

# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

SEPTEMBER, 1935.

### General, Physical, and Inorganic Chemistry.

**Excitation of some spectral lines of hydrogen by electron impact.** A. A. KRUTHOF and L. S. ORNSTEIN (*Physica*, 1935, 2, 611—622).—The excitation functions of the singlet and triplet lines at 4634 and 4617 Å., respectively, and of the  $H_\beta$  and  $H_\gamma$  lines for direct excitation from mols., have been measured. Vals. for the probability of dissociation of  $H_2$  for different electron velocities are recorded.

H. J. E.

**Infra-red spectra of noble gases (10,500—13,000 Å.).** W. F. MEGGERS (*J. Res. Nat. Bur. Stand.*, 1935, 14, 487—497).—The first spectra of He, Ne, Ar, Kr, and Xe excited by uncondensed discharges in Geissler tubes have been explored between 10,500 and 13,000 Å. using Eastman I-Z plates. Most of the new lines found represent combinations of already established spectral terms, and thus confirm the structural analyses. Two missing 2s terms are revealed for Xe and possibly one new  $f$ -type term each for Ne and for Ar.

A. R. P.

**Absorption spectrum of metastable nitrogen molecules.** A. A. FROST and O. OLDENBERG (*Physical Rev.*, 1935, [ii], 48, 66—68).—The use of special equipment and plates failed to reveal the existence of any absorption spectrum.

N. M. B.

**Influence of the chemical medium on bands of the second positive group of nitrogen.** M. DUFFIEUX (*Compt. rend.*, 1935, 201, 197—198).—A discussion of the cause of the intensity distribution in the phosphorescence spectrum observed on interrupting a discharge in  $NO_2$ .

H. J. E.

**Excitation of the Végard-Kaplan bands by electronic bombardment of a mixture of argon and nitrogen.** R. BERNARD (*Compt. rend.*, 1935, 200, 2074—2076).—Measurements are recorded.

H. J. E.

**Effect of a magnetic field on the absorption bands of sulphur.** J. GENARD (*Compt. rend.*, 1935, 200, 1926).—The absorption bands of  $S_2$  between  $\lambda\lambda$  2800 and 3300 Å. became more intense in a field of 25,500 gauss. There was no change in the rotational structure or in the predissociation. Bands between  $\lambda\lambda$  3650 and 4000 Å., attributed to  $S_4$ , were uninfluenced by the field.

H. J. E.

**Intensity relations in chromium spectra.** J. S. V. ALLEN and C. E. HESTHAL (*Physical Rev.*, 1935, [ii], 47, 926—931).—Measured relative intensities, tabulated for 4 multiplets of Cr I and 8 multiplets of Cr II, deviate in some cases from those calc. for Russell-Saunders coupling; the deviations accord

with independent observations for the Fe group, and may be due to perturbing energy levels. Two multiplets in the septet system of Cr II are corr. for excitation, the corresponding temp. of the Cr are source being 4060° abs.

N. M. B.

**Low terms in Mn v and Fe vi.** I. S. BOWEN (*Physical Rev.*, 1935, [ii], 47, 924—925).—Classifications of about 50 additional lines in Mn v and 100 lines in Fe vi, including intercombination lines, arising from transitions between  $d^3$  and  $d^24p$  configurations, and term vals. deduced from them, are tabulated. Significant coincidences with lines in nebulae and novae are discussed.

N. M. B.

**Spectra of exploded filaments in the far ultra-violet and Schumann regions.** G. VAUDET and R. SERVANT (*Compt. rend.*, 1935, 201, 195—197).—Filaments of Fe, Cu, Al, and Zn were studied; spark lines were most prominent in the spectra.

H. J. E.

**Arc spectrum of copper in the infra-red.** C. C. KIESS (*J. Res. Nat. Bur. Stand.*, 1935, 14, 519—521).—In the infra-red range up to 12,000 Å. 30 new lines of Cu have been measured by the photographic method; all, except one, are accounted for as combinations between previously known terms of Cu I.

A. R. P.

**Spectra of zinc, cadmium, and mercury in the extreme ultra-violet.** L. BLOCH and E. BLOCH (*Compt. rend.*, 1935, 201, 137—139).—Data for Zn and Cd are recorded for the regions 478—425 and 550—500 Å., respectively. The spectra were excited in a high-frequency electrodeless discharge.

H. J. E.

**Absorption band spectrum of selenium.** T. E. NEVIN (*Phil. Mag.*, 1935, [vii], 20, 347—354).—A vibrational analysis for the heads due to  $Se^{80}Se^{80}$  is given. There is probably a change in the law of force between the nuclei at the level  $v'=20$ . An isotope effect was found, and the calc. and observed positions of the isotope heads agree satisfactorily.

A. J. M.

**Intensity distribution of spectral lines excited in molecular rays.** R. MINKOWSKI and H. BRUCK (*Z. Physik*, 1935, 95, 274—283).—Lines excited by electron collision with mol. rays are much sharper than any others, and are more useful for determining excitation functions.

A. B. D. C.

**Intensity distribution of the red cadmium line excited by electron collision with molecular rays.** R. MINKOWSKI and H. BRUCK (*Z. Physik*,



1935, 95, 284—298).—This line is complex, due to isotope effects. A. B. D. C.

**Regularities in the spectrum of iodine IV.** S. G. KRISHNAMURTY (Current Sci., 1935, 3, 610—611).—The spectrum of a condensed discharge at various stages of excitation reveals the interval  $6s^3P_1-^3P_2=8252.3\text{ cm}^{-1}$  together with all terms of the  $6p$  configuration. L. S. T.

**Ultra-violet fluorescence spectra of iodine vapour: McLennan bands.** F. DUSCHINSKY and P. PRINGSHEIM (Physica, 1935, 2, 633—644; cf. this vol., 800).—Data are recorded for the variations of intensity of the bands with  $\lambda$  of the exciting light. H. J. E.

**Hyperfine structure of europium.** H. CASIMIR (Physica, 1935, 2, 719—723).—Schüler and Schmidt's observations (this vol., 804) are explained on the assumption that the nucleus has a quadrupole electrical moment. H. J. E.

**Influence of an axial magnetic field on the discharge density in mercury vapour at low pressures.** L. V. MIRLAS (J. Tech. Phys. U.S.S.R., 1934, 4, 1522—1534).—With a heated cathode a strong concn. of the electron beam was observed. CH. ABS. (e)

**Characteristics of the Pb spectrum revealed by instantaneous spectrograms.** H. NAGAOKA and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1935, 11, 171—173; cf. this vol., 676).—For different ionised states, spectral features depending on the position and shape of the electrodes and the oscillation of the discharge are discussed. N. M. B.

**Interpretation of continuous absorption of hydrogen in stars of the first spectral types.** D. BARBIER, D. CHALONGE, and E. VASSY (Compt. rend., 1935, 200, 1730—1732).—A discussion. H. J. E.

**Spectrum analysis of the hot carbon star, R Coronae Borealis.** L. BERMAN (Astrophys. J., 1935, 81, 369—425).—From a detailed spectrum analysis the composition of the star's atm. is found to be C 69, H 27, N < 0.3, metals (chiefly Mg and Fe) 4%. A list of elements identified in the spectrum is given. L. S. T.

**Absorption continuum due to quasi-molecules of calcium in dwarf stars of type M.** B. LINDBLAD (Nature, 1935, 136, 67).—The presence of excited Ca mols. is inferred. L. S. T.

**Chromospheric emission in the wings of H and K.** A. D. THACKERAY (Astrophys. J., 1935, 81, 338—340).—Two lines due to  $\text{Nd}^+$  and  $\text{Ce}^+$  are identified. L. S. T.

**Nebular spectrum of Nova Herculis.** D. BELORIZKY (Compt. rend., 1935, 201, 191—193). H. J. E.

**Red rays of oxygen in the spectrum of the night sky.** J. CABANNES (Compt. rend., 1935, 200, 1905—1908).—Line  $\sin$  in the spectrum of O I were observed ( $^1S_0 \rightarrow ^3P_{0,1,2}$ ). In the luminous layer of the upper atm. O is in the at. state, and N in the mol. state. Intensity variations are discussed. H. J. E.

**Structure of the electric arc.** N. SZULC (Compt. rend., 1935, 201, 48—50; cf. A., 1934, 1051).—Spectroscopic observations are recorded for a C arc containing  $\text{BaCl}_2$  and  $\text{CaF}_2$ . Processes taking place in different parts of the arc are discussed. H. J. E.

**True and apparent width of spectral lines.** R. MINKOWSKI and H. BRÜCK (Z. Physik, 1935, 95, 299—301).—The true width is related to that observed with the Fabry-Perot interferometer. A. B. D. C.

**Relative temperature and pressure of gases in an electric arc.** G. RIGHINI (Physica, 1935, 2, 585—590).—Assuming the Boltzmann law to hold, vals. of temp. and pressure in different parts of the arc are calc. from intensity measurements of the (1,0) and (1,1) bands of the violet  $^2\Sigma \rightarrow ^2\Sigma$  group of CN. Temp. of 3800—4800° abs. were observed. H. J. E.

**Change of temperature with time in the alternating-current arc discharge.** D. T. J. TER HORST, H. BRINKMAN, and L. S. ORNSTEIN (Physica, 1935, 2, 652—668).—Temp. measurements, based on intensity determinations for the violet CN band spectrum, are recorded as a function of phase for frequencies of 50—500 per sec. Ornstein and Brinkman's theory is supported (A., 1934, 1052). H. J. E.

**Hyperfine structure formulæ for the configuration  $p^3s$ .** M. F. CRAWFORD and L. A. WILLS (Physical Rev., 1935, [ii], 48, 69—72).—Mathematical. N. M. B.

**X-Ray wave-lengths by the plane-grating vacuum spectrograph, and the structure of the K line of carbon.** D. P. R. PETRIE (Proc. Physical Soc., 1935, 47, 626—643).—In the range 10—100 Å., experimental conditions do not justify the superior resolving power of a concave grating. A plane-grating spectrograph was designed for high-precision relative  $\lambda$  measurements; dispersion and resolving power are calc., and a no. of measurements relative to  $\text{Cu } L\alpha_{12}$  (13.310 Å.) are reported. Microphotometer curves show that the C K line has two additional components of shorter  $\lambda$ . N. M. B.

**Effect of chemical combination on the  $K\beta_1$  lines of sulphur, chlorine, and potassium.** J. VALASEK (Physical Rev., 1935, [ii], 47, 896—898).—Using a special form of target, the  $K\beta_1$  lines in the spectrum of the secondary X-radiation from a series of alkali halides and some alkaline-earth sulphides were measured, and from the electron affinities of  $\text{Cl}^-$  and  $\text{S}^{2-}$  and the ionisation potentials of  $\text{K}^+$  the vals. for the free ions are deduced by Pauling's theory. Results are compared with independent data and discrepancies are discussed. N. M. B.

**Relative ionisation of gases measured with the  $K\alpha$  line of copper.** O. GAERTNER (Ann. Physik, 1935, [v], 23, 255—258).—Data are given for Ne, Ar, Kr, Xe,  $\text{N}_2$ ,  $\text{O}_2$ , air,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ , and  $\text{C}_3\text{H}_8$ . W. R. A.

**Intensity of polarised X-rays.** W. H. GEORGE (Nature, 1935, 136, 180).—A single crystal of Cu cut parallel to the 311 planes forms a polariser for  $\text{Cu } K\alpha$  radiation which is 100- to 1000-fold more efficient than the standard methods. L. S. T.



**Absolute probability of  $K$ -electron ionisation of silver by cathode rays.** J. C. CLARK (Physical Rev., 1935, [ii], 48, 30—42).—The Ross balanced foils method was used to separate the  $K\alpha$  quanta from the thin Ag foil target radiation; the X-ray energy was absorbed in MeBr and  $\text{SO}_2$  in a standard ionisation chamber, the ionisation currents were measured, the no. of quanta absorbed in the chamber was computed, and the no. of Ag  $K$  ionisations per bombarding electron was calc. The  $K$ -electron ionisation cross-section for Ag for 70-kv. electrons is  $(4.80 \pm 0.43) \times 10^{-23}$  sq. cm. Results are compared with relative vals. (cf. Webster, A., 1933, 760) and with theory. N. M. B.

**Shapes and wave-lengths of  $K$  series lines of elements Ti 22 to Ge 32.** J. A. BEARDEN and C. H. SHAW (Physical Rev., 1935, [ii], 48, 18—30).—From measurements by double-crystal spectrometer of the widths at half-max. and the indices of asymmetry of the principal  $K$ -series lines, curves of width-at. no. and degree of asymmetry-at. no. are given. From measurements of the widths of certain satellites and of their intensities and displacements the diffraction angles of the peaks of the lines were determined and  $\lambda\lambda$  calc. N. M. B.

**Intermediate region [of the spectrum]; structure of the  $K$ -lines of the lightest elements.** A. HAUTOT (Ann. Physique, 1935, [xi], 4, 5—87).—Vac. spectrographs are described for 10—1300 Å. with max. first-order dispersion of 1 Å. per cm. The  $K$ -lines of O, N, C, B, and Be have been photographed, and the  $\lambda\lambda$  of their components and satellites measured. The mol. matrix of which the atom forms a part affects the lines by varying the no., relative intensity, or  $\lambda$  of the components; thus chemical linkings play a significant part in their emission. T. G. P.

**Intensity of X-ray lines of gold.** L. PINCHERLE (Physica, 1935, 2, 597—605).—Factors influencing the intensity of X-ray lines are discussed. Vals. in agreement with observation are calc. for the  $L$  line of Au. H. J. E.

**Theories of ionisation.** J. S. E. TOWNSEND (Phil. Mag., 1935, [vii], 20, 242—263).—The classical theory of Townsend, viz., that in which the ionisation of a gas is attributed to single collisions of electrons and positive ions with mols. of the gas, gives a satisfactory explanation of the principal phenomena of conduction by gases. The newer theories which assume the formation of metastable atoms are unnecessary, and fail to explain the properties of currents obtained in discharges under simple conditions, and of the uniform positive column in wide discharge tubes. A comparison of the classical and newer theories with regard to the conductivity of, and radiation from, He and A, and He-A mixtures shows that the newer theories do not explain why only He lines are obtained from the discharge through He, purified by ordinary methods, when the potential is the sparking potential. The mechanism of ionisation of impure He is considered, and it is shown that the classical theory explains adequately the large increase in conductivity when a small amount of A is added to He, whilst the theory of metastable atoms fails to

account for He lines becoming more prominent as the amount of impurity is reduced. A. J. M.

**Ionisation potential of the nitrogen molecule.** M. DE HEMPTINNE and J. SAVARD (Compt. rend., 1935, 200, 2147—2148).—Measurements by the method of electron impact gave potentials at 15.6, 21.2, and 23.1 volts. The energy of dissociation of  $\text{N}_2$  is 6.72 volts. H. J. E.

**Variation of mass of electrons in rapid cathode rays.** M. NACKEN (Ann. Physik, 1935, [v], 23, 313—329).—The method of deflexion of cathode rays by electric and magnetic fields was used. Results agree with the theory of Lorentz. A. J. M.

**Mean free path of metal electrons.** M. SATO (Sci. Rep. Tôhoku, 1935, 24, 14—25).—The mean velocity, collision no. of electrons with atoms, and mean free path,  $l$ , have been calc. by Fermi statistics. If the electron gas is in a highly degenerate state,  $l$  decreases with the square of the abs. temp. The results are applied to calculate electrical conductivity of metals and Brownian motion. R. C.

**Liberation of electrons from molybdenum surfaces by positive mercury ions.** S. D. GVOZDOVER (Physikal. Z. Sovietunion, 1934, 6, 415—423).—Hg ions, with velocities 100—500 volts, set free 1/6 as many electrons as do Ne ions (cf. Penning, A., 1931, 139). There may be an adsorbed Hg layer on the Mo surface analogous to that on W (cf. Sonkin, A., 1933, 657). CH. ABS. (e)

**Energy distribution of secondary electrons from molybdenum.** L. J. HAWORTH (Physical Rev., 1935, [ii], 48, 88—95).—Energy distribution curves, obtained by magnetic analysis with primary electron energies  $> 150$  volts, are given and their max. and irregularities are classified and explained. Results are correlated with curves for the no. of elastically reflected electrons as a function of primary energy. N. M. B.

