicator. With 2 ml. of 0.1N solution (micro-method, 0.05 ml. of 0.025N) and in absence of  $H_2O$ , the error is  $< 2\%$ . Examples are given. F. O. H.

Colorations given by phenols with nitrous acid. M. S. MALINOVSKI (J. Gen. Chem. Russ., 1935, 5, 1297—1298).—PhOH, cresol, and thymol do not give any coloration with aq.  $HNO_2$ , pyrocatechol gives a brown coloration with  $< 0.002\%$   $HNO_2$ , resorcinol gives a grey ppt. with 1% and a yellow coloration with 0.005—0.1%  $HNO_2$ , quinol gives a yellow coloration with 0.1%, pyrogallol with 0.001—1%, and phloroglucinol with 0.1—1%  $HNO_2$  (pink with 0.002—0.005%  $HNO_2$ ). R. T.

Volometric extraction analysis. A. BOLLIGER (J. Proc. Austral. Chem. Inst., 1935, 2, 312—317).—o-Polynitrophenols (I), e.g., picric or styphnic acid, are titrated with aq. methylene-blue hydrochloride

(II). The insol. salt formed is extracted with  $CHCl_3$ , and titration continued until (I) is completely removed from the  $H_2O$  layer. Cations forming insol. picrates or picrolonates may be so pptd., the ppt. being subsequently titrated as indicated. Other acids forming with (II) or other coloured bases salts insol. in  $H_2O$  but sol. in org. solvents may be titrated similarly. The method is suitable for about 1 mg. of material. J. S. A.

Determination of cholesterol. II. I. LIFSCHÜTZ (Biochem. Z., 1935, 282, 441—443; cf. A., 1918, ii, 179; 1935, 1363).—Cholesterol is recovered quantitatively from its compound (I) with digitonin (II) by grinding (I) with NaOAc, boiling the mixture for 30 min. with 95% EtOH, and adding excess of  $Et_2O$ . (II) and NaOAc are pptd. W. McC.

Microchemical determination [detection] of cholesterol, carbamide, glycerol, etc., based on the formation of liquid crystals. P. GAUBERT (Compt. rend., 1935, 201, 1202—1204).—A very small quantity of cholesterol (I) may be detected by melting it on a heated microscope slide together with a fragment of  $CO(NH_2)_2$ , or other substance which when mixed with (I) forms liquid crystals (cf. A., 1913, i, 264); the latter show the presence of (I). Similarly urine, or glycerol in wine, may be detected by adding fragments of (I) to a drop evaporated on a slide, and heating; if necessary the liquid crystals are made visible by pressure on the cover-slip. Lemon juice is similarly detected; in this case the liquid crystals, due to citric acid, persist at room temp. E. W. W.

Application of "Original Hanau" artificial sunlight lamp in qualitative analysis. I. Photo-analysis in pyridine and indole series. H. FREYTAG (Z. anal. Chem., 1935, 103, 334—340).—A drop of solution containing  $C_5H_5N$ , applied to filter-paper impregnated with 0.2% alcoholic 1-phenyl-3-methylpyrazolone, gives on irradiation with ultraviolet light a blue spot, due to formation of a pyridine dye from the products of photochemical oxidation. 4-Methyl- but no other methylated pyridine similarly gives a violet colour. Limit,  $10^{-5}$  g. for each. Indole, and 2-, 5-, and 7-methylindole, irradiated as drops on filter-paper, give oxidation products possessing a strong yellow-green fluorescence. With skatole a sp. bluish fluorescence is obtained.  $2 \times 10^{-6}$  g. of indole may be detected by the formation of a pink colour on irradiation of a drop of liquid on filter-paper soaked in  $H_2SO_4$ . 2-, 5-, and 4-Methylindole (sp. blue colour) may be similarly detected. J. S. A.

Specific reaction for yohimbine. L. ROSSI, A. DEL BOCA, and R. LOBO (J. Pharm. Chim., 1935, [viii], 22, 566).—The authors claim priority (cf. Anal. Farm. Biochim., 1932, 3, 51; A., 1935, 1260). J. L. D.

Aminometry of alkaloids. I. Aminometric determination in anhydrous chloroform solution. R. DIETZEL and W. PAUL (Arch. Pharm., 1935, 273, 507—515).—Alkaloids are determined by a modification of Vorländer's "aminometric" method (A., 1934, 198, 314). The amine groups are titrated in anhyd.  $CHCl_3$  with  $p-C_6H_4Me \cdot SO_2H$  in  $CHCl_3$  [standardised against  $N(CH_2Ph)_3$ ], using

$\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{Ph}$  in  $\text{CHCl}_3$  as indicator. Accurate results are obtained with brucine, strychnine, hyoscyamine, veratrine, atropine, papaverine, quinine, aconitine, cocaine, codeine, narcotino, and cinchonine. The method is applied to the determination of alkaloids in drugs and pharmaceutical preps. The drug is (if necessary) digested with aq.  $\text{HCl}$  or aq.  $\text{H}_2\text{SO}_4$  and extracted with  $\text{CHCl}_3$ . In general the alkaloid is then set free by  $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{MgO}$ , or aq.  $\text{NH}_3$ , and extracted with  $\text{CHCl}_3$  (mixed, if necessary, with  $\text{Et}_2\text{O}$ ); the dried solution is then titrated as above. Details are given of the method as applied to cortex chinae (and other quinine preps.), cortex granati, radix and tinctura ipecacuanhae, extractum and tinctura strychni, extractum belladonnae and hyoscyami, and secale cornutum (which requires special treatment). Application to semen strychni and to folia belladonnae or hyoscyami is difficult. For semen and tinctura colchici, and for caffeine and theobromine, no suitable indicator is found.

E. W. W.

**Extraction of lead by means of diphenylthiocarbazon.**—See this vol., 179.

**Glucoproteins. I. Determination of glucosamine.** R. BOYER and O. FÜRTH (Biochem. Z., 1935, 282, 242—256).—The colorimetric method of Elson and Morgan (A., 1934, 910) for determination of glucosamine (I) is adapted, with modifications, for use with the step photometer. Addition of carbohydrates or  $\text{NH}_2$ -acids to solutions of (I) causes errors; that of protein hydrolysates renders the method useless. Separation of (I) from the hydrolysates by pptn. by the  $\text{Cu-CaO}$  method is not possible, since considerable destruction of (I) occurs. For determinations of (I) in protein hydrolysates the more tedious method of Zuckerkandl *et al.* (A., 1931, 1081) must still be employed, since it is less sensitive to these errors. The structure of the pigment and its precursor is discussed.

P. W. C.

**Determination of tryptophan in proteins by means of the Pulfrich photometer.** F. BÖHM and G. GRÜNER (Biochem. Z., 1935, 282, 230—234).—A method is described and tables summarise the tryptophan contents of caseinogen and serum when determined both by the colorimetric and photometric methods.

P. W. C.

## Biochemistry.

**Carbonic acid and respiratory activity.** A. RASR (Z. Biol., 1935, 96, 615—633).—Inhalation of  $\text{CO}_2$ -rich (5—15%) air by cats and dogs markedly stimulates the respiration in both frequency and depth. The effect is increased by admixture with  $\text{O}_2$ , and occurs, although to some extent modified, after administration of certain alkaloids etc.

F. O. H.

**Equilibrium time of the gaseous nitrogen in the dog's body following changes of nitrogen tension in the lungs.** L. A. SHAW, A. R. BEHNKE, A. C. MESSER, R. M. THOMSON, and E. P. MOTLEY (Amer. J. Physiol., 1935, 112, 545—553).—The  $\text{N}_2$  content of the body  $\propto$  the partial pressure of  $\text{N}_2$  in the lungs under conditions of equilibrium at pressures up to 4 atm. The rates of  $\text{N}_2$  elimination from the completely and partly saturated body are equal, as are the saturation and desaturation times.  $\text{N}_2$  is held by the blood and tissue-fluids in a high state of supersaturation.

R. N. C.

**Intravenous injection of oxygen with the animal under ordinary and increased atmospheric pressure.** I. SINGH (J. Physiol., 1935, 84, 315—322).—Cats absorb about 5 c.c. of  $\text{O}_2$  injected intravenously in 10 min. With animals of different species the vol. absorbed per kg.  $\propto$  the size of the animal. Increase of atm. pressure increases the amount of  $\text{O}_2$  that can be absorbed.

R. N. C.

**Influence of hyperpnoea and of variations of oxygen and carbon dioxide tension in the inspired air on hearing, after images, and nystagmus.** E. GELLHORN and I. G. SPIESMAN (Amer. J. Physiol., 1935, 112, 519—527, 620—626, 662—668).

R. N. C.

**Excitability of the respiratory centre in dependence on the thyroid and spleen.** J. FELDER

(Z. ges. exp. Med., 1934, 94, 384—388; Chem. Zentr., 1935, i, 2691).

R. N. C.

**Dependence of the excitability of the respiratory centre on the thyroid.** R. SPIELMANN (Z. ges. exp. Med., 1934, 94, 378—383; Chem. Zentr., 1935, i, 2691).—The excitability of the respiratory centre of the rabbit is determined by measurement of the gross respiration in a special apparatus. Injection of thyroxine or thyrotropic hormone increases the excitability. Thyroid preps. can be evaluated biologically by the method.

R. N. C.

**Effects of suppression of the mesotergal organ on the gaseous exchange of Lepidoptera.** A. RAFFY and G. GUIGNON (Compt. rend. Soc. Biol., 1935, 120, 765—766).—Gaseous exchange is depressed by destruction of the mesotergal organ, and the increases produced by nicotine are  $<$  normal.

R. N. C.

**Neuro-central regulation of hæmatic nitrogen.** P. JEDLOWSKI (Boll. Soc. ital. Biol. speriment., 1935, 10, 225—227).—Hæmatic N is increased by destruction of one or both of the hemispherical cortices in the rabbit, and to a small extent by lesions of different parts of the encephalic base.

R. N. C.

**Evidence for a potassium shift from plasma to muscles in response to an increased carbon dioxide tension.** W. O. FENN and D. M. COBB (Amer. J. Physiol., 1935, 112, 41—55).—Experiments described indicate that increased  $\text{CO}_2$  tension tends to cause K shift from plasma to muscles, but the same increase would shift K from the muscle to Ringer's solution, because the muscle is intermediate between Ringer's solution and blood in its buffering capacity.

R. N. C.

**Kinetics of the elimination of the dye water-blue from dog plasma after intravenous injection.** A. HEMINGWAY, F. H. SCOTT, and H. N. WRIGHT (Amer. J. Physiol., 1935, 112, 56—64).—The concn. of water-blue falls rapidly in the first 2 hr. after injection, following an exponential curve; it follows a slower exponential curve during the next 48—72 hr., and proceeds at an approx. const. rate during the last 7—8 days. The equation for time and concn. is given. R. N. C.

**Erythrocyte and hæmoglobin increase in human blood during and after exercise.** E. C. SCHNEIDER and C. B. CRAMPTON (Amer. J. Physiol., 1935, 112, 202—206). R. N. C.

**Adsorption of creatine and creatinine by erythrocytes.** K. KACL (Compt. rend. Soc. Biol., 1935, 120, 916—917).—Creatine is not adsorbed by erythrocytes of cattle, and only by those of adult horses. Creatinine (I) is adsorbed by the cells of both species to the extent of 10—50%. Equilibrium is established rapidly. The abs. quantity of (I) adsorbed increases, whilst the relative quantity decreases, with rise of concn.; the phenomenon is reversible. R. N. C.

**Effect of  $p_H$  on the adsorption of creatinine by erythrocytes.** K. KACL (Compt. rend. Soc. Biol., 1935, 120, 918—920).—The optimum  $p_H$  for the adsorption is 7.3. The amount of adsorption increases with rise of temp. In presence of acids or alkalis,  $p_H$  tends to revert to its natural val. during adsorption. R. N. C.

**Permeability of erythrocytes for malonamide.** F. SCHÖNHEYDER (Skand. Arch. Physiol., 1934, 71, 39—60; Chem. Zentr., 1935, i, 2837—2838).—The permeability in buffered NaCl solution is independent of the treatment of the blood, of the composition of the outer fluid [addition of  $\text{Na}_2\text{CO}_3$  or  $\text{Hg}(\text{CN})_2$ ], or the amount of swelling, but rises with decreasing  $p_H$ . J. S. A.

**Glutathione of the erythrocytes in hyper- and hypo-thyroidism.** A. R. BEAUX (Compt. rend. Soc. Biol., 1935, 120, 822—823).—Glutathione in red corpuscles of dogs is decreased by feeding with thyroid, and increased by thyroidectomy. R. N. C.

**Alleged effect of electrical stimulation on the metabolism of red cell suspensions.** E. PONDER and J. MACLEOD (J. Gen. Physiol., 1935, 19, 265—281).—Electrical stimuli applied to red cell suspensions lead to a permanent vol. decrease (0.1%) in the system, and not to an increase in  $\text{O}_2$  consumption (cf. von Hattingberg, A., 1934, 541). The effect, which may occur in absence of red cells, disappears when platinised Pt electrodes are substituted for bright Pt. Using serum, a vol. increase occurs with platinised, not with bright, Pt electrodes. F. A. A.

**Electrokinetic potential of thrombocytes.** H. D. CREMER (Biochem. Z., 1935, 281, 345—348).—The potential is 20—42 mv. The val. varies during the day, but no certain relationship between potential and time of day, absorption of food, amount of protein, serum-albumin-globulin ratio, or plasma viscosity was detectable. P. W. C.

**Optical activity of horse's globinhæmochromogen and of hæmoglobin dissolved in 0.25N-sodium hydroxide (globin+hæmatin), with special reference to the sulphur contents.** S. SIMONOVITS and G. BALASSA (Biochem. Z., 1935, 281, 333—338).—A 0.16% solution of horse-globinhæmochromogen in 0.25N-NaOH after keeping 24 hr. has  $[\alpha]_{5780}^{20} -45.2^\circ$ ; globin+hæmatin under the same conditions has  $[\alpha]_{5720}^{20} -45.7^\circ$ . The vals. are dependent on the S content of the prep., but are independent of the concn. (0.20—0.92%) and of the methods of crystallisation. It is suggested that in globinhæmochromogen the reduced prosthetic group is coupled not with the whole globin mol., but only with the N bases of globin which are split off by NaOH. P. W. C.

**Spectrophotometric studies. II. Preparations from washed blood cells; nitric oxide-hæmoglobin and sulphæmoglobin.** D. L. DRABKIN and J. H. AUSTIN. **III. Methæmoglobin.** J. H. AUSTIN and D. L. DRABKIN. **IV. Hæmochromogens.** **V. Technique for analysis of undiluted blood and concentrated hæmoglobin solutions.** D. L. DRABKIN and J. H. AUSTIN (J. Biol. Chem., 1935, 112, 51—65, 67—88, 89—104, 105—114; cf. A., 1933, 81).—II. Solutions prepared from washed erythrocytes are preferable to hæmolysed whole blood, and absorption spectra of oxyhæmoglobin (I), hæmoglobin (II), CO-(II), cyanomethæmoglobin (III) are presented. NO-hæmoglobin (IV) solutions are prepared from reduced (II) and NO in the absence of  $\text{O}_2$ , and are converted into methæmoglobin (V) by  $\text{K}_3\text{Fe}(\text{CN})_6$ , and further into (III) by KCN. (IV) appears to be analogous to (I), but is less readily converted into (II). (I) treated with  $\text{H}_2\text{S}$  gives mixtures of (II) and sulphæmoglobin (VI). A curve for pure (VI) is deduced; from this a quant. estimate of (VI) in the blood of a patient with clinical sulphæmoglobinæmia is obtained. (VI) is formed from (II) only in the presence of  $\text{O}_2$ . It is convertible into hæmochromogens, but not into (II) or (III). Sulph-methæmoglobin is produced when (V) or (III) is treated with  $\text{H}_2\text{S}$ .

III. Absorption data are given for (V) between  $p_H$  6.0 and 9.4. Between  $p_H$  7.0 and 9.2 the change is reversible; at about  $p_H$  9.4 a reaction apparently leading to hæmatin occurs. (I) is converted into (V) in 20 min. at  $p_H$  6.0 by an equiv. amount of  $\text{K}_3\text{Fe}(\text{CN})_6$  in air. At higher  $p_H$  excess of  $\text{K}_3\text{Fe}(\text{CN})_6$  is required to complete the reaction.  $\text{NaNO}_2$ , above a crit. amount, reacts with (I) giving (V). This reaction is faster at lower  $p_H$  vals. Benzoquinone reacts slowly with (I) giving (V), and (I) in very dil. solution is partly converted into (V) in 84 hr.

IV. Spectra are given of oxidised and reduced hæmins, and of various hæmochromogens. (II) reacts slowly with NaOH, giving one of these. Another is produced when  $\text{C}_5\text{H}_5\text{N}$  is added to reduced hæmins; the reaction is complete only when excess of  $\text{C}_5\text{H}_5\text{N}$  is used. (II) and  $\text{C}_5\text{H}_5\text{N}$  yields a hæmochromogen; the reduced form of this reacts reversibly with CO, the oxidised form with KCN.

V. A spectroscopic cell, 0.07 mm. in depth, allows direct measurements to be made on undiluted blood

and solutions of (II) up to 42.7 g. per 100 c.c. Beer's law holds, no significant change in the spectrum of (II) being observed down to  $10^{-4}$  of this concn.

F. A. A.

**Physiological degradation of blood-pigments.**  
**III. Derivation of urinary pigments from hæmoglobin.** R. NOTHHAAS (Klin. Woch., 1933, 12, 1438—1441; Chem. Zentr., 1935, i, 2837).—By oxidation of hæmoglobin with  $H_2O_2$ , a pigment identical in absorption spectrum, adsorptive properties, and solubility with urochrome *B* was obtained.

J. S. A.

**Acid autoclaving of blood-albumin at 220°.**  
 V. S. SADIKOV and E. V. LINDQUIST-RISAKOVA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 271—272).—The ppt. (54 g.) obtained by acting on blood-albumin (6 kg.) with 4%  $H_2SO_4$  at 220° for 10 min. is purified by washing with  $Et_2O$  and 20 recrystallisations from hot  $EtOH$ ; the product (I) (3.4 g.) begins to sublime at 230° and to decompose at 250°; m.p. 275—276°, mol. wt. 209, 210. Analysis indicates the formula  $C_{11}H_{20}O_2N_2$ . The results of hydrolysis with 25%  $HCl$  suggest that (I) is a cyclic leucyl-isovaline,  $CPr^a \left\langle \begin{array}{c} C(OH)-NH \\ NH-C(OH) \end{array} \right\rangle CBut^b$ .

P. G. C.

**Genesis of the proteins of the blood-plasma.**  
**I. Variations in albumin and globulin in course of plasmaphoresis.** **II. Restoration of the serum-proteins after repeated plasmaphoresis.** **III. Importance of the bone-marrow in the synthesis of serum-albumin.** A. DALLA VOLTA (Boll. Soc. ital. Biol. sperim., 1935, 10, 163—166, 167—171, 342—346).—I. Repeated plasmaphoresis at 3—5-day intervals in the dog causes an initial rise followed by a fall in total serum-proteins, serum-albumin, the albumin/globulin ratio, and the vol. of circulating plasma, immediately before withdrawal of the blood, whilst the serum-proteins fall steadily for 24 hr. after replacement of the withdrawn corpuscles. Serum-globulins remain unchanged.

II. Protein and plasma regeneration takes place rapidly after repeated plasmaphoresis; albumins and globulins increase independently of each other.

III. X-Irradiation of the bone-marrow of plasma-phorised dogs induces a rapid increase of serum-albumin, whilst globulins decrease. Destructive X-irradiation of the whole body induces small variations of total serum-proteins, with a slight increase during cachexia; globulins rise whilst albumins fall. The bone-marrow is hence a place of origin of serum-albumins.

R. N. C.

**Behaviour of serum-proteins under various metabolic conditions.** H. KEILHACK (Arch. exp. Path. Pharm., 1935, 180, 1—11).—Transfer of precipitin blood from rabbits to rabbits inhibits the pptn., due probably to the presence of a non-sp., heat-stable but  $O_2$ -sensitive factor. Transfer of hæmagglutinin blood to normal, fed animals results in the detection of serum-proteins (I) in the blood after 3—4 weeks. In starved, febrile, or growing animals (I) disappear more rapidly from the blood. The difference between normal and other animals indicates that (I) can be used in an emergency to replace N loss, or consumed directly.

J. N. A.

**Determination of the isoelectric point of blood-serum.** N. I. JOUKOVSKY and W. A. L. DEKKER (Compt. rend. Soc. Biol., 1935, 120, 805—808).—The isoelectric point of cattle serum is determined by measurement of the velocity of cataphoresis of colloidal particles in the serum. Colloidal Pt, Au,  $Fe_2O_3$ , Se, and  $TiO_2$  suspension all have the same velocity in serum, although their velocities in  $H_2O$  differ; specificity of adsorption does not interfere. The isoelectric point obtained is identical with that found by the turbidity method.

R. N. C.

**Lipins of human blood.** E. M. BOYD and J. H. TWEDDELL (Trans. Roy. Soc. Canada., 1935, [iii], 29, V, 113—121).—The free cholesterol and phospholipin of whole blood remain approx. const. during the 24 hr. Cholesteryl esters are max. at 4 a.m. and lowest in the early afternoon, whilst neutral fats are highest during the day and lowest about 4 a.m.

W. O. K.

**Relation between blood-lipin level and fat content of milk in cows.** P. SCHOORL (Landbouw. Tijdschr., 1935, 47, June).—The lipin content of the blood of calves 1 week to 14 months old is 0.63—0.85%. In two herds there seemed to be a correlation between the mean fat production of the cows and the lipin content of the blood of their calves.

NUTR. ABS. (m)

**Physico-chemical state of acetylcholine in the blood.** D. BROUN and H. SCHEINER (Compt. rend., 1935, 201, 1046—1048).—When acetylcholine is added to blood-serum, the greater part is destroyed by the choline-esterase, but a small portion is inactivated by forming a complex with the serum constituents, from which it may be liberated in an active form by the addition of alkali.

W. O. K.

**Reflex influence of the content of acetylcholine in the blood of the coronary veins.** O. KRAYER and E. B. VERNEY (Arch. exp. Path. Pharm., 1935, 180, 75—92).—Electrical stimulation of the carotid sinus increases the acetylcholine (I) content of the coronary venous blood (dog) when physostigmine is previously administered. Increase of blood pressure in the isolated sinus does not increase (I), an effect achieved by adrenaline (which is inactive unless producing an arterial pressor action) in heart-lung preps. with intact vagi.

J. N. A.

**Creatine compounds. III. Phosphocreatine of the blood.** I. CLACCIO (Boll. Soc. ital. Biol. sperim., 1935, 10, 308—310).—Blood contains 0.40—0.80 mg.-% of phosphocreatine as determined by the method of Dulière; it occurs in the erythrocyte fraction.

R. N. C.

**Some recently-proposed methods for determination of glyoxaline derivatives in serum.** E. TRABUCCHI (Boll. Soc. ital. Biol. sperim., 1935, 10, 264—267).—A criticism of the method of Loeper *et al.* (cf. A., 1935, 422). The Pauly reaction in serum is considered to be due to histidine or ergothioneine, rather than to histamine, which is pptd. by phosphotungstic acid.

R. N. C.

**Alimentary post-hyperglycaemic hypoglycaemia in the normal dog.** R. SARIC, A. LACOSTE, and E. AUBERTIN (Compt. rend. Soc. Biol., 1935, 120, 1104—

1107).—The fall of blood-sugar (I) after alimentary hyperglycæmia is of regular occurrence. It may take place in one or two stages, and in some cases a second fall occurs after partial recovery; the type of curve varies with the animal. There is no correlation between the max. rises and falls of (I) or the two sections of the (I) curve. Initial hypoglycæmia never occurs before hyperglycæmia. R. N. C.

**Variations of the blood-sugar and the influence of adrenaline and insulin.** H. HOLMGREN (Acta med. Scand. Suppl., 1934, 59, 104—115).—The daily blood-sugar (I) picture of the rabbit shows regular fluctuations associated with the rhythmic changes of the liver function. Liver-glycogen (II) reaches its max. between the successive (I) max. The action of adrenaline at the (I) max. is < at the (I) min., but that of insulin is greater. The effects are associated with (II). R. N. C.

**Behaviour of blood-sugar in poisoning by potassium atractylate.** A. MARRAS (Boll. Soc. ital. Biol. sperim., 1935, 10, 355—357).—K atractylate increases blood-sugar in rabbits and pigeons when given in sublethal doses, and decreases it in lethal doses. The increase in rabbits is > in pigeons, and is reduced by atropine and ergotamine. R. N. C.

**Blood-alcohol curve after ingestion of malt beer and sugar solutions.** A. BICKEL (Arch. Verdauungskr., 1935, 57, 239—243).—After taking 400 ml. of malt beer by mouth, the blood-EtOH (Widmark's method) reached only 0.067—0.100 g. per litre. After sugar by mouth no EtOH appeared in the blood. NUTR. ABS. (m)

**General theory of the solubility of volatile acids in blood.** F. LUCE (Biochem. Z., 1935, 281, 383—394).—A theory of the solubility of foreign substances (particularly volatile acids) is developed from the physico-chemistry of hæmoglobin and from the acid-base equilibrium in blood. The difficulties due to inadequate knowledge of the influence of high concns. of protein and hæmoglobin on the individual activities of acid anions are discussed. P. W. C.

**Effect of pyruvic acid on blood-oxalic acid.** S. SUZUKI (Japan. J. Med. Sci., 1935, II, 3, 91—94).—Intravenous (but not oral) administration of  $\text{AcCO}_2\text{H}$  (< 0.05 g. per kg.) lowers the blood- $\text{H}_2\text{C}_2\text{O}_4$  in rabbits and men (cf. A., 1934, 1122). Lactic acid is ineffective. F. O. H.

**Determination of lactic acid in blood.** J. ERNST and J. TRUKA (Magyar orvosi Arch., 1934, 35, 386—391; Chem. Zentr., 1935, i, 2417).—Blood is diluted with aq. NaCl and centrifuged. The plasma is pptd. successively with  $\text{Ca(OH)}_2$  and  $\text{ZnSO}_4$ , and lactic acid in the clear filtrate is determined colorimetrically with  $\text{FeCl}_3$ . J. S. A.

**Lactic acid content of the blood in pregnancy and in puerperium.** T. J. TRUKA (Magyar orvosi Arch., 1934, 35, 482—486; Chem. Zentr., 1935, i, 2390—2391).—The normal lactic acid content of the blood varies with the season of the year. It is increased by 40—50% in the ninth month of pregnancy and returns to normal after several days of puerperium. R. N. C.

**Oxalic acid content of blood.** A. THOMSEN (Z. physiol. Chem., 1935, 237, 199—213).—The method of Merz *et al.* (A., 1931, 1440) for the determination of  $\text{H}_2\text{C}_2\text{O}_4$  in blood and serum involves a series of indifferent compounds, and the high vals. observed are due largely if not exclusively to these impurities. The content of ox serum, determined by the  $\text{Et}_2\text{O}$  extraction method, is > 0.001%. After administration of spinach to a rabbit, the max. content of  $\text{H}_2\text{C}_2\text{O}_4$  in the serum is 0.0011%. Small amounts of  $\text{H}_2\text{C}_2\text{O}_4$  are detected in the kidneys and liver. Izumi's method (A., 1934, 201) and Suzuki's modification thereof (*ibid.*, 1122) are untrustworthy. H. W.

**Acid-base balance of blood. IV. Characterisation and interpretation of displacement of the acid-base balance.** N. W. SMOCK and A. B. HASTINGS (J. Biol. Chem., 1935, 112, 239—262; cf. A., 1934, 542).—The results produced by varying the factors which control the acid-base balance in human blood indicate that individuals may be characterised in terms of the rate at which the balance is restored to normal after experimental displacement and that abnormal acid-base conditions may be characterised in terms of the physiological factors involved. W. McC.

**Blood of salmon during the spawning season.** H. OKAMURA (Japan. J. Med. Sci., 1935, II, 3, 85—89).—Analytical data are given. F. O. H.

**Changes in blood [produced] by experimental ammonia poisoning.** I. G. FAZEKAS (Arch. exp. Path. Pharm., 1935, 180, 93—104).—In rabbits there is marked hyperglycæmia, increase of serum-inorg. P, decrease of serum-Ca, pronounced acidosis, and lipæmia. J. N. A.

**Apparatus for the micro-determination of certain volatile substances. IV. Blood-ammonia, with observations on normal human blood.** E. J. CONWAY (Biochem. J., 1935, 29, 2755—2772).—Refinements in the method of determination of  $\text{NH}_3$  (A., 1933, 654) have been made. In venous blood, collected directly into the absorption vessel through a paraffined tube in an atm. of alveolar air or pure  $\text{CO}_2$ , there is practically no free  $\text{NH}_3$  for approx. 12 min.; after this time a slow rise occurs. In blood collected in an open vessel a rapid rise in  $\text{NH}_3$  content occurs, followed by a slower one; extrapolation of the curves corresponding with these rises to zero time gives in the first case a zero val. for blood- $\text{NH}_3$  and in the second 0.038 mg. of  $\text{NH}_3$ -N per 100 ml. It is concluded that there is no free  $\text{NH}_3$  in normal blood, and that that produced on shedding is due to the decomp. of a carbamino-compound. H. D.

**Blood-bromine. I. Determination. II. Control of the method and values for normal subjects.** R. INDOVINA (Boll. Soc. ital. Biol. sperim., 1935, 10, 189—191, 191—192).—I. See A., 1935, 375.

II. The sensitivity of the method (*loc. cit.*) is double that of the gravimetric or Volhard's method. The time of heating required for the destruction of org. matter does not affect the result. Vals. found for

dibromothyroxine agree with the calc. val. Vals. are given for Br in ox blood and human blood.

R. N. C.

**Detection of lead in blood.** K. HÖLL (Pharm. Ztg., 1935, 80, 1342—1343).—Various methods are discussed.

F. O. H.

**Diffusion of potassium from resting skeletal muscle following a reduction in the blood supply.** A. M. BAETJER (Amer. J. Physiol., 1935, 112, 139—146).—Blood-K in the femoral vein of the cat is not affected by reduction of the blood supply to the leg muscles to vals.  $\leq 80\%$  of the normal val., below which level it increases rapidly through loss of K from the muscles. Sympathetic stimulation increases venous plasma-K owing to reduction in the blood flow by vaso-constriction.

R. N. C.

**Inflammation and hydrogen-ion concentration of the blood.** F. LAMMERHIRT (Arch. exp. Path. Pharm., 1935, 180, 52—68).—Inflammation on the backs of rabbits, produced by mustard oil, is inhibited by intravenous injection of isotonic  $\text{Na}_2\text{CO}_3$ - $\text{NaHCO}_3$  buffer. These solutions have no appreciable effect on  $[\text{H}^+]$  of the blood.  $\text{NH}_4\text{Cl}$  and Na atophan solutions both lower the  $p_{\text{H}}$ ; the latter, however, produces alkalosis within a few hr.

J. N. A.

**Action of zinc salts on blood.** G. PIOTROWSKI (Compt. rend. Soc. Biol., 1935, 120, 830—832).—Zn salts increase the time of coagulation of blood *in vitro* but not *in vivo*. Leucocytes and the polynuclear/lymphocyte ratio are temporarily increased.

R. N. C.

**Chemical examination of moranylied or liquoidised blood.** R. NATTAN-LARRIER and P. TCHERNIAKOFSKY (Compt. rend. Soc. Biol., 1935, 120, 857—859).—Moranyl and liquoid used as anticoagulants do not affect the composition of blood except to raise the Na content.

R. N. C.

**Immunological specificity of the euglobulin and pseudoglobulin fractions of horse and human serum.** T. HARRIS and H. EAGLE (J. Gen. Physiol., 1935, 19, 383—396).—The sera of rabbits injected with either euglobulin or pseudoglobulin fractions from human and horse sera give ppts. with both, but two distinct antibodies are present. Neither fraction, as usually prepared, is free from the other. Lipins associated with the proteins do not determine the immunological specificity of the fractions.

F. A. A.

**Properties of the dried diphtheria toxin-aluminium hydroxide complex.** S. SCHMIDT (Compt. rend. Soc. Biol., 1935, 120, 1148—1150).—The complex loses its dissociability and its toxicity when dried.

R. N. C.

**Preparation of aluminium hydroxide for adsorption of toxins (anatoxins) and ultraviruses.** A. HANSEN and S. SCHMIDT (Compt. rend. Soc. Biol., 1935, 120, 1150—1152).— $\text{Al}(\text{OH})_3$  prepared by Willstätter's method does not lose its adsorbing power or gelatinous appearance if autoclaved immediately when prepared.

R. N. C.

**Adsorption of the antibodies from syphilitic and tuberculous sera.** G. D'ALESSANDRO and F. SOFIA (Boll. Soc. ital. Biol. sperim., 1935, 10,

193—195).—The antibodies are adsorbed by kaolin or animal C in presence of the corresponding antigens.

R. N. C.

**Nature of diphtheria toxin: pulverulent purified anatoxin.** S. HOSOYA, K. KAGABE, T. TANAKA, and A. MOMMA (Compt. rend. Soc. Biol., 1935, 120, 1030—1032).—The purified anatoxin does not produce flocculation with horse-serum as does the crude anatoxin, and is not an anaphylactic antigen. It does not reduce Fehling's solution except after hydrolysis with 5% HCl at 80°. An osazone, m.p. 189—191°, can be prepared from the hydrolysate after pptn. of proteins with Pb salts.

R. N. C.

**Aninsulin.** P. BARRAL (Compt. rend. Soc. Biol., 1935, 120, 993—995).—*Aninsulin*, prepared by heating insulin with  $\text{CH}_2\text{O}$ , does not produce hypoglycæmia, but is antigenic. These properties are unstable at most temp., the optimum temp. for storage being 60°.

R. N. C.

**Complement deviation reaction of aninsulin.** P. BARRAL (Compt. rend. Soc. Biol., 1935, 120, 995—998).

R. N. C.

**Nature of tubercle antibodies.** K. MEYER and A. PIC (Compt. rend. Soc. Biol., 1935, 120, 946—949).—Sera of animals prepared with tubercle bacilli contain antibodies to the proteins and fats of the bacilli, but no antibodies capable of reacting with both at once.

R. N. C.

**Precipitin titration of types I and II anti-pneumococcus sera.** L. K. VIKTOROV, L. A. GUINTZE-VERNER, and M. V. DEMIDOVA (Ann. Inst. Pasteur, 1936, 56, 52—67).—An *in-vitro* technique, using a precipitin titration with the polysaccharide fraction prepared from cultures deproteinised by  $\text{CCl}_3\cdot\text{CO}_2\text{H}$  and pptd. by 60% EtOH, is described.

F. O. H.

**Immunising power of certain soluble metallo-protein complexes, formed from anti-swine fever serum.** H. DIACONO (Compt. rend. Soc. Biol., 1935, 120, 699—701).—Cu and Hg complexes with the antiserum retain a considerable part of the immunising power.