**Secondary emission of electrons from complex targets.** P. L. COPELAND (Physical Rev., 1935, [ii], 48, 96—98; cf. A., 1934, 1149).—Investigation of secondary emission from complex targets formed by the condensation of Pt on Al, Ca on Au, and oil on Au indicate that the change in the secondary emission with the primary energy depends on the overlying element at low energies and on the base metal at high primary energies. N. M. B.

**Polarisation effects in the positron theory.** E. A. UEHLING (Physical Rev., 1935, [ii], 48, 55—63).—Mathematical. An investigation of some of the consequences of the positron theory for the special case of impressed electrostatic fields. N. M. B.

**Bragg curve of  $H$ -rays.** R. GRÉGOIRE (Compt. rend., 1935, 200, 2164—2166).—In determining the ionisation curve for  $\alpha$ -rays from Po, approx. 1% of the particles gave a max. ionisation at 31 cm. in air, the val. being 50% of that for the  $\alpha$ -particle. These rays consist of H atoms with unit charge and the same velocity as the  $\alpha$ -particles. H. J. E.

**Electron scattering by atoms.** M. GHOSH (Phil. Mag., 1935, [vii], 20, 234—242).—Theoretical. A wave-statistical formula for the scattering of elec-



trons by atoms is deduced, based on Born's method, but taking into account the excluded phase-space of the scattered electron. A. J. M.

**Effective cross-section of helium with respect to  $\text{He}^+$ .** F. WOLF (Ann. Physik, 1935, [v], 23, 285—303).—Apparatus for determining the effective cross-section of gas mols. with respect to 20—1000-volt gas ions is described. The effective cross-section of He with respect to  $\text{He}^+$  decreases linearly with increasing velocity of ions, from  $60 \text{ cm}^2 \text{ per cm}^3$  for 30-volt to  $35 \text{ cm}^2 \text{ per cm}^3$  for 980-volt ions. The effective cross-section of He with respect to  $\text{H}^+$  is considerably < this. Discharge of  $\text{He}^+$  accounts for a considerable fraction of the cross-section. A. J. M.

**Atomic mass of potassium. II. Potassium chloride-silver ratio.** C. R. JOHNSON (J. Physical Chem., 1935, 39, 781—789).—Fifteen titrimetric determinations of the  $\text{KCl}:\text{Ag}$  ratio give  $\text{K}=39.100$  ( $\text{Ag}=107.880$ ,  $\text{Cl}=35.457$ ). J. W. S.

**Systematics of isotopes.** G. BECK (Physical Rev., 1935, [ii], 48, 47—48).—A comparison and discussion of the older and the recent views on the structure of nuclei. N. M. B.

**Isotopic constitution of palladium and gold.** A. J. DEMPSTER (Nature, 1935, 136, 65).—The new mass spectrograph (cf. this vol., 909) shows that Pd consists of six isotopes with at. masses 102, 104, 105, 106, 108, and 110. No trace of  $\text{Au}^{199}$  could be detected and it is probable that the accepted at. wt. of Au is too high. L. S. T.

**Isotopic constitution of uranium.** A. J. DEMPSTER (Nature, 1935, 136, 180).—Using the spark source recently described (this vol., 677) a faint companion of at. wt. 235 to the main component at 238 has been observed with long exposures. The intensity given by the new isotope is probably < 1% of that of  $\text{U}^{238}$ .  $\text{U}^{235}$  is probably actino-U, the parent of the Ac series. L. S. T.

**Chemical elements and their atomic numbers as points on a spiral.** N. OPOLONICK (J. Chem. Educ., 1935, 12, 265—267).—The at. nos. of the elements are arranged as points on the spiral  $P=4\theta$ , where  $P$  is the position in radians and  $\theta$  the at. no. Six concentric circles are drawn through He, Ne, A, Kr, Xe, and Rn, dividing the elements into seven periods, and three additional concentric circles drawn through Ni, Pd, and Pt divide the 4th, 5th, and 6th periods into A and B series. Difficulties encountered in previous periodic arrangements of the elements are eliminated. L. S. T.

**Connexion between the emanating power of radium-containing metals and the characteristic properties of these metals.** O. WERNER (Naturwiss., 1935, 23, 456—459).—A method of using radioactive elements as indicators in metallography is described. A measured amount of the radioactive solution is evaporated to dryness on the polished metal surface, and reduced in  $\text{H}_2$  at  $750\text{--}1000^\circ$ . The activity of the substance is then determined by the streaming method. The variation of activity with temp. for different metals has been determined. The temp. coeff. of the activity is inversely  $\propto$  Debye

characteristic temp. of the metal. From the temp. coeff. curves it is possible to derive the energy content and sp. heat of alloy systems. The effect of small quantities of impurities on the characteristic temp., and the reaction velocity at transition points, may be followed. The temp. coeff. of the activity is smaller in the neighbourhood of an allotropic transition point than above or below it. A. J. M.

**Scattering of polonium  $\alpha$ -particles by oxygen and neon.** W. RIEZLER (Ann. Physik, 1935, [v], 23, 198—206).—Scattering between angles  $55^\circ$  and  $90^\circ$  was investigated, the range of incident particles being varied from 12 to 37 mm. and the energy from  $3.3$  to  $8.6 \times 10^{-6}$  erg. With Ne the classical scattering law was obeyed; with  $\text{O}_2$  the scattering was abnormally low for energies  $> 7 \times 10^{-6}$  erg. The radius of the nuclear trough is  $4.5 \times 10^{-13}$  cm. for  $\text{O}_2$  and  $4.6 \times 10^{-13}$  cm. for Ne. W. R. A.

**Anomalous scattering by suitable nuclear fields.** L. H. HORSLEY (Physical Rev., 1935, [ii], 48, 1—6).—A schematic nuclear model representing Pose's data (cf. A., 1934, 1151) on the collision of  $\alpha$ -particles and protons leads to results consistent with data on the position of nuclear energy levels and on the scattering of  $\alpha$ -particles by light elements. N. M. B.

**Registration of the ionisation curve of a single  $\alpha$ -particle.** H. ALFVÉN (Nature, 1935, 136, 70).—An experimental arrangement is described. L. S. T.

**$\beta$ -Radiation of actinium- $C''$ , mesothorium 2, and of uranium  $X_1$  and its derivatives.** M. LECORN (Compt. rend., 1935, 200, 1931—1934; cf. A., 1933, 995).—Curves showing the distribution of energy among the  $\beta$ -rays from each source are recorded, mean energies being calc. H. J. E.

**Fermi theory of  $\beta$ -radioactivity.** E. J. KONOPINSKI and G. E. UHLENBECK (Physical Rev., 1935, [ii], 48, 7—12).—Mathematical. A wt. factor is introduced into Fermi's energy distribution formula to provide required asymmetry. N. M. B.

**$\beta$ -Decay theory.** R. L. DOLECEK (Physical Rev., 1935, [ii], 48, 13—17).—Mathematical. A method of calculating the energy distribution of the  $\beta$ -electrons for any assumptions on the angular momentum balance is developed. N. M. B.

**Disintegration constant and the upper limit of the continuous  $\beta$ -spectrum.** G. J. SIZOO (Nature, 1935, 136, 142; cf. this vol., 804). L. S. T.

**$\gamma$ -Radiation from uranium-X.** E. STAHEL and D. J. COUMOU (Physica, 1935, 2, 707—718).—The absorption coeff. in Fe and Pb was measured. The calc. val. for the energy is 950,000 e.v. The abs. intensity of the radiation corresponds with the emission of 1.4 quanta per 100 atoms decomposed. H. J. E.

**Determination of self-absorption for the evaluation of weak radium-containing substances by the  $\gamma$ -ray method.** H. FRANZ and C. WEISS (Physikal. Z., 1935, 36, 486—489).—The dependence of absorption of  $\gamma$ -rays on thickness of absorbing layer has been determined, and is used as the basis



of a method for determining  $R_a$  in substances containing small quantities. A. J. M.

**Levels of the neutron.** E. SEVIN (Compt. rend., 1935, 200, 2070—2072; cf. this vol., 1050).—An expression for a series of quantised electron levels is deduced, leading to variation in mass of the neutron between 1.00784 and 1.01235 according to the electron orbit. H. J. E.

**Capture of slow neutrons by a nucleus.** L. ARTSIMOVITSCH, I. KURTSCHATOV, L. MIČOVSKI, and P. PALIBIN (Compt. rend., 1935, 200, 2159—2162).—The % of neutrons absorbed by Ag and Rh was measured after the neutrons had traversed varying thicknesses of  $H_2O$  (6—20 cm.) to reduce their energy. A const. val. of the absorption coeff. of the metals was not observed. H. J. E.

**Selective absorption of slow neutrons.** J. R. TILLMAN and P. B. MOON (Nature, 1935, 136, 66—67; cf. this vol., 802).—The absorption coeffs. of Ag, Cu, and I for slow neutrons vary with the element used as detector, indicating that selective absorption of neutrons of different velocities takes place. The ratio of the activity at  $90^\circ$  and  $290^\circ$  abs. is given for these three elements, and factors which must be considered in determining the effect of temp. on the activity of neutrons are discussed. L. S. T.

**Energy spectrum of the neutrons from the disintegration of beryllium by deuterons.** T. W. BONNER and W. M. BRUBAKER (Physical Rev., 1935, [ii], 47, 910—913).—The energy distribution investigated by the method of recoil protons in a high-pressure cloud chamber gives max. neutron energies corresponding with a disintegration of  $4.14 \times 10^6$  e.v. The calc. mass of  $Be^9$ , assuming the reaction  ${}_4Be^9 + {}_1H^2 \rightarrow {}_5B^{10} + {}_0n^1$ , is  $9.0123 \pm 0.0008$ . Other observed neutron groups of lower energy indicate that the  $B^{10}$  nucleus is left in one of several possible excited states and probably falls to the normal state by the emission of a  $\gamma$ -ray. N. M. B.

**Neutrons of mass 2?** S. FLÜGGE (Z. Physik, 1935, 95, 312—317).—Evidence is given to indicate a possible existence of particles of two neutrons combined with antiparallel spins. A. B. D. C.

**Nuclear transformations and bi-neutrons.** S. FLÜGGE and A. KREBS (Z. Physik, 1935, 95, 319—320).—Transformation phenomena observed with Be, B, Na, Cl, F, and Al nuclei are readily explained by the presence of bi-neutrons. A. B. D. C.

**Mechanism of capture of slow neutrons by light nuclei.** F. PERRIN (Compt. rend., 1935, 200, 1749—1751).—Theoretical. Diffraction may explain the large effective cross-sections in Li and B for slow neutrons. H. J. E.

**Non-observance of induced  $\beta$ -radioactivity with the light elements.** H. J. WALKER (Phil. Mag., 1935, [vii], 20, 266—274).—The possible reactions of the nuclei of light elements with neutrons are considered, with special reference to the stability of the products, and the possibility of  $\beta$ -ray disintegrations. Failure to observe  $\beta$ -radioactivity on bombarding light elements with neutrons can be

explained by their nuclear structure and isotopic constitution. A. J. M.

**Attempts to detect  $\gamma$ -radiation excited by the impact of  $\alpha$ -particles on heavy elements.** W. B. LEWIS and B. V. BOWDEN (Phil. Mag., 1935, [vii], 20, 294—304).—No  $\gamma$ -radiation could be detected when Sn and Pb were bombarded with  $\alpha$ -particles from Rn and Ra-C'. Ra-C' produces in Pb  $< 1$  pair of positive and negative electrons for 10,000  $\alpha$ -particles, and Rn  $< 1$  pair for 100,000  $\alpha$ -particles. A. J. M.

**Interaction between a neutron and a proton and the structure of  $H^3$ .** L. H. THOMAS (Physical Rev., 1935, [ii], 47, 903—909).—Mathematical. N. M. B.

**Nuclear processes in lithium on bombardment with  $\alpha$ -rays.** K. SCHNETZLER (Z. Physik, 1935, 95, 302—311).—Excitation functions on bombardment with Po  $\alpha$ -rays are given for neutrons and  $\alpha$ -rays. A. B. D. C.

**Artificial disintegration of elements.** P. SÄVEL (Ann. Physique, 1935, [xi], 4, 88—136).—The nature, energy, and conditions of emission of the radiation excited in Li,  $F_2$ , Na, Mg, Al, and  $N_2$  by  $\alpha$ -particles from Po have been studied with a 40-atm. ionisation chamber. All emit photons and all but  $N_2$  neutrons. The origin of the former is ascribed to (1) excitation without capture of  $\alpha$ -particles and without transmutation ( $Li$ ,  $N_2$ ,  $Al$ ,  $F_2$ ), (2) excitation with capture of  $\alpha$ -particles and emission of groups of protons and neutrons ( $F_2$ ,  $Al$ ,  $Na$ ,  $Mg$ ), and (3) annihilation of the positron ( $Al$ ). The mechanism of neutron emission is discussed. T. G. P.

**Life period of activated magnesium.** A. ECKARDT (Naturwiss., 1935, 23, 527).—The rate of decay of the activity of Mg activated by  $\alpha$ -rays from Th-C' is not exponential. Between 1 and 10 min. the curve is made up of two components, due to processes originating with  ${}^{25}_{12}Mg$ ,  ${}^{24}_{12}Mg$ , and  ${}^{26}_{12}Mg$ . The half-life periods of the two processes are  $1.95 \pm 0.4$  and  $7.5 \pm 1.5$  min., respectively, in agreement with Fahlenbrach (this vol., 803). A. J. M.

**Artificial radioactivity of the rare-earth elements.** J. K. MARSH and S. SUGDEN (Nature, 1935, 136, 102—103).—Additional results (cf. this vol., 559) for the half-life periods and relative intensities ( $Ag=1$ ) are: La  $1.9 \pm 0.2$  days, 0.5; Pr  $19 \pm 0.5$  hr., 0.9; Sm approx. 40 min., 0.03, and a much longer period; Eu  $9.2 \pm 0.1$  hr., 19; Tb  $3.9 \pm 0.1$  hr., 0.6; Dy  $2.5 \pm 0.1$  hr.,  $> 30$ ; Ho  $2.6 \pm 0.2$  hr.,  $> 30$ ; Er approx. 7 min., 0.03 and  $1.6 \pm 0.2$  days, 0.3; Yb approx. 3.5 hr., 0.03; and Lu  $4.0 \pm 0.1$  hr., 1.0. With Ce, Nd, and Gd the activity is  $< 0.01$  that of Ag. The results previously given (*loc. cit.*) for Er and Yb were probably due to contamination by a small amount of Ho. A specimen of ytterbia separated electrolytically from lutecia as  $YbSO_4$  gives a feeble activity indistinguishable in period from that of Lu, and probably due to residual traces of Lu. The intense activity produced by neutron bombardment of Eu, Dy, and Ho suggests a use of these elements as neutron detectors. Certain inconsistencies with Fermi's results are pointed out and the similarity in periods for Ho and Dy is discussed. L. S. T.



**Artificial radioactivity of dysprosium and other rare-earth elements.** G. VON HEVESY and H. LEVI (*Nature*, 1935, **136**, 103; cf. preceding abstract).—Bombardment by slow neutrons gives the following half-life periods and relative intensities ( $Ag=8$ ): Dy 2.5 hr., 100; Ho 35 hr., 20; Er 12 hr., 0.35; Yb 3.5 hr., 0.25; Lu approx. 5 days, approx. 1. The half-val. thicknesses in Al of the  $\beta$ -rays emitted are also recorded. The upper limit of the continuous  $\beta$ -spectrum of Dy has an energy of  $1.4 \times 10^6$  e.v. and that of Ho,  $1.6 \times 10^6$  e.v. The activities of Dy and Ho obtained with fast neutrons are, respectively, 0.01 and 0.05 of those obtained with neutrons slowed down by passage through paraffin wax. L. S. T.

**Artificial radioactivity of ruthenium bombarded by neutrons.** I. KURTSCHATOV, L. NEMENOV, and I. SELINOV (*Compt. rend.*, 1935, **200**, 2162—2163).—Bombardment of Ru with neutrons, slowed down by passage through  $H_2O$ , gave four new radioactive products of periods 40 and 100 sec. and 11 and 75 hr., respectively. Their nature is discussed. H. J. E.

**Radioactive elements formed by irradiating thorium with neutrons.** (MME.) I. CURIE, H. VON HALBAN, and P. PREISWERK (*Compt. rend.*, 1935, **200**, 2079—2080; cf. this vol., 911).—The radio-element of period 1 min. formed on irradiating Th with neutrons was shown, by pptn. with  $BaSO_4$ , to be an isotope of Ra. A new radio-element of period 2—3 min. was observed, which was an isotope of Pa, and was formed by disintegration of another radio-element, probably the isotope of Th of period 25 min., previously described. H. J. E.

**Artificial transformation products of uranium.** O. HAHN, L. MEITNER, and F. STRASSMANN (*Naturwiss.*, 1935, **23**, 544—545).—The substance of half-life 13 min. produced by the bombardment of U is probably eka-Re (at. no. 93). Comparison of the properties of the substance with those of Re shows that both form oxides sol. in NaOH [eka-Re better in  $(NH_4)_2CO_3$ ]. Both are readily pptd. by  $H_2S$  from 20% HCl solution. Like Re, eka-Re is easily converted into the septavalent form, and in this state it can be pptd. from AcOH solution by nitron, whereas the other transformation products are not pptd. The substance previously assigned half-life 50—70 min. is now assigned 100 min. It differs from the 13-min. substance in being pptd. by NaOH, and by  $H_2S$  from more strongly acid solutions. In contrast to Os, distillation with conc.  $HNO_3$  gave no volatile product. The substance is not an isotope of Pa. A third product of the bombardment of U has a half-life of 3.5 days. A. J. M.

**Artificial radioactivity.** E. FØYN (*Tidsskr. Kjemi*, 1935, **15**, 69—70).—A review. R. P. B.

**Transmutation of elements, and artificial radioactivity.** F. BÉHOUNEK (*Chem. Listy*, 1935, **29**, 2—5, 17—24).—A review. R. T.

**Absorption of cosmic-ray electrons.** J. C. STREET, R. H. WOODWARD, and E. C. STEVENSON (*Physical Rev.*, 1935, [ii], **47**, 891—895).—The interpretation that the coincident discharge of  $\approx 3$  Geiger-Müller counters in line represents the passage

of a single ionising particle through the counters and any intervening material is checked by two experimental methods. Data for absorption in Pb, Fe, and marble are extended. N. M. B.

(A) **Comparison of the intensity decrease of primary cosmic radiation in different materials.**

(B) **Absolute intensity of cosmic rays.** J. CLAY (*Physica*, 1935, **2**, 645—649, 650—651).—(A) Absorption data are recorded for  $H_2O$ , Pb, Fe, and air. The decrease in intensity of cosmic rays for equiv. layers of different materials is greatest when the density of the latter is least.

(B) A correction (cf. this vol., 426). H. J. E.

**Absorption of the soft fraction of corpuscular cosmic rays.** P. AUGER, L. LEPRINCE-RINGUET, and P. EHRENFEST (*Compt. rend.*, 1935, **200**, 1747—1749).—Vals. of the absorption coeff. of Pb, Sn, Cu, and Al are recorded. The nature of the rays is discussed. H. J. E.

**Elements of the quantum theory.** I. Quantum phenomena. II. Differential equation for a wave motion. S. DUSHMAN (*J. Chem. Educ.*, 1935, **12**, 217—224, 274—284). L. S. T.

**Waves and spin.** E. SEVIN (*Compt. rend.*, 1935, **200**, 1744—1746).—Theoretical. H. J. E.

**Quaternions, semi-vectors, and spinors.** J. BLATON (*Z. Physik*, 1935, **95**, 337—354).—Mathematical. A. B. D. C.

**Form and symmetry of the electromagnetic equations; equivalence of energy and mass.** J. URBANEK (*Compt. rend.*, 1935, **200**, 2067—2070).—Theoretical. H. J. E.

**Absolute field constant in Born's new field theory.** H. ERTEL (*Naturwiss.*, 1935, **23**, 512).—The val. of the abs. field const. is calc. to be  $b = 6.9015 \times 10^{15}$  dynes<sup>2</sup> per cm. A. J. M.

**Some conclusions from the Born-Schrödinger electron radius.** J. MEIXNER (*Ann. Physik*, 1935, [v], **23**, 371—379).—Changes in the fine structure of H and  $He^+$  lines are calc., taking into account electron spin by using Pauli's equation, and employing the Born-Schrödinger electron radius,  $r_0 = 13.6 e^2/mc^2$ . Agreement with experiment shows that the use of this radius is justified. A. J. M.

**Work functions of univalent metals.** E. WIGNER and J. BARDEEN (*Physical Rev.*, 1935, [ii], **48**, 84—87).—An approx. formula, neglecting the effect of the electric double layer on the surface, is deduced for the work functions of univalent metals in terms of heats of sublimation. Results for the alkali metals agree closely with experiment. N. M. B.

**Stokes phenomenon for the differential equations which arise in the problem of inelastic atomic collisions.** O. K. RICE (*J. Chem. Physics*, 1935, **3**, 386—398).—Mathematical. H. J. E.

**Relative transition probabilities for almost closed shells.** C. W. UFFORD (*Physical Rev.*, 1935, [ii], **47**, 931; cf. A., 1934, 1148).—Three simplifications for calculating the relative transition probabilities of different multiplets in Russell-Saunders coupling



from spectroscopic stability are given for configurations involving almost closed shells. N. M. B.

**Isotopes and nuclear structure.** M. ELSASSER (J. Chim. phys., 1935, 32, 431—432).—By relating the no. of neutrons in a nucleus to the no. of associated protons, the nuclei fall into a no. of fairly distinct groups indicating the formation of successive levels of neutrons. Certain nuclear properties are functions of the no. of neutrons. J. G. A. G.

**Masses of Be<sup>8</sup> and C<sup>12</sup>.** H. S. W. MASSEY and C. B. O. MOHR (Nature, 1935, 136, 141).—The relationship between the mass of the at. nuclei of C and Be and the binding energy of the constituent  $\alpha$ -particles is discussed. L. S. T.

**Cassioptium (lutecium) atomic nucleus and spherical symmetry.** H. SCHULER and T. SCHMIDT (Z. Physik, 1935, 95, 265—273).—The nucleus deviates from spherical symmetry approx. as the  $\cos^2$  law; its spin is 7/2. A. B. D. C.

**Nuclear model.** W. V. HOUSTON (Physical Rev., 1935, [ii], 47, 942—946).—A solution in terms of normal vibrations of the problem of a no. of bodies which attract each other with forces  $\propto$  distance gives expressions for the frequencies, and hence the quantum-mechanical energy levels, leading to a nuclear model. The instability of Be<sup>8</sup> composed of two  $\alpha$ -particles is attributed to the high zero-point energy of the system. The Pauli exclusion principle applied to the neutrons explains the limited no. of observed isotopes. N. M. B.

**Absorption spectrum of ozone in the photographic infra-red.** (MME.) L. LEFEBVRE (Compt. rend., 1935, 200, 1743—1744).—Data from 6500 to 10,000 Å. are recorded. H. J. E.

**Absorption spectrum and mechanism of the photochemical decomposition of N<sub>2</sub>O.** L. A. M. HENRY (J. Chim. phys., 1935, 32, 437—446).—The absorption spectrum of 0.5—3.5 atm. of N<sub>2</sub>O at 293—950° abs. is continuous. The long- $\lambda$  limit, 2300 Å. approx. at 20°, is displaced to longer  $\lambda$  as the temp. rises.  $\lambda < 2300$  Å. decompose N<sub>2</sub>O into NO, and NO<sub>2</sub> is produced more slowly. The energy difference between the lowest vibration level and the unstable excited state is 132,000 g.-cal., approx., and the most probable mechanism of decomp. is N<sub>2</sub>O(<sup>1</sup> $\Sigma$ ) +  $h\nu \rightarrow$  NO(<sup>2</sup> $\Pi$ ) + N(<sup>2</sup>D). J. G. A. G.

**Phosphorescence of nitrogen peroxide. Intensity of bands of the second positive group of nitrogen.** M. DUFFIEUX (Compt. rend., 1935, 201, 53—55).—The spectrum of the afterglow on interrupting a discharge in streaming NO<sub>2</sub> was continuous in the visible, and in the violet and ultra-violet showed bands of the second positive group of N<sub>2</sub> and the  $\gamma$  group of NO. The intensity distribution is discussed. H. J. E.

**Molecular emission spectra of some metallic salts.** P. MESNAGE (Compt. rend., 1935, 200, 2072—2074).—Band emission spectra from AgCl, ZnCl<sub>2</sub>, and NiCl<sub>2</sub> were excited in a high-frequency discharge in presence of a little Ne or Ar (to start the discharge). H. J. E.

**Band spectra of the hydrides of lithium.** F. H. CRAWFORD and T. JORGENSEN, jun. (Physical Rev., 1935, [ii], 47, 932—941; cf. this vol., 561).—Data for about 1000 lines, comprising 26 bands, of Li<sup>7</sup>H, with quantum assignments, are tabulated. Important consts. for the ground and upper states are given and discussed. The electronic origin isotope shift of the <sup>1</sup> $\Sigma \rightarrow$  <sup>1</sup> $\Sigma$  system is 0.0 ( $\pm 0.5$ ) cm.<sup>-1</sup> N. M. B.

**Band systems of copper hydride.** T. HEIMER (Z. Physik, 1935, 95, 321—327).—Two new band systems are analysed. A. B. D. C.

**Band spectrum of bismuth hydride.** A. HEIMER (Z. Physik, 1935, 95, 328—336).

A. B. D. C.

**Influence of the addition of calcium chloride on the absorption of solutions of Cu<sup>+</sup>, Cu<sup>2+</sup>, Fe<sup>3+</sup>, Ru<sup>3+</sup>, and Sm<sup>3+</sup>; chromophore theory.** M. PESTEMER and (FRL.) P. BERNSTEIN (Z. anorg. Chem., 1935, 223, 121—128).—Absorption data for chlorides of the above metals, with and without the addition of CaCl<sub>2</sub>, are given. The formation of chromophores as the result of incompleting electron groups is discussed. M. S. B.

**Spectrum of CO<sup>+</sup>.** H. BULTHUIS (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 604—617; cf. A., 1934, 1055).—Data for the comet-tail bands are tabulated and discussed. D. R. D.

**Band spectrum of zirconium oxide.** F. LOWATER (Phil. Trans., 1935, A, 234, 355—376).—A full rotational analysis of the 0,0, 0,1, and 1,0 bands due to Zr<sup>90</sup>O and the isotope of next abundance Zr<sup>94</sup>O is given. No A-type doubling was found. Mol. consts. for the upper and lower states are deduced. N. M. B.

**Behaviour of SiF bands in stellar spectra.** P. SWINGS (Ark. Mat. Astron. Fys., 1935, 25 B, No. 2; Chem. Zentr., 1935, i, 1010).—The intensity of the SiF bands rises continuously with the spectral type, but more slowly than that of the TiO bands. J. S. A.

**Band systems and structure of CaCl.** R. K. ASUNDI (Proc. Indian Acad. Sci., 1935, 1, A, 830—840).—Full data and vibrational analysis of the red doublet and orange band systems are given and discussed. The normal mol. dissociation energy is 3.5 volts. N. M. B.

**Causes of colour changes of cobalt salts in neutral salt solutions.** A. VON KISS and M. GESZNER (Acta Lit. Sci. Univ. Franciscus-Josephinae, Sect. Chem. Min. Phys., 1934, 4, 124—146).—Mol. extinction coeffs. for the visible spectrum were measured for CoCl<sub>2</sub>, Co(NO<sub>3</sub>)<sub>2</sub>, and CoSO<sub>4</sub> in various conc. solutions of neutral salts, HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>. Colour changes are due to the Stark effect and ion deformation. Constitutional chromophoric changes may also occur. CH. ABS. (e)

**Colour of paramagnetic crystals and solutions of the iron group.** S. DATTA (Sci. and Cult., 1935, 1, 113—114).—In hydrated crystals as well as in solutions at low temp. the absorption centres are hydrated complexes; in crystals of anhyd.



chlorides and in solutions at higher temp. the centres are undissociated mols. C. W. G.

**Zeeman effect of the absorption lines of chrome alum.** F. H. SPEDDING and G. C. NUTTING (J. Chem. Physics, 1935, 3, 369—375; cf. A., 1934, 940).—Measurements are recorded at 20° and 50° abs. with fields of 12,000—25,000 gauss. At 50° abs., but not at 20° abs., the pattern depends on the orientation of the crystal lattice with respect to the magnetic field. The energy levels appear in groups of closely spaced levels, the lowest group belonging to the quartet system. These levels split in a magnetic field, and have a *g* factor of 2. Interaction between the levels is small. H. J. E.

**Photo-dissociation of the vapours of some organo-metallic compounds.** A. TEREININ and N. PRILESHAIEVA (Acta Physicochim. U.R.S.S., 1935, 1, 759—776).—The absorption spectra of HgMe<sub>2</sub>, ZnMe<sub>2</sub>, PbEt<sub>4</sub>, HgMeI, and HgMeBr were all continuous and at  $\lambda < \text{approx. } 2800 \text{ \AA.}$  For HgMe<sub>2</sub> diffuse bands at 2125—1965 Å. were also observed. Photo-dissociation occurs at the metal-C linking. Zn and Pb were deposited on irradiating ZnMe<sub>2</sub> and PbEt<sub>4</sub> with light of  $\lambda < 2650$  and 2400—2300 Å., respectively. On illuminating the vapours of HgMeI and HgMeBr, the band fluorescence of HgCl and HgBr was observed, showing these mols. to be liberated in an excited state by photo-dissociation. H. J. E.

**Ultra-violet absorption spectrum of methylamine in the vapour state.** V. HENRI and W. LASAREFF (J. Chim. phys., 1935, 32, 353—370).—The absorption spectrum of NH<sub>2</sub>Me at 0.1—432 mm. and 18—290° lies between 2529 and 1986 Å. As the pressure is increased, the series of bands with structure change to general absorption, except on the long- $\lambda$  side of the system. Rise of temp. produces similar effects and extends the absorption to the long- $\lambda$  limit. The band spacings 650 and 2050 cm.<sup>-1</sup> are interpreted as vibration frequencies of the normal mol. (cf. A., 1933, 997) and the band spacing 1000 cm.<sup>-1</sup> is referred to the excited state. J. G. A. G.

**Relation between general absorption and residual affinity: heterocyclic compounds.** J. HOUSTON, G. CANNING, and H. GRAHAM (J.C.S., 1935, 965—966).—Pentamethylene sulphide and oxide, 1:4- and 1:3-dioxan, 1:4-thioxan, and 1:4-dithian with cyclohexane for comparison were examined spectrographically. The more chemically reactive compounds have the greater light-absorptive power. N. M. B.

**Fluorescence spectra of some hydrocarbons of the rubene family.** C. DHÉRE and (MLLE.) A. RAFFY (Bull. Soc. chim., 1935, [v], 2, 1424—1430).—The visible fluorescence spectra of tetraphenyl-, triphenyl-, and dehydro-rubene, in the solid state and in C<sub>6</sub>H<sub>6</sub> solution, have been examined. T. G. P.

**Spectrographic investigation of dyes of the benzopyrylium type.**—See this vol., 1129.

**Absorption spectra of metal complexes of dithizone and their analytical significance.** H. FISCHER and W. WEYL (Wiss. Veröff. Siemens-Werken, 1935, 14, 41—53).—The absorption spectra

of the complexes with Cu<sup>II</sup>, Cu<sup>I</sup>, Ag, Zn, Cd, Hg<sup>II</sup>, Tl<sup>I</sup>, Sn<sup>II</sup>, Pb<sup>II</sup>, Bi<sup>III</sup>, Co<sup>II</sup>, and Ni<sup>II</sup> in CCl<sub>4</sub> have been determined between 400 and 700 m $\mu$ . The possibilities of application to analysis and the structures of the complexes, are discussed. E. S. H.

**Absorption spectrum of malachite-green leucocyanide and the mechanism of the dark reaction after photolysis.** L. HARRIS, J. KAMINSKY, and R. G. SIMARD (J. Amer. Chem. Soc., 1935, 57, 1151—1154).—The absorption of the leucocyanide, base, chloride, and photo-compound of malachite-green and crystal-violet, respectively, have been determined. The fading of the coloured photo-compound in the dark has been studied and a mechanism of reaction is proposed. E. S. H.

**Fluorescence and absorption spectra of simple aromatic amines.** N. PRILESHAIEVA and R. TSCHUBAROV (Acta Physicochim. U.R.S.S., 1935, 1, 777—784).—The absorption and fluorescence spectra of NH<sub>2</sub>Ph and NHPH<sub>2</sub> have been photographed. For each the absorption bands are in the region of 2800 Å. (C<sub>6</sub>H<sub>6</sub> absorption) and at  $< 2400 \text{ \AA.}$  (NH<sub>2</sub> absorption). The bands for NHPH<sub>2</sub> are diffuse. H. J. E.