R. N. C.

**Analysis of type I pneumococcus specific precipitate.** H. O. CALVERY (J. Biol. Chem., 1935, 112, 167—169).—Analytical data for the ppt. obtained from type I pneumococcus haptene and antisera are given. The cystine and tryptophan vals. are  $>$ , and the tyrosine val. is  $<$ , those for diphtheria toxin-antitoxin flocculates.

J. N. A.

**Nature of tuberculous antibodies.** K. MEYER and A. PIC (Compt. rend. Soc. Biol., 1935, 120, 772—774).—The antibodies of antiprotein and antilipin sera are fixed by their sp. antigens, and when liberated, remain sp.

R. N. C.

**Serological flocculation rate in the region of considerable antibody excess.** S. B. HOOKER and W. C. BOYD (J. Gen. Physiol., 1935, 19, 373—378).—Mainly theoretical. When antibody concn. is  $> 3$  times the equiv. amount, the velocity of flocculation approx.  $\propto$  antigen dilution.

F. A. A.

**Microscopy of powdered desiccated endocrine organs.** H. W. YOUNGKEN (Amer. J. Pharm., 1935,



107, 463—471).—Examination and identification of thyroid, adrenal, pituitary, ovary, and corpus luteum of cattle, sheep, and hogs are described. W. McC.

**Cerium in the organs and excreta.** C. PROVINCIALI (Arch. ital. Sci. farmacol., 1932, 1, 101—119).—Ce cannot be detected in the organs with  $H_2O_2-NH_3$  owing to the interference of Fe. A solution of strychnine in  $H_2SO_4$  or of benzdine in AcOH is used under determined conditions. Ce injected intravenously remains in the blood stream for 8 hr., but later appears in most of the organs. In chronic Ce poisoning *per os*, Ce appears in the liver and kidneys, and also in the gall-bladder if administered as a double salt. It is excreted exclusively by the intestine. Resorption on oral administration is small. R. N. C.

**Distribution of chlorine in the tissues of the rabbit, after intravenous injection of sodium chloride.** F. SCICLONOFF and R. S. MACH (Compt. rend. Soc. Biol., 1935, 120, 941—942).—Max. increase of Cl in all organs appears rapidly after injection. The Cl is largely taken up by the organs that normally show high Cl contents. R. N. C.

**Occurrence of lead in the organs and bones of healthy domestic animals.** P. W. DANCKWORT and K. HÖLL (Deut. tierärztl. Woch., 1934, 42, 586—589).—Liver, spleen, kidneys, and brains, or mixed samples of these were analysed. The average Pb content of organs (200 g.) of cows and horses was 0.051 mg., and of pigs 0.33 mg. For the bones (200 g.) of cows the mean val. was 0.66 mg. and of pigs 1.15 mg. NUTR. ABS. (m)

**Silica in silicoderms.** E. KAHANE (Bull. Soc. Chim. biol., 1935, 17, 1554—1558).—Digestion by  $HNO_3-HClO_4$  of silicoderms (*Oncidium*, *Paraperonia*, *Oncidiella*) yields cryst. residues containing 55—85% of  $SiO_2$ . A. L.

**Effects of magnesium deficiency on the teeth and their supporting structures in rats.** H. KLEIN, E. R. ORENT, and E. V. MCCOLLUM (Amer. J. Physiol., 1935, 112, 256—262). R. N. C.

**Chemical composition of teeth. II. Composition of human enamel and dentine.** J. H. BOWES and M. M. MURRAY (Biochem. J., 1935, 29, 2721—2727; cf. A., 1935, 234).—N, Ca, Mg, Na, K, P,  $CO_2$ , Cl, and F were determined in the enamel and dentine from sound teeth with only a slight degree of hypoplasia. It is concluded that the enamel consists chiefly of hydroxyapatite, and that dentine contains less apatite than enamel, but more  $CO_3$ ;  $CaHPO_4$  is probably also a constituent of dentine. Only small quantities of Si and F were found in teeth. H. D.

**Early stages in the formation of the enamel organ.** E. DELORENZI (Boll. Soc. ital. Biol. sperim., 1935, 10, 279—280).—Glycogen is present in considerable quantities in early stages of formation of the organ in the guinea-pig, rabbit, and calf, but disappears with the metamorphosis into the stellate form of the cells of the central mass. R. N. C.

**Human epidermis. II. Isoelectric points of the stratum corneum, hair, and nails as determined by electrophoresis.** V. A. WILKERSON

(J. Biol. Chem., 1936, 112, 329—335; cf. A., 1934, 1381).— $p_{H_1}$ -electrophoretic mobility curves are plotted for the stratum corneum of human skin, hair, and nails, giving isoelectric points of  $p_{H_1}$  3.70, 3.67, and 3.78, respectively. H. D.

**Oxidation-reduction potential of the tissues of the ovary: effect of urine on this potential.** M. MAGARA (Compt. rend. Soc. Biol., 1935, 120, 1015—1018).—The initial  $E_h$  of the tissues of the rabbit ovary is approx. +0.3 mv., and falls in 2—3 hr. to a steady val. of +0.1 mv. In presence of urine it falls to -0.2 mv.; urine shows the same effect to a smaller degree on  $E_h$  of other tissues. R. N. C.

**Chemical composition of the muscle of marine animals. II. Nitrogenous extractives in muscle of *Mugil cephalus*.** A. CARTENI and A. MORELLI (Quad. Nutrizione, 1934—1935, 1, 433—449).—In the aq. extract of the muscle total extractive N constitutes 0.40% of the fresh tissue, the composition being:  $NH_3-N$  4.30; purine-N 4.03; albumin-N 20.73; creatine- and creatinine-N 24.74; N of other bases 23.02;  $(NH_2)_1$ -acid-N 15.16; polypeptide-N 2.05; urea-N 2.55; undetermined N 3.43%. NUTR. ABS. (m)

**Glycogen content of tape worms (cestoids).** I. A. SMORODINCEV and K. V. BEBESHIN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 413—414).—The glycogen content of *Taenia saginata* (60% of the dry solids) is 3—4 times that of *T. solium* or *Diphyllobothrium latum*. H. G. R.

**Growth and glycogen content of the foetal liver and placenta.** E. L. COREY (Amer. J. Physiol., 1935, 112, 263—267).—The foetal liver of the rat is progressively hydrated during the last third of the gestation period, placental  $H_2O$  remaining const. At foetal wt. of 0.3 g., foetal liver-glycogen (I) is > placental glycogen, which falls relatively steadily until birth, although maternal (I) varies widely, showing that the two are independent. R. N. C.

**Size, fat, and vitamin-A content of the liver of some cartilaginous fishes.** S. SCHMIDT-NIELSEN, A. FLOOD, and J. STENE (Kong. Norske Vidensk. Selsk. Forhandl., 1934, 7, 47—50; Chem. Zentr., 1935, i, 2913; cf. B., 1934, 970).—The fat content of the liver is up to 80—90% and generally  $\propto$  liver-wt. Large variations in fat and vitamin-A (I) contents occur, even in the same species. Fat melted out from the liver is poorer in (I) than the extracted liver-oil. The total (I) content is  $\leq 14$  units, sometimes >5000; in *Galens vulgaris* and *Lamna cornubia* it is >10,000—40,000, i.e., as great as in halibut etc. The (I) content of rays is < that of sharks. H. N. R.

**Separation of physeteric acid from sardine and pilot-whale oils.**—See this vol., 189.

**Effect of sex on the lipins of some marine molluscs.** J. TIMON-DAVID and G. CERESOLA (Compt. rend., 1935, 201, 853—854).—The lipin contents of the female *Eledone moschata*, *Murex brandaris*, and *Mytilus galloprovincialis* are > those of the corresponding males. R. N. C.

**Separation of selacholeic acid from cod-liver, "sukesodara" liver, sei-whale, and pilot-**

**whale oils.** Y. TOYAMA and T. TSUCHIYA (J. Soc. Chem. Ind. Japan, 1935, 38, 684—687B).—Selacholeic ( $\Delta^8$ -tetracosic) acid has been isolated as a minor component of the fatty acids from the liver oils of cod and *Theragra chalcogramma*, and from sei- and pilot-whale oils; some impure *n*-tetracosic acid was also isolated from the whale oils. H. G. M.

**Unsaponifiable matter of sei-whale oil.** Y. TOYAMA and T. TSUCHIYA (J. Soc. Chem. Ind. Japan, 1935, 38, 687—690B).—The unsaponifiable matter contains oleyl and a little cetyl alcohol and cholesterol. Hexadecanol, octadecanol, and some highly unsaturated alcohols are possibly also present. H. G. M.

**Fatty oil of *Chanoschanos* (Forsk.)**. K. KAFUKU and C. HATA (J. Soc. Chem. Ind. Japan, 1935, 38, 650B).—Analytical data for the oils from the body, liver, and intestines of this tropical fish are recorded. Only the liver oil gives a strong colour reaction for vitamin-A. J. S. A.

**Visual purple system in marine fishes.** G. WALD (Nature, 1935, 136, 913).—The visual purple system in the eye tissues of *Prionotus carolinus*, *Centropristes striatus*, and *Stenotomus chrysops* is identical chemically with that in frogs (this vol., 96). L. S. T.

**Carotenoids and the visual cycle.** G. WALD (J. Gen. Physiol., 1935, 19, 351—371).—Fuller details of work already reported (A., 1934, 913; this vol., 96) are given. The xanthophyll content of the epithelium and choroid layer of frogs' eyes falls 10—20% during light-adaptation. Light-adapted retinas contain  $0.2\text{--}0.3 \times 10^{-6}$  g. of vitamin-A. F. A. A.

**Dissociation between intestinal and glandular permeability to carotenoids in the descendance of some crossings between different species of silkworm.** C. JUCCI (Boll. Soc. ital. Biol. sperim., 1935, 10, 218—219). R. N. C.

**New phosphorus fraction in blood and tissues.** T. KALAJA (Suomen Kem., 1935, 8, B, 41—42).—The filtrate obtained from the addition of blood (but not of serum) (man, cow, rabbit, rat) and liver and muscle (rabbit, rat) to  $\text{CCl}_3\text{-CO}_2\text{H}$  gives a lower % of inorg. P by the Fiske-Subbarow method in the freshly prepared filtrate than after some hr. It is inferred that blood etc., but not serum, contains a thermo-labile compound which hydrolyses in acid or alkaline (but not neutral) protein-free filtrate. In the usual colorimetric method inorg. P must be determined immediately after filtering in the case of blood, whereas serum filtrates may be kept. The nature of the P compound is discussed. R. S. B.

**Dielectric properties and chemical constitution of phosphatides.** R. KUHN, I. HAUSSER, and W. BRYDOWNA (Ber., 1935, 68, [B], 2386—2388).—Sphingomyelin and lecithin (I) in EtOH have a dielectric const. > that of the solvent and therefore exist as zwitterions. In  $\text{C}_6\text{H}_6$  (I) and cephalin are dielectrically inactive. The inactivity of (I) is due to association. H. W.

**Lignocerylsphingosin in ox lung.** C. TROPP (Z. physiol. Chem., 1935, 237, 178—180; cf. A., 1934, 97).

—Dried ox lung contains 0.06% of lignocerylsphingosin (I) together with a phosphatide of the sphingomyelin series. (I) probably exists preformed in the spleen, the content of which is not subject to seasonal variations. (I) does not occur in the heart, kidney, lymph glands, testes, or white and red bone marrow of the ox. W. McC.

**Determination of molecule size of nucleic acids and mononucleotides by the free diffusion method. Size of the molecule of pancreatic pentosepolynucleotide and of cozymase.** K. MYRBACK and E. JORPES (Z. physiol. Chem., 1935, 237, 159—164; cf. A., 1935, 232).—The diffusion of nucleic acids (I) [yeast-nucleic acid (II), pentosepolynucleotide (III)] is not affected by  $[\text{H}^+]$ , but is greatly affected by their electric charge and by presence of salts (e.g., NaCl) which restrict the diffusion to an extent  $\propto$  the mol. size of (I). In the determination of approx. mol. wt. of (I) by the free diffusion method, comparison must be made with known substances of similar structure and tendency to ionise. The method gives a mol. wt. of about 3000 for (III), and proves that it is not a mixture of (II) with guanylic acids. The mol. wt. of cozymase is approx. 500. W. McC.

**Isolation of cystine from wool hydrolysates.** G. TOENNIES and M. A. BENNETT (J. Biol. Chem., 1935, 112, 39—50).—Yields of *l*-cystine (I) up to 44% of theoretical calc. on total S are obtained by hydrolysis of wool with 50%  $\text{H}_2\text{SO}_4$ , addition of  $\text{Na}_2\text{SO}_4$  (to salt out humins), pptn. of (I) with  $\text{Cu}^{++}$ , and its conversion into hydrochloride. Negative biuret tests, or cyanide-nitroprusside tests corresponding with the total S content of the wool, do not prove complete hydrolysis. Max. yields of (I) are obtained at stages before complete hydrolysis, owing to loss of (I) by racemisation. F. A. A.

**Distribution of cystine and cysteine in the body.** K. INATOMI (Japan. J. Med. Sci., 1935, II, 3, 115—157).—Data for the cystine-cysteine (I) content of blood and other tissues (rabbit, dog, ox, man) are tabulated. The level increases in the blood during anæmia and in the spleen (but decreases in the liver) during hunger. Splenectomy produces first a fall, then a rise (to subnormal vals.), in the content of the corpuscles, a rise in that of liver and bone-marrow (a gradual decrease commences in the latter after 1 week), and a fall in that of kidney and muscle. The origin and storage of (I) are discussed. F. O. H.

**Acetylcholine equivalent of nervous tissues.** G. S. BARSOUM (J. Physiol., 1935, 84, 259—262).—The splanchnic and vagal nerve trunks in the dog show the highest acetylcholine (I) contents of all the tissues. EtOH extracts of tissues lose their (I) activity when kept at room temp.; the activity is largely restored by addition of  $\text{CCl}_3\text{-CO}_2\text{H}$ . R. N. C.

**Carbon monoxide-ferroglutathione.**—See this vol., 194.

**Heparin.** F. LIPMANN and A. FISCHER (Z. physiol. Chem., 1935, 237, 273—274).—In agreement with Schmitz (A., 1935, 1394) highly purified hepa-

rin (I) is free from S. (I) prepared from ox lung by the method of Charles and Scott (A., 1933, 1317) gives a Ba salt which, after fractionation from neutral solution, contains Ba and org. S in the approx. ratio 2 : 3 in agreement with Jorpes' results (A., 1935, 1144), but % C and N are too high for a chondroitin-trisulphuric acid. The preps. are about 30% more active than those of Jorpes. Under the action of 0.1N-HCl at 100° loss of physiological activity is much more rapid than elimination of H<sub>2</sub>SO<sub>4</sub>.

H. W.

**Potentiometric study of hepatoflavin.** F. J. STARE (J. Biol. Chem., 1935, 112, 223—229; cf. Stern, A., 1934, 846).—The redox potentials of hepatoflavin (from horse liver) at  $p_H$  0.32—13.38 have been determined by titration with reducing agents [Ti<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>]. The titration curves branch in the more acid region. There are ionisation consts. at  $p_H$  about 6.8 (reduction) and 9.6 (oxidation). The normal potential is 0.188 volt.

W. McC.

**Dietary requirements for lactation. IV. Nature of factor-L.** W. NAKAHARA, F. INUKAI, and S. UGAMI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 28, 152—160).—Factor-L is pptd. from aq. EtOH extracts (previously treated with "acid earth"; A., 1934, 930) of liver by Ba(OH)<sub>2</sub>-MeOH. Dissolution of this ppt. by removal of Ba etc. and treatment with WO<sub>3</sub>.2H<sub>3</sub>PO<sub>4</sub> gives an active ppt. (0.176% of the liver used). The factor is not identical with glutamic acid.

F. O. H.

**Isolation of nicotinamide from heart muscle.** R. KUHN and H. VETTER (Ber., 1935, 68, [B], 2374—2375).—Protracted extraction with CHCl<sub>3</sub> of concentrates of a vitamin-B component (free from -B<sub>1</sub> and -B<sub>2</sub>) in feebly alkaline and neutral condition and heating of the residue at 150—160°/5 × 10<sup>-4</sup> mm. gives a waxy distillate from which nicotinamide is isolated.

H. W.

**Probable occurrence of tunicin in the dorsal sac of Sepia.** S. MÜLLER (Magyar chem. Foly., 1934, 40, 112—114; Chem. Zentr., 1935, i, 2551).—The product prepared by Ambronn from the dorsal sac of Sepia contains no tunicin, but a mixture of decomp. products of albumin, with a high N content.

R. N. C.

**Amide-nitrogen of ovalbumin.** A. SHORE, H. WILSON, and G. STUECK (J. Biol. Chem., 1936, 112, 407—413).—The NH<sub>2</sub> produced by the hydrolysis of ovalbumin (I) in 5, 1, and 0.2M-HCl is plotted against time and the probable amide content of (I) deduced by extrapolation to be 24 equivs. per mol.

H. D.

**Crystalline ovalbumin. II. Fractionation of peptic hydrolysis products.** H. O. CALVERY (J. Biol. Chem., 1935, 112, 171—174).—Pepsin hydrolysed one third of the peptide linkings of ovalbumin. Five distinct fractions were obtained, one of which contains free NH<sub>2</sub>-acids. Hydrolysis was also effected by erepsin, aminopolypeptidase, protaminase, and dipeptidase, the last yielding dipeptides.

J. N. A.

**Denaturation of ovalbumin by ultra-violet radiation.** J. H. CLARK (J. Gen. Physiol., 1935, 19, 199—210).—Three processes are involved, (a) a light-

denaturation, (b) a reaction between the product of (a) and H<sub>2</sub>O, (c) formation of a coagulum. (a) is unimol., independent of temp. and (largely) of  $p_H$ ; (b) has a temp. coeff. > 10, and occurs at lower temp. than does heat-denaturation.

F. A. A.

**Composition of the gelatinous mass from Rhizostoma Cuvieri.** R. ZEYNEK and A. DIMTER (Z. physiol. Chem., 1935, 237, 247—253).—The jelly is regarded as a gelatin-giving tissue differing from that of the higher animals in its ready decomp., low content of glycine (which is replaced by other NH<sub>2</sub>-acids), and high S content. It is undecided whether the L-aminobutyric acid present is to be regarded as a structural component.

H. W.

**Structure of silk fibroin.** H. MÜNCH (Angew. Chem., 1935, 48, 797—799).—A discussion of the effects of enzyme action.

E. S. H.

**Cryolysis and its relation to cell physiology.** F. F. NORD (Protoplasma, 1934, 21, 116—128).—Cryolysis of colloidal solutions followed by determination of physico-chemical vals. indicates that lyophilic colloids and their emulsions undergo irreversible changes consisting of aggregation or disaggregation according to their concns.

R. N. C.

**Physico-chemical researches on the proteins.**—See this vol., 158.

**Affinities between proteins and fatty acids, fats, and lipins.**—See this vol., 155.

**Colloid chemistry of edestin. II.**—See this vol., 158.

**Diphasic aspect of the curdling of milk by rennin.** A. G. SMITH and H. C. BRADLEY (Science, 1935, 82, 467).—A method for separating the enzymic and the aggregation phase is described. The former occupies < 60% of the time required for the appearance of the curd. Addition of CaCl<sub>2</sub> accelerates curdling by shortening the aggregation time; the enzymic activity of the rennin is unaffected. An increase in [H<sup>+</sup>] accelerates both phases.

L. S. T.

**Carotenoids of butter.** A. E. GILLAM and I. M. HEILBRON (Biochem. J., 1935, 29, 834—836).—The carotenes of various butters examined consisted of mixtures of  $\alpha$ - and  $\beta$ -forms. Lycopene and kryptoxanthin occurred in some highly coloured butters.

H. D.

**Adsorption of grass and butter carotenes on alumina.**—See this vol., 155.

**Carbon dioxide content and combining power and  $p_H$  of cervical lymph.** J. W. HEIM and O. C. LEIGH (Amer. J. Physiol., 1935, 112, 699—703).—The CO<sub>2</sub> dissociation curve of the cervical lymph of the dog is logarithmic. For a given CO<sub>2</sub> tension the combining power of the lymph is slightly > that of plasma. The average difference between the CO<sub>2</sub> contents of lymph saturated at 30 and 60 mm. of CO<sub>2</sub> tension is < the corresponding difference for separated plasma. The lymph contains about 58.8 vols. of CO<sub>2</sub> per 100 c.c. and its  $p_H$  is about 7.41 (plasma 7.34).

R. N. C.

**Substance in human seminal fluid affecting uterine muscle.** J. R. COCKRELL, E. G. MILLER, jun., and R. KURZROK (Amer. J. Physiol., 1935,

112, 579—580).—Human semen contains acetylcholine or some similar substance that in large amounts causes contraction, and is probably also responsible for the normal relaxation, of uterine muscle.

R. N. C.

**Identification of sperm in medico-legal investigations.** V. PRÉREZ (Crónica med. Valencia, 1934, 38, No. 810).—Solutions of  $\text{AuI}_3$  give characteristic crystals with dil. sperm.

CH. ABS. (e)

**Effect of intravenous injection of sucrose and glucose on the reducing power of cerebrospinal fluid, before and after hydrolysis.** M. I. GREGERSEN and L. WRIGHT (Amer. J. Physiol., 1935, 112, 97—108).—The average glucose (I) concn. of the spinal fluids of normal dogs is 77.5 mg. per 100 c.c. No hydrolysable reducing material is present; the apparent increase in reducing power on acid hydrolysis can be imitated in known (I) solutions by addition of  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$ , or neutralised  $\text{HCl}$ . Injection of (I) causes an increase in cerebrospinal fluid-(I), but sucrose (II) does not increase hydrolysable reducing material, indicating that (I), but not (II), passes the blood-spinal fluid barrier. Spectrophotometric analysis is recommended in (I) determination by Folin's micro-method.

R. N. C.

**Use of hypertonic sucrose solutions intravenously to reduce cerebrospinal fluid pressure without a secondary rise.** L. T. BULLOCK, M. I. GREGERSEN, and R. KINNEY (Amer. J. Physiol., 1935, 112, 82—96).—Hypertonic glucose or  $\text{NaCl}$  solution reduces cerebrospinal fluid pressure in the dog, but the fall is followed by a secondary rise to vals.  $>$  the initial pressure. Sucrose causes the reduction without the secondary rise.

R. N. C.

**Calcium excretion by the pancreas.** G. ÅGREN (Biochem. Z., 1935, 281, 358—362).—The  $[\text{Ca}]$  in pancreatic juice is dependent on the rate of secretion and is always  $>$  that in blood. The serum- $\text{Ca}$  curves after injection of 5—10 mg. of  $\text{CaCl}_2$  per kg. body-wt. are very different for cats before and after injection of secretin. The difference may be utilised as a test for pancreatic function.

P. W. C.

**Excretion of uric acid and urea by the pancreas and the liver under the action of secretin.** G. ÅGREN (Biochem. Z., 1935, 281, 363—366).—The uric acid and residual N contents of pancreatic juice and of bile varied from the blood concn. down to 1/15 this amount. Intravenous injection of uric acid and urea, in amounts sufficient to increase the blood concn. considerably, led to a considerable increase also in the concns. of these substances in the pancreatic juice and in bile.

P. W. C.

**Stable histochemical reaction for detection of bilirubin.** J. STEIN (Compt. rend. Soc. Biol., 1935, 120, 1136—1138).—Bilirubin in fixed sections of tissue is coloured green by I, no other oxidiser showing this reaction except  $\text{FeCl}_3$ , with which it is very feeble.

R. N. C.

**Pyrrporphyrin from ox bile.**—See this vol., 213.

**Determination of the chloride index.** A. E. LEWIN and O. B. MAKAREVIĆ (Arch. Verdauungskr., 1935, 57, 263—268).—The chloride index of a gastric juice is defined as neutral  $\text{Cl} \times 100 / \text{total Cl}$ . Hist-

amine,  $\text{EtOH}$ , or any  $\text{Cl}'$ -free test meal may be used to promote the flow of juice. The  $\text{HCl}$  of the juice and the total  $\text{Cl}'$  are determined by titration with  $\text{NaOH}$  and  $\text{AgNO}_3$ , respectively, neutral  $\text{Cl}'$  being obtained by difference. Bile-stained juice must not be used. The index remained relatively const. in the same person, in spite of wide fluctuations in  $\text{HCl}$  and total  $\text{Cl}'$ .

NUTR. ABS. (m)

**Origin and significance of neutral chloride in the secretions of the stomach and duodenum.** C. M. WILHELMJ, L. C. HENRICH, I. NEIGUS, and F. C. HILL (Amer. J. Physiol., 1935, 112, 15—20).—Neutral  $\text{Cl}'$  in the non-acid secretions of the stomach and the mixed duodenal secretions are approx. the same. When 0.1N- $\text{HCl}$  is added to the secretions, only about one third of the neutral  $\text{Cl}'$  represents neutralised  $\text{HCl}$ .

R. N. C.

**Action of gastric and duodenal juice and of bile on ascorbic acid.** A. CARTENI and A. MORELLI (Boll. Soc. ital. Biol. sperim., 1935, 10, 327—329).—Ascorbic acid is destroyed by gastric and duodenal juice and by bile, the % reduction generally  $\propto p_{\text{H}}$ .

R. N. C.

**Acidic components of wool grease.**—See B., 1936, 66.

**Formation of wax within the organism of bees.** G. BUCHNER (Fettchem. Umschau, 1935, 42, 208—209).—Shortly before the wax is discharged by the bees (*i.e.*, during its formation) the temp. of the hive rises markedly, indicating an energetic oxidation due to the  $\text{O}_2$  derived from the conversion of sugar into wax. Possible reactions are discussed.

E. L.

**Urinary modifications in the dog and rabbit following vagotomy.** E. TRIA and A. NICOLAZZO (Boll. Soc. ital. Biol. sperim., 1935, 10, 329—331).—Vagotomy induces aciduria in the rabbit and alkaluria in the dog, irrespective of the normal effect of the diet on urinary  $p_{\text{H}}$ .

R. N. C.

**Physico-chemical characters of the urine of rats on a diet of fibrin and kept in glass cages.** F. M. CHIANCONE (Boll. Soc. ital. Biol. sperim., 1935, 10, 292—294).—The urine shows decreases in  $\eta$ ,  $\sigma$ , and f.p., and increases in  $\kappa$  and the f.p./ $\kappa$  ratio, which are  $>$  those obtained when the animals are kept in metal cages. The fluorescence spectrum and spectrophotometric curve are normal.

R. N. C.

**Elimination of organic acids in urine during childhood and relation of acids to basal metabolism in adults.** S. A. SIWE (Svenska Läk. sällsk. Hand., Stockholm, 1934, 60, 157).—Elimination of org. acids, both in the total amount and in the  $\text{Et}_2\text{O}$ -sol. fraction, often varies considerably from case to case and in the same person from day to day. In premature and weak infants, in rickets, and in nutritional disturbances the vals. are high. In diabetes establishment of the org. acids in the urine presents an improved method for determining acidosis. In children elimination of org. acids seems to diminish with age and daily variations become less. There is a relatively const. ratio of 3 : 2 between the org. acids eliminated during the day and during the night. In adults there is no relation between basal metabolism and org. acid elimination.

NUTR. ABS. (m)

**Excretion of oxalic acid by guinea-pigs.** S. BORGSTROM (Biochem. Z., 1935, 281, 377—382).— $H_2C_2O_4$  is excreted even when the diet is devoid of it.  $H_2C_2O_4$  given by mouth is to a large extent decomposed in the body, but injected subcutaneously is mainly excreted in the urine. P. W. C.

**Butyric acid content of normal urine.** L. KLINC (Bull. Soc. Chim. biol., 1935, 17, 1540—1545).—In normal urine 4—8 mg. of  $Pr^bCO_2H$  (determined by oxidation to  $COMe_2$  followed by iodometric titration) are excreted daily.  $Pr^aCO_2H$  is absent. A. L.

**Water and chloride excretion of decerebrate cats.** M. SUMWALT, W. H. ERB, and H. C. BAZETT (Amer. J. Physiol., 1935, 112, 386—396). R. N. C.

**Bromine index of the urine as an indication of the normal physiological state.** N. BEZSSONOFF, A. VALLETTE, and R. SACREZ (Bull. Soc. Chim. biol., 1935, 17, 1573—1598).—The Br index of urine (mg. of Br taken up by 1 ml.) is not dependent on the concn. of mineral or org. substances, but on the presence of phenolic, indole, and glyoxaline derivatives, i.e. on the protein metabolism. The index increases with age, and reflects pathological conditions. Fever and rickets increases, and administration of vitamin-C decreases, the val. A. L.

**Renal excretion of urea.** R. DOMINGUEZ (Amer. J. Physiol., 1935, 112, 529—544).—Theoretical. R. N. C.

**Application to urine of Tollens' naphthoresorcinol test for conjugated glycuronides.** H. B. SALT (Biochem. J., 1935, 29, 2705—2709).—An improved technique is described. It is sensitive to 0.5 mg. of glycuronic acid in 5 c.c. of urine. Interfering substances are first pptd. by  $Pb(OAc)_2$ , and then the glycuronide by basic Pb acetate; the test is done on this ppt. Using aspirin as a glycurogenic drug, a method of testing the detoxicatory efficiency of the liver is described. J. N. A.

**Factors affecting appearance and duration of glycosuria.** C. S. ROBINSON, R. C. DERIVAUX, and B. HEWELL (Amer. J. Med. Sci., 1935, 189, 795—803).—In female patients without disturbance of carbohydrate metabolism and with normal fasting blood-sugar (I), after intravenous injection of 10 g. of glucose the peak (I) vals. were 0.131—0.304%. When urine excretion was small in vol., glycosuria persisted longer. The (I) level at which glycosuria ceased was usually < that at which it commenced. NUTR. ABS. (m)

**Excretion of vitamin-C in human urine.** B. AHMAD (Biochem. J., 1936, 30, 11—15).—The reducing capacity of urine excreted under diets with (a) low vitamin-C (I), (b) low protein, (c) high protein, and (d) purine-free high protein contents has been determined. Meat diets favour excretion of (I), which possibly forms most of the reducing substance of urine. J. N. A.

**Detection of small quantities of gonadotropic hormone in the urine of normal subjects.** O. THOMSEN and K. PEDERSEN-BJERGAARD (Compt. rend. Soc. Biol., 1935, 120, 1143—1147). R. N. C.

**Tungstic acid precipitation method for extraction of oestrogenic substance from urine.** S. C. FREED, I. A. MIRSKY, and S. SOSKIN (J. Biol. Chem., 1935, 112, 143—147).—Oestrogenic substances are extracted, without loss of activity, by treating urine with  $Na_2WO_4$ , acidifying with  $H_2SO_4$ , and extracting the ppt. with  $EtOH-Et_2O$ . J. N. A.

**Determination of urinary oestrin.** G. VAN S. SMITH and O. W. SMITH (Amer. J. Physiol., 1935, 112, 340—350).—Estrin (I) cannot be recovered completely from untreated pregnancy urines by  $CHCl_3$ , olive oil,  $EtOAc$ , or  $C_6H_6$ ; the largest quantity is extracted by  $C_6H_6$ . In some cases  $C_6H_6$  extracts more (I) than can be demonstrated in the untreated urines. Pregnancy urines boiled with HCl increase in their (I) content. Total (I) after boiling with HCl can be extracted completely by  $C_6H_6$ ; none is destroyed by boiling with 15% HCl. Pure "theclin" is fixed in the alkaline solution in which it is supplied, and is less potent when first diluted than if kept for 10 days; acid treatment does not increase the potency further. The action of the HCl is therefore considered to be a liberation of "bound" (I). There is no apparent relation between the "free" (I) content of the urine and its  $p_H$ . The "free" (I) of the urine of a pregnant woman varies widely daily, but total (I) increases uniformly. The procedure adopted for the assay of (I) is outlined. R. N. C.

**The Donaggio reaction. [Protective colloid in pathological urine.]** G. SOLLAZZO and V. CORTESE (Boll. Chim. farm., 1935, 74, 625—628, 631—634, 637).—The property of urine of febrile patients of inhibiting pptn. of a lake from thionine by  $(NH_4)_2MoO_4$  is due to a protective colloid, and can be imitated by gum arabic, and counteracted by addition of mannitol. The protective action is destroyed by pepsin or by dil.  $AcOH$ . Properties of the colloidal substance are discussed. E. W. W.

**Butyric acid content of faeces.** K. KLINC (Bull. Soc. Chim. biol., 1935, 17, 1546—1548).—The meconium does not contain  $PrCO_2H$ , which, however, is present in the faeces of suckling infants for a short time (until lactic acid fermentation predominates). In the adult, 40—130 mg. of  $PrCO_2H$  are present per 100 g. of faeces. A. L.

**Secreted nitrogen in the faeces and dietary protein utilisation.** W. HEURKE and F. BEIZ (Arch. Hyg. Bakteriol., 1935, 114, 56—62).—In man ingestion of various N-poor foodstuffs for 3—4-day periods indicated that faecal N (which was in all cases > the intake) tended to vary with the dry wt. of the faeces, suggesting that part of this N must be derived from intestinal secretion and that the utilisability of a foodstuff can be assessed only if the amount of the secreted N is known. About 1.5—2 g. of N are secreted per day for every 50 g. of dry wt. of faeces. NUTR. ABS. (m)

**Variation in water content of the faecal material along the colon.** F. R. STEGGERDA (Amer. J. Physiol., 1935, 112, 559—564). R. N. C.

**Disease of metabolism in sheep.** J. G. WRIGHT (Vet. Rec., 1935, 15, 1253—1255). R. N. C.

**Uric acid excretion following administration of creatinine in man under normal and pathological conditions with special reference to renal insufficiency.** R. GÄRDSTAM (*Acta med. Scand.*, 1935, Suppl. 67, 296 pp.).—In toxic and orthostatic albuminuria and in the residual condition which follows acute nephritis, in essential hypertonia and gout, and to a certain extent in congestive cardiac conditions with albuminuria the ratios conen. index of uric acid (I) : conen. index of creatinine (II) and (I) content of urine : conen. index of (II) were within normal limits. Raised vals. were found in acute and chronic nephritis, pyelonephritis, and advancing arteriosclerosis of renal origin.

NUTR. ABS. (m)

**Rôle of the pituitary in experimental chronic adrenal insufficiency.** A. GROLLMAN and W. M. FIROR (*Amer. J. Physiol.*, 1935, 112, 310—319).

R. N. C.

**Correlation between adrenals and thyroid.** I. ABELIN (*Z. ges. exp. Med.*, 1934, 94, 353—358; *Chem. Zentr.*, 1935, i, 2690).—Adrenalectomy and hyperfunction of the thyroid result in a similar series of effects. In both cases glycogen (I) falls in muscle and disappears from the liver, which undergoes fatty degeneration. A diet known to maintain liver-(I) in hyperthyroid rats has the same effect in adrenalectomised animals; di-iodotyrosine also maintains liver-(I).

R. N. C.

**Gastric secretion in anæmia.** J. W. OGILVIE (*Arch. Dis. Childhood*, 1935, 10, 143—148).—A marked diminution in the secretion of free HCl and total acidity was found in 13 out of 34 anæmic children, but there was no significant variation in the other constituents of the juice. No type of anæmia showed any const. change in secretion of free acid.

NUTR. ABS. (m)

**Effect of acute anoxæmia on hunger, digestive contractions, and the secretion of hydrochloric acid in man.** F. A. HELLEBRANDT, E. BROGDON, and S. L. HOOPES (*Amer. J. Physiol.*, 1935, 112, 451—460).—Acute anoxæmia of the pre-coma type has relatively little inhibitory effect on gastric motility or HCl secretion.

R. N. C.

**Human anthrax in Barotseland treated with novarsenobenzene.** F. W. GILBERT (*Lancet*, 1935, 229, 1283—1285).

L. S. T.

**Alimentary azotæmia in rats.** F. FUCHS (*Wien. klin. Woch.*, 1935, 48, 582—584).—In rats, a diet of green food with NaHCO<sub>3</sub> in the drinking H<sub>2</sub>O resulted in sickness and death in >14 days (high blood-N, very alkaline urine).

NUTR. ABS. (m)

**Hyperglycæmia and glycosuria associated with disease of the biliary tract.** H. LANDE and H. POLLACK (*Arch. Int. Med.*, 1935, 56, 1097—1108).—A direct correlation was obtained between the disturbance of carbohydrate metabolism and the impairment of hepatic function. Disease of the gall bladder is accompanied by diabetes, which disappears on normal functioning of the liver and adequate biliary drainage.

H. G. R.

**Cancer as a problem in metabolism.** H. H. BEARD (*Arch. Int. Med.*, 1935, 56, 1143—1170).—A review.

H. G. R.

**Blood modifications in cancer.** J. LOISELEUR (*Compt. rend. Soc. Biol.*, 1935, 120, 1038—1042).—Blood-NH<sub>2</sub>-acids and -residual N in patients with cancerous lesions are increased, whilst urea falls. The corpuscle-/plasma-Cl ratio is lowered, and is inversely  $\propto$  total Cl. The alkaline reserve approaches the lower limit of its normal vals., whilst plasma-p<sub>H</sub> approaches the upper limit. During radiological treatment residual N is increased, whilst urea, Cl, hydræmia, and alkalosis fall.

R. N. C.

**Induction of cancer by cracked mineral oils.** C. C. TWORT and J. M. TWORT (*Lancet*, 1935, 229, 1226—1228).—Mice exposed to fumes from a mineral oil cracked on a heated plate showed no definite increase in the incidence of lung tumours, but the polynuclear count is increased. Heavier Diesel oils, but not light-grade oils, are carcinogenic for the skins of mice. Lubricating oils recovered from the sump of motor cars are more carcinogenic than the original oils. The carcinogenicity of crude shale oils decreases as the cracking temp. is lowered, but oil cracked at 385° is still carcinogenic.

L. S. T.

**Growth-promoting and growth-inhibiting substances of normal organs.** J. MAISON and Y. POURBAIX (*Amer. J. Cancer*, 1935, 24, 357—385).—Addition of liver, pancreas, and intestinal mucosa to the diet of tarred mice promoted growth of tar tumours. Brain, thymus, bone marrow, dried gastric mucosa, and lymph-tissue inhibited growth. The growth-promoting substances are mostly H<sub>2</sub>O-sol. and relatively insol. in Et<sub>2</sub>O, whilst the growth-inhibiting substances are sol. in Et<sub>2</sub>O and relatively insol. in COMe<sub>2</sub>.

NUTR. ABS. (m)

**Anterior pituitary hormones and formation of experimental tar carcinoma.** J. ZELDENRUST (*Acta Brev. Néerl. Physiol.*, 1934, 4, 182—184).—Prolan stimulates growth of tumours produced in mice by tar, but the Evans alkaline pituitary extract prevents tumour formation.

R. N. C.

**Phosphoric esters in normal and malignant tissues.** E. L. OUTHOUSE (*Trans. Roy. Soc. Canada*, 1935, [iii], 29, V, 77—84).—From lymphosarcoma was isolated C<sub>6</sub>H<sub>13</sub>O<sub>8</sub>NPBa (?), [ $\alpha$ ]<sub>D</sub><sup>20</sup> +2.86°, probably the Ba salt of an aminohexahydric alcohol phosphoric acid (or possibly hexosaminephosphoric acid). From tumours other than lymphosarcomata, ethanolaminephosphoric acid has been isolated. Both these acids form insol. Pb salts. Phosphoric esters forming sol. Pb salts are present to the greatest extent in tumour tissue and least in skeletal muscle. Hexose phosphates are absent from the acid-sol. phosphates of tumour.

W. O. K.

**Copper metabolism and experimental rat cancer.** S. STMEGI (*Frankfurter Z. Path.*, 1935, 48, 35—42).—During implantation of Ehrlich—Putnoky rat cancer the Cu content of the tumour formed rises steeply until the 10th day and remains at the same level until death occurs. A disturbance of assimilation takes place in which the Cu content of

the liver rises from 34.2 to 40.8 mg. per 100 g., whilst that of the stomach falls from 38.9 to 23.2 mg. Withdrawal of Cu from normal function is advanced as a cause of cancer anæmia. When loss of Cu was compensated by injections of  $\text{CuSO}_4$  the Cu content of the stomach of tumour rats was raised to 59% > that of controls, and 11.3% < that of Cu-treated non-implanted rats. The treatment decreased the loss of red blood corpuscles and hæmoglobin and increased the no. of reticulocytes in tumour animals.

NUTR. ABS. (m)

**Determination of blood-oxalic acid in cancer.**

E. AUJALEV, F. H. COLOMBIES, and A. MONTARIOL (Compt. rend. Soc. Biol., 1935, 120, 954—955).— $\text{H}_2\text{C}_2\text{O}_4$  is determined by the method of Maugeri. In cases of hyperoxalæmia, blood-sugar and cholesterol are generally increased, but not  $\propto \text{H}_2\text{C}_2\text{O}_4$ ; urea remains normal.

R. N. C.

**Intimate mechanism of diabetes from superabundance.** M. WIERZUCHOWSKI, Z. BORKOWSKI, and A. GOSTYNSKA (Compt. rend. Soc. Biol., 1935, 120, 1133—1135).—Absorption by the organs from the blood-stream of continuously-injected glucose in the dog increases with the rate of injection up to the extreme limit of tolerance.

R. N. C.

**Effect of total thyroidectomy on experimental diabetes insipidus in dogs.** W. MAHONEY and D. SHEEHAN (Amer. J. Physiol., 1935, 112, 250—255).

R. N. C.

**Calorigenic action of fat and carbohydrate in pancreatic diabetes.** G. C. RING (Amer. J. Physiol., 1935, 112, 124—129).

R. N. C.

**Effect of equivalent amounts of glucose and starch on glycæmia and glycosuria in diabetics.** M. WISHNOFSKY and A. P. KANE (Amer. J. Med. Sci., 1935, 189, 545—550).—No significant difference was observed.

NUTR. ABS. (m)

**Lipase content of the normal liver and the liver in fatty degeneration.** N. FIESSINGER and A. GAJDOS (Compt. rend. Soc. Biol., 1935, 120, 766—768).—The lipase content of the human liver decreases considerably in fatty degeneration.

R. N. C.

**Pathogenic mechanism of the green diarrhoea of pigeons in avitaminosis.** G. RENOSTO (Boll. Soc. ital. Biol. sperim., 1935, 10, 297—299).—The capacity of strains of *B. coli*, isolated from the intestines of pigeons in avitaminosis-B, to ferment carbohydrates, liberate  $\text{H}_2\text{S}$ , and cause hæmolysis is equal to that of strains from normal pigeons.

R. N. C.

**Fine structure of the striated muscular fibres in normal and pathological conditions. I. Lipidosis of the striated muscular fibres and localisation of the lipin material in some toxic infections.** A. BASILE (Boll. Soc. ital. Biol. sperim., 1935, 10, 302—304).—Intoxication of guinea-pigs by diphtheria toxin, *B. typhosus*, P, or As provokes a slow rise of lipins in the striated muscular fibres.

R. N. C.

**Influence of progressive toxæmic liver damage on the glucose tolerance curve.** S. SOSKIN and L. A. MIRSKY (Amer. J. Physiol., 1935, 112, 649—

656).—The curves obtained in dogs after administration of diphtheria toxin do not show the normal increase in tolerance. The cycle of events following the onset of toxæmia depends on the amount of sugar used; the curve becomes alternately normal and "diabetic" in type.

R. N. C.

**Infantile allergic eczema. II. Serum-lipins; saturation of the fatty acids.** H. K. FABER and D. B. ROBERTS (J. Paediat., 1935, 6, 490—493).—In eczema, serum-fatty acids tend to be less unsaturated than normally.

NUTR. ABS. (m)

**Hyperoxalæmia in acute eczema and dermatitis.** S. SUZUKI (Japan. J. Med. Sci., 1935, II, 3, 95—97).—A slight hyperoxalæmia occurs.

F. O. H.

**Treatment of hæmorrhagic disorders with vitamin-C.** H. ENGELKES (Lancet, 1935, 229, 1285—1287).—Capillary hæmorrhages are successfully treated.

L. S. T.

**Pathological physiology of infarct. III. Ammonia and lactic acid during necrosis and autolysis.** G. BORGER, H. BAYERLE, T. MAYR, and E. PETERS (Z. physiol. Chem., 1935, 237, 113—120; cf. A., 1935, 1269).—The  $\text{NH}_3$  content of normal and infarct kidney remains fairly const. for 50 hr., whilst that of autolysing kidney steadily increases. The lactic acid levels vary, both that of autolysing and infarct kidney being > normal for the first 2 hr., after which (2—96 hr.) the infarct content alone decreases to normal levels.

F. O. H.

**Non-diabetic ketosis with acidosis.** D. C. DARROW and M. K. CARY (J. Paediat., 1935, 6, 676—694).

NUTR. ABS.

**Ketosis in cows.** G. F. BODDIE (Vet. Rec., 1935, 15, 1539—1546).—Blood-sugar in a normal cow is not increased after parturition; it falls in severe cases of post-parturient dyspepsia. Blood-ketones are slightly increased after parturition; in severe post-parturient dyspepsia there is a considerable increase due to formation of  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{H}$ , which is low in normal animals.

R. N. C.

**Flocculation of sera in distilled water and Henry reaction.** R. O. PRUDHOMME (Compt. rend. Soc. Biol., 1935, 120, 944—946).—Malaria sera contain a substance that is pptd. by  $\text{H}_2\text{O}$ ; it is present in normal serum in smaller quantities, demonstrable by melanin.

R. N. C.

**Pathology of infantile marasmus.** Z. VON GUTÁCSY (Arch. Kinderheilk., 1935, 105, 43—53).

NUTR. ABS.

**Blood- and cerebrospinal fluid-sugar. Permeability to sugar of the brain-membranes in meningitis.** A. V. TSHERKASSOV and E. E. JOLKVER (Rev. franç. Pédiat., 1935, 11, 350—364).

NUTR. ABS.

**Renal elimination of vitamin-C in experimental nephritis.** F. PINOTTI (Boll. Soc. ital. Biol. sperim., 1935, 10, 314—317).—Vitamin-C elimination by the kidneys is increased by intoxication with  $\text{UO}_2(\text{OAc})_2$  or  $\text{HgCl}_2$ , the increase from  $\text{HgCl}_2$  persisting longer.

R. N. C.

**Uric acid crystals in the blood plasma of a fowl suffering from pyo-nephrosis consequent**

on vitamin-A deficiency. G. SANKARAN (Current Sci., 1935, 4, 314).—A fowl fed during 12 weeks on a diet deficient in vitamin-A had 375 mg. of uric acid per 100 c.c. of plasma (control 8.34 mg.).

F. R. G.

Cerebrospinal fluid in periodic paralysis. G. GUILLAIN, L. ROUQUÈS, and C. RIBADEAU-DUMAS (Compt. rend. Soc. Biol., 1935, 120, 841—842).—The cerebrospinal fluid shows hyperalbuminosis, a slightly positive Pandy reaction, and a broadening of the colloidal benzoin pptn. curve.

R. N. C.

Specific value of crude iron compounds in the treatment of "pine" in cattle and sheep. J. BROWN (Vet. Rec., 1935, 15, 1233—1234).

R. N. C.

Rheumatic disease (osteo-arthritis and allied conditions) in the horse. W. M. MITCHELL (Vet. Rec., 1935, 15, 1501—1507).—A lecture. Vitamin deficiency is the probable cause.

R. N. C.

Rickets due to strontium. (A) Nature of injury to calcifying mechanism. (B) Phosphatase activity and calcification. A. E. SOBEL, J. COHEN, and B. KRAMER (Biochem. J., 1935, 29, 2640—2645, 2646—2650).—(A) With Sr rickets in rats, a marked diminution occurs in *in-vitro* calcifying power of the bones, an injury removed both *in vivo* and *in vitro* by bathing the bone cells in Sr-free fluids. Sr<sup>++</sup> directly inhibits calcification, apparently combining with a factor involved in this process.

(b) No significant difference occurs in the phosphatase activities of bones from rats with Sr- or Ca-rickets, whilst Sr<sup>++</sup> (up to 0.08%) does not influence the hydrolysis by bone-phosphatase preps.; hence the loss of *in-vitro* calcifying power due to Sr<sup>++</sup> is not related to the phosphatase activity.

F. O. H.

Activity of *p*-aminophenylsulphonamide on experimental streptococcal infections in the mouse and rabbit. J. TRÉFOUËL, (MME.) J. TRÉFOUËL, F. NITTI, and D. BOVER (Compt. rend. Soc. Biol., 1935, 120, 756—758).—Resistance to hæmolytic streptococci is increased.

R. N. C.

Bordet-Wassermann reaction: inhibiting power of the fraction of the serum precipitated by hydrochloric acid. C. AUGUSTE (Compt. rend. Soc. Biol., 1935, 120, 885—886).—Complement-fixation by syphilitic sera is increased considerably by pptn. with HCl; it is reduced to normal by the return of the pptd. fraction.

R. N. C.

Relation of diet and serum-calcium to tetany in the parathyroidectomised rat. M. M. HOSKINS (Endocrinol., 1935, 19, 453—460).—Rats are protected from tetany by diets with high Ca/P ratios, which keep serum-Ca (I) high. In cases where (I) is low, tetany cannot be correlated closely with the blood-Ca level, and apparently depends on some endogenous factor.

R. N. C.

Thrombo-angiitis obliterans (Buerger) X. Reduction in blood volume following bilateral oophorectomy. M. FRIEDLANDER, N. LASKEY, and S. SILBERT (Endocrinol., 1935, 19, 461—465).—Cholesterol, fibrinogen, and  $\gamma$  are increased.

R. N. C.

Metabolism of tonic and non-tonic muscle. H. SCHÖNFELDER (Arch. exp. Path. Pharm., 1935,

180, 24—27).—Under anaërobic conditions the lactic acid (I) produced by finely minced muscle from newborn rabbits is increased by 28% by addition of glucose (II), but by only 5% by glycogen (III). With mature muscle, (II) increases (I) by only 7%, whilst (III) increases it by 116%; if the same muscles have been paralysed by section of the nerves 3—4 weeks before, the yield of (I) is increased by 30% by (II), and only by 1% by (III).

J. N. A.

Rôle of tissue metabolism in the radio-sensitivity of the thymus of the guinea-pig. M. CHEVRE-MONT (Arch. Biol., 1935, 46, 507—598).

Chemical mediation of sympathetic vasodilator nerve impulses. A. ROSENBLUETH and W. B. CANNON (Amer. J. Physiol., 1935, 112, 33—40).

R. N. C.

Water metabolism in normal and hypophysectomised frogs. M. E. JONES and F. R. STEGGERDA (Amer. J. Physiol., 1935, 112, 397—400).

R. N. C.

Colloid model for illustration of biological processes. I. Triple salt effect in the germination of crustacean eggs and with phosphatides. H. G. B. DE JONG, J. VAN DER MEER, and L. G. M. B. BECKING (Kolloid-Beih., 1935, 42, 384—407).—The concn. region of the system KCl—MgCl<sub>2</sub>—NaCl—H<sub>2</sub>O in which the germination of crustacean eggs is possible has been determined. Analogous regularities have been found in the behaviour of a desensitised, EtOH-insol. plant phosphatide as regards stability and reversal of change in these solutions. The biological significance of the results is discussed.

E. S. H.

Rôle of phosphatides in nutrition. A. K. PICKAT, O. J. KURTSINA, and N. S. ZENIN (Problems of Nutrition, Moscow, 1935, 4, No. 2, 30—37).—Small doses of lecithin (I) had no beneficial effect on the growth of rats receiving also all vitamins. (I) is probably not essential to the diet.

NUTR. ABS. (m)

Nutrient value of cow's milk and of modified milk for various mammals. R. JACQUOT and H. TRIMBACH (Bull. Soc. Sci. aliment., 1934, 22, 134—156; Chem. Zentr., 1935, i, 2553—2554).—Varying levels of utilisation of milk by animals receiving an all-milk diet are discussed. For smaller and more rapidly growing animals cow's milk is deficient in Ca, P, Fe, and lactalbumin (lysine). Lactose is relatively poorly utilised even by calves. Isoenergetic replacement of milk-fat by starch improves growth and increases N retention.

Digestibility of foodstuffs. H. STEUDEL (Z. ges. exp. Med., 1935, 95, 580—588; Chem. Zentr., 1935, i, 2553).—A discussion.

A. G. P.

Influence of rations low in minerals on the composition of the blood and milk of cows, and on the blood of their progeny. J. W. GROENEWALD (Onderstepoort J. Vet. Sci., 1935, 4, 93—165).—The only mineral element, a shortage of which in the ration was reflected in the composition of the blood of the heifers, was P, the blood-inorg. P decreasing from 7.2 to 3.4 mg. per 100 ml. The average composition of the blood-minerals of all the cows except those on low P intake was: Ca 8.4, P 7.2,



Mg 2.7, K 58.7, Na 302, Cl 314 mg. per 100 ml. Slight depressions occurred in these levels during lactation. The variations in the composition of the rations had no effect on the mineral composition of the milk. In the calves, the blood-Ca was > that of the dam during the first month, and the inorg. P higher during the first 3 months. The K, which was very high in calf's blood at birth, declined rapidly and steadily, reaching the adult level at 10 weeks, whereas for Na the reverse was true.

NUTR. ABS. (m)

Effects of a diet poor in salts on the growth and composition of the incisors of the rat. M. F. CLARKE and A. H. SMITH (Amer. J. Physiol., 1935, 112, 286—293). R. N. C.

Relation between the motor and secretory functions of the human fasting stomach. F. A. HELLEBRANDT (Amer. J. Physiol., 1935, 112, 162—165). R. N. C.

Reserve store of hæmoglobin-producing substances in growing dogs as influenced by diet. F. S. ROBSCHT-ROBBINS and G. H. WHIPPLE (Amer. J. Physiol., 1935, 112, 27—32).—Growing dogs can store hæmoglobin-producing substances on a diet of liver or ox skeletal muscle. R. N. C.

Phytin in human nutrition. R. A. McCANCE and E. M. WIDDOWSON (Biochem. J., 1935, 29, 2694—2699).—Small amounts of phytin (I) can be determined by extraction with HCl, pptn. as the Fe<sup>III</sup> salt, and determination of the P in the latter after H<sub>2</sub>SO<sub>4</sub>-HClO<sub>4</sub> incineration. The (I) content of 64 foodstuffs has been determined, in many cases 40—50% of the total P being in the form of (I). Green leaf and stem vegetables and the pulp of fresh and dried fruits contain no (I). When (I) is ingested, 20—60% is excreted unchanged in the fæces. (I)-P constitutes < 5% of the total P of the average diet in this country. J. N. A.

Permeability of frog capillaries to protein. R. E. CONKLIN (Amer. J. Physiol., 1935, 112, 401—404).—The skin capillaries are highly permeable to protein, but normally do not admit protein mols. from the lymph spaces. R. N. C.

Deaminating and urea-forming power of the liver in normal pregnancy; intermediary protein metabolism. L. HEROLD (Arch. Gynakol., 1935, 159, 166—171).—Compared with normal women, normal pregnant women exhibit a delay in the decline of the free NH<sub>2</sub>-N of the blood and a delayed rise in the bound NH<sub>2</sub>-N following intravenous injection of 1 g. of glycine. NUTR. ABS. (m)

Effect of restricted diet on deamination in the organism. I. Effect of high-carbohydrate diet. R. AGNOLI and L. UNTERSTEINER (Arch. Sci. biol. Napoli, 1934, 20, 474).—Deaminative power is reduced. NUTR. ABS. (m)

Nitrogen metabolism in protein starvation. G. MOUROT (Compt. rend., 1935, 201, 1044—1046).—In N starvation the relative amount of the various N fractions excreted is a function of the total N excreted per kg. body-wt. per 24 hr. (i). Thus, as i increases, the proportion of urea also increases at

first rapidly, then more slowly, becoming const. at about 80% of the total N, when i is 400 mg. Conversely the amount of undetermined N falls with increasing i and becomes insignificant at the above val. of i. The nature of the N products excreted is thus determined primarily by the intensity of the oxidation process in the tissues. W. O. K.

Tyrosine metabolism of *Bombyx mori* (silkworm). J. HOLTZMANN (Biochem. J., 1936, 30, 28—30).—There is no need to assume synthesis of tyrosine (I) by the grubs, as the (I) intake in the ingested mulberry leaves exceeds the amount of (I) in the cocoon and contained grub. J. N. A.

Effect of an alkaline reaction and of the physico-chemical environment on the oxidation of uric acid. J. SULA (Compt. rend. Soc. Biol., 1935, 120, 911—915).—Uric acid (I) is oxidised by O<sub>2</sub> in pure solutions at p<sub>H</sub> > 7.6, the extent of oxidation increasing with p<sub>H</sub>. Oxidation takes place in human serum at p<sub>H</sub> > 7.6 only if the (I) concn. is > 3 mg. per litre; otherwise it begins at p<sub>H</sub> 8.0. The inhibition is not due to the sp. proteins, since serum-globulins and -albumins and ovalbumin in pure solutions permit oxidation at p<sub>H</sub> 7.6. R. N. C.

Absorption of gluten peptone and of glutamic acid introduced into a Vella intestinal loop. G. SARZANA (Boll. Soc. ital. Biol. sperim., 1935, 10, 173—175).—The rate of absorption of gluten peptone in the dog is < that of Witte's peptone, but > that of glutamic acid. R. N. C.

Feeding experiments with mixtures of highly purified amino-acids. VII. Dual nature of the "unknown growth essential." M. WOMACK and W. C. ROSE. VIII. Isolation and identification of an essential amino-acid. R. H. MCCOY, C. E. MEYER, and W. C. ROSE (J. Biol. Chem., 1935, 112, 275—282, 283—302; cf. A., 1935, 113).—VII. The unknown substance essential for growth is a mixture of isoleucine (I) and a substance (II) less sol. in Bu<sup>4</sup>OH than is (I).

VIII. The isolation of pure (II) from blood-fibrin is described. (II) is  $\alpha$ -amino- $\beta$ -hydroxybutyric acid, m.p. 255—257° (decomp.) (N-benzoate, m.p. 151°, picrate m.p. 139.5—141°), which with red P and HI gives *d*- $\alpha$ -aminobutyric acid. An otherwise adequate diet must contain < 0.6% of (II) for max. growth. Bromination of methoxyethylmalonic acid (Palmaa *et al.*, A., 1931, 710) followed by heating at 150° gives  $\alpha$ -bromo- $\gamma$ -methoxybutyric acid, b.p. 145—148°/5 mm., which, with conc. aq. NH<sub>3</sub> gives  $\alpha$ -amino- $\gamma$ -methoxybutyric acid (III), m.p. 224—225° (decomp.). (III) boiled for 3 hr. with 48% HBr gives  $\alpha$ -amino- $\gamma$ -hydroxybutyric acid, which has no growth-promoting effect. Hydroxyglutamic acid and citrulline are not essential constituents of food. W. McC.

Amino-acid metabolism. I. Fate of glycine, *dl*- and *d*-alanine in the normal animal. J. S. BUTTS, M. S. DUNN, and L. F. HALLMAN (J. Biol. Chem., 1935, 112, 263—274; cf. Wilson *et al.*, A., 1930, 367).—Those NH<sub>2</sub>-acids, fed to male rats, favour the production of glycogen, *d*- being twice as effective as *dl*-alanine (I), which is much more effective than is glycine. The ketone-suppressing activities

of the acids are in the same order. Probably the *l*-component of (I) has no effect on glycogen production.

W. McC.

**Model experiment in respiration using croton oil in the presence and absence of carotenoids.** R. RETOVSKY (Bull. Soc. Chim. biol., 1935, 17, 1614—1628).—A study is made of the autoxidation of croton oil in the presence and absence of carotenoids (I). The length of the period of incubation  $\propto$  the intensity of the light, and is shorter in absence of (I). With daylight the course of the autoxidation in absence of (I) eventually follows that in presence of (I).

A. L.

**Behaviour in the body of peat extracts (humic substances) after oral or intravenous administration.** R. SCHMID (Biochem. Z., 1935, 281, 329—332).—Humic substances, orally administered to man, were absorbed to a small extent and led to an increase in the normal urinary excretion of humic substances. 1% aq. solutions injected intravenously into rabbits were lethal but smaller concns. were tolerated.

P. W. C.

**Action of choline and other substances in the prevention and cure of fatty livers.** C. H. BEST and H. J. CHANNON (Biochem. J., 1935, 29, 2651—2658).—The influence of dietary constituents (*e.g.*, protein) on the fat content of the liver and the correlation and significance of available data are discussed (cf. A., 1935, 244, 524, 890).

F. O. H.

**Influence of caseinogen content of diets on the nature of "cholesterol" fatty liver.** A. W. BEESTON, H. J. CHANNON, and H. WILKINSON (Biochem. J., 1935, 29, 2659—2667).—In rats fed on a diet containing 20% of fat, 2% of cholesterol, and only small amounts of choline (I), variations in the protein (II) content cause marked changes in the contents of the various lipins in the resulting fatty livers. Dosage with (I) (80 mg. per day per rat) largely prevents deposition of glycerides, but not that of cholesteryl esters. (II), but not (I), increases liver-phosphatides.

F. O. H.

**Metabolism of polycyclic compounds. I. Production of dihydroxydihydroanthracene from anthracene.** E. BOYLAND and A. A. LEVI (Biochem. J., 1935, 29, 2679—2683).—Rats fed on a diet containing anthracene excrete 1:1:2-dihydroxy-1:2-dihydroanthracene (I),  $C_{14}H_{12}O_2$ , m.p. 160—161°,  $[\alpha]_D^{20} -154^\circ$  in  $COMe_2$ ,  $-100^\circ$  in dioxan (diacetate,  $C_{18}H_{16}O_4$ , m.p. 149°,  $[\alpha]_D^{20} -375.5^\circ$  in  $C_6H_6$ ,  $-362^\circ$  in dioxan; dibenzoate,  $C_{28}H_{20}O_4$ , m.p. 138°,  $[\alpha]_D -452^\circ$ ), yielding  $\alpha$ -anthrol on boiling with dil. acid. Hydrogenation of (I) yielded dihydroxytetrahydroanthracene (II), m.p. 149°,  $[\alpha]_D +99^\circ$  in dioxan (diacetate, m.p. 91°,  $[\alpha]_D^{20} -74^\circ$  in dioxan). Oxidation of (II) gave 3- $\beta$ -carboxyethyl-2-naphthoic acid (III), m.p. 210° (decomp.). On boiling with dil. acid, (II) affords 2-ketotetrahydroanthracene. Rabbits fed on the same diet excreted a *d*-form of (I), m.p. 184°,  $[\alpha]_D^{20} +16^\circ$  in dioxan (diacetate, m.p. 184°,  $[\alpha]_D +309^\circ$  in dioxan). Hydrogenation yielded a dihydroxytetrahydroanthracene, m.p. 162°,  $[\alpha]_D^{20} -1^\circ$  (diacetate, m.p. 84°,  $[\alpha]_D^{20} -3^\circ$ ), which on oxidation yielded (III). Rats probably excrete 1(or 2)-hydroxy-1:2-dihydroanthracene in addition to (I).

J. N. A.

**Comparison of the actions of certain dietary lipins in producing acetonaemia.** R. LECOQ and R. CAREL (Compt. rend., 1935, 201, 1154—1156).—Ingestion of castor oil in man, dog, rabbit, and rat is followed by a rise of the total ketones in the blood and especially of  $\beta$ -hydroxybutyric acid, similar to that following administration of butter-fat or olive oil.

W. O. K.

**Effect of ingested fat on the sterol metabolism of the white rat.** H. C. ECKSTEIN and C. R. TREADWELL (J. Biol. Chem., 1936, 112, 373—378).—Rats on diets supplemented with soya-bean or maize oils showed increased concns. of sterols in their livers which were not due to mobilisation from the tissues. The supplements appear to increase the difference between faecal and ingested sterols.

H. D.

**Fat metabolism in fishes. VIII. Changes in the fat of ripening salmon eggs.** J. A. LOVERN (Biochem. J., 1936, 30, 20—24).—At all stages of the ripening the degrees of unsaturation of the  $C_{20}$  and  $C_{22}$  acids are higher than in the depôt fat, and two possible explanations are discussed. During ripening there is a marked rise in the amount of  $C_{18}$  acids together with a fall in the mean unsaturation of this group.

J. N. A.

**Dicarboxylic acids as intermediates in the biological degradation of normal saturated fatty acids and their derivatives.** P. E. VERKADE and J. VAN DER LEE (Rec. trav. chim., 1935, 54, 893—898).—Mainly a priority claim against Flaschen-träger *et al.* (A., 1935, 1151) and a recapitulation of the authors' views on biological oxidation of fatty acids (cf. A., 1933, 417; 1935, 1273, etc.).

J. W. B.

**Fat metabolism. VII.  $\beta$ -Oxidation of normal saturated dicarboxylic acids administered *per os*.** P. E. VERKADE, J. VAN DER LEE, and A. J. S. VAN ALPHEN (Z. physiol. Chem., 1935, 237, 186—190; cf. A., 1934, 1393).—Suberic and adipic acid were detected in the urine of a dog to which Na sebacate had been administered; similarly azelaic and pimelic acids were found after administration of Na undecanedicarboxylate. The incidence of  $\beta$ -oxidation is thus established.

H. W.

**Absorption in phloridzinised animals. I. Absorption of fats.** G. SARZANA (Boll. Soc. ital. Biol. sperim., 1935, 10, 197—198).—Fat excretion in the faeces of pigeons given high doses of phloridzin increases, but the % of fat absorbed is not displaced considerably.

R. N. C.

**Spontaneous ketonuria and ketonuria from administration of stearic acid in normal subjects and hepatic patients.** L. CANNVÒ (Boll. Soc. ital. Biol. sperim., 1935, 10, 180—182).—Ketonuria is min. in normal subjects on a mixed diet, but is increased to non-pathological vals. by ingestion of Na stearate (I). It is increased in patients with hepatic parenchymatic trouble and after carbohydrate-rich food. (I) acts according to the type of hepatic lesion; ketonuria appears in local lesions where large parts of the parenchyma are functioning normally, and in more extensive lesions associated with cellular degeneration. The keto-acids are mostly eliminated as  $\beta$ -hydroxybutyric acid. (I) provokes in

most cases an increase in total org. acids in the urine, but there is no relation existing between ketonuria and aciduria.

R. N. C.

**Fat and calcium metabolism. III. Influence of butter and margarine on the faecal output of calcium in full-grown rats.** A. WESTERLUND (Lantbrukshögsk. Ann., 1935, 2, 51—70).—In rats on low or moderate Ca diets the faecal but not the urinary Ca excretion was much greater in those receiving margarine as sole source of fat than in those receiving butter.

NUTR. ABS. (m)

**Glycogen formation from lower fatty acids with an even number of carbon atoms. III. Fate of acetoacetic acid in the animal organism.** R. STÖHR (Z. physiol. Chem., 1935, 237, 165—170; cf. A., 1933, 1193; Snapper *et al.*, A., 1929, 94).—The respiration of surviving rat's liver and kidney is restricted and that of diaphragm is increased by addition of  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{H}$ . The glycogen content of the livers of fasting rats is not increased by feeding  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Na}$  and  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$  + glucose.

W. McC.

**Ketosis. VII. Quantitative studies on  $\beta$ -oxidation. Glycogen formation from various fatty acids.** H. J. DEUEL, jun., J. S. BUTTS, L. F. HALLMAN, and C. H. CUTLER (J. Biol. Chem., 1935, 112, 15—23).—Liver-glycogen (I) of fasting male rats rises approx. 100% following the ingestion of the Na salts of fatty acids with an odd no. of C. No such rise follows the ingestion of the Na salts of the even acids. Trivalerin causes an increase in (I) > that caused by tributyrin; Wesson oil causes no increase. Oleic acid does not cause an increased (I) formation, but nonoic acid does, indicating that fissure of the double linking is not a primary change in the metabolism of oleic acid.

F. A. A.

**Effect of administration of fat on blood-sugar.** H. SCHÖNFELD (Monatsschr. Kinderheilk., 1935, 61, 432—435).—Olive oil caused a fall in blood-sugar in fasted children and rabbits, but when fasted for 24—48 hr. after the administration, hyperglycaemia occurred.

NUTR. ABS. (m).

**Conversion of fat into sugar.** W. HAARMANN (Biochem. Z., 1935, 282, 406—418; cf. A., 1933, 94).—The production of lactic acid (I) by surviving organs (skeletal and heart muscle, liver, brain of rabbit, dog, pig) is increased (optimal with 0.005—0.01M solutions) by addition of  $\text{Pr}^a\text{CO}_2\text{Na}$  and Na  $\beta$ -hydroxybutyrate (II), the increases being > equiv. to the corresponding decrease in the degradation of carbohydrate. When glucose is added this degradation is increased by addition of  $\text{Pr}^a\text{CO}_2\text{Na}$  and to a smaller extent by that of (II) but the production of (I) from carbohydrate is usually decreased.

W. McC.

**Fat metabolism. IV. Acetoacetic acid breakdown in the kidney.** J. H. QUASTEL and A. H. M. WHEATLEY (Biochem. J., 1935, 29, 2773—2786).—The breakdown of  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{H}$  (I) by the kidney cortex *in vitro* under the conditions previously described (A., 1935, 1408) is investigated. The anaerobic breakdown of (I) is similar to the aerobic breakdown in the presence of  $\text{CN}'$  or glucose, and is

accelerated by glutathione but not by ascorbic acid. The aerobic breakdown of (I) is inhibited by salts of  $\text{AcOH}$ ,  $\text{EtCO}_2\text{H}$ ,  $\text{PrCO}_2\text{H}$ , and malonic acid (II). The inhibition by (II) may be neutralised by Na fumarate and lactate and by alanine. The aerobic inhibition by  $\text{BzOH}$  with guinea-pig kidney is much > that with rat kidney.  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$  and  $\text{H}_3\text{AsO}_3$  inhibit strongly under aerobic conditions. Mincing the kidney decreases the breakdown of (I). Production of  $\beta$ -hydroxybutyric acid accounts chiefly for the anaerobic decomp. of (I) and for about 1/3 to 1/4 of the aerobic decomp.