**Pyrrole-blues. Absorption spectra.** See this vol., 1134.

**Vitamin-E. Measurement of absorption band.**—See this vol., 1037.

**Chlorophyll derivatives [absorption spectra].** See this vol., 1177.

**Spectrometric measurements on various carotenoids.** A. E. GILLAM (Biochem. J., 1935, 29, 1831—1836).—Spectrometric data are recorded for the absorption bands in the visible and ultra-violet of various carotenoids in CHCl<sub>3</sub> and in CHCl<sub>3</sub>-SbCl<sub>3</sub> solution. W. O. K.

**Absorption spectra of adsorbed materials.**  
**I. Adsorption spectra of dyes adsorbed on colloids.** E. B. FODIMAN and V. A. KARGIN (Acta Physicochim. U.R.S.S., 1934, 1, 220—231).—The absorption of methylene-blue (I), thionine, Me-blue, and erythrosin, adsorbed on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, and gelatin sols, are modified in cases where the dye ion is charged oppositely to the colloid particles, but not when similarly charged. The absorption of dyes adsorbed on SiO<sub>2</sub> and TiO<sub>2</sub> changes on removal of the charge from the sol particles, but (I) on gelatin shows no corresponding change. J. W. S.

**OH band in the very near infra-red.** A. NAHERNIAC (Compt. rend., 1935, 200, 1742—1743).—A band at  $\lambda$  9500—9800 Å., attributed to OH, was observed in the absorption spectrum of the vapours of HCO<sub>2</sub>H, AcOH, other fatty acids, BzOH, cyclohexanol, resorcinol, (CH<sub>2</sub>·OH)<sub>2</sub>, and glycerol. It is not observed in the absorption spectra of the liquids or their solutions. This fact may be due to association. H. J. E.

**Far infra-red spectrum of H<sub>2</sub>O.** R. B. BARNES, W. S. BENEDICT, and C. M. LEWIS (Physical Rev., 1935, [ii], 47, 918—921).—The absorption of atm. H<sub>2</sub>O vapour mapped in the range 38—170  $\mu$  is in good



agreement with Mecke's analysis of the vibration-rotation bands, and these results are extended.

N. M. B.

**Extreme infra-red absorption of  $D_2O$ , ice, and  $D_2O$  in dioxan.** C. H. CARTWRIGHT (Nature, 1935, 136, 181).— $D_2O$  and  $H_2O$  have the same absorption between 60 and 200  $cm^{-1}$ . The absorption band near 160  $cm^{-1}$  can therefore be assigned to a hindered translational frequency of  $D_2O$  or  $H_2O$  mols. as predicted by Bernal and Tamm (this vol., 432). The existence of the 160  $cm^{-1}$  band in ice at  $-10^\circ$  provides additional evidence for a quasi-cryst. structure in  $H_2O$ , and indicates that the intermol. forces in  $H_2O$  and ice are approx. the same. The 160  $cm^{-1}$  band disappears for  $H_2O$  dissolved in dioxan, confirming the view that its presence is due to a structure in  $H_2O$  rather than to the individual mols.

L. S. T.

**Vibration frequencies of ethylene and ethane.** E. TELLER and B. TOPLEY (J.C.S., 1935, 885—889).—From a summary of existing experimental data on the infra-red and Raman spectra, sets of vibration frequencies for the  $C_2H_4$  and  $C_2H_6$  mols. are derived.

N. M. B.

**Absorption of acetylene and dideuteroacetylene in the photographic infra-red.** C. A. BRADLEY, jun., and A. MCKELLAR (Physical Rev., 1935, [ii], 47, 914—917; cf. A., 1934, 1288).—Using an absorbing column 9 m. long and  $C_2D_2 > 90\%$  pure at 85 cm. pressure, no absorption bands in the range 7000—11,500 Å. were observed. A 7.5-m. column of  $C_2H_2$  at 90 cm. pressure gives a new absorption band with origin at 7859 Å. Possible vibrational transitions giving rise to this are discussed.

N. M. B.

**Low-frequency fundamental bands of methyl chloride, bromide, and iodide.** E. F. BARKER and E. K. PLYLER (J. Chem. Physics, 1935, 3, 367—368; cf. A., 1934, 1288).—The  $\nu_5$  bands of MeCl, MeBr, and MeI have been observed at  $\lambda$  13.7, 16.4, and 18.8  $\mu$ , respectively, that of MeI having a sharp zero branch suitable for use in calibration. Isotope effects were observed.

H. J. E.

**Vibration frequencies of chlorine derivatives [of some aliphatic compounds].** H. C. CHENG and J. LECOMTE (Compt. rend., 1935, 201, 199—201).—A discussion of the Raman and infra-red spectra of halogenated derivatives of MeR. The influence of the radical R on the C—Cl vibrational frequency is small in the  $Cl_1$ , considerable in the  $Cl_2$ , and preponderant in the  $Cl_3$ -derivatives. The C—H vibrational frequency undergoes no systematic variation with change in R or the no. of Cl atoms in the mol.

H. J. E.

**Modes of vibration of dihalogen derivatives of ethane.** H. C. CHENG and J. LECOMTE (Compt. rend., 1935, 201, 50—52).—Raman and infra-red spectra of  $(CH_2Cl)_2$ ,  $CH_2Cl-CH_2Br$ ,  $(CH_2Br)_2$ ,  $CH_2Cl-CH_2I$ , and  $(CH_2I)_2$  support the hypothesis of *cis*- and *trans*-forms of these mols. One infra-red frequency is observed in the infra-red which should theoretically be inactive. Factors causing this anomaly are discussed.

H. J. E.

**Infra-red absorption spectra of proteins.** F. VLÈS and E. HEINTZ (Compt. rend., 1935, 200, 1927—1929).—Data are recorded for serin, oxy-haemoglobin, excelsin, edestin, gelatin, and casein. The chief absorption regions were at approx. 3—5  $\mu$  and 6  $\mu$ . The calc. and observed positions of bands corresponding with the isoelectric points agreed (cf. this vol., 444).

H. J. E.

**Raman spectra of some metallic halides.** C. S. VENKATESWARAN (Proc. Indian Acad. Sci., 1935, 1, A, 850—858).—Raman data for the halides of Cd and Zn and for  $MgCl_2$ ,  $MgBr_2$ , and  $AlCl_3$  are given.  $ZnCl_2$  and  $ZnBr_2$  and the halides of Cd give lines showing the existence of homopolar binding. The spectra of  $ZnCl_2$  and  $CdI_2$  were fairly intense and indicate a linear triat. model analogous to those of the  $Hg^{II}$  halides. Intensity, sharpness, and frequency for  $ZnCl_2$ ,  $CdBr_2$ , and  $CdI_2$  vary markedly from crystal to solution, and with different solvents; the presence of halogen ions in solution also affects the spectra. Results are attributed to the change in degree of ionisation in different solvents and to the influence of solvent mols. on the fundamental oscillation frequencies of the compounds.  $MgCl_2$ ,  $MgBr_2$ , and  $AlCl_3$  gave no Raman lines; a marked effect on the  $H_2O$  bands was found in each case.

N. M. B.

**Raman spectra of bromine compounds of germanium and tin.** A. TCHAKIRIAN and H. VOLKRINGER (Compt. rend., 1935, 200, 1758—1760).—Data are recorded for  $GeBr_4$ .  $GeHBr_3$  gave results similar to a solution of  $SnBr_2$  in HBr. Formation of the acidic compounds  $HSnBr_3$  and  $HGeBr_3$  is indicated.

H. J. E.

**Raman spectra in solutions. I. Solutions of arsenic trichloride in carbon tetrachloride and benzene.** A. E. BRODSKI, A. M. SACK, and S. F. BESUGLI (Ber. Ukrain. Wiss. Forsch. physikal. Chem., 1935, 4, 135—142).—Raman frequencies are given for  $AsCl_3$ ,  $CCl_4$ ,  $C_6H_6$ , a 39% solution of  $AsCl_3$  in  $CCl_4$ , and a 35% solution of  $AsCl_3$  in  $C_6H_6$ . The  $CCl_4$  and  $C_6H_6$  frequencies appear unchanged in the mixtures, but the  $AsCl_3$  vals. show deviations which are attributed to the polar character of  $AsCl_3$ .

R. S.

**Doppler effect in light scattered by liquids. I. Variation with temperature.** B. V. R. RAO (Proc. Indian Acad. Sci., 1935, 1, A, 765—767; cf. this vol., 565).—For  $CCl_4$  at  $70^\circ$ , the Doppler components become fainter and broader, merging with the central undisplaced component which increases in intensity; at  $0^\circ$  the components become sharper and move away from the central component. Results support the hypothesis of loosely-bound, or "vapour," and closely-bound or "cryst.," mol. groups in a liquid.

N. M. B.

**Raman spectrum of heavy chloroform.** R. W. WOOD and D. H. RANK (Physical Rev., 1935, [ii], 48, 63—65).—The spectrum was photographed and line shifts were measured. Three types of isotope effects were observed. Calc. and observed vals. for the isotope displacements agree.

N. M. B.



**Vibrational Raman scattering in liquids.** S. BHAGAVANTAM and A. V. RAO (Physical Rev., 1935, [ii], 47, 1935, 921—923).—The intensity distribution in the wings accompanying the depolarised vibrational Raman line  $656\text{ cm}^{-1}$  in  $\text{CS}_2$  is similar to that in the wings accompanying the Rayleigh lines and falls to zero from a max. near the centre. Results are contrary to the predictions of theories of the rotational Raman effect. N. M. B.

**Raman frequency of the C:C linking in alkylidene-cyclohexanes and -cyclohexenes.** T. HAYASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 27, 99—108).—The Raman frequency of the C:C linking in nerol was 1670 and in geraniol  $1669\text{ cm}^{-1}$ . No effect of the spatial arrangement of the  $\text{CH}_2\text{OH}$  on the C:C frequency was observed, indicating that the latter is mainly determined by the no. of substituents. The frequencies in methylene-, ethylidene-, and isopropylidene-cyclohexanes were 1655, 1676, and  $1674\text{ cm}^{-1}$ , respectively, showing that when one C of the C:C linking is a member of the cyclohexane ring, the inner frequencies near  $1665\text{ cm}^{-1}$ , due to the valency oscillation of the various C:C linkings, remain nearly the same as those corresponding in the aliphatic olefines. The frequency in 1:2-dimethylcyclohexene was  $1675\text{ cm}^{-1}$ , hence when the C:C linking is part of the cyclohexene ring the inner C:C frequencies near  $1665\text{ cm}^{-1}$  are nearly as in the corresponding aliphatic series types. N. M. B.

**Raman spectra of the isomeric cis- and trans-1:3- and 1:4-dimethylcyclohexanes and of 1:1-dimethylcyclohexane.** O. MILLER and L. PIAUX (Compt. rend., 1935, 201, 76—77; cf. A., 1933, 998).—Data are recorded, the spectra of the cis- and trans-isomerides having certain lines in common, but showing characteristic differences.

H. J. E.

**Raman spectra of the esters of some derivatives of  $\beta$ -ketobutyric acid.** II. M. MILONE (Gazzetta, 1935, 65, 339—349).—Raman spectrum of derivatives of the type  $\text{COMe}\cdot\text{CRR}'\cdot\text{CO}_2\text{Et}$  show that the enolic form is present in large amount when  $\text{R}=\text{H}$  and  $\text{R}'=\text{Cl}$  or  $\text{COPh}$ , in small amount when  $\text{R}=\text{H}$  and  $\text{R}'=\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$  or  $\text{CH}_2\text{Ph}$ , and absent when both R and  $\text{R}'$  are alkyl. O. J. W.

**Raman effect of organic substances. IV. Raman effect of cedrene.** K. MATSUNO and K. HAN (Bull. Chem. Soc. Japan, 1935, 10, 220—231).—A complicated spectrum of 119 lines is discussed, and by correlating with existing data an attempt is made to assign the various Raman frequencies. It is impossible to decide from Raman effect measurement whether cedrene contains a 1-methylcyclopentene or -hexene ring. W. R. A.

**Raman effect of some organic substances.** G. B. BONINO and R. MANZONI-ANSIDEI (Mem. R. Accad. Sci. Ist. Bologna, 1934, [ix], 1, 10 pp.; Chem. Zentr., 1935, i, 1197).—The Raman spectra of 96 compounds of various classes are described.

H. N. R.

**Anti-Stokes fluorescence of aniline vapour.** N. PRILESHAEVA (Acta Physicochim. U.R.S.S., 1935, 1, 785—794).—The anti-Stokes fluorescence of  $\text{NH}_2\text{Ph}$

reaches max. at  $250^\circ$ , and disappears at  $350\text{--}400^\circ$ . The spectral region for excitation is at  $\lambda 2900\text{--}3900\text{ \AA}$ . (max. 3600). The excitation mechanism is discussed. On irradiating a mixture of  $\text{NH}_2\text{Ph}$  and indigotin vapours with white light, the blue indigotin fluorescence bands and those of  $\text{NH}_2\text{Ph}$  are observed, indicating a sensitised anti-Stokes fluorescence.

H. J. E.

**Depolarisation factor of light scattered by liquids.** A. BOUTARIC and PEYROT (Rev. gén. Sci., 1934, 45, 564—565; Chem. Zentr., 1935, i, 858).—Vals. for the depolarisation factor ( $\rho$ ) of various liquids are recorded.  $\rho$  is raised by introduction of a C:C linking. Introduction of Me or Et in a saturated cyclic series increases  $\rho >$  does a corresponding increase in the no. of ring C atoms.  $\rho$  can be used as a test of purity and, in certain cases, for studying binary mixtures. Very pure  $\text{H}_2\text{O}$  shows a small fluorescence, but pure  $\text{C}_6\text{H}_6$  does not.

H. J. E.

**Depolarisation of light by colloidal solutions, crystalline precipitates, and solid deposits on glass.** S. PROCOPIU (Compt. rend., 1935, 201, 55—58).—Observations are recorded for the depolarisation produced by various colloids and suspensions and by films on glass. The min. particle size to produce depolarisation is approx.  $0.8\text{ }\mu$ . The method may be used to study cryst. ppt. formation or the orientation of thin solid films.

H. J. E.

**Raman spectrum of rubber.** S. D. GEHMAN (J. Amer. Chem. Soc., 1935, 57, 1382—1383).—A spectrum, with intense frequencies at 1672, 1460, and  $1382\text{ cm}^{-1}$ , has been observed. E. S. H.

**Quenching of iodine fluorescence by benzene vapour.** J. P. HOWE and W. A. NOYES, jun. (J. Amer. Chem. Soc., 1935, 57, 1262—1265).—The quenching is not of the simple type encountered in monat. vapours. Probably several excited states are involved.

E. S. H.

**Fluorescence of some pure substances.** E. CANALS, P. PEYROT, and R. NOËL (Compt. rend., 1935, 201, 208—210; cf. A., 1934, 830).—Vals. for the depolarisation factors ( $\rho$ ) and the relative intensities of fluorescence for a series of fatty acids are recorded.  $\rho$  decreases as the homologous series is ascended, except in the case of  $\text{Pr}^{\text{c}}\text{CO}_2\text{H}$  and  $\text{BuCO}_2\text{H}$ . The fluorescence spectrum in each case was at  $4400\text{--}4900\text{ \AA}$ .

H. J. E.

**Influence of nitrogen on the fluorescence of cyanogen.** A. JAKOVLEVA (Acta Physicochim. U.R.S.S., 1934, 1, 296—304).—The presence of 20 mm. pressure of  $\text{N}_2$  decreases to half the intensity of the blue fluorescence of  $(\text{CN})_2$ , produced by illumination of ICN with ultra-violet light. The changes in relative intensities of the (1,1) and (0,0) bands indicate that a transition from the state  $v'=1$  to  $v'=0$  occurs on collision. The probabilities of quenching and of the transfer of vibration on collision are about 0.1.

J. W. S.

**Fluorescence spectra of hepatoflavin before and after irradiation.**—See this vol., 1145.

**Connexion between absorption and luminescence in concentrated dye solutions.** V. L.



LEVSHIN (*Acta Physicochim. U.R.S.S.*, 1935, 1, 685—712; cf. A., 1931, 1353).—Measurements on the absorption and fluorescence of rhodamine-G (extra) solutions are recorded. The absorption spectrum changes with increasing concn., due to association. The associated mols. are incapable of fluorescence and the intensity decreases. The concn. solutions on heating resemble dil. solutions. In Bu<sup>o</sup>OH solution changes in absorption spectrum occur only at high concn. This method of studying association is discussed. H. J. E.

**Temperature optima of phosphorescent dye solutions.** P. FRÖHLICH (*Acta Lit. Sci. Univ. Francisco-Josephinae, Sect. Chem. Min. Phys.*, 1934, 4, 1—17).—Vals. of the temp. at which max. phosphorescence was observed are recorded for EtOH and glycerol solutions of erythrosin, eosin-A, rhoduline-orange, and rhodamine-S. There was a steady transition between fluorescence and phosphorescence phenomena. CH. ABS. (e)

**Fluorescence of zinc oxide-iron oxide mixtures and its dependence on the temperature of heat-treatment.** A. KUTZELNIGG (*Z. anorg. Chem.*, 1935, 223, 251—252; cf. this vol., 1085).—The fluorescence of equimol. ZnO + Fe<sub>2</sub>O<sub>3</sub> mixtures heated at different temp. passes through a min. for mixtures heated at 500—550° as does that of ZnO, but rises to a max. at about 700°. J. S. A.

**Influence of the passage of an electric current on the phosphorescence of zinc sulphide.** G. DÉCHÈNE (*Compt. rend.*, 1935, 201, 139—142).—The phosphorescence of thin layers of various types of phosphorescent ZnS, spread on metal electrodes separated by conducting Cellophane, was reduced on passing a current after illuminating. The effect increased with the applied voltage (1000—3000 volts). H. J. E.

**Light-dark effect, with reference to the adsorptive power of phosphors.** J. A. HEDVALL and I. AFZELIUS (*Svensk Kem. Tidskr.*, 1935, 47, 156—161).—Phosphorescent ZnS containing Ag or Cu adsorbed 10—75% more lanasol-green when illuminated than when in the dark. Non-phosphorescent ZnS or BaSO<sub>4</sub> gave no such effect. H. J. E.

**Radiation accompanying the dehydration of quinine sulphate.** M. PROST (*Compt. rend.*, 1935, 201, 143—144; cf. A., 1931, 996).—A magnetic field of 600 gauss produced a 90% reduction in the ionisation current. The effect may be due to the production of large ions during the dehydration. H. J. E.

**Emission of radiation in chemical and biological phenomena.** R. AUDUBERT and O. VIKTORIN (*Coll. Czech. Chem. Comm.*, 1935, 7, 261—272; cf. A., 1933, 764).—Audubert and Van Doormaal's results were confirmed. Data are recorded for the dependence on time of the no. of photons emitted in the anodic polarisation of Al, and on the applied voltage. The intensity of the radiation cc the anode c.d. Preliminary vals. are given for the spectral distribution of the radiations, using photocathodes of Al and CuI. Radiation was observed from nerves excited electrically or mechanically. H. J. E.

**Hyperbolic law of decay of phosphorescence.** M. CURIE (*Compt. rend.*, 1935, 201, 142—143).—Theoretical. H. J. E.

**Quantitative tetrachromatic theory [of colour vision].** I. J. F. SCHOUTEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1935, 38, 590—603). D. R. D.

**Ionisation potential of acetone vapour.** W. A. NOYES, jun. (*J. Chem. Physics*, 1935, 3, 430—432).—The val. found by the electron bombardment method was 10.1 volts, agreeing with one val. predicted from spectroscopic data. H. J. E.

**Electrical behaviour of the rectifying layer of lead sulphide.** W. SCHADE (*Physikal. Z.*, 1935, 36, 499—508).—On varying the tuning of a circuit in which a PbS detector was connected in series with a milliammeter, the current in the circuit at first increased, reached a max., then decreased to zero, and finally the current was reversed. The greatest current flows in the detector for small alternating p.d. if the positive half-phase travels from the point to the surface. A virgin spot is less sensitive than one which has been previously used. Direct photographic demonstration of the emission of electrons from the PbS surface has been obtained. A. J. M.

**New photo-electric effect of cuprous oxide.** I. K. KIKOIN (*Physikal. Z. Sovietunion*, 1934, 6, 478—489; cf. A., 1934, 1291).—Experiments on the dependence of the effect on magnetic field strength, light intensity,  $\lambda$ , and temp. are described. CH. ABS. (e)

**External photo-electric effect in cuprous oxide.** E. VASSER (*Physikal. Z. Sovietunion*, 1934, 6, 351—367).—Vals. for the long- $\lambda$  limit and photo-electric yield are recorded and discussed. CH. ABS. (e)

**Influence of occluded gas and vapours on the electrical conductivity of cuprous oxide.** L. DUBAR (*Compt. rend.*, 1935, 200, 1923—1925).—The conductivity decreases as a result of adsorption of gases, particularly H<sub>2</sub>O, which produces approx. a tenfold decrease. H. J. E.

**Electrical conductivity of water.** A. KLING and A. LASSIEUR (*Compt. rend.*, 1935, 201, 203—204).—The conductivity of H<sub>2</sub>O varies, distillation in Pt giving a higher val. than that in glass. The presence of small quantities of dissolved CO<sub>2</sub> cannot be detected conductometrically. H. J. E.

**Dipole moment of deuteroammonia.** J. M. A. DE BRUYNE and C. P. SMYTH (*J. Amer. Chem. Soc.*, 1935, 57, 1203—1205).—The triple point of ND<sub>3</sub> is at -73.6° and 48.6 mm. The dipole moments of NH<sub>3</sub> and ND<sub>3</sub>, calc. from dielectric const. measurements, are  $1.46 \times 10^{-18}$  and  $1.49 \times 10^{-18}$ , respectively. E. S. H.

**Dipole moment and structure of organic compounds. Moment of the N:C group.**—See this vol., 976.

**Electrical moments of isobutyl, isopropyl, and phenylchlorosulphites.** P. TRUNEL (*Compt. rend.*, 1935, 200, 2186—2187; cf. this vol., 430).—Vals. of 2.66, 2.83, and 2.43 Debye units, respectively, were obtained. The difference between the vals. for



the  $\text{Pr}^{\alpha}$  and  $\text{Pr}^{\beta}$  derivatives is attributed to their different influences on the free rotation of  $\text{O}\cdot\text{SO}\cdot\text{Cl}$ . The change due to the introduction of the Ph group is discussed. H. J. E.

**Electric moments of alkyl monohalides.** P. C. MAHANTI (Phil. Mag., 1935, [vii], 20, 274—287).—The effect of temp. on the dielectric const. of the vapours of Me, Et, and Pr halides and of  $\text{C}_3\text{H}_5\text{Cl}$  has been determined by a heterodyne method, and the dipole moments have been calc. Since the moment of  $\text{EtCl}$  is  $>$  that of  $\text{MeCl}$ , and the moment of  $\text{Pr}^{\alpha}\text{Cl}$  is approx. the same as that of  $\text{EtCl}$ , the induction effect due to the principal doublet associated with the C-halogen linking of a  $n$ -alkyl monohalide is transmitted only as far as the second C in the chain. A. J. M.

**Dielectric constants of acetylenic compounds.** VI. **Acetylenic acids.** C. J. WILSON and H. H. WENZKE (J. Amer. Chem. Soc., 1935, 57, 1265—1267; cf. A., 1934, 1292).—Electric moments have been determined for propiolic, tetrolic, phenyl-,  $o$ - and  $p$ -chlorophenyl-,  $o$ - and  $p$ -nitrophenyl-propionic, phenyl-acetic, benzoic,  $p$ -nitro-,  $o$ -,  $m$ -, and  $p$ -hydroxybenzoic acids. The presence of the triple linking has a pronounced effect on the moments of  $\text{CO}_2\text{H}$  in the propiolic acids and on the ionisation consts. of these acids. H is more positive in  $\text{CO}_2\text{H}$  of the acetylenic acids than in  $\text{AcOH}$ . E. S. H.

**Covalency angles of oxygen and sulphur in organic compounds.** L. E. SUTTON and G. C. HAMPSON (Trans. Faraday Soc., 1935, 31, 945—957).—The dipole moments of  $\text{Ph}_2\text{O}$ ,  $p$ -mono- and  $pp'$ -dibromodiphenyl ether, and  $\text{PhBr}$  in  $n$ -hexane at  $25^\circ$  are 1.18, 1.75, 0.65, and 1.60, respectively; those of  $p$ -bromophenyl  $p$ -tolyl ether,  $p$ -mono- and  $pp'$ -dichlorobenzophenone in  $\text{C}_6\text{H}_6$  at  $25^\circ$  are 1.98, 2.71, and 1.70, respectively. The valency angles of O and S in  $\text{Ph}_2\text{O}$  and  $\text{Ph}_2\text{S}$  are  $128 \pm 4^\circ$  and  $113 \pm 3^\circ$ , respectively. An explanation for the abnormally high val. for O is proposed, based on the probable resonance of the ordinary structure with others in which O forms a double linking with one nucleus. E. S. H.

**Dipole moments of vapours.** II. L. G. GROVES and S. SUGDEN (J.C.S., 1935, 971—974; cf. A., 1934, 944).—The following vals., in Debye units, were obtained:  $\text{H}_2\text{O}$   $1.84 \pm 0.01$ ,  $\text{D}_2\text{O}$   $1.84 \pm 0.01$ ,  $\text{PhCl}$   $1.73 \pm 0.01$ ,  $\text{PhBr}$   $1.71 \pm 0.01$ ,  $\text{EtOBz}$   $1.95 \pm 0.02$ ,  $\text{COPhMe}$   $3.00 \pm 0.01$ ,  $\text{PhNO}_2$   $4.24 \pm 0.02$ ,  $\text{PhCN}$   $4.37 \pm 0.02$ ,  $\text{Bu}^n\text{CN}$   $4.09 \pm 0.01$ . A survey of available data shows that in homologous series the moment of the terminal group tends to approach a const. val. on passing from Me to higher homologues and that Sutton's relation (cf. A., 1931, 1354) is confirmed. N. M. B.

**Dipole moments of 1:4-dinitro-, 1:3:5-trinitro-, and certain 2:4:6-trisubstituted 1:3:5-trinitro-benzenes.** (MRS.) C. G. LE FÈVRE and R. J. W. LE FÈVRE (J.C.S., 1935, 957—965).—Measurements were made at  $25^\circ$  and  $45^\circ$ , in  $\text{C}_6\text{H}_6$ ,  $\text{CHCl}_3$ , and dioxan solution, having regard to at. polarisations in the evaluation of the final moments. For the two first-named compounds moments were finite but  $>0.5$ ; for the other compounds vals. were

larger. Results are explained by reference to a non-planar configuration of the  $\text{NO}_2$  group. N. M. B.

**Molecular polarisation of solutes and dielectric constant of solvents.** R. J. W. LE FÈVRE (Nature, 1935, 136, 181—182).—From the Raman-Krishnan formula for the vol. polarisation of a dielectric (A., 1928, 348) it is deduced that the polarisations of most substances in solution should be  $<$  those in the vapour state. Substances with a negative Kerr const. should exhibit polarisations which are greater in the dissolved than in the gaseous condition. L. S. T.

**Density and refractive index of benzene at varying temperatures.** ("Allotropy" of benzene.) B. PESCE (Gazzetta, 1935, 65, 440—447).— $d$  and  $n$  of  $\text{C}_6\text{H}_6$  are measured from  $25^\circ$  to  $79^\circ$ :  $d_4^\circ = 0.89983 - 1.0193 \times 10^{-3}t - 1.252 \times 10^{-6}t^2 - 6.044 \times 10^{-9}t^3$ ;  $n_{D_570}^\circ = 1.51431 - 0.644 \times 10^{-3}t + 0.033 \times 10^{-6}t^2 - 2.391 \times 10^{-9}t^3$ . The graphs of these functions present no singular points, and give no evidence of two liquid forms of  $\text{C}_6\text{H}_6$ . E. W. W.

**Spectrochemistry of organic fluorine compounds.** K. VON AUWERS (Z. physikal. Chem., 1935, 173, 345—348).—Schiemann's (A., 1931, 1355) vals. for the equiv. refractive power of F are confirmed for  $o$ -,  $m$ -, and  $p$ - $\text{C}_6\text{H}_4\text{F}\cdot\text{NO}_2$  and  $o$ -,  $m$ -, and  $p$ -fluoronitroaniline, but his dispersion equiv. is too large. T. G. P.

**Origin of optical rotatory power.** T. M. LOWRY (Nature, 1935, 136, 191—192).—A review of recent theoretical investigations, with illustrative examples. L. S. T.

**Analysis of rotatory dispersion of chemically analogous substances.** P. A. LEVENE and A. ROTHEN (Science, 1935, 81, 623—624).—The partial rotations of the individual absorption regions in substances of the general type of  $\text{CHRR}'\cdot[\text{CH}_2]_n\cdot\text{X}$ , where R and R' are alkyl, and X is a functional group  $\text{CHO}$ ,  $\text{N}_3$ ,  $\text{SH}$ , halogen ( $n=0$  or an integer), are tabulated and discussed. L. S. T.

**The  $\text{NO}^+$  radical.** W. R. ANGUS and A. H. LECKIE (Trans. Faraday Soc., 1935, 31, 958—962).—Conductivity measurements show that solutions of  $\text{NOHSO}_4$  or  $\text{NOCIO}_4$  in nitromethane are electrolytes, confirming the deduction from band spectra and Raman spectra data that  $\text{NO}^+$  is a stable radical. E. S. H.

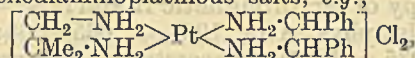
**Shape of the  $\text{NO}_2$  molecule.** G. B. B. M. SUTHERLAND and W. G. PENNEY (Nature, 1935, 136, 146—147).—Closer investigation (cf. A., 1934, 829) of the electronic structure indicates a  $\text{O}\cdot\text{N}\cdot\text{O}$  angle of approx.  $110$ — $120^\circ$ . A wide-angled structure for  $\text{NO}_2$  is also to be preferred from a study of force fields in triat. mols. Difficulties regarding the contours of the infra-red bands suggest that a re-examination of these bands is necessary. L. S. T.

**Structure of telluric acid.** L. PASSERINI and M. A. ROLLIER (Atti R. Accad. Lincei, 1935, [vi], 21, 364—368; cf. A., 1934, 1161).—Cubic  $\text{H}_6\text{TeO}_6$  has a  $15.68 \text{ \AA}$ ,  $d_{\text{calc.}}$  3.158, 32 mols. in the unit cell, and space-group  $\text{O}_h^8$ . The structure is  $\text{Te}(\text{OH})_6$ , with the OH arranged symmetrically around the Te, and not  $\text{H}_2\text{TeO}_4\cdot 2\text{H}_2\text{O}$ . D. R. D.



**Structure of phosphorus pentachloride and phosphorus pentamide.** H. MOUREU and P. ROCQUET (Compt. rend., 1935, 201, 144—147).— $\text{PCl}_5$  (fused, gaseous, or in solution) may consist of mols. in which P is surrounded by a shell of 10 electrons, in equilibrium with a small proportion of mols. with two singlet linkings, the latter being responsible for the ready dissociation and the formation of  $\text{POCl}_3$ . Similar considerations may apply to  $\text{P}(\text{NH}_2)_5$ , which readily loses 2 mols. of  $\text{NH}_3$  forming a polymeride of  $\text{PN}_3\text{H}_4$ . It is shown from the electronic structures that  $\text{PN}_3\text{H}_4$ ,  $\text{PNCl}_2$ , and  $\text{PN}(\text{OH})_2$  should all polymerise readily. H. J. E.

**Configuration of the valencies of 4-covalent platinum.** Optical resolution of *meso*-stilbene-diaminoisobutylenediaminoplatinous salts. W. H. MILLS and T. H. H. QUIBELL (J.C.S., 1935, 839—846).—The diphenyldimethyl derivatives of bisethylenediaminoplatinous salts, e.g.,



have been resolved, by means of diacetyltartaric acid, into antimeric optically active forms showing a high degree of optical stability. This shows that the 4-covalent Pt must have a planar configuration of its valencies, since the regular tetrahedral arrangement would give a symmetrical configuration for the complex cation. The planar arrangement also gives a practically strainless five-ring system composed of C and N atoms and one Pt. O. J. W.

**Wave-mechanical treatment of the Mills-Nixon effect.** L. E. SUTTON and L. PAULING (Trans. Faraday Soc., 1935, 31, 939—945).—Theoretical. E. S. H.