H. D.

**Relation of the spleen to formation of glycogen in the liver; rate of absorption of glucose and lactic acid.** M. KERLY and C. REID (J. Physiol., 1935, 84, 302—314).—Glycogen (I) formation in the liver in normal or splenectomised cats under chloralose takes place with equal readiness when glucose (II) or lactic acid (III) is injected into a vein or absorbed from the intestine. Unanaesthetised normal and splenectomised rats form (I) in the liver after administration of (II) or (III) by stomach tube. Anaemia after splenectomy reduces (I) formation. (I) formation after feeding with (III) is < that after (II) and less regular. Acetylcholine and choline chloride do not increase (I) formation. Cats absorb 1.1N-(II) and -(III) from the intestine at the same mol. rate, but rats absorb 50—60% (II) from the stomach 6—7 times as fast as 10—17% (III); the rate of (III) absorption is not increased by the use of more conc. solutions, and the unabsorbed fraction is mostly found in the stomach, suggesting that control by this organ is responsible for the different rates of absorption in cats and rats.

R. N. C.

**Cyclic changes in liver-glycogen of rats after removal of the adrenals.** G. ÅGREN (Biochem. Z., 1935, 281, 367—369).—The periodic changes in the liver-glycogen level normally observed in rats are not obtained after adrenalectomy.

P. W. C.

**Functional and anatomical state of the endocrine pancreas, and its insulin content, in dogs subjected to prolonged fasting.** E. AUBERTIN, A. LACOSTE, R. SARIC, and E. CASTAGNOU (Compt. rend. Soc. Biol., 1935, 120, 1107—1110).—The alimentary blood-sugar curve in dogs subjected to prolonged fasting resembles that of diabetic dogs, but a subsequent hypoglycaemia is observed. The insulin (I) of the pancreas is > in normal animals.

R. N. C.

**Comparison of the influence of fasting on the tolerance to glucose and galactose.** E. M. MACKAY, H. C. BERGMAN, and R. H. BARNES (Amer. J. Physiol., 1935, 112, 591—594).—The blood-sugar curve in the rabbit following administration of galactose (I) is not influenced by fasting, whereas that after glucose (II) is lower. The alimentary hyperglycaemia produced by (I) is not affected by previous administration of (II), nor is the blood-sugar curve of a second dose of (I) essentially different from that of the first. The data support the theory that metabolism of (I) and (II) is fundamentally different.

R. N. C.

**Rate of absorption of glucose from the intestinal tract of the rabbit.** E. M. MACKAY, H. C.

BERGMAN, and R. H. BARNES (Proc. Soc. Exp. Biol. Med., 1934, 32, 323—326).—The rate of absorption decreases with time after the glucose is administered, and is related to the amount of glucose available for absorption.  
R. N. C.

**Origin of the specific dynamic action of intravenous fructose at the three levels of assimilation in a normal dog.** M. WIERZUCHOWSKI (Compt. rend. Soc. Biol., 1935, 120, 1127—1130).—Fructose (I) assimilation, fructolysis, and fat formation are dependent on the levels of assimilation, whilst the sp. dynamic action and oxidation quotient of (I) are independent of these and hardly variable. The sp. dynamic action hence originates from none of the above factors.  
R. N. C.

**Utilisation of carbohydrate during aerobic activity in isolated frogs' muscle.** C. L. GEMMILL (Amer. J. Physiol., 1935, 112, 294—300).—The average utilisation of carbohydrate by muscles stimulated at regular short intervals for long periods in oxygenated Ringer's solution accounts for only 42% of the total energy exchange as calc. from the  $O_2$  consumption, so that other material besides carbohydrate is oxidised to supply the energy for aerobic contraction of muscle.  
R. N. C.

**Carbohydrate changes following recovery from muscular contraction.** J. SACKS and W. C. SACKS (Amer. J. Physiol., 1935, 112, 565—572).—The lactic acid (I) formed during anaerobic activity in the muscle diffuses into the blood during recovery, no glycogen (II) being formed. The "Meyerhof cycle" is of no significance in recovering mammalian muscle. Hexose phosphate formed during contraction is resynthesised directly to (II) during recovery, at a practically const. rate. Further evidence is shown that the sole function of phosphocreatine hydrolysis is the maintenance of const.  $p_H$  in the fibre. The data confirm the theory that the energy of muscular activity is derived primarily from oxidative reactions.  
R. N. C.

**Hypothalamic nuclei in the regulation of chloride and sugar metabolism.** F. H. LEWY and F. K. GASSMAN (Amer. J. Physiol., 1935, 112, 504—510).  
R. N. C.

**Hexose monophosphate changes in muscle in relation to rate of stimulation and work performed.** R. E. FISHER and G. T. CORI (Amer. J. Physiol., 1935, 112, 5—14).—The work output and lactic acid (I) formation by rapidly-stimulated, isolated frogs' gastrocnemii are the same as by slowly-stimulated muscle, but hexose monophosphate (II) formation is increased, indicating an increased breakdown of glycogen (III); a short tetanus causes an even greater increase. (I) and (II) formation in unloaded muscle is < in muscles attached to a tension spring. (II) formation is not directly related to the work performed. The increase per mg. of (I) formed is greatest in contractions without load, and decreases as the work output increases; it is concluded that a muscle exhibits max. working efficiency with reference to (III) expenditure if it is producing max. tension at a slow rate of stimulation. Short tetani against a spring permitting considerable con-

traction do not produce delayed (I) or (II) formation, but after-formation of (I) is observed.  
R. N. C.

**Aerobic and anaerobic production of lactic acid and degradation of carbohydrate in tissues.** W. HAARMANN and H. BRINK (Biochem. Z., 1935, 282, 419—433).—Production of lactic acid (I) and degradation of carbohydrate in organs (heart and skeletal muscle, brain of ox, dog, rabbit) are differently affected by  $O_2$ , being restricted in some cases and unaffected or increased in others. In some case the production of (I) after addition of glucose (II) and glycogen (III) is decreased in presence of  $O_2$ . Usually the degradation of carbohydrate in absence of  $O_2$  is more than equiv. to the amount of (I) produced. Oxidation of (II) and (III) in some organs is decreased by  $O_2$ , but is unaffected in others. Production by the organs of (I) from  $AcCO_2H$  and  $AcCHO$  is not prevented by  $O_2$  and that from fumaric and succinic acid (IV) is increased by  $O_2$  [no (I) is produced anaerobically from (IV)].  
W. McC.

**Aerobic and anaerobic disappearance of lactic acid in tissues.** W. HAARMANN and H. BRINK (Biochem. Z., 1935, 282, 434—440).—The amount of added lactate which disappears from pulped tissues in 3 hr. is the same whether or not  $O_2$  is present.  
W. McC.

**Vascular balance of lactic acid in the organs of the dog, after saturation of the organism with glucose.** M. WIERZUCHOWSKI and T. CHMIELEWSKI (Compt. rend. Soc. Biol., 1935, 120, 1131—1133).—Lactic acid is discharged into the blood-stream from the motor apparatus, head organs, and portal vein system, and is absorbed in small quantities by the liver.  
R. N. C.

**Resynthesis of phosphocreatine after muscular contraction.** J. SACKS and W. C. SACKS (Amer. J. Physiol., 1935, 112, 116—123).—Removal of lactic acid (I) and resynthesis of phosphocreatine (II) proceed *pari passu* in the early stages of recovery of the muscle of the cat and the rabbit after contraction. The amounts of (I) removed and (II) synthesised in a given time are equiv. (II) resynthesis from its hydrolysis products after contraction takes place at a rate much < that required by Lundsgaard's hypothesis. Reconversion of hexose phosphate-P into (II)-P is slow in the early stages of recovery.  
R. N. C.

**Liver-ketogenesis and its auto-regulation.** S. LEITES and A. I. ODINOV (Biochem. Z., 1935, 282, 345—361).—In rabbit's liver pulp kept at 37—38° for 24 hr. autoxidation produces  $CH_2Ac\cdot CO_2H$  (I) and  $\beta$ -hydroxybutyric acid (II). Ketogenesis is more pronounced in the liver pulp of fasting than in that of non-fasting rabbits. With non-fasting rabbits production of (I) is optimal at  $p_H$  5.6 and of (II) at 7.0, whilst with fasting rabbits the val. for (I) and (II) is 5.6. When the amount of preformed ketone in the pulp is low, ketogenesis is > when it is high.  $Pr^cCO_2H$  added to the pulp produces (II) if ketogenesis was previously slight. Addition of  $NaOAc$  and  $AcCO_2Na$  has no effect on ketogenesis. These results indicate that the intermediate products of fat metabolism directly control ketogenesis in the liver to an extent dependent on that of previous

ketogenesis. The auto-regulation also depends on the glycogen content. W. McC.

**$\alpha$ -Glycerophosphoric acid and brain metabolism.** R. E. JOHNSON (Biochem. J., 1936, 30, 33—42).—In the presence of  $\text{Na}_4\text{P}_2\text{O}_7$  (I) the extra  $\text{O}_2$  uptake by pigeon's brain tissue *in vitro* due to the addition of  $\alpha$ -glycerophosphate (II) is additive to that due to lactate (III). (I) increases the rate of disappearance of (II); (III) has little effect. There is no interaction between  $\text{AcCO}_2\text{H}$  and (II) with or without added (I), so it is concluded that the Embden-Meyerhof scheme does not apply to pigeon's brain tissue. The 2 : 4-dinitrophenylhydrazones of  $\text{AcCHO}$  and of a compound containing probably 6 C were isolated from the reaction products of brain with (II). H. D.

**Rôle of glutathione in anaerobic tissue glycolysis.** A. GEIGER (Biochem. J., 1935, 29, 811—823).—Aq. KCl extracts and suspensions of muscle, brain, liver, and heart of rats, dialysed free from glutathione (I), produced no lactic acid (II) from glucose (III) or  $\text{AcCHO}$ , but did so if glycogen (IV) was the substrate. Addition of reduced (I) caused (II) formation from (III) and  $\text{AcCHO}$ , but slightly inhibited that from (IV). Oxidised (I) inhibited (II) formation from (III),  $\text{AcCHO}$ , and (IV). Inhibition of glycolysis by oxidising agents is probably due to the formation of oxidised (I). Borate inhibits glycolysis by brain, the effect being counteracted by  $\text{CaCl}_2$ . Probably inorg. P is not essential for glycolysis. H. D.

**Intermediate metabolism of internal secretory glands. IV. Proteolysis and ammonia formation.** S. EPSTEIN and E. MIMA (Biochem. Z., 1935, 281, 339—344).—The proteolytic activity and  $\text{NH}_3$  formation in the thyroid, thymus, adrenal, and pancreatic glands were investigated. Proteolysis was very feeble (except with the pancreas), but was more marked at acid reactions. P. W. C.

**Nitrogen metabolism of pre-school children.** L. C. KUNG and W. Y. FANG (Chinese J. Physiol., 1935, 9, 375—381).—In children on a controlled diet supplemented with soya-bean milk or cow's milk, the N intake and retention were 0.47—0.53 and 0.046—0.140 g. per kg., respectively; with a freely chosen diet the vals. were 0.39—0.56 and 0.030—0.054. H. G. R.

**Chemical changes in metabolism in severe malnutrition in infants. V. Nitrogen metabolism.** L. GAROT, R. VIVARIO, and (Mlle.) COMHAIRE (Rev. franç. Pédiat., 1935, 11, 1—36).—Absorption of protein in malnutrition is little altered, the recovery of N from the faeces being < 20% of the intake. N retention is often increased in spite of stationary body-wt. Excretion in the early stages is normal, but in more severe cases the partition of urinary N is altered. Urea-N falls below 60% of the total,  $\text{NH}_3$ -N is almost absent, and  $\text{NH}_2$ -acid and residual N are greatly increased. Possibly intermediary metabolism is deranged. NUTR. ABS. (m)

**Phosphorus metabolism of invertebrate nerve.** G. L. ENGEL and R. W. GERARD (J. Biol. Chem., 1936, 112, 379—392).—The P of the nerves of

*Homarus americanus* was determined as inorg., arginine (I), adenylypyrophosphate (II), and stable (resistant to 7 min. acid hydrolysis) fractions. The changes in these fractions during recovery in  $\text{O}_2$  after dissection are interpreted as being due to the reaction :  $(\text{II}) + 2 (\text{I}) \rightarrow 2 (\text{I}) \text{ phosphate} + \text{adenylic acid}$ . If the time of dissection was long the synthesis of (I) phosphate was > the apparent breakdown of (II), due probably to the re-synthesis of (II) at a later stage. During anoxia extensive hydrolysis of (II) and (I) phosphate occurs; on aerobic recovery from anoxia all the (I) phosphate is re-formed in 5 hr. and 2/3 of the (II) in 1 hr. H. D.

**Minimum endogenous sulphur metabolism : magnitude, origin, character.** R. RAZAFIMAHERY (Ann. Physiol. Physicochim. biol., 1935, 11, 261—300).—Administration to pigs, rats, rabbits, and dogs of a carbohydrate diet sufficient for energy requirements but deficient in N and S led to a continual loss of N and S from the body. The N : S ratio of the negative balance was always different from that found in the tissues, being higher in the dog and rabbit and lower in the rat and pig. When the total energy expenditure was lowered the loss of both N and S per unit of body-wt. was also lowered. The partition of S between faeces and urine differed from that of N, the gut excreting a higher proportion of S than N. In the dog the faecal S was 66% of the total output, in the rat 50, in the rabbit 33, and in the pig 20%. 30—50% of urinary S was neutral S. In all species observed about 15% of the total acid S consisted of conjugated S; it persisted in the urine even with a protein-free diet. NUTR. ABS. (m)

**Sulphur metabolism. I. Absorption and excretion of flowers of sulphur.** J. H. KELLERMANN (Onderstepoort J. Vet. Sci., 1935, 4, 199—228).—The rates of absorption and excretion of S flowers, when fed to rats or sheep, were relatively low. When the S was removed from the ration there was a very marked lag before the urinary inorg.  $\text{SO}_4$  returned to its normal level, and also a long retention of S in the digestive tract. When the basal ration was relatively high in easily available S the absorption of the S flowers was low and vice versa, and thus the level of the food-S may control the toxic level of S flowers when added to the ration. NUTR. ABS. (m)

**Continuous nitrogen and mineral balances during pregnancy, puerperium, and lactation.** H. A. HUNSCHER, F. COPE, H. R. STERNBERGER, B. N. ERICKSON, and I. G. MACY (Proc. Amer. Inst. Nutrition, J. Nutrition, 1935, 9, No. 6, Suppl., 13—14).—During the latter half of pregnancy in a healthy woman the mean daily intakes were : Ca 3.1, Mg 0.6, Na 5.0, K 6.6, N 19.0, P 2.7, Cl 7.7, S 1.5 g., and the corresponding daily retentions : 0.37, 0.11, 0.56, 1.40, 3.06, 0.26, 0.60, and 0.34 g. During the first 53 days of lactation the daily balances were often negative; the averages were : Ca -0.48, Mg -0.03, Na +0.47, K +0.87, N -0.56, P -0.37, Cl +0.30, S -0.22 g. NUTR. ABS. (m)

**Calcium, phosphorus, and nitrogen retention of rats on soya bean-egg powder and whole milk powder diets.** E. REID (Chinese J. Physiol., 1935,

9, 307—313).—Soya bean-egg powder promotes Ca and P retention equal to, and N retention and digestibility  $>$ , that of whole milk powder. H. G. R.

**Composition and action on calcium metabolism of Ah-Chiao (donkey-skin) glue and commercial gelatin.** T. G. NI (Chinese J. Physiol., 1935, 9, 329—338).—Donkey-skin glue contains N 16.49, ash 0.92, Ca 0.099, lysine 6.2—7.0, arginine 7, lysine 0.41—2.19, and cystine 0.15%. Donkey-skin glue, pure gelatin, and glycine all increase the absorption and retention of Ca. H. G. R.

**Serum-calcium response to ingested calcium.** S. FREEMAN, E. R. KANT, and A. C. IVY (J. Biol. Chem., 1935, 112, 1—7).—The serum-Ca of fasting adults is raised 5—6% 2 hr. after ingestion of 2.3 g. of  $\text{CaCl}_2$  or 10 g. of Ca gluconate (I). Daily ingestion of  $\text{CaCl}_2$  for one month before the experiment does not affect this response. In dogs the serum-Ca response increases with Ca dosage, and  $\text{CaCl}_2$  produces a greater max. response than (I), but the increase produced by (I) persists longer. F. A. A.

**Magnesium deficiency in animals. VII. Effects of magnesium deprivation, with a superimposed calcium deficiency, on the animal body, as revealed by symptomatology and blood changes.** H. G. DAY, H. D. KRUSE, and E. V. MCCOLLUM (J. Biol. Chem., 1936, 112, 337—359; cf. A., 1934, 1253).—Dogs on a diet deficient in Mg and Ca show decreases in serum-Ca, -Mg, -alkali reserve, - $p_{\text{H}}$ , and -inorg. P, and erythrocyte vol. and increases in blood-Cl, -fibrinogen, and -non-protein-N, and no changes in serum-Na, -K, -lipins, -bile pigments, -albumin, and -globulin. H. D.

**Metabolism of inorganic substances in the liver of calves during foetal development. I. Iron, phosphorus, and calcium.** Z. GRUZEWSKA and M. G. ROUSSEL (Ann. Physiol. Physicochim. biol., 1935, 11, 176—198).—There appears to be a local reserve of Fe in the foetal liver; the content is at a min. at 6—7 months, rising suddenly at 8½—9 months. The P content (chiefly org.) at about the 4th month is approx. 0.9%; it then decreases throughout gestation, at first rapidly, then more slowly. The Ca content showed only small variations throughout development. NUTR. ABS. (m)

**Disappearance of digestive inhibition with the repetition of exercise.** F. A. HELLEBRANDT, E. BROGDON, and S. L. HOOPES (Amer. J. Physiol., 1935, 112, 442—450).—The inhibition of HCl secretion disappears with the repetition of all but extreme grades of work. It disappears also in extremely severe work when the response has been conditioned. R. N. C.

**Some immediate physiological effects of reduced cooling powers on human subjects.** D. H. K. LEE and A. G. MULDER (J. Physiol., 1935, 84, 279—295).—Exposure in the post-absorptive state to high temp. in dry or humid atm. causes similar responses. Respiratory changes become marked after 3 hr. Alveolar  $\text{CO}_2$  tension falls only after the respiratory vol. has increased. Urinary acid excretion is lowered from the 3rd to the 6th hr.  $\text{CO}_2$  in cutaneous venous blood from the forearm

falls before alveolar  $\text{CO}_2$  tension, probably due to increased  $\text{CO}_2$  excretion through the skin; the fall may be increased when the tension falls. The evidence for a true arterial alkalæmia is not conclusive. Blood-lactate is not increased. After ingestion of food the response in dry atm. is  $>$  than in humid atm. R. N. C.

**Nervous system and remote action of ultra-violet rays.** G. VIALE and E. RONCALLO (Boll. Soc. ital. Biol. sperim., 1935, 10, 311—314).—Irradiation of the normal rabbit's foot depresses blood-sugar, but scarcely affects it in the denervated foot. R. N. C.

**Diuresis associated with direct stimulation of the pituitary.** W. R. INGRAM and R. W. BARRIS (Endocrinol., 1935, 19, 432—440). R. N. C.

**Comparative study of sodium chloride and blood pressure changes induced by adrenal insufficiency, trauma, and intraperitoneal administration of glucose.** W. M. PARKINS, A. R. TAYLOR, and W. W. SWINGLE (Amer. J. Physiol., 1935, 112, 581—590; cf. A., 1935, 1422). R. N. C.

**Comparative values of butter and margarine in medical nutrition.** S. BADILKES, E. EINHORN, V. KUDASCHEVITSCH, and V. SIKOV (Arch. Verdauungskrankh., 1934, 56, 293—306; Chem. Zentr., 1935, 1, 2694). R. N. C.

**Physiological action of silage on the digestive process of farm animals.** A. KRATNOV (Probl. Tierzucht, 1933, 5, 18—25; Bied. Zentr., 1935, A, 5, 615).—Silage stimulates the gastric and salivary glands of cows, sheep, and pigs and induces changes in the composition of digestive juices, whereby digestion is improved. A. G. P.

**Influence of ingestion of raw pancreas on the blood-lipins of completely depancreatized dogs maintained with insulin.** I. L. CHAIKOFF and A. KAPLAN (J. Biol. Chem., 1935, 112, 155—165).—The blood-lipin level is lowered soon after pancreatectomy, but addition of raw pancreas to the diet increases it to a val.  $>$  the normal, which is maintained as long as the tissue is supplied. Ingestion of raw pancreas after a low lipin level has been established causes a rapid and pronounced rise in all lipin constituents and fatty acids, particularly the cholesteryl esters. J. N. A.

**State of bismuth in body-fluids and tissues.** P. J. HANZLIK and A. P. RICHARDSON (J. Pharm. Exp. Ther., 1935, 55, 447—463).—Electromigration experiments show that the Bi of  $\text{Na}_2\text{BiO}_3$ ,  $\text{Na}_2\text{BiI}_5$ , and Na Bi tartrate and thioglycollate (I) exists in the electronegative state in aq., glycol, or sucrose solutions, in the presence of salt and of acidity or alkalinity according to the Bi compound, in urine, blood, and liver-tissue *in vitro*, and in the urine, plasma, and liver of rabbits after intramuscular injection of toxic and fatal doses. The  $\text{BiI}_5$  ion exists as such in both solutions and body-fluids. Bi of  $\text{BiOCl}$  and Bi hydroxysalicylate in aq. suspension migrates electropositively in traces only, but in the presence of salt and the above body-fluids and tissues *in vitro*, and after intramuscular injection, the Bi is strongly electronegative. Bi always exists in the

electronegative state in the body, the originally electro-positive ions being transformed slowly into electro-negative complexes by the action of salts. Blood-Bi is mostly in plasma solution, only traces occurring in the corpuscles; the highest concn. of plasma-Bi is obtained after administration of (I). R. N. C.

**Incidents and toxic accidents of calcium intravenotherapy.** L. TOCCO (Boll. Soc. ital. Biol. sperim., 1935, 10, 348—350).—The disturbances produced during Ca therapy, or immediately after, are the result of rapid reaction or saturation of the blood with Ca, and have no connexion with the toxic effects sometimes encountered, which are probably due to micro-crystals present in the Ca solution, or produced by contact with the blood. R. N. C.

**Effect of potassium and calcium on the contractions of mammalian skeletal muscle.** A. M. BAETJER (Amer. J. Physiol., 1935, 112, 147—151). R. N. C.

**Effect of potassium and calcium ions on the blood-sugar.** K. KIYOHARA, M. MORITA, and S. MUTA (Compt. rend. Soc. Biol., 1935, 120, 1011—1014).—Perfusion of the isolated pancreas of the dog with blood containing KCl or CaCl<sub>2</sub> does not affect blood-sugar (I). Both increase (I) in rabbits when injected intravenously; the increase is not affected by atropine, and is not reduced after double adrenalectomy. R. N. C.

**Biochemistry of copper. XI. Pigmentation of skin and hair.** U. SARATA. XII. Beneficial effect on blood-transfusion. M. ITIZYO (Japan. J. Med. Sci., 1935, II, 3, 79—84, 99—113).—XI. The Cu content of non-pigmented skin of cats and dogs (approx. 0.0004% of the dry wt.) is < that of pigmented skin. This fact, together with the increase in oxidation of *l*-3 : 4-dihydroxyphenylalanine by skin extracts due to certain concns. of Cu (A., 1931, 1186), indicate that Cu is concerned with melanin formation. XII. Blood-regeneration due to blood-transfusion in hæmorrhagic rabbits is accelerated by addition of Cu (0.6—2.0 mg. per kg. body-wt.), but not of Mn, Fe, Co, or Ni, to the transfused blood. F. O. H.

**Effect of fluorine on the phosphatase content of plasma, bones, and teeth of albino rats.** M. C. SMITH and E. M. LANTZ (J. Biol. Chem., 1935, 112, 303—311; cf. Phillips, A., 1932, 1278).—Feeding of harmful doses of NaF and injection of doses sufficient to cause acute poisoning have no significant effect on the phosphatase content of their plasma, bones, and teeth. W. McC.

**Effect of ammonia on acid-base equilibrium.** F. VENULET, F. GOEBEL, and R. TISLOWITZ (Compt. rend. Soc. Biol., 1935, 120, 1139—1142).—NH<sub>3</sub> added to milk or distilled or tap-H<sub>2</sub>O ingested by dogs abolishes alkalosis and displaces the acid-base equilibrium of the blood towards the acid side. The alkalosis produced by ingestion of NaHCO<sub>3</sub> or alkaline salt mixture is also decreased by addition of NH<sub>3</sub>, and intravenous injection of NH<sub>3</sub> decreases the alkaline reserve. R. N. C.

**Apparent intoxication in poultry, due to nitrogenous bases.** S. F. COOK and K. G. SCOTT (Science, 1935, 82, 465—467).—Intoxication induced

by N bases apparently occurred in poultry fed on a special diet which included functionally low-S fish-meal. Replacement of the latter by meat scrap, casein, skim-milk, or high-S fish-meal relieved the hæmorrhagic symptoms. Addition of NMe<sub>3</sub>, NHMe<sub>2</sub>, NH<sub>2</sub>Me, NHEt<sub>2</sub>, etc., ergot, and nicotine to a non-hæmorrhagic diet produced symptoms similar to those resulting from the special diet. Methylamines were present in the low-S fish-meal in amounts sufficient to produce the intoxication. The S compounds in the high-S fish-meal were sufficient to detoxicate the methylamines. Addition of dried blood, S, cystine, or cysteine to hæmorrhagic diets alleviated the symptoms. L. S. T.

**Effect of intravenous injections of amino-acids on the motility of the stomach in normal and fasting dogs.** H. BOWMAN, J. F. REGAN, and E. U. STILL (Amer. J. Physiol., 1935, 112, 438—441). R. N. C.

**Sensitivity to acetylcholine and velocity of hydrolysis by blood of acetylcholine in man.** G. INGVARSSON (Biochem. Z., 1935, 281, 370—376).—No difference could be detected in the rate of hydrolysis of acetylcholine (I) by bloods of sensitive and resistant individuals or in blood taken before and after injection of (I). Such differences in sensitivity arise in the nervous system rather than in any varying degree of inactivation of (I) by blood. P. W. C.

**Pharmacological properties of the acetylene linking.**—See this vol., 188.

**Action of acetylcholine on gaseous metabolism.** C. ZUMMO, D. ELIA, and A. PAGANO (Boll. Soc. ital. Biol. sperim., 1935, 10, 195—197).—Acetylcholine (I) does not affect gaseous metabolism in rats or pigeons; hence the increase caused by pilocarpine is not due to liberation of (I). R. N. C.

**Co-operative action of sympathetic nerve impulses, adrenaline, and sympathin on the nictitating membrane of the cat.** A. C. LIU (Amer. J. Physiol., 1935, 112, 690—694). R. N. C.

**Tyramine. II. Moderating effect on human basal metabolism : therapeutic assays in hyperthyroidism. III. Effects on the different systems of the human organism.** P. JACCHIA and F. CAPOCASALE (Boll. Soc. ital. Biol. sperim., 1935, 10, 201—204, 205—208).—II. Tyramine (I) depresses basal metabolism in hyperthyroid patients when given orally or intramuscularly; metabolism remains low when (I) is administered over long periods.

III. (I) given as above reduces gastric acidity, and in some cases increases blood-sugar. R. N. C.

**Derivatives of aminomethyldihydro-oxazine which exhibit adrenaline-like action.**—See this vol., 214.

**2 : 4-Dinitrophenol and respiration of tissues *in vitro*.** G. DOMINI (Boll. Soc. ital. Biol. sperim., 1935, 10, 362—364).—Sections of surviving liver and spleen show no change in their metabolism *in vitro* if taken from animals treated with fatal doses of 2 : 4-dinitrophenol (I). Metabolism is unaffected by addition of small quantities of (I) to the respiratory medium, but is depressed by higher concns. If the (I)

is added to the medium during the development of the manometric registration, small quantities are still ineffective, moderate quantities cause a rise of metabolism followed by a fall, whilst large quantities inhibit it, and  $O_2$  consumption falls. R. N. C.

**Influence of sodium taurocholate, hepatic bile, and gall-bladder bile on the absorption of oleic acid from the small intestine.** C. RIEGEL, K. O. ELSOM, and I. S. RAVDIN (Amer. J. Physiol., 1935, 112, 669—672).—Oleic acid introduced alone into an intestinal loop in the dog is practically unabsorbed, but the absorption is increased by the presence in the loop of Na taurocholate, and to a small degree by hepatic or gall-bladder bile. R. N. C.

**Therapy of poisoning by the active principle (potassium atractylate) of *Carlina gummifera*.** A. MARRAS (Boll. Soc. ital. Biol. sperim., 1935, 10, 357—359).—Correction by glucose or adrenaline of the hypoglycaemia induced in rabbits poisoned by K atractylate prevents or delays death, which is, however, due to other causes besides hypoglycaemia. R. N. C.

**Variations of the absorption spectrum of the blood of leucæmic fowls after intravenous injection of a lecithin-hydrogen peroxide complex.** J. MAGAT, D. ABRAGAM, and M. MAGAT (Compt. rend. Soc. Biol., 1935, 120, 1091—1093).—The absorption curve of the leucæmic fowl after injection of lecithin- $H_2O_2$  complex lies above that of the normal fowl between 450 and 600  $m\mu$ , with a feeble max. at 510  $m\mu$ , whilst the band at 600—640  $m\mu$  is less intense. The leucæmic blood probably contains a principle that inhibits the formation of peroxyhaemoglobin. R. N. C.

**Toxic action of pyrethrins on marine animals.** M. O. GAUDIN (Compt. rend. Acad. Agric. France, 1935, 21, 277—281).—Effects of administration of pyrethrins by injection or through respiratory organs are examined. A. G. P.

**Action of tetralin, 5-tetralol, and 5-tetralone on body temperature and metabolism.** H. R. KANITZ, A. LOHMEYER, and J. SCHOLZ (Arch. Hyg., 1935, 113, 234—244; Chem. Zentr., 1935, i, 2841).—Administration of tetralin caused a moderate fall in body temp., followed by a more permanent rise;  $O_2$  consumption was not changed, while the urinary quotient was increased. H. N. R.

**Action of chlorophyll on the mobilising effects of adrenaline with respect to sugar.** K. E. LARSSON (Compt. rend. Soc. Biol., 1935, 120, 1124—1126).—Injection of large doses of chlorophyll in rabbits suppresses to some extent the hyperglycaemic action of adrenaline. R. N. C.

**Hæmatopoietic action of Ah-Chiao (donkey-skin glue).** T. G. NI (Chinese J. Physiol., 1935, 9, 383—393).—The hæmatopoietic action was of a similar order to that of gelatin and was independent of Fe and Cu. H. G. R.

**Solvents of the active principles of chamæpitium.** A. BORSANI (Boll. Soc. ital. Biol. sperim., 1935, 10, 240—242).— $COMe_2$ , EtOH, Et<sub>2</sub>O, and  $CHCl_3$  extracts of *Ajuga chamæpitys* show a transitory

depressor effect, whilst the corresponding residues show a depressor effect without an initial rise, indicating the presence of two active principles. The depressor principle is sol. in  $H_2O$  and is pptd. by EtOH.

R. N. C.

**Synergism of narcotic poisons.** R. J. LESZCZYŃSKI (Poznań. Towarz. Przyj. Nauk. Prace Kom. Lek., 1934, 4, 1—16; Chem. Zentr., 1935, i, 2559).—Morphine, scopolamine, and the *Cannabis indica* alkaloids act synergistically with one another in the production of narcosis in dogs. R. N. C.

**Theories of narcosis.** (A) K. H. MEYER and H. HEMMI. (B) I. TRAUBE. (C) K. H. MEYER (Biochem. Z., 1935, 282, 444, 445—446, 447).—Polemical.

W. McC.

**Absorption of bilirubin, rose Bengal, and tetrabromophenolsulphonaphthalein by the liver.** M. ROYER (Compt. rend. Soc. Biol., 1935, 120, 809—812).—Absorption of bilirubin by the liver of the normal dog is > that of rose Bengal or tetrabromophenolsulphonaphthalein; all three diminution coeffs. are < that of urobilin, and are reduced by intoxication with  $CHCl_3$ . R. N. C.

**Toxic action of local anæsthetics on the amphibian heart.** L. DONATELLI (Arch. Farm. sperim., 1935, 60, 482—496).—Comparative data are given for the lethal and toxic action of novocaine, stovaine, cocaine, pantocaine, and percaïne on the heart of frogs and toads. F. O. H.

**Influence of diuretics on the chlorine of rat organs.** K. A. WINTER (Med. Klinik, 1934, 30, 1727—1728; Chem. Zentr., 1935, i, 2842—2843).—Salyrgan causes no diminution in tissue-Cl, but kidney-Cl falls by 75%. Euphyllin causes a considerable general fall in Cl. H. N. R.

**Action of curare and atropine on the secretions of the pancreas.** R. GAYET and M. GUILLAUME (Ann. Physiol. Physicochim. biol., 1934, 10, 532—533; Chem. Zentr., 1935, i, 2841).—The action of the two drugs is similar. H. N. R.

**Percaïne.** F. FALCO (Rev. Fac. Quím. Ind. Agric., 1934, 3, 185—191).—Percaïne (I) is extracted from viscera with EtOH. Photomicrographs are reproduced of the compounds of (I) with picric acid, Mayer's reagent,  $K_2Cr_2O_7$ ,  $HgCl_2$ ,  $AuCl_3$ , and  $K_4Fe(CN)_6$ . F. R. G.

**Fate of procaine in the dog.** J. G. DUNLOP (J. Pharm. Exp. Ther., 1935, 55, 464—481).—Procaine (I) in the normal dog disappears rapidly from the circulation, and is excreted slowly in the urine as non-toxic end-products; in the absence of the kidneys these are found in the blood during survival. Blood alone does not affect (I). The liver is not essential for detoxication of (I), but its action is more rapid and efficient than that of other tissues. R. N. C.

**Phenanthrene derivatives. VI. Amino-alcohols of the ethanalamine and propanolamine type.** N. B. EDDY (J. Pharm. Exp. Ther., 1935, 55, 419—429).—The pharmacological properties of 3- $\beta$ -diethylamino- $\alpha$ -hydroxyethylphenanthrene are described. Similar derivatives with the  $NH_2$  unsubstituted, or with the  $NEt_2$  attached to an Ac or a



hydroxy-*n*-propyl side-chain are less effective analgesics, and less like morphine in other respects. Phenanthrene and  $\text{NEt}_2 \cdot [\text{CH}_2]_2 \cdot \text{OH}$  are not analgesic.