**Dissociation of some molecules with free valencies.** H. LESSHEIM and R. SAMUEL (Current Sci., 1935, 3, 610; cf. A., 1934, 477).—Conclusions reached from the correlation between the electronic terms of mols. of the type  $\text{BeO}$ ,  $\text{BeF}$ , and  $\text{NO}$  and those of the constituent atoms are summarised. L. S. T.

**Electronic structure and valency.** C. PRÉVOST (Bull. Soc. chim., 1935, [v], 2, 1119—1148).—Current views of valency are modified. The no. of electronic doublets in the outer shell, except for the *K* ring, is regarded as equal to the no. of corners of a polyhedron (4, 6, etc.), and electronic shells can be completed by borrowing from an inner shell even when this is the *K* ring. Ionic forces are inferior to covalent. O may be singly covalently linked, as in  $\text{O} \cdot \text{P}(\text{OH})_3$  [the electrostatic energy between  $\text{O}^-$  and  $\text{P}^+$  in the formulation  $\text{O}^- \cdot \text{P}^+(\text{OH})_3$  is considered to be negligible],  $\text{O} \cdot \text{S} \cdot \text{O}$ ,  $\text{O} \cdot \text{S}(\cdot \text{O})_2$ , etc. Co-ordination is represented on the basis of covalency and not as electrostatic action on dipoles, and the co-ordination no. never exceeds 4 when the underlying ring is *K*, and when the central atom and satellites belong to the same row of the periodic table. Deficient octets, as in  $\text{BF}_3$ , are considered to be completed from the *K* ring, except in the active form, and thus possess tetrahedral symmetry. Oxidation and autoxidation are discussed. Prototropy is generalised on the basis of the structural insignificance of the electrovalent linking, the stable structure not necessarily

corresponding to the neutralisation by the  $\text{H}^+$  of the effective charge, e.g., in the ion  $\text{O}^-\text{N}^+\text{O}^+$  the negative charge is carried by O, but the stable form is  $\text{O} \cdot \text{N}(\cdot \text{O}) \cdot \text{H}$ ; so with  $(\text{HO})_2\text{P}(\cdot \text{O}) \cdot \text{H}$ . Many mols. usually written with triple linkings are supposed to have singlet linkings, e.g.,  $\text{:N} \cdot \text{N} \cdot$ , electrons being drawn from the *K* rings, explaining the acidity of  $\text{C}_2\text{H}_2$  and  $\text{HCN}$ . The theory is supported by stereochemical evidence. R. S. B.

**Electronic theories of Lewis and Kossel.** W. A. NOYES (Science, 1935, 81, 628—629).—Lewis' theory provides a simple explanation for many facts which are less easily reconciled with that of Kossel. L. S. T.

**Orientation of unsymmetrical molecules at interfaces.** S. H. BAUER and A. POLLACK (J. Chem. Physics, 1935, 3, 401—405).—Theoretical. H. J. E.

**Electronic structures of polyatomic molecules and valency. VI. Method of molecular orbitals.** R. S. MULLIKEN (J. Chem. Physics, 1935, 3, 375—378; cf. A., 1934, 14).—Theoretical. A qualitative framework into which chemical and spectroscopic data can be fitted is described. H. J. E.

**Vibrations of polyatomic molecules in excited electronic states.** A. B. F. DUNCAN (J. Chem. Physics, 1935, 3, 384—385).—The strongest vibrational frequencies observed in the excited states of  $\text{CO}_2$ ,  $\text{CS}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{ClO}_2$ ,  $\text{SO}_2$ ,  $\text{O}_2$ ,  $\text{NH}_3$ ,  $\text{PCl}_3$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_6\text{H}_6$ , and  $\text{COMe}_2$  are totally symmetrical. These are usually the only frequencies observed. H. J. E.

**Molecular structure of benzene.** G. B. BONINO (Gazzetta, 1935, 65, 371—423).—Modern conceptions of the structure of the  $\text{C}_6\text{H}_6$  ring are reviewed, with special reference to results obtained from the study of spectra (including infra-red and Raman) and to the application of quantum mechanics to the problem. It is considered that a conception of structure which is both acceptable on physical grounds and useful in interpreting the chemical behaviour of cyclic compounds is now available. H. F. G.

**Calculation of the fundamental frequencies of vibration of a molecule  $\text{X}_6\text{Y}_6$ , having plane hexagonal symmetry.** C. MANNEBACK (Ann. Soc. Sci. Bruxelles, 1935, 55, B, 129—159).—Mathematical. W. R. A.

**Calculation of the vibration frequencies of  $\text{C}_2\text{H}_4$  by the method of symmetrical co-ordinates.** J. M. DELFOSSE (Ann. Soc. Sci. Bruxelles, 1935, 55, B, 114—128).—Mathematical. W. R. A.

**Periodic groups of non-hydride di-atoms.** C. H. D. CLARK (Trans. Faraday Soc., 1935, 31, 1017—1036; cf. this vol., 432).—Non-hydride di-atoms are classified into periods (determined by non-bonding groups of electrons) and groups or sub-groups (dependent on electrons derived from the incomplete systems of the constituent atoms). Regularities and progressions of spectroscopic consts. are traced through different groups and periods. E. S. H.

**Rational systematisation of chemical compounds.** H. G. GRIMM (Z. ges. Naturwiss., 1935, 1,



178—186; cf. this vol., 448).—A review of the author's method of classification. H. J. E.

**Maximum valency of elements and atomic structure. I, II.** B. ORMONT (*Acta Physicochim. U.R.S.S.*, 1935, 1, 745—751, 752—758).—A general discussion of the influence of electron arrangements in compounds on their stability. Numerous compounds are discussed. H. J. E.

**Electron affinity of the radicals  $\text{HO}_2$  and  $\text{OH}$ , and the oxygen molecule.** J. WEISS (*Trans. Faraday Soc.*, 1935, 31, 966—969).—Theoretical. The electron affinities, calc. with the aid of certain assumptions, are  $\text{HO}_2 + 4.6$ ,  $\text{OH} + 3.7$ ,  $\text{O}_2 + 2.7$  electron volts. E. S. H.

**Constitution of water in solutions of weak electrolytes. I. Formic and acetic acids.** C. S. S. RAO (*Phil. Mag.*, 1935, [vii], 20, 310—322).—The effect of dissolving weak electrolytes in  $\text{H}_2\text{O}$  on its constitution has been investigated in the case of  $\text{AcOH}$  and  $\text{HCO}_2\text{H}$  by examining the intensity distribution along the Raman  $\text{H}_2\text{O}$  band in these solutions. With increasing concn. of solute the band sharpens, and the max. moves towards higher frequencies. Addition of a weak electrolyte to  $\text{H}_2\text{O}$  causes a decrease in  $[(\text{H}_2\text{O})_3]$  and an increase in  $[\text{H}_2\text{O}]$ . The proportion of  $(\text{H}_2\text{O})_3$  in  $\text{HCO}_2\text{H}$  is  $>$  in  $\text{AcOH}$  at the same concn. A. J. M.

**Electron affinity of free radicals. V. Aromatic derivatives of dixanthyl and  $pp'$ -diphenylenedi(diphenylmethyl).** H. E. BENT and R. G. GOULD, jun. VI. **Strength of the carbon-carbon linking in certain substituted dixanthyls.** H. E. BENT and E. S. EBERS. VII. **Triphenylboron and tri- $\alpha$ -naphthylboron.** H. E. BENT and M. DORFMAN (*J. Amer. Chem. Soc.*, 1935, 57, 1217—1220, 1242—1246, 1259—1261; cf. A., 1932, 1191).—V. The electron affinities of phenylxanthyl and  $\alpha$ -naphthylxanthyl differ little from the vals. for org. free radicals previously reported. Na is added more easily to  $pp'$ -diphenylenedibenzhydryl than to  $\text{CPh}_3$ . This observation is interpreted in terms of single linking energies and resonance energy.

VI. The electron affinities of dibenzyl-, diphenylethyl-, and di- $n$ -butyl-dixanthyl have been determined. The heat of dissociation of C-C in these compounds is calc. as 16—17 kg.-cal. The variability of single linking energies is discussed.

VII.  $\text{BPh}_3$  and tri- $\alpha$ -naphthylboron (I) behave like free radicals in adding Na, but the reaction is slow and the free energy change small. (I) adds 2 Na atoms, the second of which is held much less firmly than the first. E. S. H.

**Concept of "chemical compound."** J. A. A. KETELAAR (*Chem. Weckblad*, 1935, 32, 58—64).—The structure of intermetallic compounds and of cryst. substances in general is discussed in relation to the conception of a compound as containing certain elements in const. stoicheiometric proportions. Thermal analysis alone does not adequately reveal the composition of all phases which may occur in the former case; the application of e.m.f. measurements and of activity considerations is demonstrated. H. F. G.

**Nature of chemical force.** H. HELLMANN (*Acta Physicochim. U.R.S.S.*, 1934, 1, 333—353).—A summary of recent news. J. W. S.

**Theory of liquids. III.** T. S. WHEELER (*Proc. Indian Acad. Sci.*, 1935, 1, A, 795—814; cf. A., 1934, 1295).—An examination of Edser's theory regarding a liquid as composed of a no. of force centres or mols. each vibrating within an associated spherical space kept free from other mols. by the thermal motion of the occupying mol. The vibratory motion is considered, and the amplitude has been linked with density, internal latent heat of vaporisation, surface tension, viscosity, and v.p. Formulae relating viscosity with surface tension, and v.p. with internal latent heat, and equations for the coeff. of thermal expansion and compressibility are derived. Results are verified for a no. of substances. N. M. B.

**Mechanical requirements and complementary anisotropy of ferromagnetic materials.** A. PERRIER (*Helv. phys. Acta*, 1934, 7, 665—668; *Chem. Zentr.*, 1935, i, 1015).—Theoretical. The production of anisotropy by mechanical working is related to the author's theory of ferromagnetic induction.

J. S. A.  
**Comparison of action of heat on platinum oxide obtained chemically and in the electric discharge.** J. PIAZZA (*An. Soc. cient. Santa Fe*, 1934, 6, 23—25; *Chem. Zentr.*, 1935, i, 1028).—Pt oxide (I) obtained by electric discharges in  $\text{O}_2$  at low pressure decomposes between 530° and 600°;  $\text{Pt}(\text{OH})_2$  at 560°;  $\text{PtO}_2$  at 630°. (I), of composition  $\text{Pt}_2\text{O}_3$ , is probably a mixture of Pt and  $\text{PtO}_2$ .

J. S. A.  
**Compound of platinum and helium. Probable size of colloidal particles.** H. DAMIANOVICH (*An. Soc. cient. Santa Fe*, 1934, 6, 17—19; *Chem. Zentr.*, 1935, i, 1027—1028).—The mol. size calc. from at. dimensions is of colloidal order. To obtain products of high He content, rapid condensation on a cooled surface is desirable.

J. S. A.  
**Electronic states of the carbon atom and the calculation of binding energies.** W. LASAREFF (*Physica*, 1935, 2, 737—742).—The energies of the C-C linking in diamond and in aliphatic compounds are  $132 \pm 3.5$  and 128 kg.-cal., respectively. H. J. E.

**(C-C) diamond linking energy.** W. LASAREFF (*J. Physical Chem.*, 1935, 39, 913; see preceding abstract).—From recent data the energy of the  $\text{C}(^5\text{S})$ - $\text{C}(^5\text{S})$  linking in the diamond lattice is calc. as  $123 \pm 5$  kg.-cal. J. W. S.

**Dynamical theory of the diamond lattice. II. Elastic constants of diamond.** N. S. N. NATH (*Proc. Indian Acad. Sci.*, 1935, 1, A, 841—849; cf. this vol., 150).—Mathematical. Expressions for the three elastic consts. of the diamond in terms of the mol. force consts. and approx. numerical vals. are deduced. N. M. B.

**Variation method of calculating the energy of atomic systems.** A. A. SCHUCHOVITZKI (*Acta Physicochim. U.R.S.S.*, 1934, 1, 212—219).—Mathematical. J. W. S.

**Correction to the Eötvös constant.** D. G. DERVICHIAN (*Compt. rend.*, 1935, 200, 2065—2067).—



The val. of the Eötvös const. for a series of fatty acids and alcohols is approx. 1.2 if, in place of the expression  $(M/N\rho)^{2/3}$  for the surface area, the val. of the cross-section of the mol., deduced from X-ray measurements, is used. These substances all give discordant vals. using the normal method of calculating the const. H. J. E.

**Interpretation of the Eötvös constant and of its different values.** D. G. DERVICHIAN (Compt. rend., 1935, 201, 130—133; cf. preceding abstract).—Theoretical. An expression is derived similar to the Eötvös equation with the Ramsay and Shields correction term. Vals. for the const. are calc. and compared with experimental vals. H. J. E.

**Surface tension of heavy water.** H. LACHS and I. MINKOW (Nature, 1935, 136, 186—187).—Preliminary measurements with 94—99.2% D<sub>2</sub>O indicate that the surface tensions of H<sub>2</sub>O and D<sub>2</sub>O are probably equal. L. S. T.

**Parachor and chemical constitution. II. Structure of the triphenylmethane dyes.** S. K. RAY (J. Indian Chem. Soc., 1935, 12, 248—257; cf. this vol., 283).—The surface tension and  $d$  of the hydrochlorides and coloured carbinol bases of rosaniline, crystal-violet, and malachite-green have been determined in solution. The parachor vals. support the quinonoid structure. O. J. W.

**Additivity of the parachor.** A. H. W. ATEN, jun. (Rec. trav. chim., 1935, 54, 666—670).—From the law of corresponding states it is shown that the parachor defined by  $P=\gamma^{1/4}M/(D-d)$  should also be given by  $P=Ka^{1/4}b^{1/2}$ , where  $a$  and  $b$  are the van der Waals consts. for the substance and  $K$  is a const. for all substances. Vals. of  $P$  calc. by the two formulæ show satisfactory agreement for the 30 substances examined. Additivity of  $P$  is traced to the additivity of the function  $a^{1/4}b^{1/2}$ . S. J. G.

**Fine structure of X-ray absorption edges in close-packed cubic and close-packed hexagonal crystal lattices.** D. COSTER (Physica, 1935, 2, 606—610).—The cubic close-packed and the hexagonal close-packed crystal lattices give the same X-ray absorption edge fine structure as regards the position of max. and min. relative to the main edge. The form of the max. and min. show typical differences. Data for Ca and Ti and for  $\alpha$ - and  $\epsilon$ -brass are quoted. H. J. E.

**Lattice state of reacting crystal phases in the X-ray diagram.** W. BÜSSEM (Naturwiss., 1935, 23, 469—472).—The methods of obtaining  $F$ -curves for reacting crystal phases are discussed. A. J. M.

**X-Ray extinction in piezoelectrically oscillating crystals.** G. W. FOX and W. A. FRASER (Physical Rev., 1935, [ii], 47, 899—902). N. M. B.

**New crystallography.** W. L. BRAGG (Proc. Roy. Soc. Edin., 1934—1935, 55, 62—71).—Bruce-Preller lecture. N. M. B.

**Photo-elastic effect of cubic crystals.** H. MUELLER (Physical Rev., 1935, [ii], 47, 947—957).—Assuming that elastic deformations produce optical anisotropy, the Ewald-Born theory of double refraction of crystals is applied to the calculation of

the photo-elastic properties of  $D$  lattices. An explanation of the change of  $n$  with density, and of the different photo-elastic properties of NaCl, KCl, CaF<sub>2</sub>, and diamond is deduced. N. M. B.

**Equilibrium form and growth form of crystal.** I. N. STRANSKI and R. KAISCHEV (Ann. Physik, 1935, [v], 23, 330—338).—Theoretical. The equilibrium and growth forms of a crystal and the effect of degree of supersaturation on the equilibrium form are discussed on the basis of the theory of crystal growth previously put forward (this vol., 816). A. J. M.

**Growth of very thin crystals. I. Qualitative investigation. II. Quantitative study. III. Theoretical.** L. KOWARSKI (J. Chim. phys., 1935, 32, 303—331, 395—405, 469—495; cf. A., 1930, 1111, 1366; 1932, 796).—I. Full details are given of the growth, contraction, and drop phenomena observed with  $p$ -toluidine (I) crystals sublimed on to the edge of a razor blade, and mica, using the apparatus described. Two types of crystals are distinguished. Type (i) are large isolated crystals of uniform sp. thickness (approx. 1  $\mu$ ) with geometrically definable curved edges. These crystals grow when a carefully cleaned blade and rapid cooling are employed. When a disturbance occurs, such as making contact with a growing crystal, increments of thickness spread radially over the surface from the point of contact. Type (ii) occur in oriented groups. Each crystal is in stratified layers of different thickness and grows simultaneously in thickness and area. The edges are rectilinear. Such crystals are produced on blades contaminated with (I) and by slow cooling. Liquid drops formed below the m.p. are mobile and do not enlarge on type (ii), but are stationary and enlarge on type (i) (cf. A., 1933, 557). The unit cell of (I),  $a$  5.93,  $b$  8.91,  $c$  23.3 Å., contains 8 mols.

II. Growing crystals of (I) are photographed at intervals of 10—15 sec.. Each crystal passes through three stages of growth. Initially, the area,  $S$ , increases parabolically with respect to time, then linearly, and finally the rate tends to zero; concomitantly, the ratio  $S^{\frac{1}{2}}/\text{breadth}$  ( $=f$ ) decreases, becomes const., and then increases. In general, these phenomena are independent of changes of thickness.

III. The theories of crystal growth are reviewed. The surface of a "curve-type" crystal of (I) is covered with a film of mobile mols. of which the surface density probably increases with time, and "homothetic" growth ( $f$  const.) is interpreted as an isotropic phenomenon. The theory leads to a growth equation of the form  $S=S_{\infty}e^{-\frac{1}{2}kt}$ , which accords with the above data, where  $S$  is the surface area at time  $t$ . In general, crystal growth is anisotropic, but isotropy supervenes when the velocity of crystallisation is in the neighbourhood of its max. J. G. A. G.

**Oriented intergrowth and overgrowth in relation to the modification of crystal habit by adsorption.** C. FRONDEL (Amer. J. Sci., 1935, [v], 30, 51—56).—In the case of regular intergrowths of crystals of different kinds, the lattice dimensions on certain planes are comparable; it is suggested that the same is true when impurities adsorbed from solu-



tion have an influence on the habit of the growing crystal. L. J. S.

**Analytical method for determining preferred orientations of crystals in mechanically worked cubic metals.** C. B. POST (Z. Krist., 1935, 90, 330—340).—An addition to the established method, which involves X-ray pinhole photographs along and perpendicular to the direction of rolling. Mainly mathematical, with detailed reference to the orientation analysis of rolled Ag. B. W. R.

**Recrystallisation of silver of different degrees of purity.** E. OSSWALD (Z. Metallk., 1935, 27, 101—104).—The recrystallisation temp. of Ag determined by X-ray methods agrees closely with that determined from curves showing the recovery of physical properties with annealing temp. Chemically pure Ag recrystallises at room temp. within 24 hr. of rolling and is completely recryst. in about 3 weeks. Even minute quantities of impurity raise the recrystallisation temp. considerably. Ag with 0.1% Fe recrystallises at 80° when annealed immediately after rolling, but will recrystallise at 20° in 14 days. A. R. P.

**Twinning of single crystals of tin.** B. CHALMERS (Proc. Physical Soc., 1935, 47, 733—746).—The conditions under which parts of the crystals can be caused to twin by impact or tension are investigated, and the determination of the energy relations for certain controlled cases is described. The energy of twinning is  $8 \times 10^5$  ergs converted into heat per c.c. of crystal twinned. The process is discussed in relation to the crystal structure of Sn. N. M. B.

**Microstructure of platinum after action of helium, oxygen, and hydrogen in the electric discharge.** H. DAMIANOVICH (An. Soc. cient. Santa Fe, 1934, 6, 20—22; Chem. Zentr., 1935, i, 1028).—After the action of He, Pt shows a fine-grained structure with isolated coarse growths due to the ease of recrystallisation of Pt in He. In H<sub>2</sub> and other gases a uniform large-grained structure results. J. S. A.

**Properties of crystalline magnesium oxide.** R. W. DITCHBURN and J. HARDING (Nature, 1935, 136, 70—71).—Heating for 1 hr. in a vac. with metals at the specified temp. had no effect on cryst. MgO in the case of K (400°), Na (500°), Pb (1050°), Mg (1100°), and Al (1100°); Ca (1050°) and Cu (1100°) etched the surface slightly. The crystal is thus more resistant to metallic vapours than is glass or quartz. It can be ground and polished, and sealed into soda-glass of high expansion coeff. L. S. T.

**Crystal structure of Au<sub>2</sub>Bi.** T. JURRIANSE (Z. Krist., 1935, 90, 322—329).—A definite phase Au<sub>2</sub>Bi exists; its structure is cubic face-centred, space-group  $O_h^1$ ,  $a_0$  7.942 Å.,  $d$  (X-ray) 15.70, m.p.  $373^\circ \pm 2^\circ$ . The equilibrium diagram of the system Au—Bi is revised accordingly. B. W. R.

**X-Ray investigation of austenite and martensite in some special steels.** Z. NISHIYAMA (Sci. Rep. Tôhoku, 1935, 24, 128—140).—Steels containing Cr, Ni, or Mn and quenched from the  $\gamma$ -phase have been examined. The austenite has a face-centred cubic and the  $\alpha$ -martensite a body-centred tetragonal

lattice, the consts. of each lattice varying with C content as in C steels. The martensite formed from austenitic Ni steel by cooling in liquid N<sub>2</sub> has the same tetragonal lattice. The martensite-like structure observed in quenched and tempered high-C high-Mn steel has a hexagonal lattice and has been formed from austenite during polishing. R. C.

**Structure of manganite.** J. GARRIDO (Bull. Soc. Franç. Min., 1935, 58, 224—241).—Manganite from Illfeld has  $a$  4.42,  $b$  5.23,  $c$  2.87 Å. The X-ray diagram indicates the existence of a multiple cell with  $A$  8.84,  $B$  5.23,  $C$  5.74 Å., and 4 mols. of Mn<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O making 1 mol. of Mn<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O in each of the four smaller cells. Each Mn is surrounded by 6 O at 1.95 Å. L. S. T.

**Transition point of sodium cyanide due to rotation of the CN group.** J. M. BJVOET and H. J. VERWEEL (Rec. trav. chim., 1935, 54, 631—632).—The lattice of NaCN is of the rock-salt type at room temp., but changes to orthorhombic on cooling, the transition point being 11—16°, since the kinetic energy is no longer sufficient to permit the free rotation of the CN groups, which become oriented parallel to one another. This also explains why the crystal does not fall to pieces when the lattice form changes, despite a contraction of 1.5%. S. J. G.

**Crystallography of complex salts.** E. STOICOVICI (Bull. Soc. Ştiinţe Cluj, 1934, 8, 140—144; Chem. Zentr., 1935, i, 997).—[Cu en<sub>2</sub>][Mn(SCN)<sub>4</sub>] is triclinic holohedral,  $a : b : c = 1.260 : 1 : 0.972$ ,  $\alpha$  90° 32',  $\beta$  115° 59',  $\gamma$  101° 32'. [Ni en<sub>3</sub>][Ni(SCN)<sub>6</sub>] is monoclinic holohedral,  $a : b : c = 1.067 : 1 : 1.143$ ,  $\beta$  111° 50'. J. S. A.

**Crystal structure of calcium chloride.** A. K. VAN BEVER and W. NIEUWENKAMP (Z. Krist., 1935, 90, 374—376).—By cooling fused dehydrated CaCl<sub>2</sub> slowly in vac., single crystals were obtained, having rhombic pseudotetragonal structure,  $a_0$  6.24,  $b_0$  6.43,  $c_0$  4.20 Å., space-group  $Pnmm$ . At. parameters are given. A powder photograph does not agree with this structure, but corresponds with a second modification, arising from the first by mechanical disturbance. B. W. R.

**Crystal structure of aluminium arsenate AlAsO<sub>4</sub>. Isomorphism of Si and As<sup>v</sup> in crystals.** F. MACHATSCHKI (Z. Krist., 1935, 90, 314—321).—Powder diagrams of AlAsO<sub>4</sub> indicate a hexagonal structure,  $a_0$  5.030,  $c_0$  5.612 Å., disagreeing with the tetragonal structure previously found, and corresponding with that of quartz if the 3 Si of quartz are replaced by Al<sup>III</sup> and As<sup>v</sup> statistically in the ratio 1 : 1. B. W. R.

**Crystallographic relations of aluminium iodate nitrate.** K. SZTRÓKAY (Z. Krist., 1935, 90, 381—382).—Morphological and optical properties of the crystals Al(IO<sub>3</sub>)<sub>2</sub>NO<sub>3</sub>·6H<sub>2</sub>O are described. B. W. R.

**Complex anion formation by tervalent elements: structure of caesium thallic enneachloride.** H. M. POWELL and A. F. WELLS (J.C.S., 1935, 1008—1012).—The structure of Cs<sub>3</sub>Tl<sub>2</sub>Cl<sub>9</sub> has been determined. The rhombohedral unit cell has 2 mols.; space-group  $C_{3v}^1$  or  $D_{3d}^2$ . The structure is



based on a hexagonal close-packing of the Cs and Cl ions, with Tl occupying some of the positions between 6 Cl. The complex anion  $\text{Tl}_2\text{Cl}_9^{3-}$ , distinguished in the structure, is formed by two octahedral groups of 6 Cl around one Tl sharing the 3 Cl of one face between two octahedra. The comparative instability of  $\text{A}_3\text{MHl}_6$  halides is attributed to the structure, and the formation of more complex compounds to greater structural compactness. The relation of the structure to that of  $\text{Cs}_3\text{As}_2\text{Cl}_9$  is discussed.

N. M. B.

**Scattering of X-rays in solutions of heavy molecules and the structure of complex ions.** V. DANILOV, V. FINKELSTEIN, and D. SIROTENKO (Ber. Ukrain. wiss. Forsch. physikal. Chem., 1935, 4, 125—133).—The theory of the scattering of X-rays by gases can be applied to a solution of heavy mols. in a solvent of light mols. A study of X-ray scattering by aq.  $\text{K}_2\text{Hg}_2\text{I}_4$  indicates that  $\text{HgI}_4^{2-}$  consists of 4 I' arranged tetrahedrally about a central Hg<sup>++</sup>.

R. S.

**Crystallographic investigation of**  $2[\text{HgClMnO}_4], 3\text{HgO}$ . C. LAURO (Rend. Fac. Sci. Cagliari, 1933, 3, 148; Chem. Zentr., 1935, i, 1027).—The compound has  $a : b : c = 1.74805 : 1 : 0.62872$ .

J. S. A.

**Two-dimensional crystals of cristobalite.** W. NIEUWENKAMP (Z. Krist., 1935, 90, 377—380).—Photographs are given which confirm the author's theoretical treatment of two-dimensional X-ray diffraction. The cristobalite specimens examined have a two-dimensional lattice, with only arbitrary phase relations between adjacent sheets.

B. W. R.

**Crystal structure of lepidocrocite.** F. J. EWING (J. Chem. Physics, 1935, 3, 420—424).—The crystals are orthorhombic ( $a$  3.87,  $b$  12.51,  $c$  3.06 Å.; space-group  $V_h^{17}$ -*Amam*; 4 mols. of  $\text{FeO}(\text{OH})$  in the unit cell). Interat. distances are calc. The structure consists of Fe-centred O octahedra, joined by the sharing of edges into two-dimensionally infinite layers, with the successive layers held together by H linkings.

H. J. E.

**Crystallography and structure of hexamethylenetetramine salicylate.** A. ŁASZKIEWICZ (Arch. Chem. Farm., 1935, 2, 219—236).—Crystallographic data are recorded.

R. T.

**Crystal structure of dodecahydrobenzanthracene.** J. IBALL (Chem. and Ind., 1935, 716).—The cell is triclinic,  $a_0$  7.84,  $b_0$  8.71,  $c_0$  11.71 Å.,  $\alpha$  108.0°,  $\beta$  96.6°,  $\gamma$  81.5°,  $d$  (floatation) 1.123. Space-group probably  $P\bar{1}$ . The probable shape of the mol. is discussed.

B. W. R.

**X-Ray studies of products of nitration of starch.** I. M. KOŁACZKOWSKA and T. URBANŃSKI (Rocz. Chem., 1935, 15, 339—342).—Starch nitrates prepared from potato and sol. (amorphous) starch show the formation of similar crystallites in both cases.

R. T.

**Molecular structure in sisal, coir, and oak.** E. N. M. THOMAS and J. HEWITT (Nature, 1935, 136, 69—70).—X-Ray photographs are reproduced. Sisal fibres give the usual cellulose pattern and stretch-

ing appears to act on the crystallites (or micelles) in the same way as it does on cotton. The coir pattern gives two cellulose patterns at right angles to each other, and may be interpreted either as one spiral of crystallites running at 45° around the fibre, or as two spirals at right angles to each other, each running at 45° in opposite directions around the fibre. Chlorination has no great effect on the X-ray patterns, supporting the view that lignin is amorphous. In oak, it is inferred that the crystallites lie parallel to the longitudinal axis of the tracheids and that they are almost perfectly oriented. The results for oak agree, to some extent, with those for the summer wood of ash and the spring wood of fir (A., 1931, 1360).

L. S. T.

**Electron diffraction as a means for determining the structure of organic substances.** G. NATTA, M. BACCAREDDA, and R. RIGAMONTI (Monatsh., 1935, 66, 64—75).—The electron diffraction diagrams of many highly polymerised org. substances are very susceptible to the presence of thin films of fatty impurities. Special precautions are necessary to obtain characteristic diagrams of such substances.

O. J. W.

**Structure of the benzene molecule and some of its methyl derivatives.** P. L. F. JONES (Trans. Faraday Soc., 1935, 31, 1036—1039).—The vapours of  $\text{C}_6\text{Me}_6$ , mesitylene, *p*-xylene, and  $\text{C}_6\text{H}_6$  have been examined by the electron-diffraction method. The results are in agreement with the assumption of a plane mol. with a regular hexagonal structure for the  $\text{C}_6\text{H}_6$  nucleus.

E. S. H.

**Scattering of fast electrons from thin foil.** H. SAEGUSA and K. KIKUCHI (Sci. Rep. Tōhoku, 1935, 24, 30—44).—The angular distribution of electrons scattered at angles of 30—120° by non-elastic collision from celluloid films has been determined, with accelerating voltages of 1 to  $2.8 \times 10^4$  volts; the no. of electrons so scattered passes through a max. at about 53° and a min. at 45°, and at 90° is about 110% of the no. scattered by elastic collision. For angles of 30—50° the results agree with Möller's theory (A., 1931, 1100) as well as do Klemperer's (A., 1933, 109).

R. C.

**Diffraction of X-rays and electrons by carbon tetrachloride vapour.** C. DEGARD, J. PIÉCARD, and W. VAN DER GRINTEN (Nature, 1935, 136, 142—143; cf. A., 1934, 946, 1163).—New X-ray and electron-diffraction analyses of  $\text{CCl}_4$  agree with theory and give the same vals. for interat. distances, viz., Cl-Cl  $2.85 \pm 0.03$  Å.,  $2.86 \pm 0.03$  Å., and C-Cl  $1.74 \pm 0.02$  Å.,  $1.75 \pm 0.02$  Å., respectively. The influence of thermal vibrations could be detected in the electron-diffraction photographs.

L. S. T.

**Contact difference of potential between tungsten and barium. External work function of barium.** P. A. ANDERSON (Physical Rev., 1935, [ii], 47, 958—964).—Highly rigorous conditions of outgassing and of obtaining clean surfaces lead to the vals.  $2.13 \pm 0.05$  volts for the contact p.d. between W and Ba, and  $2.39 \pm 0.05$  equiv. volts for the external work function of Ba.

N. M. B.



**Molecular orientation in thin layers of anisotropic liquids and measurement of constants characterising their elastic properties.** V. FRÉDERIKS and V. ZVETKOV (Physikal. Z. Sovietunion, 1934, 6, 490—504; cf. A., 1934, 948).—Experiments with *p*-azoxyanisole are described, vals. for its elasticity consts. as a function of temp. being given.

CH. ABS. (e)

**Plasticity of crystals.** E. W. ZECHNOWITZER (Naturwiss., 1935, 23, 511).—Recrystallisation of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  from  $\text{HNO}_3$  solution gives large prismatic crystals which can be bent in the fingers. When thus treated, the crystals become opaque and rough. Undeformed crystals lose their plasticity on keeping in air.