R. N. C.

**Removal of cardiac glucosides from the frog's ventricle.** G. KINGISEPP (*J. Pharm. Exp. Ther.*, 1935, 55, 377—389).—Washing-out of cardiac glucosides from the heart produces recovery; the combination between the drugs and heart muscle resembles an absorption, but hysteresis must be assumed to occur.

R. N. C.

**Mechanism of the action of fish serum on warm-blooded animals.** A. VON BEZNAK and L. VON TÓTH (*Arch. exp. Path. Pharm.*, 1935, 180, 69—74).—Intravenous or subcutaneous injection of shad serum causes death, the min. lethal dose for rabbits being  $1.2 \pm 0.2$  c.c. per kg. There is a decrease in respiration, temp., and blood pressure. The lytic and lethal factors are retained by an ultrafilter. The toxic action is reduced by atophan.

J. N. A.

**Effect of poisons of different pharmacological types on the chromatic function of frog's skin.** R. J. LESZCZYŃSKI (*Poznań. Powarz. Przyj. Prace Kom. Lek.*, 1934, 4, 17—44; *Chem. Zentr.*, 1935, i, 2559).—Adrenaline lightens, and pituitrin (I) darkens, the colour of the skin by peripheral action. Ergotamine lightens the colour by sympathetic action; (I) abolishes, but does not invert, this action. Pilocarpine, eserine, acetylcholine,  $\text{CHCl}_3$ ,  $\text{Et}_2\text{O}$ ,  $\text{BaCl}_2$ , strophanthin, papaverine, Ca, K, and conc.  $\text{NaCl}$  solution produce a temporary lightening followed by darkening;  $\text{NaNO}_2$  lightens, and  $\text{C}_5\text{H}_{11}\text{NO}_2$  darkens, the colour, whilst atropine is without effect. The characteristic action is shown only by poisons that affect the sympathetic system.

R. N. C.

**Detoxification of strychnine by sodium pentobarbital.** E. E. SWANSON (*J. Amer. Pharm. Assoc.*, 1935, 24, 959—961).—Na pentobarbital is an antidote for strychnine poisoning in rabbits; the effect is < that of Na amytal.

F. O. H.

**Potassium polythionates as antidotes for hydrocyanic acid poisoning.** A. CHISTONI and B. FORESTI (*Arch. int. Pharm. Théor.*, 1935, 49, 439—444; *Chem. Zentr.*, 1935, i, 2843).— $\text{K}_2\text{S}_4\text{O}_6$  and  $\text{K}_2\text{S}_5\text{O}_6$  are not suitable antidotes for HCN poisoning, since the K<sup>+</sup> assists the paralytic action of the poison on the nerve centres.

H. N. R.

**Enzyme chemistry.** R. WILLSTÄTER (*Scientia*, 1935, 57, 210—220; *Chem. Zentr.*, 1935, i, 2548).—The nature, constitution, and specificity of enzymes are discussed.

A. G. P.

**Progress in enzyme chemistry.** ANON. (*Nature*, 1936, 137, 53—55).—An expansion of the paper read by E. Waldschmidt-Leitz before the British Association.

L. S. T.

**Enzyme activity and anion effects.** W. KOPACZEWSKI (*Bull. Sci. Pharm.*, 1934, 41, 391—402; *Chem. Zentr.*, 1935, i, 2383).—Activity is influenced by  $[\text{H}^+]$  and by the associated ions, but much more by the age of the prep., the concn. and physical condition of the substrate, and the purity of the enzyme.

A. G. P.

**Thermodynamics of enzymic equilibria. Aspartase system.** K. P. JACOBSON and J. TAPADINHAS (*Biochem. Z.*, 1935, 282, 374—382; cf. *A.*, 1935, 121, 1530; Quastel *et al.*, *A.*, 1926, 868).—The position of equilibrium attained in the aspartase (I) system is dependent on temp. and since the heat of amination (calc. from the temp. coeff. of *K*) accords with the val. for the difference in the heats of formation of the components of the system, it follows that (I) is a true catalyst.

W. McC.

**High-pressure ultrafiltration with Cellophane as a means of enzyme purification and determination of particle size.** G. GORBACH and K. NITSCHÉ (*Biochem. Z.*, 1935, 281, 306—309).—The prep. of the membrane and its application to the concn. of invertase in yeast autolysates are described.

P. W. C.

**Stereochemical specificity and equilibrium in the fumarase system. Biochemical production of *d*-malic acid.** K. P. JACOBSON and M. SOARES (*Biochem. Z.*, 1935, 282, 383—386).—In solutions containing aspartase and relatively high  $[\text{NH}_4\text{Cl}]$ , fumarase produces *d*-malic acid in 100% yield from *dl*-malic acid and hence exhibits abs. configurative specificity.

W. McC.

**Uricase and its action. VIII. Extraction and precipitation of ox-kidney uricase.** R. TRUSKOWSKI and S. GUBERMANÓWNA (*Biochem. J.*, 1935, 29, 2787—2797; cf. *A.*, 1934, 451).—Uricase (I) powder is prepared by thorough washing of minced kidney with  $\text{H}_2\text{O}$ ,  $\text{EtOH}$ , and  $\text{Et}_2\text{O}$  and drying at 30°. The apparent activity of the preps. depends on the availability of  $\text{O}_2$ . Active solutions are obtained by extracting the powder with aq.  $\text{Na}_2\text{CO}_3$  at  $p_{\text{H}} > 9.8$  for 48 hr. at room temp.  $\text{AcOH}$  and  $(\text{NH}_4)_2\text{SO}_4$  ppt. (I) from the extracts. (I) has an optimum  $p_{\text{H}}$  of 8.8 and is completely inactivated at  $p_{\text{H}} < 5.8$  or by tryptic digestion. The quantity of P removable by 2% aq.  $\text{NaOH}$  in the powder approx.  $\propto$  the activity.

H. D.

**Uricase, amino-acid oxidase, and xanthine oxidase.** D. KELLIN and E. F. HARTREE (*Proc. Roy. Soc.*, 1935, B, 119, 114—140).—Uricase (I) and  $\text{NH}_2$ -acid oxidase (II), like xanthine oxidase (III), function as true dehydrogenases. (I) is prepared by drying minced pig's liver with  $\text{COMe}_2$ . This prep. shows optimum activity at  $p_{\text{H}}$  9.25. Its inhibition by  $\text{CN}'$  is reversible.  $\text{CO}$ ,  $\text{Na}_2\text{S}$ ,  $\text{NaF}$ , and urethane have very small or no inhibitory effects.  $\text{P}_2\text{O}_7^{4-}$  has a slight activating effect. Small amounts of Cu and Fe inhibit (I), but this inhibition is abolished when the metals are added in phosphate buffer containing  $\text{P}_2\text{O}_7^{4-}$ . (I) is sp. for uric acid (IV); alkyl derivatives of (IV) are not oxidised, although they may act as competitive inhibitors.  $\text{H}_2\text{O}_2$  is formed when  $\text{O}_2$  is the H acceptor for the oxidation. On the addition of *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$  (V) and peroxidase (VI) a coupled oxidation of (V) by  $\text{H}_2\text{O}_2$  occurs, doubling the  $\text{O}_2$  uptake due to the oxidation of (IV) alone. (V) alone increases the  $\text{O}_2$  uptake owing to the (VI) activity of hæmatin compounds in (I) preps. It is suggested that the primary stage of the reaction is the oxidation of (IV) to uric acid 4:5-glycol; this then rearranges to form hydroxyacetylenediureinecarboxylic acid,

which gives allantoin on decarboxylation. The Michaelis const. for (II) with *dl*-alanine as substrate is about  $5 \times 10^{-3} M$ . (II) is irreversibly inhibited by  $H_2S$  in the presence of  $O_2$ . An inhibition by ethylurethane may be only a salt effect as other narcotics have no effect. (II) is inhibited by various tissue extracts such as liver-(I) and heart-muscle oxidase. Incubation with (III) almost completely inhibits (II), but this effect is considerably reduced if (III) is first boiled. Destruction of (III) by incubation with  $CN'$  does not affect this inhibition. A similar inhibition is shown by charcoal. The rate of oxidation of *l*-alanine by (II) is unaffected by the addition of *d*-alanine. The formation of  $H_2O_2$  on aerobic dehydrogenation is best shown by the coupled oxidation of EtOH (cf. following abstracts). (II) oxidises *N*-monomethyl- but not *N*-dimethyl- or  $\alpha$ -methyl-alanine. In addition to oxidative deamination, kidney slices promote the oxidation of *d*- and *l*-dihydroxyphenylalanine due to their polyphenol-oxidase content.

E. A. H. R.

**Coupled oxidation of alcohol.** D. KEILIN and E. F. HARTREE (Proc. Roy. Soc., 1935, B, 119, 141—159).—Addition of EtOH to mixtures of uricase (I) and uric acid (II), or of  $NH_2$ -acid oxidase (III) and  $NH_2$ -acids, doubles the  $O_2$  uptake; xanthine oxidase (IV) and hypoxanthine or MeCHO do not show the same effect unless catalase (V) is also present. EtOH undergoes a coupled oxidation to MeCHO by the  $H_2O_2$  formed in the dehydrogenation. This coupled oxidation requires the formation of nascent  $H_2O_2$  and a factor found in (I), (III), and (V) but not in (IV). This factor is probably (V) activating nascent  $H_2O_2$  so that it can oxidise EtOH. In the system (IV)+MeCHO+EtOH+(V), the  $H_2O_2$  formed promotes the secondary oxidation of EtOH to MeCHO, and MeCHO in turn is oxidised by the enzyme so that the  $O_2$  uptake is much more than doubled and may continue as long as any EtOH remains unoxidised if (IV) remains intact. Such reactions are termed "cyclic oxidations." When purines are the substrates cyclic oxidation does not go beyond tripling the  $O_2$  uptake, due perhaps to competitive inhibition by (II).

E. A. H. R.

**Action of cyanide and other respiratory inhibitors on xanthine oxidase.** M. DIXON and D. KEILIN (Proc. Roy. Soc., 1935, B, 119, 159—190).—Xanthine oxidase (I) is inactivated on incubation with  $CN'$ . This inactivation differs from normal  $CN'$  inhibition in that it is produced relatively slowly, is irreversible, and affects both aerobic and anaerobic oxidation, so that the dehydrogenase, and not some O-activating catalyst, is poisoned. Inactivation is much slower at  $20^\circ$  than at  $38^\circ$ . If sufficient time is allowed for the  $CN'$  to act, inactivation is complete. Aerobically (I) is protected against  $CN'$  by purines, so that addition of  $CN'$  subsequent to the addition of hypoxanthine (II) has no effect on the oxidation of (II). Anaerobically uric acid (III), adenine, and guanine protect (I) against  $CN'$ , but (II) protects (I) only in the presence of a H-acceptor, without which it may enhance the effect due to  $CN'$ . No inhibition is produced by  $CO_2$ ,  $H_2S$ ,  $P_2O_7^{''''}$ , or  $NaN_3$  even on incubation.  $NaN_3$ , but not the other three, produces a

large inhibition on anaerobic incubation in presence of (II).  $H_2S$  doubles the  $O_2$  uptake owing to its coupled oxidation by the  $H_2O_2$  formed. The identity of (I) and the Schardinger enzyme (IV) is supported by the fact that (IV) undergoes the same type of inactivation by  $CN'$ , and to the same extent, as (I). (IV) is also completely protected against  $CN'$  poisoning by (III).

E. A. H. R.

**Existence of dehydrogenases of the fatty acids in the human placenta.** G. TESAURO (Boll. Soc. ital. Biol. sperim., 1935, 10, 325—326).—Extracts and sections of human placenta show dehydrogenase activity with succinic acid but not with fatty acids; the placenta is therefore not a site of fatty acid oxidation.

R. N. C.

**Enzymic dehydrogenation of glycerophosphoric acid.** T. WAGNER-JAUREGG and H. RAUEN (Z. physiol. Chem., 1935, 237, 233—235).—The dehydrogenation of Na glycerophosphate (I) by the dehydrase (II) of cucumber seeds is greatly accelerated by the flavin enzyme (III) (inactivated by heating to  $100^\circ$ ). The reaction is further hastened by simultaneous addition of the co-enzyme (IV), which by itself is much less active in the reduction of methylene-blue. HCN, even in high concn., has no influence on the rate of dehydrogenation of (I) by the system (II)-(III)-(IV).

H. W.

**Dehydrogenation of citric acid and isocitric acid by cucumber-seed dehydrase.** T. WAGNER-JAUREGG and H. RAUEN (Z. physiol. Chem., 1935, 237, 227—232; cf. A., 1935, 1023).—The action of citricodehydrase is greatly enhanced by the presence of flavin enzyme, and in this dehydrogenating system  $O_2$  is absorbed. The enzymic oxidation of citric acid (I) proceeds thus:  $(I) + \frac{1}{2} O_2 = CO_2 + X$ . The possibility that  $X = CO(CH_2 \cdot CO_2H)_2$  (II) is excluded since it is scarcely attacked under the experimental conditions. Fission of (I) into (II) and  $HCO_2H$  is a mode of anaerobic enzymic fission of (I), which may be a primary, but is certainly not a secondary, reaction.  $CH_2Ac \cdot CO_2H$ , ketipinic, aconitic, itaconic, hydroxyfumaric, and hydroxymaleic acid, and AcOH do not behave as substrate to the dehydrase. *iso*Citric [ $\alpha$ -hydroxypropane- $\alpha\beta\gamma$ -tricarboxylic] acid is dehydrogenated more rapidly than (I) and the reaction is greatly accelerated by Warburg's yellow enzyme.

H. W.

**Liver enzymes. V. Aldehyde of liver.** L. REICHEL and K. ECKHOFF (Z. physiol. Chem., 1935, 237, 214—220; cf. A., 1934, 693, 807).—The methods of obtaining preps. of the dry enzyme cause destruction of the indophenol oxidase (I) and almost complete removal of flavin. Such preps. under aerobic or anaerobic conditions can therefore only immediately catalyse the dismutation process; this is related to the presence of cozymase, which occurs in considerable amount. Dehydrogenation takes place in the systems aldehyde (+co-enzyme) (II)-aldehyde (III)-cytochrome *Bc* (A., 1934, 453)-(I)- $O_2$  and (II)-(III)-flavoprotein, lactoflavin, or 9-*d*-araboflavin. Metabolism in the organism can therefore proceed through one or other intermediate systems. If the intermediate acceptors are not present in optimal concn. in the

dehydrase system, dehydrogenation is accompanied by dismutation. H. W.

**Constitution of starch and mode of action of starch-splitting enzymes.**—See this vol., 194.

**Destruction of certain hydrolytic enzymes in the course of their action.** R. BONNET and B. NATAF (Compt. rend., 1935, 201, 1060—1062).—Various amylase and invertase preps. lose activity during their action. As this takes place even in the absence of proteolytic enzymes it is not to be attributed to destruction of the active mols. by the latter. W. O. K.

**Action of the two amylases of barley.** C. S. HANES (Canad. J. Res., 1935, 13, 185—208).—Van Klinkenberg's results (cf. A., 1932, 91, 1062; 1933, 92) for the hydrolysis of starch, prepared by his method, by  $\beta$ -amylase (I) are confirmed. This method of prep. produces some reducing substances. Small's method gives a starch which, when completely hydrolysed by (I), has only 60% of the reducing power of maltose (II). Erythrogranulose (III) with  $\alpha$ -amylase (IV) gives only 40% of (II); one third of the reducing power of the products is not removed by *Monilia tropicalis*, and is thus not due to (II) or glucose; some of the reducing products are rapidly hydrolysed by (I). The production of reducing products from starch by (IV) is much faster than from the amount of (III) which is assumed to be present therein. (IV) thus does not act preferentially on (III). The non-maltose reducing products are formed preferentially in the initial stage of the hydrolysis. Possibly both  $\beta$ -starch [the portion susceptible to (I)] and (III) are formed by (I) and do not pre-exist as such in starch. R. S. C.

**Biochemical changes in wheat grain under the action of high temperatures.** V. L. KRETOVITSCH and E. N. RIAZANCEVA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 409—412).—Heating the grain to 105—130° causes partial denaturation of the gliadin and a decrease in the hydration of the gluten and in catalase and diastatic activities. Heating to 60—90° causes an increase in diastatic activity. H. G. R.

**Hydrolysis of the phosphoric ester of starch and glycogen.** H. PRINGSHEIM and S. GINSBURG (Bull. Soc. Chim. biol., 1935, 17, 1599—1606).—The hydrolysis of starch by pancreatic diastase may give 100% yield of maltose without liberation of  $H_3PO_4$ . With glycogen, on the other hand, 10—23% dephosphorylation occurs. A. L.

**Emulsin. XXV. Coffee emulsin.** B. HELFERICH and F. VORSATZ (Z. physiol. Chem., 1935, 237, 254—260).—It is advocated that the term "emulsin" should be used generally for enzymes capable of hydrolysing glucosides and not to express a sp. action. Coffee emulsin is obtained by extraction of ground raw coffee (with or without pre-treatment with  $CO_2$ ) with  $H_2O$ , pptn. with tannin, and detannising the ppt. by  $CO_2$ . The behaviour of the product towards phenyl- $\alpha$ -D-mannoside,  $\alpha$ -D-galactoside, and  $\beta$ -D-galactoside indicates the presence of three enzymes; a feeble diastatic action is also detectable. It resembles lucerne emulsin, from which

it differs in its feeble  $\beta$ -D-glucosidase action. The  $\beta$ -D-glucosides of protocatechualdehyde, caffeic acid, and vanillin are so much more rapidly hydrolysed than phenyl- $\beta$ -D-glucoside or salicin by the  $\beta$ -glucosidase of coffee emulsin that the enzyme can thus be detected and to some extent determined, whereas its certain detection by salicin is impossible. The existence of different  $\beta$ -D-galactosidases is thus confirmed. H. W.

**Polysaccharides synthesised by micro-organisms.**—See this vol., 193.

**Glucoside syntheses with emulsin.**—See this vol., 56.

**Hydrolysis of  $\beta$ -glucosides and conjugated glycuronic acids by enzymes of liver and kidney.** E. HOFMANN (Biochem. Z., 1935, 281, 438—443).—Salicin,  $\beta$ -naphtholglycuronic acid,  $\beta$ -phenol-xyloside, -galactoside, and -glucoside, lactoseureide, and glycyrrhizic acid are all hydrolysed by enzyme preps. from horse's and rabbit's liver and kidney. With salicin, the  $p_H$  optimum appears to be dependent on the nature of the buffer solution, but the reaction does not occur below  $p_H$  5. P. W. C.

**Hydrolysis of lactose by enzymes of liver and kidney.** C. NEUBERG and E. HOFMANN (Biochem. Z., 1935, 281, 431—437).—Various enzyme preps., obtained as autolysates and as powders (dried with  $EtOH-Et_2O$ ) from horse's and rabbit's liver and kidney, which hydrolyse lactose to glucose and galactose are described. P. W. C.

**Invertase. II. Purification of invertase by adsorption methods.** N. TAKETOMI (J. Soc. Chem. Ind. Japan, 1935, 38, 559B).—Invertase (I) may be purified and separated from amylase (II) in aq.  $EtOH$  solution by adsorption on activated clay at 30°.  $Al(OH)_3$  and cholesterol readily adsorb (I), (II), and proteins, but not selectively. Active C is unsatisfactory for the separation of (I) from (II). H. G. M.

**Thiol compounds and their significance in the enzymic conversion of carbohydrates.** T. BERSIN (Z. Spiritusind., 1935, 58, 393—394).—The presence of oxidised and reduced forms of compounds of the cystine and glutathione types in living cells is noted, and the literature dealing with the effects of such autoxidisable compounds in the enzymic conversion (hydrolysis, fermentation, oxidation) of carbohydrates is reviewed and discussed. I. A. P.

**Influence of cations on fermentation by tumour cells. V. Calcium and magnesium.** I. A. LASNITZKI and O. ROSENTHAL (Biochem. Z., 1935, 281, 395—401).—Whereas K increases considerably the intensity of anaerobic fermentation of rat implantation tumours, Ca and Mg under the same conditions have no effect. P. W. C.

**Nature and specificity of Ricinus lipase.** H. E. LONGENECKER and D. E. HALEY (J. Amer. Chem. Soc., 1935, 57, 2019—2021).—Dry *Ricinus* lipase loses only a portion of its activity in many years. The activity is favoured by factors favouring the stability of  $H_2O$ -in-oil emulsions. For 14 oils examined there was no specificity when the no. of mols. hydrolysed is considered. R. S. C.

which gives allantoin on decarboxylation. The Michaelis const. for (II) with *dl*-alanine as substrate is about  $5 \times 10^{-3}M$ . (II) is irreversibly inhibited by  $H_2S$  in the presence of  $O_2$ . An inhibition by ethylurethane may be only a salt effect as other narcotics have no effect. (II) is inhibited by various tissue extracts such as liver-(I) and heart-muscle oxidase. Incubation with (III) almost completely inhibits (II), but this effect is considerably reduced if (III) is first boiled. Destruction of (III) by incubation with  $CN'$  does not affect this inhibition. A similar inhibition is shown by charcoal. The rate of oxidation of *l*-alanine by (II) is unaffected by the addition of *d*-alanine. The formation of  $H_2O_2$  on aerobic dehydrogenation is best shown by the coupled oxidation of EtOH (cf. following abstracts). (II) oxidises *N*-monomethyl- but not *N*-dimethyl- or  $\alpha$ -methyl-alanine. In addition to oxidative deamination, kidney slices promote the oxidation of *d*- and *l*-dihydroxyphenyl-alanine due to their polyphenol-oxidase content.

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**Liver enzymes. V. Aldehyde dehydrogenase of liver.** L. REICHEL and K. ECKHOFF (Z. physiol. Chem., 1935, 237, 214—220; cf. A., 1934, 693, 807).—The methods of obtaining preps. of the dry enzyme cause destruction of the indophenol oxidase (I) and almost complete removal of flavin. Such preps. under aerobic or anaerobic conditions can therefore only immediately catalyse the dismutation process; this is related to the presence of cozymase, which occurs in considerable amount. Dehydrogenation takes place in the systems aldehydease (+co-enzyme) (II)–aldehyde (III)–cytochrome *Bc* (A., 1934, 453)–(I)– $O_2$  and (II)–(III)–flavoprotein, lactoflavin, or 9-*d*-araboflavin. Metabolism in the organism can therefore proceed through one or other intermediate systems. If the intermediate acceptors are not present in optimal concn. in the

dehydrase system, dehydrogenation is accompanied by dismutation. H. W.

**Constitution of starch and mode of action of starch-splitting enzymes.**—See this vol., 194.

**Destruction of certain hydrolytic enzymes in the course of their action.** R. BONNET and B. NATAF (Compt. rend., 1935, 201, 1060—1062).—Various amylase and invertase preps. lose activity during their action. As this takes place even in the absence of proteolytic enzymes it is not to be attributed to destruction of the active mols. by the latter. W. O. K.

**Action of the two amylases of barley.** C. S. HANES (Canad. J. Res., 1935, 13, 185—208).—Van Klinkenberg's results (cf. A., 1932, 91, 1062; 1933, 92) for the hydrolysis of starch, prepared by his method, by  $\beta$ -amylase (I) are confirmed. This method of prep. produces some reducing substances. Small's method gives a starch which, when completely hydrolysed by (I), has only 60% of the reducing power of maltose (II). Erythrogranulose (III) with  $\alpha$ -amylase (IV) gives only 40% of (II); one third of the reducing power of the products is not removed by *Monilia tropicalis*, and is thus not due to (II) or glucose; some of the reducing products are rapidly hydrolysed by (I). The production of reducing products from starch by (IV) is much faster than from the amount of (III) which is assumed to be present therein. (IV) thus does not act preferentially on (III). The non-maltose reducing products are formed preferentially in the initial stage of the hydrolysis. Possibly both  $\beta$ -starch [the portion susceptible to (I)] and (III) are formed by (I) and do not pre-exist as such in starch. R. S. C.

**Biochemical changes in wheat grain under the action of high temperatures.** V. L. KRETOVITSCH and E. N. RIAZANCEVA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 409—412).—Heating the grain to 105—130° causes partial denaturation of the gliadin and a decrease in the hydration of the gluten and in catalase and diastatic activities. Heating to 60—90° causes an increase in diastatic activity. H. G. R.

**Hydrolysis of the phosphoric ester of starch and glycogen.** H. PRINGSHEIM and S. GINSBURG (Bull. Soc. Chim. biol., 1935, 17, 1599—1606).—The hydrolysis of starch by pancreatic diastase may give 100% yield of maltose without liberation of  $H_3PO_4$ . With glycogen, on the other hand, 10—23% dephosphorylation occurs. A. L.

**Emulsin. XXV. Coffee emulsin.** B. HELFERICH and F. VORSATZ (Z. physiol. Chem., 1935, 237, 254—260).—It is advocated that the term "emulsin" should be used generally for enzymes capable of hydrolysing glucosides and not to express a sp. action. Coffee emulsin is obtained by extraction of ground raw coffee (with or without pre-treatment with  $COMe_2$ ) with  $H_2O$ , pptn. with tannin, and detannising the ppt. by  $COMe_2$ . The behaviour of the product towards phenyl- $\alpha$ -*D*-mannoside,  $\alpha$ -*D*-galactoside, and  $\beta$ -*D*-galactoside indicates the presence of three enzymes; a feeble diastatic action is also detectable. It resembles lucerne emulsin, from which

it differs in its feeble  $\beta$ -*D*-glucosidase action. The  $\beta$ -*D*-glucosides of protocatechualdehyde, caffeic acid, and vanillin are so much more rapidly hydrolysed than phenyl- $\beta$ -*D*-glucoside or salicin by the  $\beta$ -glucosidase of coffee emulsin that the enzyme can thus be detected and to some extent determined, whereas its certain detection by salicin is impossible. The existence of different  $\beta$ -*D*-galactosidases is thus confirmed. H. W.

**Polysaccharides synthesised by micro-organisms.**—See this vol., 193.

**Glucoside syntheses with emulsin.**—See this vol., 56.

**Hydrolysis of  $\beta$ -glucosides and conjugated glycuronic acids by enzymes of liver and kidney.** E. HOFMANN (Biochem. Z., 1935, 281, 438—443).—Salicin,  $\beta$ -naphtholglycuronic acid,  $\beta$ -phenol-xyloside, -galactoside, and -glucoside, lactoseureide, and glycyrrhizic acid are all hydrolysed by enzyme preps. from horse's and rabbit's liver and kidney. With salicin, the  $p_H$  optimum appears to be dependent on the nature of the buffer solution, but the reaction does not occur below  $p_H$  5. P. W. C.

**Hydrolysis of lactose by enzymes of liver and kidney.** C. NEUBERG and E. HOFMANN (Biochem. Z., 1935, 281, 431—437).—Various enzyme preps., obtained as autolysates and as powders (dried with  $EtOH-Et_2O$ ) from horse's and rabbit's liver and kidney, which hydrolyse lactose to glucose and galactose are described. P. W. C.

**Invertase. II. Purification of invertase by adsorption methods.** N. TAKETOMI (J. Soc. Chem. Ind. Japan, 1935, 38, 559B).—Invertase (I) may be purified and separated from amylase (II) in aq.  $EtOH$  solution by adsorption on activated clay at 30°.  $Al(OH)_3$  and cholesterol readily adsorb (I), (II), and proteins, but not selectively. Active C is unsatisfactory for the separation of (I) from (II). H. G. M.

**Thiol compounds and their significance in the enzymic conversion of carbohydrates.** T. BERSIN (Z. Spiritusind., 1935, 58, 393—394).—The presence of oxidised and reduced forms of compounds of the cystine and glutathione types in living cells is noted, and the literature dealing with the effects of such autoxidisable compounds in the enzymic conversion (hydrolysis, fermentation, oxidation) of carbohydrates is reviewed and discussed. I. A. P.

**Influence of cations on fermentation by tumour cells. V. Calcium and magnesium.** I. A. LASNITZKI and O. ROSENTHAL (Biochem. Z., 1935, 281, 395—401).—Whereas K increases considerably the intensity of anaerobic fermentation of rat implantation tumours, Ca and Mg under the same conditions have no effect. P. W. C.

**Nature and specificity of Ricinus lipase.** H. E. LONGENECKER and D. E. HALEY (J. Amer. Chem. Soc., 1935, 57, 2019—2021).—Dry *Ricinus* lipase loses only a portion of its activity in many years. The activity is favoured by factors favouring the stability of  $H_2O$ -in-oil emulsions. For 14 oils examined there was no specificity when the no. of mols. hydrolysed is considered. R. S. C.

**Voltinism of the silkworm (*Bombyx mori*, L.).**  
**I. Activity of the lipase in relation to voltinism.** H. SATO and I. CHINO (Bull. Sericult. Japan, 1935, 8, 403).—The lipase of eggs incubated at 15° has an activity > that of eggs incubated at 25°. This and similar phenomena are due to instability of the voltinism determiner.  
 P. G. M.

**Influence of oral administration and injection of various nutrients on enzyme actions of body-fluid of the silkworm.** S. MATSUMURA and T. OKA (Bull. Sericult. Japan, 1935, 8, 403—404).—Enzyme activity is increased by feeding or injection of the appropriate substrate only.  
 P. G. M.

**Activation of enzymes. III. Rôle of metal ions in activation of arginase. Hydrolysis of arginine induced by certain metal ions with urease.** L. HELLERMAN and M. E. PERKINS (J. Biol. Chem., 1935, 112, 175—194).—A method for obtaining an arginase (I) prep. of high activity is described. So obtained it is neither activated nor, after treatment with oxidising agents, reactivated by cysteine, but it is activated by Ni<sup>++</sup>, Mn<sup>++</sup>, Fe<sup>++</sup>, and especially by Co<sup>++</sup>, and Co<sup>++</sup> effects complete reactivation after H<sub>2</sub>S inactivation. Arginine, without (I), best in presence of urease and any of the above ions, is hydrolysed. The effect is diminished by CN<sup>-</sup>, which, however, does not prevent hydrolysis of any urea in the mixture. The mol. of (I) probably contains a metallic component which can be separated by oxidising or other agents. The pronounced effect of Co<sup>++</sup> may be due to its ability to form complex mols.  
 J. N. A.

**Quantitative measurement of tyrosinase.** M. GRAUBARD and J. M. NELSON (J. Biol. Chem., 1935, 112, 135—141).—A method for determining the activity of tyrosinase (I) is described. A unit is the amount of (I) which under specified conditions will bring about an uptake of 10 cu. mm. of O<sub>2</sub> per min. (I) appears to consist of one enzyme, the oxidation of *p*-cresol and dehydrogenation of pyrocatechol being both effected by active O<sub>2</sub>.  
 J. N. A.

**Peptidase system of *Aspergillus parasiticus*.** M. J. JOHNSON and W. H. PETERSON (J. Biol. Chem., 1935, 112, 25—34).—The aminopolypeptidase (I) is preferentially pptd. from mixtures with dipeptidase by addition of 1.5—2.5 vols. of 95% EtOH. The (I) of *A. parasiticus* attacks peptide linkings adjacent to free NH<sub>2</sub>. Dipeptides are not attacked unless decarboxylated, and peptides composed entirely of glycine are not attacked. The crude enzyme from the mould also contains three distinct peptidases, capable of hydrolysing peptides in which Cl or Me is substituted in the NH<sub>2</sub>. The apparent basic dissociation consts. × 10<sup>12</sup> of leucyldiglycine, leucylglycine, triglycine, and diglycine are 19.0, 16.0, 19.0, and 14.0, respectively.  
 F. A. A.

***a*- and *b*-Thymonucleic acid and the enzyme transforming the *a*- into the *b*-form (nucleogelase).** R. FEULGEN (Z. physiol. Chem., 1935, 237, 261—267).—Na *a*-thymonucleate (I) is transformed into the *b*-salt (II) by nucleogelase (pancreatic prep.) at *p*<sub>H</sub> 6.8—6.9. The tetranucleotide structure of the product follows, since (*a*) elimination of H<sub>3</sub>PO<sub>4</sub> or

purines does not occur, (*b*) protracted exposure of (II) to the action of the enzyme does not diminish the amount pptd. by mineral acid or increase the solubility in acid, (*c*) the at. ratio P : Na = 4 : 4 in both (I) and (II), (*d*) [α] of (II) resembles that of (I) in its unusual dependence on temp., and in its disappearance after addition of NaOH and return after neutralisation, (*e*) complete hydrolysis of (I) or (II) yields identical products in identical amounts, and (*f*) the analytical data for (II) are those required for a tetranucleotide based on the presence of deoxyribose as carbohydrate.  
 H. W.

**Enzymic histochemistry. II. Micro-method for determination of tryptic activity.** L. WEIL (Biochem. J., 1936, 30, 5—10).—The CO<sub>2</sub>H groups liberated by the action of trypsin on tissue sections are determined by titration with 0.05*N*-NMe<sub>4</sub>-OH, the NH<sub>2</sub> having been blocked by CH<sub>2</sub>O. The reproducibility of the method is ±0.00007 mg. of NH<sub>3</sub>-N. The tryptic activity in tumour tissue is independent of the thickness of the slice and time of extraction.  
 J. N. A.

**Platinum potential corresponding to the inactivation of the proteolytic power of papain by oxidisers.** P. REISS (Compt. rend. Soc. Biol., 1935, 120, 908—910).—The proteolytic action of papain is arrested by oxidisers above a definite *E*<sub>h</sub>, which increases with fall of *p*<sub>H</sub>.  
 R. N. C.

**Isolation and properties of pepsin and trypsin.** J. H. NORTHROP (Current Sci., 1935, 4, 370—376).—A summary.

**Acetylation of tyrosine in pepsin.** R. M. HERRIOTT (J. Gen. Physiol., 1935, 19, 283—299; cf. A., 1934, 1239).—“Cryst. 60% active acetylpepsin” contains 7 Ac per mol.; 3 of these may be removed by hydrolysis at *p*<sub>H</sub> 0.0 or 10. The phenolic OH of glycytyrosine is acetylated by keten under the conditions used for pepsin, and it is probable that the 3 labile Ac, responsible for the decrease in activity, are attached to tyrosine phenolic groups in the pepsin mol.  
 F. A. A.

**Enzymic histochemistry. XVI. Digestion of keratin by the larva of the moth *Tineola biselliella*, Humm.** K. LINDERSTRÖM-LANG and F. DUSPIVA (Z. physiol. Chem., 1935, 237, 131—158; cf. A., 1935, 784).—The intestinal cells and juice (*p*<sub>H</sub> 9.6—10.2) of the larvæ contain a proteinase (I) which degrades caseinogen (optimum *p*<sub>H</sub> 9.3) but does not attack wool (at *p*<sub>H</sub> 9.2 or 9.6—10.2). Juice from larvæ which have eaten wool, but not that from fasting larvæ and larvæ on diets poor in S (cotton wool, caseinogen), contains a ·SH compound (or compounds) which rapidly oxidises in air. At *p*<sub>H</sub> 10, in presence of reducing agents (LiSH, SH·CH<sub>2</sub>·CO<sub>2</sub>H), (I) attacks wool liberating equiv. amounts of NH<sub>2</sub> and CO<sub>2</sub>H. When trypsin-kinase replaces (I) the wool remains unaffected. The mid-gut cavity contains a reducing agent the presence of which is independent of that of ·SH compounds. The action of (I) is not inhibited by low concns. (0.01*N*) of ·SH compound.  
 W. McC.

**Changes of wheat proteins under the action of flour and yeast enzymes.** A. V. BLAGOVESHCHENSKI and M. P. YURGENSON (Biochem. J., 1935, 29, 805—

810).—Variations on treatment with flour enzyme (A., 1933, 1331) in the leucosine- and non-protein-N, gliadin, globulin, and glutenin fractions of flour and baking mixtures (obtained by extracting with H<sub>2</sub>O, 72% EtOH, 10% NaCl, and 2% NaOH, respectively) indicate that the solvent effect of the enzyme is one of disaggregation as opposed to the proteolytic action of yeast enzymes. H. D.

**Does protease secretion occur in bacteria?** W. MOYCHO (Compt. rend., 1935, 201, 859—860).—Cultures of *B. prodigiosum* in peptone media develop to a greater extent if shaken, and the appearance of the red colour of prodigiosin is delayed. The secretion of proteases (I) does not occur until after the death of the cell. (I) are not liberated if the bacteria are killed by PhMe, CHCl<sub>3</sub>, or Et<sub>2</sub>O. R. N. C.

**Action of proteases on the protein of ungerminated cereals and on amylolytic activity** T. CHRZĄSZCZ and J. JANICKI (Biochem. Z., 1935, 281, 408—419).—The action of trypsin, papain, pepsin, and rennin on the protein and active amylase (I) content of ungerminated cereals was investigated. (I) is present in cereals, and the activity is increased by the action of proteases to an extent varying with different proteases and cereals. No abs. relationship exists between the increase of active (I) and the extent of protein degradation. The increase depends not exclusively on these factors, but also on the formation of substances having elutriant and kinase activity. Rennin, since it degrades oat- and buckwheat-protein (unattacked by pepsin), must contain protease. P. W. C.

**Phosphatases of the brain.** K. V. GIRI and N. C. DATTA (Current Sci., 1935, 4, 324).—In brain (of sheep) both "acid" (I) and "alkaline" phosphatase (optimum p<sub>H</sub> 5.0 and 9.6, respectively) are present. (I) is not activated by Mg<sup>++</sup>, and is therefore not identical with erythrocyte phosphatase (cf. Waldschmidt-Leitz, A., 1935, 534). F. R. G.

**Variations of serum-phosphatase after ingestion of chloroform.** H. METZGER, P. BARTHELMÉ, and M. URBAN (Compt. rend. Soc. Biol., 1935, 120, 896—897).—CHCl<sub>3</sub> ingested by dogs daily for long periods causes an increase of serum-phosphatase, which disappears with cessation of administration. Bile secretion is not affected. R. N. C.

**Serum-phosphatase during gestation.** J. CAYLA and F. FABRE (Compt. rend. Soc. Biol., 1935, 120, 748—750).—Phosphatase increases by about 136% in pregnancy, and does not depend on the age of the mother. CaO fixation by the foetus is increased 7-fold during the last 2 months. R. N. C.

**Action of some chemical compounds on vegetable phosphatases.** J. COURTOIS (Compt. rend., 1935, 201, 855—856).—The affinity of any phosphatase for glycerophosphate depends on its origin; emulsin (I) and white mustard phosphatase react differently from takadiastase (II). NaF accelerates hydrolysis by the grain enzymes, and restrains that by (II); EtOH exhibits an inverse activity to NaF, whilst glycerol restrains (II) without affecting (I). AsO<sub>4</sub><sup>'''</sup> and PO<sub>4</sub><sup>'''</sup> inhibit all three to equal degrees. All these agents influence the affinity of each enzyme

for both glycerophosphates to the same degree. Mg<sup>++</sup> does not accelerate any of the three, nor does 8-hydroxyquinoline (cf. A., 1935, 122). R. N. C.

**Phosphatase activity of tissues and plasma in tumours of bone.** C. C. FRANSEEN and R. McLEAN (Amer. J. Cancer, 1935, 24, 299—317).—The phosphatase activity of the blood-plasma is raised significantly in the osteoblastic type of osteogenic sarcoma, and on removal of the tumour mass the plasma-phosphatase val. falls to normal, rising again with recurrence of the tumour. The tumour tissue is also higher in phosphatase than are all other types of tumour tissue examined. The results support the theory of the synthesis of phosphatase by the osteoblasts. NUTR. ABS. (m)

**Micro-determination of phosphatase in serum.** E. MÜLLER (Z. physiol. Chem., 1935, 237, 35—39).—Amidol or metol is suitable as reducing agent in the colorimetric [(NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub>-sulphite] determination of PO<sub>4</sub><sup>'''</sup> by the step-photometer. With Na β-glycerophosphate as substrate, the application of the method to phosphatase activity in serum (0.5 c.c.) is described. F. O. H.

**Energy relationships in the enzymic formation of lactic acid and synthesis of phosphagen.** O. MEYERHOF and W. SCHULZ (Biochem. Z., 1935, 281, 292—305).—The reaction phosphopyruvic acid (I)+creatine → creatinephosphoric acid + AcCO<sub>2</sub>H is associated with a negative heat val. of -3000 g.-cal., whereas the analogous reaction (I)+arginine → argininephosphoric acid + AcCO<sub>2</sub>H is almost thermo-neutral. P. W. C.

**Enzymic synthesis of creatinephosphoric acid by phosphate transfer from phosphopyruvic acid.** H. LEHMANN (Biochem. Z., 1935, 281, 271—291).—The synthesis of creatinephosphoric acid (I) in muscle poisoned with CH<sub>2</sub>I-CO<sub>2</sub>H on addition of phosphoglyceric acid (II) and phosphopyruvic acid (III) is investigated using dialysed muscle extracts. The synthesis, which takes place only in presence of adenylic acid (IV) or adenylic pyrophosphate (V), occurs particularly in old extracts dialysed for a long time in which spontaneous dephosphorylation no longer occurs. PO<sub>4</sub><sup>'''</sup> transfer occurs in two stages: (IV)+(III) → (V)+AcCO<sub>2</sub>H; (V)+creatine → (I)+(IV). A small amount of (IV) may thus generate 100 times its amount of (I). Mg is necessary for both reactions. (III) permits a quicker and more complete transfer of PO<sub>4</sub> than does (II). The reaction may be used for the prep. of (I) and also for the synthesis of argininephosphoric acid in crab's muscle extract. P. W. C.

**Dephosphorylation of starch by phosphatase.** H. PRINGSHEIM and F. LOEW (Bull. Soc. Chim. biol., 1935, 17, 1607—1613).—Complete dephosphorylation of amylopectin without maltose formation is not effected by several phosphatase preps. The dephosphorylation becomes proportionately easier, however, as diastatic action proceeds. A. L.

**Cozymase.** H. VON EULER, H. ALBERS, and F. SCHLENK (Z. physiol. Chem., 1935, 237, I—II; cf. A., 1935, 1024; Warburg *et al.*, *ibid.*, 400).—Improved methods of purification enable cozymase

(I) to be obtained almost pure and not as a mixture of isomerides. On acid hydrolysis (I) yields adenine (19.5%), nicotinamide, and  $\text{NH}_3$  (but no  $\text{CO}_2$ ). (I), which is probably a dinucleotide,  $\text{C}_{24}\text{H}_{35}\text{O}_{18}\text{N}_8\text{P}_2$ , is a monobasic acid. W. McC.

**Stability of the heat-stable glycolysis activator in cozymase, and of Warburg's co-enzyme.** H. VON EULER and G. GÜNTHER (Svensk Kem. Tidskr., 1935, 47, 285—290).—The glycolysis-activating power of cozymase is slightly enhanced when its oxidation-reduction activation is destroyed by heat. A study of lactic acid production indicates that the mechanism of glycolysis activation is the same for both "active" and "inactive" cozymase. The glycolysis activation is only slowly inactivated by 0.1*N*- $\text{NaOH}$  at 100°, 0.5*N*- $\text{NaOH}$ , or 0.5*N*- $\text{HCl}$ . The relative activities at  $p_{\text{H}}$  5 (from fermentation measurements) after 1 hr. at 85° are approx. : cozymase 85%, Warburg's co-enzyme 30%. M. H. M. A.

**Cozymase as a hydrogen carrier.** H. VON EULER, E. ADLER, and H. HELLSTRÖM (Svensk Kem. Tidskr., 1935, 47, 290—293).—Substrate-dehydrogenase-cozymase systems give a reduced cozymase stable to atm.  $\text{O}_2$ , and reoxidised by flavin-enzyme. Cozymase is thus identified with the co-enzyme in the system substrate-dehydrogenase-co-enzyme-flavin-enzyme-acceptor. M. H. M. A.

**Action of cozymase.** H. VON EULER and R. VESTIN (Z. physiol. Chem., 1935, 237, 1—7).—Cozymase (I) [both highly purified ( $AC_0 = 4 \times 10^5$ ) and relatively crude preps.] rendered fermentation-inactive by heat (A., 1935, 782, 1162, 1165, 1278) and normal (I) promote phosphorylation and formation of lactic acid by rat muscle in presence of hexose diphosphate (II) to approx. the same extent. Adenosine triphosphate can replace (I)+(II) in muscle glycolysis but not in yeast fermentation (cf. A., 1932, 778). Direct phosphorylation of  $\text{AcCO}_2\text{H}$  by yeast enzyme system (apozymase) in presence of (I) does not occur. Phosphorylation in muscle extract-glycogen-(I) preps. with (II) equals that with  $\text{AcCO}_2\text{H}$ . The nature of the various active centres of (I) (which are differentiated by reagents, e.g.,  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ , as well as by heat) is discussed. F. O. H.

**Oxidative inactivation of cozymase with Schar-dinger enzyme preparations.** F. LIPMANN (Nature, 1935, 136, 913—914).—An inhibition of fermentation occurs when yeast macerate is mixed with a milk prep. containing xanthine oxidase in presence of  $\text{O}_2$ . Fermentation recommences on addition of boiled yeast macerate or purified cozymase. L. S. T.

**Activators of glycolysis. II.** H. VON EULER and G. GÜNTHER (Z. physiol. Chem., 1935, 237, 221—226; cf. A., 1035, 1162).—Repetition of previous work with a much purer cozymase prep. shows that the ability to accelerate glycolysis is increased by heating the material at 100°. H. W.

**Fermentative enzymes. IV. Specificity of yeast-phosphatase.** E. BAUER, A. SCHÄFFNER, and F. KRUMBEY (Z. physiol. Chem., 1935, 237, 191—198; cf. A., 1935, 661).—Repetition of previous work following criticisms of Schuchardt (*ibid.*, 1026) and

Collatz (*ibid.*, 1026) shows that dried yeast of various origins yields phosphatase preps. identical within the limits of experimental error with those described previously with respect to sp. action on  $\alpha$ -glycerophosphate.  $\beta$ -Glycerophosphate is relatively slowly attacked. H. W.

**Phosphate transference by means of phosphopyruvic acid in alcoholic fermentation of sugar.** O. MEYERHOF and W. KIESSLING (Biochem. Z., 1935, 281, 249—270).—The velocity of degradation of phosphopyruvic acid (I) by yeast is increased by addition of sugar to an extent dependent on the fermentation velocity of the latter, to which  $\text{PO}_4'''$  of (I) is transferred. In presence of  $\text{NaF}$ , 2 mols. of (I), 2 mols. of hexose, and 2 mols. of  $\text{PO}_4'''$  are used and 2 mols. of  $\text{CO}_2$ , 2 mols. of  $\text{EtOH}$ , 1 mol. of hexose diphosphate (II), and 2 mols. of phosphoglyceric acid (III) are formed. The velocity is similarly increased in presence of  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$  and (II) is again formed. The  $\text{MeCHO}$  arising remains, however, as such, the conversion into (III)+ $\text{EtOH}$  not taking place. By using different sugars as  $\text{PO}_4'''$  acceptors in systems containing  $\text{NaF}$  or  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ , the velocity of degradation of (I) is shown to correspond with the fermentation velocities of the various sugars. The latter velocity must therefore be determined by the ability and readiness of the sugar to act as  $\text{PO}_4'''$  acceptor. Including this new reaction in the general mechanism of alcoholic fermentation, a scheme is obtained which accounts both for the fermentation velocity of the sugars and for the requirements of the Harden-Young equation. P. W. C.

**Theory of mitogenetic radiation. V. Yeast as detector for mitogenetic rays.** M. MOISSEJEVA (Biochem. Z., 1935, 281, 349—357).—Using liquid yeast cultures as detector in a chamber with quartz base or wall and using blood which had been dried on filter-paper and immersed in  $\text{H}_2\text{O}$  as inductor, the detector and inductor being hermetically separated, a positive induction effect (max. 50%, average 21%) on the multiplication of the yeast occurs. P. W. C.

**Preparation and determination of trehalose in yeast.** A. STEINER and C. F. CORI (Science, 1935, 82, 422—423).—Treatment of yeast with  $\text{N}\cdot\text{H}_2\text{SO}_4$  followed by pptn. with  $\text{HgSO}_4 + \text{Fe}_2(\text{SO}_4)_3$  in 7.5%  $\text{H}_2\text{SO}_4$  completely extracts the trehalose (I), and only traces of polysaccharide which are pptd. on neutralisation with  $\text{BaCO}_3$ . After removal of the added metals, concn. in vac., and addition of  $\text{EtOH}$ , cryst. (I) is obtained in 0.3—0.7% yield. A method for the determination of (I) in yeast is outlined. L. S. T.

**Relation of oxygen tension and temperature to the time of reduction of cytochrome.** T. J. B. STIER (J. Gen. Physiol., 1935, 19, 339—350).—The time for the appearance of the cytochrome absorption band in yeast suspensions at various temp. is linearly related to the  $\text{O}_2$  tension. Crit. tensions, increasing with rise of temp., are found below which the cytochrome band appears. The  $\text{O}_2$  tension within the suspension is lowered by respiration by the cells; the rate of lowering can be calc. from the data and agrees approx. with direct measurements. F. A. A.



**Constitution of cytochrome c.** J. ROCHE and M. T. BÉNEVENT (Bull. Soc. Chim. biol., 1935, 17, 1473—1493).—Hæmatin, prepared from pig's blood, successively oxidised and reduced with  $K_3Fe(CN)_6$  and  $Na_2S_2O_4$  gives a hæmochromogen with  $C_5H_5N$  which has an absorption spectrum almost identical with that of the corresponding hæmochromogen of cytochrome c from yeast. A. L.

**Fixation and exchange of cations in living organisms. General character of the laws of base exchange.** J. LAVOLLAY (Compt. rend., 1935, 201, 1150—1152).—If  $x$  is the concn. of a cation in a medium and  $Y$  the concn. in the organisms cultivated thereon, then the equation  $Y = Kx^{1/p}$  (where  $K$  and  $p$  are consts. and  $1/p < 1$ ) holds within certain limits of concn. for  $K$  in *Penicillium glaucum*,  $Mg$  in *Aspergillus niger*, and for  $Ca$  and  $Pb$  in brewer's yeast. If  $C_1$  and  $C_2$  represent the concns. of two cations, then in certain cases  $[C_1/C_2]_{fixed} = [C_1/C_2]_{medium}$ . The formal similarity of these laws to those controlling base exchange in zeolites and in soil indicates a close relationship to these phenomena. W. O. K.

**Yield of citric acid from sugar as a basis for estimating the schemes of its formation from the latter.** V. S. BUTKEVITSCH and M. S. GAJEVSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 405—408).—Yield tests show that, with *A. niger*, the whole of the sugar is converted into citric acid, according to the scheme of either Raistrick or Virtanen.

H. G. R.

**Diffusible nature of the inhibitory agent produced by fungi.** J. C. CARTER (Phytopath., 1935, 25, 1031—1034).—Agar media staled by growth of *Helminthosporium sativum* and a bacterium inhibit the further growth of *H. sativum*. The inhibitory agent is diffusible and thermostable, and retains its activity after sterilisation. A. G. P.

**Biochemistry of micro-organisms. XLVII. Production of polysaccharides by *Penicillium luteum*.** ZUKAL. C. G. ANDERSON and H. RAISTRICK (Biochem. J., 1936, 30, 16—19).—When *P. luteum*, Zukal, is grown on a Czapek-Dox medium with glucose as sole source of C, the principal metabolic product is luteic acid, a malonylpolyglucose. In the early stages of growth a polymannose is present which tends to be replaced by a polygalactose with increasing age of the culture. No pentose is produced. J. N. A.

**Vitamin-A activity of the stem of a *Mucor*.** W. H. SCHOPFER and A. JUNG (Compt. rend. Soc. Biol., 1935, 120, 1093—1095).—The stem of *Phycomyces blakesleeianus* when completely developed contains carotene and exhibits considerable vitamin-A activity. R. N. C.

**Slime-mould pigment as indicator of acidity.** W. SEIFRIZ and M. ZETZMANN (Protoplasma, 1935, 23, 175—179).—The yellow pigment,  $C_{13}H_{13}O_2N_4$ , of *Physarum polycephalum* changes from greenish-yellow at  $p_H$  8 to orange-red at  $p_H$  1. Within the mould the pigment shows changes in the plasmodium from  $p_H$  8 when fruiting to  $p_H$  1.6 when a sclerotium is formed. The pigment is probably a flavin. A. G. P.

**Nature of inhibition between certain fungi parasitic on citrus.** J. G. ARRILLAGA (Phytopath., 1935, 25, 763—775).—Inhibitory action of *Diaporthe citri* towards *Phytophthora parasitica* or *P. citrophthora* results from the action of metabolic products of *D. citri*. The inhibitory agent is not an enzyme, is diffusible, filterable, and relatively thermostable, and is constantly produced in various substrates whether *Phytophthora* is present or not. A. G. P.

**Influence of *Phytomonas tumefaciens* and *P. rhizogenes* on the actual acidity of certain liquid and agar substrates.** A. R. WILSON (Phytopath., 1935, 25, 854—863).—Differences in the rate and direction of  $p_H$  changes effected by these organisms in a no. of media are determined. On carrot infusion free  $NH_3$  is produced. A. G. P.

**Relation between sulphur in various forms and rate of growth of the colourless flagellate *Chilomonas paramecium*.** S. O. MAST and D. M. PACE (Protoplasma, 1935, 23, 297—325).—*Chilomonas* synthesises starch (I), fat, protein, and protoplasm from inorg. compounds, without intervention of light. Energy is probably derived from oxidation of  $NH_3$ . With all S compounds examined the rate of fission increases to a max. and subsequently declines as the S source is progressively increased. The optimum concn. of S varies with the source. Growth, fission, and synthesis of (I) and fat continue in the absence of S. With insufficient S fat accumulates (defective oxidation) and death ultimately occurs. Insufficient C causes death through (I)-starvation. Excessive S or C causes the formation of substances inhibiting cell division. Neither S nor C is necessary for fission. A. G. P.

**Rôle of bacteria, particularly anaërobes, in the corrosion of steel.** R. VEILLON (Compt. rend. Soc. Biol., 1935, 120, 1045—1047). R. N. C.

**Action of microbes on fats.** L. M. HOROVITZ-VLASOVA and M. J. LIVSCHITZ (Zentr. Bakt. Par., 1935, II, 92, 424—435).—Lipolysis by a no. of bacteria and fungi is indicated principally by the increased acid val. of the fatty phase. Glycerol is not detectable in cultures. The Nile-blue and "potash" tests are suitable for detecting lipolysis. Oxidation of fats by the organisms yields peroxides, OH-acids, and aldehydes and is indicated by the presence of labile O compounds (pyrogallol test), increased acidity in the aq. phase, lowered I val., and increased  $n$ . Neither the lipase nor the oxidative enzyme of moulds appears in the substrate. Bacterial lipase is thermostable. A. G. P.

**Phytochemical reduction of lactaldehyde.**—See this vol., 191.

**Optical properties of fermentation lactic acids. I. Bacteria producing inactive lactic acid.** H. KATAGIRI and K. KITAHARA (J. Agric. Chem. Soc. Japan, 1935, 11, 997—1007).—Yeast mashes for saké manufacture contain both *d* and *l*-lactic acid formers; the resultant lactic acid from the saké produced is optically inactive. P. G. M.

**Formation of succinic acid by *B. coli*. Production of succinic acid in relationship to synthesis of proteins.** M. MICHAELIS (Z. physiol. Chem., 1935,

237, 181—185).—Determination of lactic and succinic acid (I), EtOH, AcOH, and HCO<sub>2</sub>H formed by the growth of *B. coli* in sucrose solutions in presence of increasing amounts of NH<sub>3</sub> shows that only in the case of (I) does a relationship between yield and [NH<sub>3</sub>] exist; with increasing [NH<sub>3</sub>] the yield of (I) declines. No relationship exists between the yields of (I) and AcOH. Apparently (I) is a product of the fission of the sugar, and in presence of sufficient NH<sub>3</sub> is transformed by aspartase through fumaric acid into aspartic acid and thence into proteins. H. W.

Nature of the "sporogenes vitamin," an essential growth factor for *Cl. sporogenes* and related organisms. A. M. PAPPENHEIMER, jun. (Biochem. J., 1935, 29, 2057—2063; cf. Fildes *et al.*, this vol., 113).—The isolation of a highly conc. prep. of the *sporogenes* growth factor (I) from a conc. HCl extract of the C<sub>5</sub>H<sub>5</sub>N—Et<sub>2</sub>O solution of the saponifiable and unsaponifiable material of mare's urine is described. (I) is probably an unsaturated OH-acid of mol. wt. 200, and is purified by distillation of its Me ester, which is inactive. 0.04 × 10<sup>-6</sup> g. of (I) per ml. added to an NH<sub>2</sub>-acid medium promoted visible growth of *sporogenes*. (I) is distinct from other growth factors previously described. A. L.

*Leptothrix echinata*, a new iron bacterium, precipitating principally manganese. H. BEGER (Zentr. Bakt. Par., 1935, II, 92, 400—406).—The Mn-accumulating properties of the organism are described. A. G. P.

Carotenoids of purple bacteria. I. P. KARRER and U. SOLMSEN (Helv. Chim. Acta, 1935, 18, 1306—1315).—The isolation (by extraction with various solvents and chromato-absorption) of the following cryst. carotenoids from purple bacteria (called strain Z, as yet unidentified) is described: *rhodoviolascin*, m.p. 218° (max. at 573.5, 534, 496 m $\mu$ ); SbCl<sub>3</sub> compound, max. at 642 m $\mu$  (C 84.15, H 10.23%), *rhodopin*, m.p. 159—160° (547, 508, 478 m $\mu$ ) (C 82.83, H 10.58%), both of which contain 2 O, which is not OH, and *rhodopurpurin*, m.p. 161—162°, C<sub>40</sub>H<sub>56</sub>(58) (550, 511, 479 m $\mu$ ). An amorphous pigment *flavorhodin* (502, 472 m $\mu$ ) was also isolated. All absorption max. are in CS<sub>2</sub>. J. W. B.

Action of some sulphur compounds on fermentation of glucose by propionic bacteria (*Propionibacterium* II). P. CHAIX (Compt. rend., 1935, 201, 857—858).—*Propionibacterium* II does not affect glucose in absence of S derivatives, but ferments it in presence of cystine, cysteine, or glutathione (I). Max. action occurs with a (I) concn. of 1 : 25,000. R. N. C.

Photochemical reactions of SH-compounds in solution.—See this vol., 171.

Utilisation of CO<sub>2</sub> in the dissimilation of glycerol by propionic acid bacteria. H. G. WOOD and C. H. WERKMAN (Biochem. J., 1936, 30, 48—53).—The mechanism of formation of the products of fermentation of glycerol (I) is investigated. Yeast is incubated anaerobically with (I) and CaCO<sub>3</sub> and the volatile and non-volatile acids formed, and the CO<sub>2</sub> and (I) utilisation, are determined. AcOH, EtCO<sub>2</sub>H, PrCO<sub>2</sub>H, succinic and sometimes lactic acid were

isolated; CO<sub>2</sub> obtained from CaCO<sub>3</sub> is utilised by propionic bacteria in the fermentation of (I). H. D.

Sulphur bacteria in the "pink" waters of the Surakhani oil fields.—See this vol., 48.

New autotrophic and thermophilic sulphur-bacteria association. V. CZURDA (Zentr. Bakt. Par., 1935, II, 92, 407—414).—In sulphated hot springs (Pystian) organisms utilising S as an energy source included two variants of *Thiobacterium* and a new *Thiospirillum* (*T. pistiense*). A. G. P.

Specific polysaccharide from the bacillus Calmette-Guerin (BCG). E. CHARGAFF and W. SCHAEFFER (J. Biol. Chem., 1936, 112, 393—405).—Sp. polysaccharides were obtained from BCG by the Heidelberger-Menzel method and separated into H<sub>2</sub>O-sol. and -insol. fractions which on purification gave polysaccharide A, [ $\alpha$ ]<sub>D</sub> + 77.4°, containing mannose, arabinose, and small quantities of inositol, and polysaccharide S, sol. in acids, and containing Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. A protein, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -50°, is also prepared with weak tuberculin activity. The A and S fractions are haptens without antigenic activity. H. D.

Refractometric study of diphtheria toxin. C. SIEBENMANN (Trans. Roy. Soc. Canada, 1935, [iii], 29, V, 41—43).—Under const. conditions, the quantity of toxin produced by cultures of *B. diphtheriae*  $\propto$  the amount of bacterial growth, which in turn is correlated with the fall in *n* of the medium. In general, high toxin production is associated with low vals. of *n*. W. O. K.

Variations of p<sub>H</sub> in culture media designed for the production of staphylococcal toxin. J. SCHWARTZ (Compt. rend. Soc. Biol., 1935, 120, 1085—1086). R. N. C.

Relation of growth to toxin production of the Dochez N.Y. 5 strain of hæmolytic streptococcus. H. C. PLUMMER (Trans. Roy. Soc. Canada, 1935, [iii], 29, V, 45—52).—With various carbohydrate-free media, the quantity of toxin formed is related to the extent of growth. In presence of glucose or maltose, growth, but not necessarily the quantity of toxin produced, is increased; at neutral reactions both growth and toxin are regularly increased. W. O. K.

Neutralising action of two streptococcal antisera. F. H. FRASER and H. C. PLUMMER (Trans. Roy. Soc. Canada, 1935, [iii], 29, V, 63—68).—Of the toxins produced by 174 strains of hæmolytic streptococci, 157 were neutralised by N.Y. 5 antitoxin, 15 of the remainder by Smith antitoxin, whilst 2 strains were neutralised only by a mixture of the two antitoxins. One toxin was neutralised by each of the two antitoxins separately. W. O. K.

Action of quinoline derivatives on pneumococci and streptococci *in vitro*. I. BÜHRMANN (Z. Immunität., 1935, 84, 300—307; Chem. Zentr., 1935, i, 2833—2834).—18 quinoline derivatives [mostly 6-hydroxyquinoline-4-carboxylic acid (I) and 4-amino-2-phenylquinoline (II) derivatives] were examined in 0.01% solution. The growth of pneumococci was inhibited by the hydrochlorides of (I) Pr<sup>a</sup> ester, 4-amino-6-hydroxyquinoline (III), (II), 4-amino-2-*p*-tolylquinoline (IV), Bu<sup>B</sup> 3-2-phenyl-4-

quinolylaminoacetate, and 3:4-dihydro-1:2-naphth-acridineamine (V). Growth of streptococci was inhibited by (II), (III), (IV), and (V). J. S. A.

**Lipins of tubercle bacilli. XL. Presence of sterols.** R. J. ANDERSON, R. SCHOENHEIMER, J. A. CROWDER, and F. H. STODOLA (Z. physiol. Chem., 1935, 237, 40—45).—Only traces of sterol-like substances were found in the  $\text{COMe}_2$ -sol. fat and crude  $\text{CHCl}_3$ -sol. waxes. They probably arise from extraneous sources (cf. A., 1935, 407, 663).

F. O. H.

**Active immunisation in poliomyelitis.** S. FLEXNER (Science, 1935, 82, 420—421). L. S. T.

**Nature of filterable viruses.** R. G. GREEN (Science, 1935, 82, 443—445). L. S. T.

**Titration of the L and S antigens of vaccinia virus in extracts of the vaccinated skin of the rabbit, calf, and guinea-pig.** J. CRAIGIE and F. O. WISHART (Trans. Roy. Soc. Canada, 1935, [iii], 29, V, 57—62).—Extracts of infected skin contain both the L (heat-labile) and S (heat-stable) antigens as demonstrated by reaction with pure anti-L- and anti-S-serum. The presence of the same L and S antigens in the infected skin of three different species suggests that the antigens of vaccinia are sp. products of the virus analogous to bacterial antigens. W. O. K.

**Purification of bacteriophage by electrophoresis and its therapeutic use.** L. MARMIER and V. GRYZEZ (Ann. Inst. Pasteur, 1935, 55, 641—653).—Details are given for obtaining bacteriophage preps. free from protein material, which on intravenous injection do not produce anaphylactic shock. The bacteriophage loses but little of its activity in purification. P. G. M.

**Action of medicinal substances on the cell.** G. ROSKIN (Z. Immunität., 1935, 84, 251—267; Chem. Zentr., 1935, i, 2697).—The action of medicinal substances on trypanosomes can be detected by failure to form the blue dye from Rongalit-white, and by the shifting of the isoelectric point of the cells (indicator, methylene-blue). The sensitivity of *Paramecia* to quinine (I) fluctuates periodically; saccharated  $\text{Fe}_2\text{O}_3$  renders them more sensitive to (I) in acid than in alkaline solution. The sensitivity of *Paramecia* to ultra-violet light is increased in presence of dil. (I) solutions. R. N. C.

**[Trypanocidal action of] antimony compounds.** F. G. CAWSTON (Vet. Rec., 1935, 15, 1280).—Stibilase and trystibine are more effective than tartar-emetie against trypanosomes and schistosomes. R. N. C.

**Synthesis of chemotherapeutic compounds.**  
I. Synthetic "Naganin" in the U.S.S.R. I. L. KRITSCHIEVSKI and I. S. MEERSON. II. Quinoline derivatives [for use] against malaria. I. L. KRITSCHIEVSKI and E. J. STERNBERG (Z. Immunität., 1933, 79, 180—186, 438—459; Chem. Zentr., 1935, i, 2843).—I. The synthesis of a compound as active against trypanosomes as "Founeau 309" is claimed.

II. A no. of 8-substituted aminoquinolines have been studied with regard to their action against bird-malaria. 8- $\gamma$ -Diethylaminopropylamino-6-methoxyquinoline ("Plasmizide") has a therapeutic

index of 26.6; the corresponding OH-compound is also active. Lengthening of the C-chain in position 8 and the introduction of branched chains lower the val. of the product. H. N. R.

**Germicidal efficiency of chloramine-T and calcium hypochlorite.**—See B., 1936, 46.

**Integration of the endocrine system.** (SIR) W. LANGDON-BROWN (Lancet, 1935, 229, 1155—1161).—A lecture. L. S. T.

**Endocrine organs of the blue whale.** A. P. JACOBSEN (Nature, 1935, 136, 1029).—The presence of various hormones in the pituitary, thyroid, pancreas, ovary, and corpus luteum graviditatis is described. L. S. T.

**Reversion of the action of adrenaline and other active substances.** V. SUSANNA (Arch. Int. Pharm. Ther., 1935, 49, 460—469; Chem. Zentr., 1935, i, 2836).—Ergotamine reverses the pressor action of adrenaline, pituitrin, eserine, ephedrine, racedrine, strychnine,  $\text{NMe}_3$ , and  $\text{NH}_2\text{Bu}$ . Ethylurethane and chloral are without influence. A. G. P.

**Comparative study of sympathin and adrenaline.** W. B. CANNON and A. ROSENBLUETH (Amer. J. Physiol., 1935, 112, 268—276).—The effects of sympathin from different sources in the cat are compared with those of adrenaline (I) on physiological indicators. It is concluded that there are two sympathins, one excitatory and the other inhibitory; the latter differs from acetylcholine, and both differ from (I). R. N. C.

**Response of the hyperthyroid heart to adrenaline.** C. H. McDONALD, W. L. SHEPARD, M. F. GREEN, and A. F. DE GROAT (Amer. J. Physiol., 1935, 112, 227—230).—Prolonged thyroid feeding to terrapins increases the rate of  $\text{O}_2$  consumption in the isolated heart and the response of the rate of  $\text{O}_2$  consumption to adrenaline. R. N. C.

**Action of the hormone of adrenal cortex on the glycogen content of the liver.** H. A. HOCHFELD (Biochem. Z., 1935, 282, 392—398).—In rats the glycogen content of the liver, after a 24-hr. fast, is progressively increased by administration of fat, of the hormone, and of fat + hormone. Possibly the hormone stimulates conversion of fat into carbohydrate. W. McC.

**Adrenaline and sugar content of foetal blood.** O. MACCHIARULO (Arch. Gynäkol., 1935, 159, 349—354).—Variable amounts of adrenaline (I) were detected in the blood and urine of infants following birth; comparable amounts were present 8 days later. There was no relationship between the sugar and (I) of the blood. (I) was present in the maternal blood several days before delivery and increased during labour. NUTR. ABS. (m)

**Tono-glycaemic index of adrenaline.** B. ENOCKSSON and A. GIERTZ (Acta med. Scand., 1934, 59, Suppl., 116—126).—There is a relation ("tono-glycaemic index") in normal men between the hyperglycaemic and pressor actions of adrenaline, injected subcutaneously. This is about 3 in normal men and about 7 in normal women. Its variability depends chiefly on that of the pressor effect. The

hyperglycæmic and pressor effects in women are respectively  $>$  and  $<$  those in men. The dissociation of the two effects becomes manifest in certain diseases; the index rises in hypertonia and asthma, and falls in jaundice. R. N. C.

**Adrenaline in the venom of *Bufo arenarum*.** V. DEULOFEU (Z. physiol. Chem., 1935, 237, 171—172).—0.18 mg. of adrenaline was isolated from 45 g. of the dried venom. W. McC.

**Effect of continuous injection of adrenaline on the ketone content of the urine.** A. BAUDOIN, H. BÉNARD, J. LEWIN, and J. SALLET (Compt. rend. Soc. Biol., 1935, 120, 860—862).—Urinary ketones in the dog are increased slightly by chloralose anaesthesia, and very considerably by continuous injection of adrenaline. The acidosis produced is  $<$  in diabetics. R. N. C.

**Inactivation of histamine in perfused organs.** F. R. STEGGERDA, H. E. ESSEX, and F. C. MANN (Amer. J. Physiol., 1935, 112, 70—73).—The kidneys and (less) the liver are most effective in inactivating histamine. R. N. C.

**Effect of dietary lipæmias on the insulin and adrenaline blood-sugar curves.** H. J. HAMBURGER (Klin. Woch., 1935, 14, 96—97).—The insulin blood-sugar curve in children fed with albumin paste containing cholesterol and pig's bile shows a fall  $>$  normal; the rise produced by adrenaline is weakened. R. N. C.

**Hypoglycæmic action of insulin in dogs with the pancreatic duct ligatured, and with or without secondary fatty degeneration of the liver.** E. AUBERTIN and E. CASTAGNOU (Compt. rend. Soc. Biol., 1935, 120, 1101—1104).—Ligature of the pancreatic ducts does not diminish the response to insulin in an otherwise healthy animal. Fatty degeneration of the liver causes a broadening of the blood-sugar curve, recovery being much slower. R. N. C.

**Hypoglycæmic action of insulin phosphotungstate and phosphotungstic acid administered by mouth.** H. N. MUKHERJEE (J. Physiol., 1935, 84, 362—366).—Insulin phosphotungstate suspension in phosphotungstic acid (I) solutions, or (I) alone, produces hypoglycæmia when administered to rabbits by mouth; the effect is apparently due to both constituents. R. N. C.

**Augmentation of the physiological response to insulin.** L. C. MAXWELL and F. BISCHOFF (Amer. J. Physiol., 1935, 112, 172—175).—The response to insulin in rats and rabbits is augmented by addition of basic  $\text{Fe}^{III}$  chloride to the insulin. R. N. C.

**Continuous injection of insulin in the dog: threshold dose by the intra-arterial and the mesenteric-intravenous routes.** A. BAUDOIN, J. LEWIN, and E. AZÉRAD (Compt. rend. Soc. Biol., 1935, 120, 865—866).—The threshold dose by either route is approx. 0.01 unit per kg. per hr. R. N. C.

**Effect of hypophysectomy and cerebral manipulation in the dog on the response of the blood-sugar and -inorganic phosphorus to insulin.** I. L. CHAIKOFF, F. L. REICHERT, P. S. LARSON, and M. E. MATHES (Amer. J. Physiol., 1935, 112, 493—

503).—The response of blood-sugar and -inorg. P to insulin is augmented to successively increasing extents by craniotomy, radial incision of the dura, retraction of the right temporal lobe, and complete hypophysectomy. R. N. C.

**Continuous injection of insulin in the dog. Threshold dose by the peripheral intravenous route.** A. BAUDOIN, E. AZÉRAD, and J. LEWIN (Compt. rend. Soc. Biol., 1935, 120, 769—771).—The threshold dose is about 0.05 unit per kg. per hr. R. N. C.

**Excretion of insulin by the dog.** J. A. SHANNON (Amer. J. Physiol., 1935, 112, 405—413).—The rate of insulin (I) excretion  $\propto$  plasma concn. of (I) between 0.013 and 0.565%. Intravenous injection of (I) does not affect the urea, xylose (II), or creatinine (III) excretion. The simultaneous excretion ratio of (III) and (I) is about 0.994. (II) excretion with moderate to high urine vols. is  $<$  the simultaneous (I) excretion (mean ratio 0.734). Phloridzin raises the glucose excretion to the level of that of (III) or (I), the excretion of (II) increasing to  $>90\%$  of that of (I). R. N. C.

**Reactions of ammonolysed parathyroid hormone.** R. G. ROBERTS, W. R. TWEEDY, and G. H. SMULLEN (J. Biol. Chem., 1935, 112, 209—214).—Parathyroid hormone (I) reacts as a typical protein with Na in liquid  $\text{NH}_3$ . The activity of (I) varies inversely with the liberation of the acidic  $\text{H}_2$ , and is diminished by the action of  $\text{NH}_3$  alone; it is not dependent on  $\cdot\text{S}\cdot\text{S}\cdot$  or any linkings readily reduced by Na- $\text{NH}_2$ . (I) has no prosthetic group (either with or without Fe) which catalyses the action of Na on  $\text{NH}_3$ . J. N. A.

**Action of small doses of parathyroid hormone on the magnesium of the organism.** M. COPPO and M. PISA (Z. ges. exp. Med., 1935, 95, 675—678; Chem. Zentr., 1935, i, 2390).—Total Mg and ash in the body of the rat are reduced by administration of 1 unit of parathormone (I) a day. The action of (I) on mineral metabolism probably results from its effect on Mg. R. N. C.

**Relation of contracture and tetany to experimentally-produced calcium deficiency in cats, with and without lesions of the cortical motor areas.** H. C. COOMBS, F. H. PIKE, and D. S. SEARLE (Endocrinol., 1935, 19, 421—431). R. N. C.

**Idiopathic hypoparathyroidism and tetany in the fowl.** F. B. HUTT and W. L. BOYD (Endocrinol., 1935, 19, 398—402).—A case is reported of a pullet with tetany and low blood-Ca, due to temporary idiopathic hypoparathyroidism. Parathormone, but not Ca gluconate, showed a curative effect. R. N. C.

**Depressor hormone as the origin of protein shock.** G. DE NITO (Deut. med. Woch., 1935, 61, 339—341).—Lymphoganglin (I), formed in the lymph glands, is considered to be the most important depressor factor of the animal organism. Injection produces effects characteristic of protein shock. Protein shock is probably due to (I) being discharged by the lymph glands on stimulation of the lymphatic

system by the foreign protein. A (I)-like substance can be extracted from plants. R. N. C.

**Existence of prosecretin.** V. B. SCOTT and E. U. STILL (Amer. J. Physiol., 1935, 112, 511—517).—Of the secretin (I) present in untreated duodenal mucosa one fraction is extracted by neutral 0.9% NaCl, and the other completely by acids, and partly by weak bases and aq. EtOH. (I) is present in the mucosa if digestive acids have been excluded. The prosecretin (II) theory of Bayliss and Starling is not considered to be entirely tenable; the acid-sol. (I) is probably held by adsorption on the protein mols., and, if (II) exists, by combination. R. N. C.

**Rôle of duodenal hormones (secretin) in carbohydrate metabolism.** J. LA BARRE (Bull. roy. Acad. Méd. Belg., 1934, 14, 469—486).—A lecture. R. N. C.

**Effect of lactogenic hormone preparations on the blood-sugar level of rabbits and monkeys.** W. O. NELSON, C. W. TURNER, and M. D. OVERHOLSER (Amer. J. Physiol., 1935, 112, 714—717).—Lactogenic hormone preps., believed to be relatively free from other pituitary hormones, do not affect blood-sugar in either species. R. N. C.

**Action of pituitrin on venous blood pressure.** V. I. VON GÖNCZY and J. KISS (Z. ges. exp. Med., 1934, 94, 400—404; Chem. Zentr., 1935, i, 2835).—In most cases the pressure is increased by injection of pituitrin. Negative results sometimes obtained are associated with a predominance of histamine-like substance in the pituitrin prep. A. G. P.

**Acetonuria after administration of the (pituitary) fat-metabolism hormone.** K. J. ANSELMINO and F. HOFFMANN (Z. ges. exp. Med., 1934, 94, 305—308; Chem. Zentr., 1935, i, 2835; cf. A., 1935, 411).—Administration of the hormone increased the  $\text{COMe}_2$ , AcOH, and  $\beta$ -hydroxybutyric acid contents of blood and urine. A. G. P.

**Erythrophore and melanophore hormone.** A. JORES and G. WILL (Z. ges. exp. Med., 1934, 94, 389—393; Chem. Zentr., 1935, i, 2690).—The melanophore hormone (I) is not identical with Zondek's erythrophore hormone (II). (I) is > (II) in the basophile section of the pre-pituitary, whilst in the anterior lobe the (I)/(II) ratio is inverted.  $\text{H}_2\text{O}$  extracts only a small quantity of (I) from pituitary powder, but the activity of the extract is increased considerably by treatment with alkali or contact with blood, suggesting that the extract contains an inactive precursor of (I). The (II) potency of the extract is weakened by this treatment. (II) is extracted completely, but (I) only partly, from the powder by repeated treatment with 0.6% NaCl. (II) is readily sol. in EtOH, but (I) only with difficulty. R. N. C.

**Melanophore hormone and adrenals.** A. JORES and H. BECK (Z. ges. exp. Med., 1934, 94, 293—299; Chem. Zentr., 1935, i, 2690).—The adrenal cortex is increased in size in rabbits or rats by injection of melanophore hormone (I). The adrenaline content is also increased. (I) may be identical with the corticotropic hormone. R. N. C.

**Influence of various hormones on spread of melanophores caused by posterior pituitary lobe extract.** H. MATSUDA (Folia Pharmacol. Japon., 1935, 19, 377—393). CH. ABS. (*p*)

**Effect of the thyrotropic hormone of the pituitary on blood-function.** S. THADDEA and A. WALY (Z. ges. exp. Med., 1934, 94, 359—369; Chem. Zentr., 1935, i, 2690). R. N. C.

**Comparison of the actions of the corticotropic hormone of the anterior pituitary in different species of animals.** K. J. ANSELMINO, L. HEROLD, and F. HOFFMANN (Z. ges. exp. Med., 1934, 94, 323; Chem. Zentr., 1935, i, 2690).—The hormone acts similarly on the adrenals in rats, guinea-pigs, rabbits, and mice. The growing male mouse is best suited for assay. R. N. C.

**Action of alkaline anterior pituitary extract on the mineral substances of the plasma.** R. GERSONMAN and A. D. MARENZI (Compt. rend. Soc. Biol., 1935, 120, 817—820).—In normal and thyroidectomised dogs the extract evokes an increase of total plasma- $\text{CO}_2$ , sugar, Ca, Mg, and inorg. P, and a fall of Cl and Na. The Ca increase appears in hypophysectomised, but not thyro-parathyroidectomised, dogs. R. N. C.

**Cows' milk as a possible excretory source of the anterior pituitary-like hormone.** A. I. WEISMAN, I. S. KLEINER, and E. ALLEN (Endocrinol., 1935, 19, 395—397).—The hormone is absent from pregnancy milk. R. N. C.

**Influence of pituitary growth-hormone on the phosphatase activity of bone and kidney.** W. E. WILKINS, J. A. CALHOUN, C. PILCHER, and E. M. REGEN (Amer. J. Physiol., 1935, 112, 477—480).—The phosphatase activity of the bones and kidney of the adult rat is slightly reduced. R. N. C.

**Growth-promoting hormone and tumour growth.** P. ENGEL (Z. Krebsforsch., 1935, 41, 488—496; Chem. Zentr., 1935, i, 2835).—The tumour-stimulating action of the pituitary growth-hormone is lowered by simultaneous injection of "prepitran," but not by that of gonadotropic hormone. The direct inhibitory action of the latter on tumour growth is due to its influence on metabolic changes. A. G. P.

**Action of posterior pituitary hormone on the blood-sugar of the rabbit.** H. C. ELLSWORTH (J. Pharm. Exp. Ther., 1935, 55, 435—438).—Pitressin increases blood-sugar in very high doses only; pitocin is without effect. R. N. C.

**Posterior pituitary and carbohydrate metabolism.** F. HÖGLER and F. ZELL (Wien. Arch. inn. Med., 1935, 27, 141—158).—In rabbits the posterior pituitary hormone affects carbohydrate metabolism. Tonephin acts on the liver cell, mobilising glycogen and raising blood-sugar. Hence injuries to the posterior pituitary may cause disturbances of carbohydrate metabolism. NUTR. ABS. (*m*)

**Chemistry of the pituitary gonadotropic hormone.** L. C. MAXWELL and F. BISCHOFF (J. Biol. Chem., 1935, 112, 215—221; cf. Wallen-Lawrence, A., 1934, 1039).—Partial or complete inactivation

of pituitary powder results from treatment with powerful oxidising agents and substances which react with  $\text{NH}_3$ ,  $\text{NH}_2$ , and  $\text{OH}$ , but mild oxidising and reducing agents have no effect. In 3 hr. at  $37^\circ$  0.1N-NaOH produces complete, whilst 0.033N-NaOH and 0.1N-HCl produce partial, inactivation. There is no evidence that the preps. contain two hormones, and  $\text{CH}_2\text{O}$ , although it produces inactivation, does not exert a selective destructive action.

W. McC.

**Prolan excretion in senility.** H. SAETHRE (Acta med. Scand., 1934, 59, Suppl., 440—442).—Prolan excretion is high in old women, but absent in girls of 13—15 years. Healthy men excrete about 5 mouse units per litre of urine, but elderly men almost as much as elderly women.

R. N. C.

**Effect of adrenals and pituitary on regulation of blood-pressure and inversion of the sex characters in man.** J. BAUER (Acta brev. Néerl. Physiol., 1934, 4, 157—161).—Theoretical.

R. N. C.

**Oxytocic properties of blood extracts and their physiological significance.** G. H. BELL and J. M. ROBSON (J. Physiol., 1935, 84, 351—361).—Oxytocic activity has been found in a no. of extracts from the blood of pregnant cows, women in labour, and rabbits before and after injection of posterior pituitary extract. The extracts also contain a factor inhibiting the reaction of the uterus to oxytocin *in vitro*; this activity increases on keeping.

R. N. C.

**Chemistry of oestrogenic substances.** J. W. COOK, E. C. DODDS, and F. L. WARREN (Nature, 1935, 136, 912—913).—Previous work is confirmed (cf. A., 1935, 1033, 1173).

L. S. T.

**Pineal gland and gonadotropic hormone.** P. ENGEL (Z. ges. exp. Med., 1934, 94, 333—345; Chem. Zentr., 1935, i, 2692).—The extract from  $\text{CO}_2$ -dried pineal powder with 0.5% alkali acts antagonistically to the gonadotropic hormone (pre-pitan).

R. N. C.

**Rate of disappearance and fate of mare's gonadotropic hormone following intravenous injection.** H. R. CATCHPOLE, H. H. COLE, and P. B. PEARSON (Amer. J. Physiol., 1935, 112, 21—26).—The hormone (I) after injection in large quantities in the rabbit and gelding disappears from the blood without being excreted or stored. The rate of disappearance in the gelding is  $>$  in the pregnant mare. Castration of the rabbit does not affect the rate of disappearance of (I). Thus (I) is not prolan, which is excreted in the urine.

R. N. C.

**Influencing of the time of coagulation of blood by the sex hormone and its variation in hormonal hermaphroditism and experimental sex changes.** E. LUNDBERG (Acta med. Scand., 1934, 59, Suppl., 432—438).—Injection of folliculin in growing female rabbits shortens the time of coagulation of the blood by approx. 50%; the effects appear 1—2 hr. after injection, and persist for  $>$  24 hr. In man the time is shortened by approx. 20%. There is little reaction in young female animals, and none in infants.

R. N. C.

**Hormones of the corpus luteum.** E. JARLÖV (Acta med. Scand., 1934, 59, Suppl., 438—440).—Corner's corpus luteum extract is adsorbed on excess of kieselguhr and the powder exhaustively extracted with  $\text{H}_2\text{O}$ . The extract, which should contain only folliculin (I), exhibits an action ("pre-pregnancy reaction") on the rabbit's uterus. Pure (I) preps. give the reaction only at certain places in the uterus.

R. N. C.

**Crystalline by-product obtained in large-scale extraction of theelin and theelol.**—See this vol., 214.

**Presence, in the urines of certain women, of a substance antagonistic to the oestrous hormones.** A. DURUPT, J. LAGARDE, and P. BREGOUT (Compt. rend. Soc. Biol., 1935, 120, 852—853).—The antagonistic substance appears in the urine of dysmenorrhoeics.

R. N. C.

**Standardisation of sex-stimulating substances: therapeutic efficiency.** E. LAQUEUR (Klin. Woch., 1935, 14, 339—341).—The min. dose of ketohydroxy-oestrin (I) necessary to produce "heat" in the castrated rat is 10—16 times that necessary for mice, whilst the rat unit of oestradiol monobenzoate (II) is 4 times the mouse unit. Hence the rat is 4—5 times as sensitive to (II) as to (I); in mice the two substances are equally potent.

R. N. C.

**Effects of the oestrogenic and the galactopoietic hormones on the mammary gland of the rabbit.** W. U. GARDNER, E. T. GOMEZ, and C. W. TURNER (Amer. J. Physiol., 1935, 112, 673—683).

R. N. C.

**Effect of injection of residual ovarian extracts.** H. W. MARLOW and F. GROETSEMA (Endocrinol., 1935, 19, 415—420).

R. N. C.

**Inhibition of thyroid activity by the follicular hormone (menformone).** J. G. HEYL, S. E. DE JONGH, and R. KOOR (Acta brev. Néerl. Physiol., 1934, 4, 126—127).

R. N. C.

**Inhibition of the oestrogenic effect of follicular hormone by progestin.** P. DE FREMERY, S. KOBER, and M. TAUSK (Acta brev. Néerl. Physiol., 1934, 4, 119—121).—The effect of the min. oral dose of oestrin in spayed mice is inhibited by 3 rabbit units of progestin injected simultaneously.

R. N. C.

**Isolation of folliculin and equilenin by chromatographic adsorption.** R. DUSCHINSKY and E. LEDEKER (Bull. Soc. Chim. biol., 1935, 17, 1534—1539).— $\alpha$ -Folliculin (I) is readily isolated from the  $\text{C}_6\text{H}_6$  extract of pregnant mares' urine after adsorption on  $\text{CaCO}_3$ ; with  $\text{Al}_2\text{O}_3$ , (I) and equilenin (II) are adsorbed, (II) being isolated as picrate.

A. L.

**Equilin prepared from pregnant mare urine.** G. F. CARTLAND and R. K. MEYER (J. Biol. Chem., 1935, 112, 9—14).—Equilin (I) prepared by Girard's method and further recrystallisation from EtOH has m.p. 238—240°,  $[\alpha]_D^{25} +331^\circ$  in EtOH. Assayed biologically in 10% aq. EtOH + 0.5%  $\text{Na}_2\text{CO}_3$ , the product has approx. 75% of the activity of standard theelin (II); assayed without the addition of  $\text{Na}_2\text{CO}_3$  its biological activity is only 30% that of (II). Colorimetrically (cf. A., 1935, 791) (I) has approx. 11% o

the val. of (II); this val. is not altered during the final recrystallisations. F. A. A.

**Difference between "male hormone" extracts from urine and from testicles in hypophysectomised rats.** J. FREUD (Acta brev. Néerl. Physiol., 1934, 4, 145—147).—The response of the seminal vesicles, ventral prostate, and periurethral tissue in hypophysectomised rats to testicle extracts is considerably > to male urine extracts. The "male hormone" of the testicle extracts is considered therefore to be different from that of the urine, or to be associated with some "co-substance" which acts synergistically. R. N. C.

**Use of gonadotropic hormones in the treatment of imperfectly-migrated testes.** A. W. SPENCE and E. F. SCOWEN (Lancet, 1935, 229, 1335—1338). L. S. T.

**Enzymic determination of vitamins.** F. PIRORONE (Annali Chim. Appl., 1935, 25, 292—309).—The action of solutions of vitamin-A, -B, -C, and -D, of known biological activity, on the alcoholic fermentation of sucrose is studied by means of the CO<sub>2</sub> evolved. Acceleration of the fermentation (X) ∝ concn. of the vitamin. The vitamin units are given by the following expressions: for -A and -D,  $11.36 \times (X-100)+23$ ; for -B,  $0.0823(X-100)+2.34$ ; for -C,  $0.0625(X-100)+0.19$ . T. H. P.

**Absorption of carotene and vitamin-A.** J. C. DRUMMOND, M. E. BELL, and E. T. PALMER (Brit. Med. J., 1935, ii, 1208—1210).—The carotene (I) and vitamin-A (II) content of the chylous fluid of a patient suffering from an effusion of chyle into the thoracic cavity were studied before and after oral administration, on separate occasions, of (II) (0.125 mg. in 9 days) and (I) (100 mg. in 7 days). A rise of the level of both followed the administration, but, relative to the amount ingested, was much more marked in the case of (II). Little (I) and (II) could be extracted directly from the fluid with Et<sub>2</sub>O, but treatment with EtOH rendered (I) easily extractable. (II) was present as ester. NUTR. ABS. (m)

**Do the ascorbic acid contents of the organs of the rat vary according to the presence or absence of vitamin-A in the diet?** L. RANDOIN, A. GROUD, and C. P. LEBLOND (Compt. rend. Soc. Biol., 1935, 120, 1082—1085).—Ascorbic acid is high in the organs of the rat, the presence or absence of vitamin-A causing no important variations. R. N. C.

**Determination of vitamin-A in body-fluids.** E. ROSENTHAL (Klin. Woch., 1935, 14, 307; Chem. Zentr., 1935, i, 2554).—Wendt's method gives uncertain results. The author's colour test (A., 1934, 1145, 1413) is suitable for sera and other body-fluids. A. G. P.

**Determination of vitamin-A by means of its influence on the vaginal contents of the rat.** K. H. COWARD, M. R. CAMDEN, and E. M. LEE (Biochem. J., 1935, 29, 2736—2741).—The disappearance of keratinised cells from the vaginal smears of rats deficient in vitamin-A on feeding -A is used as a basis for the assay of -A. Results are rather less accurate than by the growth response method. H. D.

**Antineuritic vitamin. IV.** A. WINDAUS, R. TSCHESCHE, and R. GREWE (Z. physiol. Chem., 1935, 237, 98—104; cf. A., 1934, 1415).—Oxidation with BaMn<sub>2</sub>O<sub>8</sub> of the sulphate of the vitamin, removal of Ba, SO<sub>4</sub><sup>2-</sup>, and Mn oxides from the solution, concn. in a vac., and treatment with picrolonic acid yields the picrolonate (I) of a base (II), C<sub>6</sub>H<sub>10</sub>N<sub>4</sub> (probably 5:6-diamino-2:4-dimethylpyrimidine) [hydrochloride (III), m.p. 265° (decomp.); picrate, m.p. 224.5° (decomp.)]. The liquors from (III) yield a second base, subliming at 110—120°/13 mm. (hydrochloride, m.p. 224°), probably the Ac derivative of (II). The liquors from (I) yield two cryst. fractions, m.p. 180° and 225°, of acidic character, containing N but free from S and Cl. The structure of vitamin-B<sub>1</sub> is discussed. F. O. H.

**Consumption of the antineuritic factor in the oryzanin feeding of different birds.** G. MARTINO (Boll. Soc. ital. Biol. sperim., 1935, 10, 300—302; cf. A., 1934, 460, 706). R. N. C.

**Is lactic impregnation of the tissues the true cause of avian polyneuritis?** R. LECOQ (Compt. rend. Soc. Biol., 1935, 120, 958—961).—Addition of lactic acid to the diet increases the vitamin-B requirements of the pigeon, and the normal protective doses of yeast for polyneuritis are no longer effective. R. N. C.

**Isolation of pyruvic acid from the blood of vitamin-B<sub>1</sub>-deficient pigeons.** R. E. JOHNSON (Biochem. J., 1936, 30, 31—32).—AcCO<sub>2</sub>H has been isolated as the 2:4-dinitrophenylhydrazone from the blood of vitamin-B<sub>1</sub>-deficient pigeons. AcCHO is not present. J. N. A.

**Content of vitamin-B<sub>1</sub> in (A) germinating wheat, (B) Italian wheats.** V. FAMIANI (Atti R. Accad. Lincei, 1935, [vi], 22, 84—85, 86—88).—(A) The vitamin-B<sub>1</sub> content of wheat tends to increase during germination.

(B) Data for 8 varieties are given. F. O. H.

**Gastro-intestinal symptoms of vitamin(-B) deficiency.** E. SCHRÖDT (Acta med. Scand., 1935, 84, 456—495). R. N. C.

**Extraction and stabilities of vitamin-B<sub>1</sub> and of lactoflavin.** B. BISBEY and H. C. SHERMAN (J. Biol. Chem., 1936, 112, 415—420).—Vitamin-B<sub>1</sub> is almost completely extracted from dried milk by 80% EtOH but scarcely at all by abs. EtOH; about half of the lactoflavin is extracted by 80% EtOH, the remainder being found active in the residue. H. D.

**Lactoflavin (vitamin-B<sub>2</sub>).** R. KUHN (Angew. Chem., 1936, 49, 6—10).—A lecture.

**Growth-promoting activity of *l*- and *d*-araboflavin [6:7-dimethyl-9-*l*-(or *d*-)1'-arabitylisoalloxazine].** H. VON EULER, P. KARRER, and M. MALMBERG (Helv. Chim. Acta, 1935, 18, 1336—1338; cf. A., 1935, 1286).—Growth in rats given 10—40 × 10<sup>-6</sup> g. daily doses of *l*-araboflavin (*ibid.*, 1134) ceases after 30—40 days, and even with the latter dose no const. growth-promoting activity is observed. Doses of 10 × 10<sup>-6</sup> g. of *d*-araboflavin produce a const. wt. increase of 0.8 g. per day over the period of observation (50 days). Doses of 10 × 10<sup>-6</sup> g. of *l*-riboflavin

and  $3 \times 10^{-6}$  g. of the *d*-form produce wt. increases of 1.3 g. and 0.9 g. per day, respectively. The synthetic stereoisomeride thus exhibits higher growth-promoting activity than does natural lactoflavin, although it differs only in the stereoisomerism of one OH in the sugar residue.  
J. W. B.

**Vitamin- $B_2$  complex.** Differentiation of anti-blacktongue and "P.-P." factors from lactoflavin and vitamin- $B_6$  ("rat pellagra" factor). I—VI. T. W. BIRCH, P. GYÖRGY, and L. J. HARRIS (Biochem. J., 1935, 29, 2830—2850).—Data for the distribution of human pellagra-preventing ("P.-P.") factor (I), vitamin- $B_6$  ("rat pellagra" factor) (II), and lactoflavin (III) in various foodstuffs are tabulated. Rats fed on (I)-producing diets (A., 1929, 476) remain free from skin lesions; such diets cure (II)-deficiency disease. Hence rat pellagra is not analogous to human pellagra, rats having no need of, or being able to synthesise, (I). With maize diets (*ibid.*) containing (II), dogs develop "blacktongue," a condition rapidly cured by administration of autoclaved yeast, fresh fish, or anti-anæmia prep., but not of (III). The anti-blacktongue factor is therefore distinct from (II) and (III), but may be identical with (I). The "chicken pellagra" of Elvehjem and Koehn (A., 1935, 669) appears to be distinct from (II)-deficiency; its relation to human pellagra and blacktongue is not clear. The term "rat acrodynia factor" is proposed for (II). The extrinsic factor for pernicious anæmia (A., 1932, 1156) appears to be different from (II) or (III). Factors in the vitamin- $B_2$  complex are discussed.  
F. O. H.

**Maintenance nutrition in the pigeon.** Influence of dietary protein and vitamin- $B_3$ . C. W. CARTER and J. R. O'BRIEN (Biochem. J., 1935, 29, 2746—2754).—For the normal growth of pigeons a diet of polished rice plus vitamin- $B_1$  must be supplemented with protein and  $-B_3$  (liver concentrates).  
H. D.

**Maintenance nutrition in the pigeon.** Vitamin- $B_3$  concentrates. C. W. CARTER and J. R. O'BRIEN (Biochem. J., 1936, 30, 43—47).—A prep. containing vitamin- $B_3$  activity is obtained by extraction of liver with 97% EtOH, concn. and addition of Et<sub>2</sub>O, extraction with H<sub>2</sub>O, and addition of COMe<sub>2</sub>.  
H. D.

**"Enteral" vitamin- $I-B_7$ .** Behaviour of the vitamin towards primary alcohols. E. CENTANNI (Biochim. Terap. sper., 1935, 22, 137, 153).—The extract obtained from rice polishings with 95—100% EtOH, administered to pigeons on a diet of polished rice, did not protect from progressive emaciation ending fatally, but prevented digestive disturbances. The same extract, administered orally or intravenously, stimulated appetite markedly. The existence of an "enteral" vitamin ( $I-B_7$ ) regulating the digestive functions is therefore affirmed. MeOH (most effective), Pr<sup>o</sup>OH, Bu<sup>o</sup>OH, and C<sub>5</sub>H<sub>11</sub>·OH extracted the vitamin from rice polishings, in varying degree. The vitamin probably consists of several factors.  
NUTR. ABS. (m)

**Behaviour of the enteral vitamin towards solvents.** E. MONTEVECCI (Biochim. Terap. sper., 1935, 22, 143).—The vitamin is insol. in fat solvents,

but sol. in 95% EtOH, which does not extract the antineuritic and growth-promoting vitamins. With 70% EtOH, the last two are completely, the first partly, extracted from rice polishings.

NUTR. ABS. (m)

**Synthesis of ascorbic acid in the tissues *in vitro*.** M. LAPORTA and E. RINALDI (Boll. Soc. ital. Biol. sperim., 1935, 10, 319—322).—Minced animal tissues in Ringer-Locke solution at  $p_H$  7.38 in presence of sugars, or their H<sub>2</sub>O or glycerol extracts, show no definite increase in their ascorbic acid content; the results of Guha and Ghosh (cf. A., 1935, 416) are not confirmed.  
R. N. C.

**Cellular fixation and non-fixation of ascorbic acid in dystrophies from avitaminosis-C.** G. MOURIQUAND and A. COEUR (Compt. rend. Soc. Biol., 1935, 120, 1007—1009).—The Giroud-Leblond reaction after administration of ascorbic acid in avitaminosis-C is negative in certain cases.  
R. N. C.

**Effect of thyroxine on vitamin-C metabolism.** J. MOSONYI (Z. physiol. Chem., 1935, 237, 173—177; cf. Demole *et al.*, A., 1935, 1423).—In guinea-pigs (but not in rats) administration of thyroxine or extract of thyroid gland markedly decreases the ascorbic acid (I) content of the adrenals and slightly decreases that of the liver. Simultaneous administration of vitamin-A counteracts the effect. In rats extirpation of the thyroid gland increases the (I) content of the adrenals (but not that of the liver), apparently due to increased synthesis in the adrenals.  
W. McC.

**Seasonal variation in vitamin-C content of the organism.** F. IPPEN (Schweiz. med. Woch., 1935, 66, 431—432).—In healthy people receiving 200 ml. of orange juice by mouth or 0.1 g. of ascorbic acid orally or intravenously the urinary excretion of vitamin-C (I) showed a max. in all cases after 1 hr. Low curves are held to indicate a (I) deficit in the organism.  
NUTR. ABS. (m)

**Polyploidy and vitamin-C.** F. W. SANSOME and S. S. ZILVA (Biochem. J., 1936, 30, 54—56; cf. A., 1934, 227).—There is no evidence that the ascorbic acid content of tomatoes is conditioned by their size (McHenry, A., 1935, 1287).  
H. D.

**Effect of incomplete diets on concentration of ascorbic acid in the rat's organs.** Identity of ascorbic acid and the reducing agent of rat's gut. F. G. HOPKINS [with B. R. SLATER and G. A. MILLIKAN] (Biochem. J., 1935, 29, 2803—2819).—With rats on a normal mixed diet, the concn. of ascorbic acid (I) in liver and gut is 0.26 mg. per g. After a 48-hr. fast, the level in the gut rises to 0.40 mg., whilst that in the liver is unaffected. With diets of carbohydrate (II) alone, the concn. of (I) in the liver rises to 0.33 mg., whilst that in the gut remains normal; with protein+fat or fat alone, the liver and gut vals. are 0.19 and 0.37 mg., respectively. Diets of protein+(II) or of fat+(II) produce no significant effect. Determination of the velocity of reduction of 2:6-dichlorophenol-indophenol indicates the identity of the reducing agent in CCl<sub>3</sub>·CO<sub>2</sub>H extracts of rat's gut with (I). The bimol. coeff. of reduction



is unaffected over a considerable range of concn. of (I) and dye (cf. A., 1934, 1145). F. O. H.

**Reversible oxidation of vitamin-C in biological media.** N. BEZSSONOFF and M. WOLOSZYN (Compt. rend. Soc. Biol., 1935, 120, 893—895).—Vitamin-C (I) forms a reversible oxidation-reduction system with its oxidation product, which contains no dienolic group and is probably dehydroascorbic acid (II).  $E_h \propto$  the (I) concn., the variation being due to considerable ionisation differences between (I) and (II). The characteristic reducing agents of biological media increase the stability of the system and modify the properties of (I) from those observed in pure solution. R. N. C.

**Oxidation-reduction processes in experimental deficiency. I. Alteration of capacity of tissues to reduce 2:6-dichlorophenol-indophenol in avian heriberi.** M. MITOLO (Arch. Fisiol., 1934, 34, 102).—The capacity of tissues to reduce the indophenol is diminished in all organs, and particularly in the lungs and intestine. NUTR. ABS. (m)

**Variations of the power of vitamin-C in biological media to decolorise dichlorophenol-indophenol.** N. BEZSSONOFF and M. WOLOSZYN (Compt. rend. Soc. Biol., 1935, 120, 890—892).—The results obtained by dichlorophenol-indophenol titration of urine, milk, and cerebrospinal fluid to which known quantities of ascorbic acid have been added are untrustworthy. R. N. C.

**Reeds as a source of vitamin-C.** S. BALACHOVSKI (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 270).—Leaves of the common reed (*Phragmites communis*) contain up to 0.2% of ascorbic acid. Anaerobic treatment of an aq. extract with lactic bacilli resulted in an increased reducing power. P. G. C.

**Vitamin-C (ascorbic acid) content of [East] Indian fruits.** J. P. SPRUYT and W. F. DONATH (Geneesk. Tijds. Nederl.-Indie, 1935, 75, 1944—1950).—The ascorbic acid content of various fruits was determined by the 2:6-dichlorophenol-indophenol titration method, both before and after treatment with  $H_2S$ . Addition of  $Hg(OAc)_2$  has no effect on the result. *Capsicum annum* (0.07—0.25%) and the banana (0.04—0.15%) have the highest vitamin-C contents. S. C.

**Origin of the vitamin-C in the organs of rats fed on vitamin-C-free diets.** H. VON EULER, C. GARTZ, and M. MALMBERG (Biochem. Z., 1935, 282, 399—405; cf. Guha *et al.*, A., 1935, 131).—*In vitro* rat's liver and brain do not convert mannose (I) into ascorbic acid. Brain- and liver-hexosedehydrase, after addition of cozymase (II), dehydrogenate (I) and glucose. The (II) of the liver undergoes rapid spontaneous destruction. W. McC.

**Vitamin-C in invertebrates.** A. GIROUD and R. RATSIMAMANGA (Compt. rend. Soc. Biol., 1935, 120, 763—765).—Vitamin-C (I) is high in the hepatopancreas and sex glands of invertebrates, low in the muscles, and scarcely detectable in the intestine and gills. The ovaries of *Pecten maximus*, which contain a carotenoid, contain more (I) than the carotenoid-free testicles. R. N. C.

**Ascorbic acid content of certain organs of chicks raised on vitamin-C-deficient ration.** H. C. HOV (Science, 1935, 82, 423).—Chicks fed on such a diet, with or without ultra-violet irradiation, showed a high ascorbic acid (I) content in the adrenals, intestine, and intestinal mucosa; pancreas and kidney had approx. one third of the content of the liver or intestine, whilst muscle contained none. Part of (I) appeared to be excreted through the intestinal wall to the lumen. L. S. T.

**Examination of the cerebrospinal fluid for the detection of hypovitaminosis-C.** F. PLAUT and M. BÜLOW (Klin. Woch., 1935, 14, 276—277).—Young patients on a vitamin-C-deficient diet exhibit a low -C content of the cerebrospinal fluid. -C falls in old age. R. N. C.

**Reduction of 1-phospho-18-tungstic acid by ascorbic acid.** M. LAPORTA (Boll. Soc. ital. Biol. sperim., 1935, 10, 318—319).—Ascorbic acid and reductone are the only substances that reduce 1-phospho-18-tungstic acid (I) in the cold to any considerable extent; in neutral or alkaline solution it is reduced by many other substances. With org. liquids containing vitamin-C the intensity of the blue colour  $\propto$  -C content. The reduction is quantitatively reversible, and (I) can be determined by titration of the reduced (I) with 2:6-dichlorophenol-indophenol or I. R. N. C.

**Reactions of vitamin-C.** E. PITTARELLI and M. PITTARELLI (Biochem. Terap. sper., 1935, 22, 100).—Three reactions are described for the identification of ascorbic acid, based on the reduction of  $Fe(CNS)_3$ ,  $Cu(CNS)_2$ , and  $HgCl_2$ . The first and last might be used quantitatively. NUTR. ABS. (m)

**Determination of ascorbic acid.** M. VAN EEKELLEN and A. EMMERIE (Biochem. J., 1936, 30, 25—27).—In determining the ascorbic acid content of various substances and fluids by the  $Hg(OAc)_2$  method the extract must be made with  $CCl_3 \cdot CO_2H$ , and the  $Hg(OAc)_2$  added at  $p_H$  5, an excess being avoided. The time between the pptn. and passage of  $H_2S$  must be  $>$  5—10 min. Other methods are criticised. J. N. A.

**Conditions for the silver nitrate reaction as a test for ascorbic acid.** A. GIROUD, C. P. LEBLOND, R. RATSIMAMANGA, and M. RABINOWICZ (Compt. rend. Soc. Biol., 1935, 120, 967—968). R. N. C.

**Provitamin-D from plant and animal sources.** R. M. BETHKE, P. R. RECORD, and O. H. M. WILDER (J. Biol. Chem., 1935, 112, 231—238; cf. Waddell, A., 1934, 1043).—In chicks, irradiated cholesterol (I) is more efficacious in preventing rickets than is irradiated ergosterol (II) and calciferol (III), irradiated (II) and (III) being equally efficacious. Irradiated (I) is as potent as is cod-liver oil. Since equiv. rat units of vitamin-D (IV) from irradiated animal products (hog-brains, butter, lard) are more efficacious than (IV) from irradiated plant products (cottonseed oil, wheat middlings, lucerne leaf meal, yeast, fungus mycelium), it follows that the pro-(IV) of animal is not identical with that of plant products. The (IV) efficiencies of irradiated products from higher and lower plants are equal. W. McC.

**Vitamin-D content of egg yolk. II. Influence of various sources of vitamin-D on the antirachitic value. III. Antirachitic value of market eggs.** H. D. BRANION, T. G. H. DRAKE, and F. F. TISDALL (U.S. Egg and Poultry Mag., 1934, 40, No. 8, 22, 23, 58; No. 9, 22, 23, 52, 54).—Egg yolks are a good source of the antirachitic vitamin. Addition of 1% of cod-liver oil to the ration of hens increased the antirachitic potency of yolks 6–8 times. Large quantities of irradiated ergosterol (I) are transferred to the yolk with relative inefficiency. Small doses of (I) are transferred to the yolk as efficiently as is cod-liver oil. Ultra-violet irradiation of the birds, or exposure to sunshine during summer, causes only slight increase in the antirachitic val. of the eggs. Cold-storage for 8–11 months has little or no effect on the vitamin-D content of the eggs. NUTR. ABS. (m)

**Effect of vitamin-D on the calcium content of dentine.** E. W. FISH (J. Physiol., 1935, 84, 272–278).—Max. doses of vitamin-D administered with CaCO<sub>3</sub> to dogs over long periods do not affect the Ca content of the dentine. Blood-Ca and the opacity of the bones to X-rays are increased, and new deposits of highly-calcified bone matrix are produced. R. N. C.

**Comparative antirachitic efficiency of irradiated milk, yeast milk, and cod-liver oil.** R. M. BETHKE, W. E. KRAUSS, P. R. RECORD, and O. H. M. WILDER (Proc. Amer. Inst. Nutrition, J. Nutrition, 1935, 9, No. 6, Suppl., 7).—Irradiated milk and cod-liver oil, fed to chicks, showed the same antirachitic potency, but the milk from cows fed on irradiated yeast had only about 10% of this val. When fed to rachitic infants, the two milks were equally efficient. NUTR. ABS. (m)

**Vitamin-D activity of cacao shell. I. Effect of fermenting and drying of cacao on the vitamin-D potency of cacao shell. II. Origin of vitamin-D in cacao shell.** A. W. KNAPP and K. H. COWARD (Biochem. J., 1935, 29, 2728–2735).—Vitamin-D is absent from the shell of the cacao bean dried in the dark, whether previously allowed to ferment or not; 21 I.U. per g. were found in that which had fermented and dried in the sun for 22 days. It is concluded that the occurrence of -D in the cacao bean is associated with the growth of ergosterol-producing yeast on it during fermentation. H. D.

**Use of purpurin as an indicator of the action of vitamin-D.** L. BUTTURINI (Boll. Soc. ital. Biol. sperim., 1935, 10, 215–217).—Purpurin colours the bone sections of rachitic rats whether or not vitamin-D is administered. R. N. C.

**Physiological system of products eliminated by plants.** A. FREY-WYSSLING (Protoplasma, 1935, 23, 393–409).—Secretions, excretions, and resorbed materials which are not subsequently assimilated ("recretions") are differentiated and their nature is discussed. A. G. P.

**Osmotic ratios of some Bengalese plants.** J. SEN-GUPTA (Ber. deut. Bot. Ges., 1935, 53, 783–795).—Cryoscopic determinations of the osmotic

pressure of saps of a no. of species from various localities and at different periods are recorded. A. G. P.

**Mechanism of salt absorption by plant cells.** (A) W. J. V. OSTERHOUT. (B) F. C. STEWARD (Nature, 1935, 136, 1034–1035, 1035).—Discussions. L. S. T.

**Intake of caesium by potato plants.** K. HELLER, K. PEH, and J. PINDUR (Z. Pflanz. Düng., 1935, 41, A, 36–37).—Addition of Cs salts to nutrient media for potatoes had no appreciable effect on the % of dry matter or of K, but increased the % of Cs in the plants. In higher proportions Cs tended to lower the total wt. of the plants. A. G. P.

**Incorporation of deuterium into growing organisms. II.** O. REITZ and K. F. BONHOEFFER (Z. physikal. Chem., 1935, 174, 424–434).—The experiments with green algæ (A., 1935, 661) have been continued, using water of higher D content. It has been possible to replace > half the H in the dry substance of the organisms with D without the algæ being killed. As the D content of the culture solution increases, the rate of growth of the algæ falls, and at a D content of 85–90% growth of *Scenedesmus acutus* ceases. After many days in culture solutions made with practically pure D<sub>2</sub>O, however, a considerable proportion of the organisms start to grow again if placed in water of lower D content. Under conditions where any growth by chlorophyll assimilation occurs the assimilation of D is only half as rapid as that of H. R. C.

**Isotope exchange in soya beans.** K. OKABE and T. TITANI (Bull. Chem. Soc. Japan, 1935, 10, 552–554).—The exchange of H in soya beans by D has been observed by leaving the beans in contact with dil. D<sub>2</sub>O. The exchange corresponds with a H<sub>2</sub>O content of 25%, whereas analysis gives 10%, probably because of the replacement in the beans of H other than those of H<sub>2</sub>O by D. R. S. B.

**Chlorophyll deficiencies in rice.** K. RAMIAH and S. RAMANUJUM (Proc. Indian Acad. Sci., 1935, 11, B, 343–368).—Genetic factors are examined. A. G. P.

**Action of electromagnetic short waves on the development of the plant embryo.** A. HERZUM (Magyar Orvosi Arch., 1934, 35, 392–395; Chem. Zentr., 1935, i, 2387–2388).—Exposure to short waves (12 m.) retards the growth of embryos of *Lupinus albus*. The action is sp. and increases with the period of exposure. The direct thermal effect is secondary. Brief exposure has a stimulative action. A. G. P.

**Hydrocyanic acid and nitrates in the germination of sorghum.** C. HAMANT (Compt. rend., 1935, 201, 1503–1505).—The total N in the grains, which contain an emulsin-like enzyme, is about 0.535%, of which about 0.046% is NO<sub>3</sub>-N. NO<sub>3</sub>-N of the germinating plant first increases and then decreases, the loss being found as HCN in a glucoside, formed exclusively in the plant, which also contains fructose and a hydroxybenzaldehyde as components. J. L. D.

**Occurrence of methoxyl, ethoxyl, and methylenedioxy-groups in substances of vegetable**

origin; mechanism of their formation by the plant. C. A. BROWNE and M. PHILLIPS (J. Washington Acad. Sci., 1935, 25, 517—524).—A theoretical discussion. Pictet's conception of the formation of OMe and CH<sub>2</sub>O<sub>2</sub> from CH<sub>2</sub>O in plants is inapplicable to *Penicillium*. The groups may be derived from hexoses by changes involving, in turn, hydrolysis, oxidation, reduction, and dehydration. Lignin, derived from carbohydrates, may be the precursor of many OMe-containing constituents of plants. A. G. P.

**Relationship between vitamin-A and plastids.** P. J. LAVERGNE (Compt. rend., 1935, 201, 1042—1044).—The plastids of the cells of *Elodea canadensis* and other plants give locally the SbCl<sub>3</sub> reaction for vitamin-A. W. O. K.

**Physiology of delayed germination in *Avena fatua*.** L. P. V. JOHNSON (Canad. J. Res., 1935, 13, C, 283—300).—Delayed germination is associated with a condition of the seed-coat tissues (brought about by post-fertilisation agencies) which restricts access of O<sub>2</sub> to the embryo. Normal germination may be restored by breaking the seed coat over the embryo or by soaking in 1—2% aq. KNO<sub>3</sub>. Exposure to artificially increased [O<sub>2</sub>] under germinating conditions had a stimulative effect. Treatment with pure O<sub>2</sub>, Et<sub>2</sub>O, or NaCNS produced irregular results. CH<sub>2</sub>Cl·CH<sub>2</sub>·OH and C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> were injurious. After-ripening probably induces changes in the seed coat which increase its permeability to O<sub>2</sub>. A. G. P.

**Chemical studies on methods of mulberry culture for young silkworms.** C. NAKASONE (Bull. Sericult. Japan, 1935, 8, 398). P. G. M.

**Concentration of cell sap of mulberry leaves.** Y. IMAMURA, K. KOIKE, and M. FURUYA (Bull. Sericult. Japan, 1935, 8, 396—397).—An investigation of cell sap concn. in different varieties by a method of plasmolysis. The concn. is lower in spring than in autumn. P. G. M.

**Atomic dynamics of plant growth.** G. HEVESY, K. LINDERSTRÖM-LANG, and C. OLSEN (Nature, 1936, 137, 66—67; cf. A., 1935, 1531).—Using radioactive P as indicator, it is found that the P atoms of maize leaves are present in a mobile state, and that during growth a continuous interchange of P occurs between different leaves. L. S. T.

**Action of follicular hormone on the growth of culture plants.** K. SCHARRER and W. SCHROPP (Biochem. Z., 1935, 281, 314—328).—The effects of increasing amounts (500—1000 mouse units) of cryst. preps. [both phenolic and the Na salt (I)], free from auxin but not completely free from equilin and hippulin, were investigated. With wheat, increased yields of grain and straw resulted, the effect being greater with (I). With rye and barley, the increases were within the limits of error except with 1000 units of (I). Positive results were not obtained with oats. With horse beans, 500 units led to an increase of 24% and 1000 units of 39% in the fruit, but the yield of straw was decreased. No significant effects were obtained with rape-seed or soya bean, but with sugar beet the yield was increased by 14%. This increase, however, affected only the dry substance wt., no increase in sugar or leaf being obtained. P. W. C.

**Developmental growth and the amino-acids.**  
I. *l*-Histidine. F. S. HAMMETT (Protoplasma, 1935, 23, 326—336).—*l*-Histidine (I) has no direct action on developmental growth, anabolism, or catabolism in *Obelia geniculata*. In concns. of *M*/31,000—21,000 (I) sustains the metabolic activity of maintenance. It is toxic in concns. > *M*/16,000. A. G. P.

**Influence of season on photosynthesis in the tropics.** B. N. SINGH and K. KUMAR (Proc. Indian Acad. Sci., 1935, 11, B, 437—456; cf. A., 1935, 794).—Seasonal variations are recorded in the intensity of assimilation of CO<sub>2</sub> by radish leaves of different ages under controlled conditions. Artificially increased illumination accelerates photosynthesis more effectively in winter than in summer. Summer rates of assimilation are increased by rise of temp. in the range 29—37°, but are not greatly affected by increases of [CO<sub>2</sub>]. The temp. coeff. of assimilation (21—31°) does not vary much from season to season, but at higher temp. ranges vals. are high in summer and low in winter. The chlorophyll content of leaves reaches max. during rains, is smaller, although still high, in winter, and is least in summer. The dry matter content and total leaf area in winter are > in summer. A. G. P.

**Role of potassium in the production of plant substance.** K. MAIWALD and A. FRANK (Z. Pflanz. Düng., 1935, 41, A, 8—28).—A discussion. A. G. P.

**Growth substance and cell division.** L. JOST (Ber. deut. Bot. Ges., 1935, 53, 733—750).—The response (elongation or division) of plant cells to growth substance (I) from various sources (bean sap, extracts of *Boletus edulis*) and of yeast preps. varies with the nature, position, age, and physiological condition of the cell, and with the concn. of (I) applied to it. Cell division may be induced by indolylacetic acid, and also by many unrelated substances, e.g., citric acid, NaCl, fructose. The possibility of the necessary presence of co-substances for the activity of (I) is discussed. The concn. of (I) necessary to cause cell division is approx. 1 in 10<sup>3</sup>—10<sup>4</sup>, whereas cell elongation is stimulated by 1 in 10<sup>7</sup>. A. G. P.

**Ascorbic acid (vitamin-C) and phytocarcinoma.** L. HAVAS (Nature, 1935, 136, 989; cf. A., 1935, 1431, 1548).—Injection of ascorbic acid into tomato plants increased the size of the tumours produced in them by *B. tumefaciens*. No marked change in *p<sub>H</sub>* of the sap of treated plants occurred. L. S. T.

**Pathological histology and phytochemistry of Psyllid yellows.** J. R. EYER (Phytopath., 1935, 25, 895).—Tissue surrounding feeding stylets of the potato psyllid nymph is examined. Sheath materials are of animal origin and contain chitosan and mucin. Surrounding tissue contains plant degradation products, arginine, tryptophan, and tyrosine. Diseased leaves and stems have abnormally high starch contents. The relationship between hexoses and starch in healthy plants is disturbed by the disease. Sucrose, the principal sugar of translocation, is absent or its formation is inhibited in diseased plants. A. G. P.

**Biochemical modifications in phytopathology. Disequilibrium of organic and mineral composition in parasite infections.** R. SALGUES (Compt. rend. Soc. Biol., 1935, 120, 780—782).—Fats, insol. carbohydrates (I), and ash in *Medicago lupulina*, L., are reduced during infection by *Septoria medicaginis*, Rob. and Desm., whilst proteins and sol. (I) are increased. Ca falls and P and K rise in the ash. The increase in sol. (I) is due to one of reducing sugars, whilst the fall in insol. (I) is due to disappearance of amyloids and hemicelluloses. R. N. C.

**Low-temperature masking of tobacco mosaic symptoms.** J. GRAINGER (Nature, 1936, 137, 31—32).—These symptoms are masked when the host plant is grown at a temp.  $< 11^{\circ}$  approx. L. S. T.

**Effect of tannic acid on infectivity of tobacco-mosaic virus.** H. H. THORNBERRY (Phytopath., 1935, 25, 931—937).—Inhibition of the virus by tannic acid (I) depends on the concn. of acid applied and the period of action. Removal of (I) by pptn. with gelatin or by ultrafiltration restores virus activity. Treatment of plants with (I) prior to inoculation inhibits infection to extents of the concn. of (I) used. When applied after inoculation, (I) in concns. of 0.01—10% has little effect on infection. A. G. P.

**Virus of tobacco mosaic. IV. Effects of different chemical agents on infectivity. V. Optimum hydrogen-ion concentration for purification by precipitation with lead acetate.** W. M. STANLEY (Phytopath., 1935, 25, 899—921, 922—930).—IV. Substances directly inactivating the virus are usually oxidising agents, protein precipitants, or agents inducing a change in  $[H^+]$  known to inactivate the virus. Prolonged action of  $HgCl_2$  in germicidal concns. did not affect the virus. In higher concns.  $HgCl_2$  affected purified virus preps. more markedly at  $p_H$  6—8 than at  $p_H$  3—5. The infectivity of the virus on *Phaseolus vulgaris* was increased by  $PO_4^{3-}$  buffers at  $p_H$  7.0, but on *Nicotiana* was unaffected or somewhat decreased. Charcoal completely adsorbed the virus from solutions, notably at  $p_H$  3—5.

V. The optimum  $p_H$  for pptn. by basic Pb acetate was 9.0, and for  $Pb(OAc)_2$ , 5.5. For elution from  $Pb(OAc)_2$  ppts. the optimum  $p_H$  was 7.0. A. G. P.

**Inhibiting influence of a virus on one of its mutants.** H. H. MCKINNEY (Science, 1935, 82, 463—464).—Tobacco plants inoculated with virus mixtures in which the extract of yellow mosaic is much  $>$  that of the common mosaic develop at first symptoms of the former, but ultimately show those of the latter. With plants having yellow mosaic reinoculation with the common mosaic eventually suppresses symptoms of the former. L. S. T.

**Toxicity of ethyl alcohol towards dried and germinating seeds.** S. LALLEMAND and S. LALLEMAND (Bull. Soc. Chim. biol., 1935, 17, 1509—1521).—The toxicity of EtOH towards germinating seeds of *Lens esculenta* is  $<$  that towards the dry seeds, although in the former case the EtOH concn. is greater. A. L.

**Biological distribution of metals.** H. RAMAGE (Nature, 1936, 137, 67).—Spectroscopic determin-

ations of various metals in apple seeds, india-rubber tree seeds, Brazil nuts, etc. are recorded and discussed. L. S. T.

**Influence of soil sand on the determination of radium in plants.** K. G. KUNASCHEVA and B. K. BRUNOVSKI (Trav. Lab. biogeochem. Acad. Sci. U.R.S.S., 1935, 3, 45—48).—The anomalously high Ra content of *Struthiopteris germanica* does not depend on the presence of a large amount of sand, which has no influence on the Ra content of plants. CH. ABS. (e)

**Iodine contents of Chinese marine algæ.** P. S. TANG and C. S. CHANG (Chinese J. Physiol., 1935, 9, 369—374).—The I content of 12 further species (cf. A., 1935, 1436) is determined. H. G. R.

**Mode of combination of acetic acid in ginkgo wood (*Ginkgo biloba*).** K. KÜRSCHNER (Cellulosechem., 1935, 16, 107).—Polemical against Tang *et al.* (this vol., 123). R. S. C.

**Fructose anhydride from the leaves of the barley plant.** H. K. ARCHBOLD and A. M. BARTER (Biochem. J., 1935, 29, 2689—2693).—An aq. extract of barley leaves yielded a fructose anhydride (or a mixture of anhydrides) which on hydrolysis yielded reducing sugar equiv. to 105% of the wt. of anhydride taken, of which 94% was fructose. The more sol. fractions had  $[\alpha]_D^{25} -27^{\circ}$  and were more readily attacked by invertase than the less sol., which had  $[\alpha]_D^{25} -37^{\circ}$ . J. N. A.

**Pectin of ramie bast.** F. EHRLICH and R. HAENSEL (Cellulosechem., 1935, 16, 97—107, 109—114).—This pectin is much "altered." It contains much cyclic tetragalacturonic (pectolic) acid as  $H_2O$ -insol. Ca salt and only small amounts of  $\alpha$ -D-galacturonic acid, whilst most of the  $H_2O$ -sol. portion is a non-cyclic digalacturonic acid bound to carbohydrates, which include a disaccharide, large amounts of D-galactose, and some L-arabinose and methylpentose (? D-fucose). R. S. C.

**Properties of kelp colloids.** G. B. RIGG and B. DUNSFORD (Proc. 5th Pacific Sci. Congr., 1934, 3, 2115—2121).—Colloidal preps. from *Nereocystis* were dialysed in collodion sacs. The solid matter in the initial and dialysed preps. averaged 0.079 and 2.4%, respectively. The respective  $p_H$  were 5.58 and 6.43. The dialysed preps. gave a flaky ppt. with electrolytes, but no ppt. on boiling. CH. ABS. (e)

**Unsaponifiable matter of algæ fats. I. Sterol.** K. SHIRAHAMA (J. Agric. Chem. Soc. Japan, 1935, 11, 980—984).—A sterol, "pervesterol," was isolated from various algæ and named. The const. given agree with those reported by Heilbron *et al.* for fucosterol (A., 1934, 1347). The sterol from *Chishima nori* could not be purified. P. G. M.

**Chemical investigation of the seeds of *Allanblackia klainei*, Pierre.** L. ADRIAENS (Mat. grasses, 1933, 25, 9961—9962; Chem. Zentr., 1935, i, 2911—2912).—The acids from the seed-fat are 62.5% saturated (mainly stearic acid) and 37.5% unsaturated

(almost wholly oleic acid). Fractional crystallisation of the fat from COMe<sub>2</sub> affords an *oleodistearin*, m.p. 43.9—44.5°, I val. 27.8. H. N. R.

African oil seeds.—See B., 1936, 66.

Wheat-germ oil.—See B., 1936, 67.

Essential oil from the rhizomes of *Cyperus rotundus*, Linn.—See B., 1936, 44.

Crystalline substance from the essential oil of *Lachnophyllum gossypinum*, Bge. V. V. VIJLAMS, V. S. SMIRNOV, and V. P. GOLMOV (J. Gen. Chem. Russ., 1935, 5, 1195—1204).—The oil contains β-pinene, camphene, and about 30% of a cryst. ester (I), CPr<sup>a</sup>:C:C<sup>c</sup>:C:CH:CH:CO<sub>2</sub>Me, m.p. 32.6—32.8°, which when hydrolysed with aq. NaOH yields a mixture of products, of which COMeBu<sup>a</sup>, *n*-valeric and maleic acids were identified. When heated at 100° with 50% HNO<sub>3</sub> (I) yields Pr<sup>a</sup>CO<sub>2</sub>H and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. Catalytic hydrogenation (Pd-C) of (I) affords CH<sub>2</sub>Me[CH<sub>2</sub>]<sub>7</sub>CO<sub>2</sub>Me. R. T.

Diterpene, from leaf- and wood-oil of *Sciadopitys verticillata*, S. and Z.—See this vol., 207.

Carotenoids from the anthers of *Lilium tigrinum*: antheraxanthin. P. KARRER and A. OSWALD (Helv. Chim. Acta, 1935, 18, 1303—1305).—Hydrolysis (NaOEt-EtOH) of the ligroin extract of the anthers affords a mixture of pigments separated by chromato-absorption from EtOH solution by Ca(OH)<sub>2</sub> into capsanthin, and *antheraxanthin*, C<sub>20</sub>H<sub>58(56)</sub>O<sub>3</sub>, m.p. 211° (corr.), which has absorption max. at 490.5, 460.5, and 428 mμ in CHCl<sub>3</sub>, and gives a blue colour (max. 587 mμ) with SbCl<sub>3</sub>. J. W. B.

New type of plant lipochrome. I. M. HELBRON, B. LYTGOE, and R. F. PIPHERS (Nature, 1935, 136, 989).—A pigment, *myoxanthin*, m.p. 117—118° (uncorr.), has been isolated from the unsaponifiable fraction of *Rivularia nitida*. Unlike other phyto-carotenoids, it exhibits only one absorption band (max. 488—490 mμ) in CS<sub>2</sub>, resembling astacene in this respect, but differing from it in other respects. No hypophasic xanthophylls were detected in *R. nitida*. L. S. T.

Plastid pigments of marsh dodder. G. MACKENNEY (J. Biol. Chem., 1936, 112, 421—424).—2—3 mg. of rubixanthin, 4—6 mg. of lycopene, and 20—25 mg. of γ-carotene per kg. of fresh wt. were isolated from *Cuscuta subinclusa* and *salina*; traces of chlorophyll were detected. H. D.

Hanfangchin B.—See this vol., 217.

Alkaloids obtained from jaborandi leaves.

Synthesis of pilocarpidine.—See this vol., 215.

Chemical investigation of the liana "Efiri." IV. E. CASTAGNE (Congo, 1935, I, 32—37; Chem. Zentr., 1935, i, 2828; cf. this vol., 133).—From the EtOH extract of the stem of *Trichlisia gillettii* are isolated two alkaloids, *trichlisine*, C<sub>16</sub>H<sub>31</sub>O<sub>10</sub>N, m.p. about 255—260° (decomp.), [α]<sub>D</sub> +116.66° in 0.5*N*-HCl, and *trichliseine*, C<sub>28</sub>H<sub>40</sub>O<sub>7</sub>N, m.p. 135°, [α]<sub>D</sub> +68.49° in 0.5*N*-HCl. H. N. R.

"Sotetsu" (*Cycas revoluta*, Thunb.). IV. Sotetsu-emulsin. K. NISHIDA (Bull. Chem. Soc. Japan, 1935, 10, 524—530).—Sotetsu seed contains

a glucoside of CH<sub>2</sub>O, which splits off CH<sub>2</sub>O under the influence of an emulsin (I) which is also present. The isolation of (I) is described. (I) effects complete hydrolysis of salicin, the optimum conditions being *p*<sub>H</sub> 5.1 and 55—60°; the unimol. coeff. for the reaction increases with time and the velocity α the amount of (I) used (cf. following abstract). J. W. B.

"Sotetsu" (*Cycas revoluta*, Thunb.). V. Sotetsu pollen. I. K. NISHIDA (J. Agric. Chem. Soc. Japan, 1935, 11, 143—148).—The pollen does not contain starch, protamine, or spermine. Free adenine and choline are present, 2.24 g. of the latter (as aurichloride) being obtained from 1 kg. of pollen. P. G. M.

Proteins of the cowpea (*Vigna sinensis*). W. H. ADOLPH and H. C. CHIANG (Chinese J. Physiol., 1935, 9, 347—353).—The protein has been fractionated into vignin (globulin A) 45, glutelin 25, albumin 15, globulin B 10, and globulin C 5%, and the distribution of N determined in each fraction by the Van Slyke method. H. G. R.

Artificial medium for epithelial cells and fibroblasts. L. E. BAKER (Compt. rend. Soc. Biol., 1935, 120, 932—934). R. N. C.

Air analysis apparatus. T. C. SHEN (Chinese J. Physiol., 1935, 9, 363—368). H. G. R.

Manometric device for gas analysis. B. N. SINGH and P. B. MATHUR (Current Sci., 1935, 4, 313—314).—A simplified apparatus alternative to that of Haldane for measuring the respiratory gaseous exchange in plants is briefly described. N. M. B.

Technique of toxicology. R. FABRE (Chem. Weekblad, 1935, 32, 691—697).—Various techniques used in the isolation of foreign substances from tissues (destruction of org. matter, electro-dialysis, extraction with solvents, etc.) are discussed. F. O. H.

Determination of protein-nitrogen.—See this vol., 219.

Determination of salicylates in body-fluids. L. E. ONTANEDA and A. V. J. FERLONI (Compt. rend. Soc. Biol., 1935, 120, 820—822).—Salicylates are determined as phenol in blood by Marenzi's modification of the method of Theiss and Benedict, and in urine by the method of Marenzi. R. N. C.

Determination of phenols in blood and urine. R. F. BANFI and A. D. MARENZI (Compt. rend. Soc. Biol., 1935, 120, 812—814).—More exact details are given for some of the steps in Marenzi's modification of the method of Theiss and Benedict. R. N. C.

Modification of Young's method for the determination of inositol in animal tissues. R. A. GREGORY (Biochem. J., 1935, 29, 2798—2802).—The method (A., 1934, 1246) is modified by replacing the COMe<sub>2</sub> extraction by dissolution of the tissue in 10% KOH followed by pptn. of impurities by ZnCl<sub>2</sub>. H. D.

Modification of the copper-lime technique for the separation and recovery of carbohydrates from biological fluids. R. M. ARCHIBALD (Trans. Roy. Soc. Canada, 1935, [iii], 29, V, 97—103).—A modification of the Van Slyke's CuSO<sub>4</sub>-Ca(OH)<sub>2</sub>

method for removing carbohydrates from solution is described which allows small quantities to be separated from urine and recovered in good yield. At most only a small fraction of the fermentable sugar originally present is converted into non-fermentable reducing material. W. O. K.

**So-called normal alcohol of the body.** R. N. HARGER and A. L. GOSS (Amer. J. Physiol., 1935, 112, 374—381).—Steam-distillates of fresh urine, blood, or minced tissues contain reducing substances. Any EtOH added to the fluid distils over in the first fraction of distillate, so that the reducing material of the second fraction cannot be EtOH. The difference between the reducing powers of the first and second fractions represents the normal EtOH of the tissue or fluid used, and is never  $> 0.3$  mg.-%; vals. are given for blood, urine, and certain tissues. The reducing substances of the first fraction of distillate are increased by storing the tissues in the refrigerator before distillation. R. N. C.

**Determination of thiocyanates in biological fluids by double distillation.** P. R. ORELLA (Anal. Farm. Bioquím., 1935, 6, No. 2, 41—51).—In this rapid modification of Chelle's method, the sample is distilled with 0.1N-H<sub>3</sub>PO<sub>4</sub> or -H<sub>2</sub>SO<sub>4</sub> to separate CN', and then aq. K<sub>2</sub>CrO<sub>4</sub> and dil. H<sub>2</sub>SO<sub>4</sub> are added to decompose CNS', liberating HCN, which is distilled separately. The HCN is collected in each case in NaOH and determined colorimetrically as Prussian-blue. CNS' was detected in human and horse's saliva and cow's milk, but not in human urine or human milk. No cyanides were found in any of these fluids. E. L.

**Rapid titrimetric determination of arsenic in biological material.** R. ALLCROFT and H. M. GREEN (Biochem. J., 1935, 29, 824—833).—Org. matter is destroyed with HClO<sub>4</sub> and HNO<sub>3</sub>, and As is distilled into aq. AgNO<sub>3</sub> as AsH<sub>3</sub> by addition of SnCl<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, and Zn. 88% of As added to various org. materials in concns. of 1.3 p.p.m. was recovered. H. D.

**Application of the nitro-sulpho-perchloric acid method in the destruction of organic matter for the toxicological determination of arsenic.** E. KAHANE and M. POURTOY (J. Pharm. Chim., 1936, [viii], 23, 5—22).—Loss of As by entrainment during distillation is more liable with As<sup>III</sup> than with As<sup>V</sup> and during wet destruction of org. matter the tendency for the formation of As<sup>III</sup> should be prevented by using excess of oxidising agent. In the H<sub>2</sub>SO<sub>4</sub>-HNO<sub>3</sub>-HClO<sub>4</sub> method (B., 1934, 380) this is attained by continuous addition of HNO<sub>3</sub> or HNO<sub>3</sub>-HClO<sub>4</sub>. Redistillation of the distillate is then unnecessary except as a precaution. E. H. S.

**Determination of chlorides in biological fluids by the use of adsorption indicators. Use of dichlorofluorescein for the volumetric micro-determination of chlorides in cerebrospinal fluids and blood-serum.** A. SAIFER and M. KORNBELUM (J. Biol. Chem., 1935, 112, 117—122).—The liquid is treated with EtOH-Et<sub>2</sub>O, an EtOH solution of dichlorofluorescein is added, and then

titrated with standard AgNO<sub>3</sub>. 1 mg. of NaCl can be rapidly determined with an error  $\pm 2\%$ .

J. N. A.

**Micro-methods for the determination of magnesium.** B. BASSANI and V. ZAMBOTTI (Boll. Soc. ital. Biol. sperim., 1935, 10, 261—263).—The presence of Zn in plasma and tissues introduces an error that may reach 2.5% in determinations of Mg by pptn. as MgNH<sub>4</sub>PO<sub>4</sub> (I) after ashing. ZnNH<sub>4</sub>PO<sub>4</sub> is pptd. at a lower  $p_{II}$  than (I), and either fails to redissolve on addition of excess NH<sub>3</sub>, or more probably is carried down or adsorbed by the pptd. (I), since there is no definite ratio between the total and pptd. Zn, and the amount of Zn pptd. increases with the Mg/Zn ratio.

R. N. C.

**Extraction of lead by means of diphenylthiocarbazono.**—See this vol., 179.

**Determination of potassium in organs and parts of organs.** H. WILLSTAEDT (Acta med. Scand., 1934, 84, 104—107; Chem. Zentr., 1935, i, 2860).—The sample is dried at 110° and ashed in presence of H<sub>2</sub>SO<sub>4</sub>. The ash is extracted with little H<sub>2</sub>O, and K determined by the method of Jendrassik and Szél.

J. S. A.

**Determination of small quantities of zinc.**—See this vol., 178.

**Spectrophotometric micro-determination of zinc in organic material.** J. DABROWSKI and L. MARCHLEWSKI (Biochem. Z., 1935, 282, 387—391).—After destruction of org. matter (cf. Ridge *et al.*, B., 1933, 858) the part of the ash sol. in HCl is freed from Cu by treatment with H<sub>2</sub>S, and the Zn, after pptn. as ZnS and dissolution in HCl, is repptd. with 8-hydroxyquinoline (I). The amount of (I) (and hence the Zn content) in the ppt. is determined spectrophotometrically after separating the components by dissolving in HCl.

W. McC.

**Determination of copper in organs.** Z. GRUZEWSKA and G. ROUSSEL (Compt. rend. Soc. Biol., 1935, 120, 934—936).—Cu is determined in organs after incineration by extraction of the ash with H<sub>2</sub>O, oxidation of Fe with HNO<sub>3</sub> and pptn. with excess of NH<sub>3</sub>, and pptn. of Cu with 1-nitroso- $\beta$ -naphthol in AcOH. The ppt. is ignited in presence of (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and Cu weighed as CuO. The Cu of rabbit liver remains in the insol. ash, Fe passing into the sol. fraction.

R. N. C.

**Determination of total phosphorus in organs and organic liquids.** I. Technique. S. FIANDACA. II. Technical observations and physiological values. S. FIANDACA and I. CAPIZZI (Boll. Soc. ital. Biol. sperim., 1935, 10, 183—185, 185—186).—I. The sample is incinerated with HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>, and Ca removed from the neutral solution with (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. P is pptd. as MgNH<sub>4</sub>PO<sub>4</sub>, which is washed with H<sub>2</sub>O, dissolved in 20% H<sub>2</sub>SO<sub>4</sub>, and N determined by the micro-Kjeldahl method.

II. Vals. obtained with solutions of Na<sub>2</sub>HPO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> + Na glycerophosphate oscillate between limits on either side of the calc. val. Vals. are given for the P of the blood and organs of the rabbit.

R. N. C.