A. J. M.

**Elastic modulus of ferromagnetic metals.** M. KÆRSTEN (Z. Metallk., 1935, 27, 97—101).—Recent work on the effect of internal stress on the elastic modulus of metals is reviewed and its bearing on the variation of the modulus of ferromagnetic metals under the influence of magnetic fields is discussed mathematically.

A. R. P.

**Weakening of a deformed single crystal by annealing.** M. O. KORNFELD (Physikal. Z. Sovietunion, 1934, 6, 329—342; cf. A., 1934, 1296; this vol., 433).—Single-crystal wires of Al were strengthened by tensile deformation and then weakened by annealing for various periods at temp. (*t*) from 150° to 650°. The velocity of weakening rises rapidly with *t* in the range 150—250°, but does not vary greatly with the initial degree of deformation for *t*=200°. For 20-hr. annealing periods the flow limit decreases linearly with fall of *t* up to 400° and above 550°, but the state of the crystal does not vary with *t* in the interval 400—550°. Annealing near the m.p. restores the deformed crystal to its initial state.

CH. ABS. (e)

**Continuity of the solid and the liquid states.** J. FRENKEL (Nature, 1935, 136, 167—168).—The solid, liquid, and gaseous states must be regarded as forming one continuous sequence, the sharp transition points, i.e., m.p. and b.p., being substitutes for continuous transitions through unstable intermediate states corresponding with the hook-like parts of the *p*-*v* curve.

L. S. T.

**Coalescence in stages between two drops of a liquid.** I. W. WARK and A. B. COX (Nature, 1935, 136, 182).

L. S. T.

**Determination of mol. wt. of cellulose by a dynamic osmotic method.** J. MARCHLEWSKA (Rocz. Chem., 1935, 15, 331—338).—A dynamic method is described, which gives vals. of 27,000—37,000 for various samples of cellulose acetate.

R. T.

**Relation between vitrification temperature and mol. wt. of organic compounds.** F. K. GORSKI (Physikal. Z. Sovietunion, 1934, 6, 513—514).—The relation  $T_g = BM^{2/3}$  ( $T_g$ =abs. temp. of vitrification, *M*=mol. wt., *B*=const.) holds for 17 org. compounds with  $T_g$ =94—250° abs., the mean val. of *B* being 6.77. A similar expression is proposed for two-component systems.

CH. ABS. (e)

**Absorption of sound in gases.** V. O. KNUDSEN (Science, 1935, 81, 578—581).—A summary.

L. S. T.

**Tracing of standing sound and ultra-sonic waves in gases.** O. BRANDT and H. FREUND (Z. Physik, 1935, 95, 415—416).

A. B. D. C.

**Rendering visible ultra-sonic waves in gases and determination of their intensities.** R. POHLMAN (Naturwiss., 1935, 23, 511).—A method for photographing ultra-sonic waves of small intensities is described. The intensity can be determined photometrically.

A. J. M.

**Effect on supersonic dispersion in gases, of (A) pressure.** W. RAILSTON and E. G. RICHARDSON. (B) Temperature. H. L. PENMAN (Proc. Physical Soc., 1935, 47, 533—542, 543—548).—(A) Measurements of  $\lambda\lambda$  and absorption for supersonic radiation of frequencies 40—2000 kc. per sec. at pressures  $> 2$  atm. were made in  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{SO}_2$ .

(B) Measurements of  $\lambda\lambda$  of supersonic radiation of frequencies 40—140 kc. per sec. were made in  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{SO}_2$  for the range room temp.—200°. Calc. velocities at const. density plotted against temp. show supersonic dispersion by a sharp fall of velocity in  $\text{CO}_2$  at a temp. which increases with the frequency of the source. The relation of results to theories of supersonic dispersion is discussed.

N. M. B.

**Crystal structure and electrical properties.** VI. The eight principal parameters of electrical conductivity of bismuth single crystals in magnetic fields. O. STIERSTADT (Z. Physik, 1935, 95, 355—364).

A. B. D. C.

**Influence of pressure on the electrical resistance of hard-drawn gold wire in different stages of annealing, and of soft gold wire.** A. MICHELS and M. LENSSEN (Physica, 1935, 2, 591—596; cf. A., 1930, 281).—Measurements are recorded from 1 to 2900 atm. of the resistance of drawn Au wire at 25°, 50°, 75°, and 100° after annealing at 25—400°. After the application of pressure hysteresis was observed.

H. J. E.

**Theory of electrical resistance anomaly of ferromagnetic substances.** T. HIRONE (Sci. Rep. Tôhoku, 1935, 24, 122—127).—The accelerated decrease of the resistance with temp. below the crit. temp. is attributed to the mean free path of the conduction electron being decreased by the rotational vibration of the mol. magnets in the Honda-Ôkubo model of a ferromagnetic substance (Physical Rev., 1917, 10, 705). This is confirmed by existing data.

R. C.

**Electrical resistance of iron below the Curie point and the resistance anomaly of ferromagnetic materials.** A. DRIGO (Atti R. Ist. Veneto Sci., 1934, 93, 1163—1172; Chem. Zentr., 1935, i, 1186—1187).—The electrical resistance of Fe below the Curie point depends on the spontaneous magnetisation and is  $\propto$  the temp. Fe resembles Ni, the observations agreeing with theory.

H. J. E.

**Thermo-electric effect and the superconducting state.** E. F. BURTON, F. G. A. TARR, and J. O. WILHELM (Nature, 1935, 136, 141).—With Sn and



Pb no thermo-electric effect exists when both junctions are in the superconducting state. The effect appears when either one of the junctions is raised above the superconducting point of one of the metals. L. S. T.

**Thermo-electromotive force produced by magnetisation.** T. KOUSMINE (Helv. phys. Acta, 1934, 7, 732—772; Chem. Zentr., 1935, i, 863).—Data are recorded for the thermo-e.m.f. in the system Fe or Ni—Cu, with a const. temp. gradient, when the ferromagnetic material was magnetised up to saturation. H. J. E.

**Influence of magnetisation while hot and of crystallisation on the shape of the thermo-magnetic curves.** A. MICHEL and G. CHAUDRON (Compt. rend., 1935, 200, 2171—2173).—The stabilisation temp. for rhombohedral  $\text{Fe}_2\text{O}_3$  and for ferrites of Ba and Pb are  $1250^\circ$  and  $950^\circ$ , respectively. H. J. E.

**Thermomagnetic behaviour of ferromagnetic powders.** H. FORESTIER (Compt. rend., 1935, 201, 45—47; cf. A., 1926, 566).—The effects of grain size and of crystal structure are described for  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ . H. J. E.

**Mechanical damping of ferromagnetic materials in magnetisation.** M. KERSTEN (Z. tech. Physik, 1934, 15, 463—467; Chem. Zentr., 1935, i, 1186). H. J. E.

**Transition metals on the basis of quantum mechanics.** N. F. MOTT (Proc. Physical Soc., 1935, 47, 571—588).—Theoretical. The magnetic susceptibilities and electrical conductivities of Co, Ni, and Pd and of their alloys with Cu, Ag, and Au are considered. The no. of electrons in the outermost  $s$  state must be about 0.6 per atom in the transition metals and 1 in the noble metals, explaining certain magnetic properties. A quantum-mechanical explanation, supported by resistance measurements, is given of the relatively high resistance of the transition metals. N. M. B.

**Magnetic resistance variation of metal crystals.** M. KOHLER (Z. Physik, 1935, 95, 365—382).—Magnetic variation of resistance depends on the current passing and on crystallographic orientation (cf. Stierstadt, this vol., 1062). A. B. D. C.

**Number of electrons contributing to the paramagnetism of nickel.** L. NÉEL (Compt. rend., 1935, 201, 135—137).—The effects of metals alloyed with Ni on its paramagnetism are  $\propto$  the nos. of their valency electrons. The electrons of the alloyed metal annul the magnetic contribution of the Ni electrons. H. J. E.

**Gadolinium, a new ferromagnetic metal.** G. URBAIN, P. WEISS, and F. TROMBE (Compt. rend., 1935, 200, 2132—2134).—The Curie point is at  $16 \pm 2^\circ$ . The sp. magnetisation of Gd in strong fields is  $>$  that of Fe. Data are recorded. The at. moment of Gd is 35.4 magnetons, that of Fe being 11. H. J. E.

**Diamagnetism of elements in the powdered state.** M. R. VERMA and I. C. GUPTA (Current Sci., 1935, 3, 611).—Red and grey Se powdered under  $\text{C}_6\text{H}_6$  or PhMe showed only in an extreme case a fall

in diamagnetic susceptibility from  $-3.03 \times 10^{-7}$  to  $-2.69 \times 10^{-7}$  at a particle size of  $0.4 \mu$  (cf. A., 1934, 1159). Washing with dil. HCl restored the original val. Red Se passes into the black form on prolonged exposure to light, and the decrease in diamagnetic susceptibility reported in certain cases may be due to transition to a metastable allotrope on powdering. Rao's results (A., 1931, 1357) are criticised. L. S. T.

**Magnetic properties of solutions of cadmium in molten cadmium chloride and of molten calomel.** J. FARQUHARSON and E. HEYMANN (Trans. Faraday Soc., 1935, 31, 1004—1010).—The absence of paramagnetism excludes the existence of  $\text{CdCl}$ ; the probability of the existence of either  $\text{Cd}_2\text{Cl}_2$  or an at. solution of Cd in  $\text{CdCl}_2$  is discussed. Comparison of the magnetic properties with the electrical conductivity of molten calomel suggests that it consists of  $\text{Hg}_2\text{Cl}_2$  mols. which are partly dissociated into  $\text{Hg}_2^{++}$  and  $\text{Cl}^-$ . A marked rise in diamagnetic susceptibility occurs when  $\text{CdCl}_2$ ,  $\text{PbCl}_2$ , or  $\text{Hg}_2\text{Cl}_2$  melts. E. S. H.

**Magnetic susceptibilities of salts of the iron group elements.** R. B. JAMES (Physical Rev., 1935, [ii], 48, 78—83).—Measurements of paramagnetic susceptibilities of powdered crystals over the temp. range  $80$ — $300^\circ$  abs. are given for  $\text{K}_3\text{Cr}(\text{SCN})_6 \cdot 4\text{H}_2\text{O}$ ,  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO})_2 \cdot 4\text{NH}_3$ ,  $\text{Ni}(\text{CN})_2 \cdot \text{C}_6\text{H}_6 \cdot \text{NH}_3$ ,  $\text{NiO}$ ,  $\text{K}_2\text{Co}(\text{SCN})_4 \cdot 4\text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6\text{NH}_3$ ,  $\text{CoSO}_4 \cdot 6\text{NH}_3$ ,  $\text{Co}(\text{CN})_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$ . The results agree with Van Vleck's predictions. N. M. B.

**Magnetic susceptibility of cerium chloride in aqueous solution and its variation with temperature.** J. LIQUIER-MILWARD (Proc. Physical Soc., 1935, 47, 559—570).—Using a slightly modified Quincke ascension method, measurements were made for the concn. range  $8$ — $37.5\%$  anhyd. salt, and temp.  $7$ — $70^\circ$ . The variation of mol. susceptibility with temp. follows a Curie-Weiss law,  $\chi_c(T + \Delta) = C$ , where  $C = 0.762$  irrespective of concn.;  $\Delta$ , however,  $\propto$  no. of ions present per unit vol., and increases from 45 to 63 in the range considered. The effective magneton no. of the ion  $\text{Ce}^{++}$ , if calc. from  $\mu_{\text{eff}} = 14.07 \sqrt{\chi_c(T + \Delta)}$ , has a const. val. 12.36. Results are compared with available data from the spectroscopic ground states of the rare-earth group. N. M. B.

**Determination of the m.p. of calcium, strontium, and barium.** F. HOFFMANN and A. SCHULZE (Z. Metallk., 1935, 27, 155—158).—Determinations in an A atm. using vac.-sublimed metal gave the following vals.: Ca  $851^\circ$ , Sr  $771^\circ$ , Ba  $704^\circ$  ( $\pm 1^\circ$  in each case). Vals. are also given for the commercial metals. A. R. P.

**Heat capacities at low temperatures. I. Heat capacities of some organic substances.** S. AOYAMA and E. KANDA (Sci. Rep. Tôhoku, 1935, 24, 116—121).—The mol. heats of  $\text{C}_6\text{H}_6$ ,  $\text{Et}_2\text{O}$ , PhMe, PhOH, and PhI have been determined at  $80$ — $230^\circ$  abs. R. C.

**Heat capacity of potassium chloride from  $2.3^\circ$  to  $17^\circ$  abs.** W. H. KEESOM and C. W. CLARK



(Physica, 1935, 2, 698—706).—Data are recorded. Blackman's theory (this vol., 573) is partly confirmed.

H. J. E.

Heat capacity of methane and its halogen derivatives from spectroscopic data. R. D. VOLD (J. Amer. Chem. Soc., 1935, 57, 1192—1195).—The mol. heat capacities of  $\text{CH}_4$ ,  $\text{MeCl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and  $\text{CCl}_4$  over the range 0—500° have been calc., with an accuracy of about 3%, from their Raman spectra, using the equation for a polyat. gas.

E. S. H.

Relationships between constitution and magnitude of mol. heat of fusion of organic compounds. II. Synthesis of 1:4-endoazocyclohexane.—See this vol., 1133.

Homology in long-chain compounds. I. Oleic acid and *n*-alkyl oleates. L. KEEFER and J. H. McLEAN (J.S.C.I., 1935, 54, 178—185t).—The prep. of oleic acid and the *n*-alkyl oleates is described, and densities, mol. vols., and heat of combustion have been determined.

Vapour pressures of solid krypton. W. H. KESOM, J. MAZUR, and J. J. MEIHZEN (Physica, 1935, 2, 669—672).—Data are recorded from the triple point (115.94° abs.,  $p=54.9$  cm.) to 78° abs. Vals. agree with theory except near 115° abs.

H. J. E.

Vapour pressures of the isotopic forms of water. M. H. WAHL and H. C. UREY (J. Chem. Physics, 1935, 3, 411—414).—The ratio of v.p. of  $\text{H}_2\text{O}^{16}$  and  $\text{HDO}^{16}$  and that of  $\text{H}_2\text{O}^{16}$  and  $\text{H}_2\text{O}^{18}$  has been measured at 11.25°, 23.00°, 35.6°, and 46.35°, using the method of fractional distillation of dil. solutions of  $\text{D}_2\text{O}$  in  $\text{H}_2\text{O}$  under conditions such that the Rayleigh distillation formula held. Separation of the H isotopes by fractional distillation of  $\text{H}_2\text{O}$  is possible; that of the O isotopes would be more difficult.

H. J. E.

Certain physical properties of cyanogen and its halides. R. P. COOK and P. L. ROBINSON (J.C.S., 1935, 1001—1005).—The prep. and purification of  $\text{C}_2\text{N}_2$ ,  $\text{CNCl}$ ,  $\text{CNBr}$ , and  $\text{CNI}$ , used for obtaining vals. for v.p. and density, liquid density, and surface tension, are described. The temp. coeff. of the liquid density and surface tension is given. Physical properties of these compounds and of  $\text{HCN}$  are tabulated, and are discussed with reference to structure and association in the liquid state.

N. M. B.

Comparison of physical properties of hydrogen and deuterium iodides. J. R. BATES, J. O. HALFORD, and L. C. ANDERSON (J. Chem. Physics, 1935, 3, 415—420).—Data for the absorption coeffs. and v.p. of  $\text{HI}$  and  $\text{DI}$  are recorded. Absorption by  $\text{HI}$  occurs at longer  $\lambda$  than that of  $\text{DI}$ . The v.p. of  $\text{DI}$  is slightly > that of  $\text{HI}$  at a given temp. Theoretical reasons for these differences are discussed.

H. J. E.

Vapour pressure of hexachloroethane. P. J. VAN DER LEE (Z. anorg. Chem., 1935, 223, 213—216).—Between 62° and 216°, the v.p. of solid  $\text{C}_2\text{Cl}_6$  is given by  $\log_{10} p = 8.640 - 2636.1/T$ ; for the liquid,  $\log_{10} p = 7.483 - 2103.6/T$ . The triple point is 186.8°. Latent heats of sublimation, evaporation,

and fusion are 12.0, 9.6, and 2.4 kg.-cal. per mol., respectively.

J. S. A.

Sublimation pressures of solid oxygen and nitrogen. S. AOYAMA and E. KANDA (Sci. Rep. Tôhoku, 1935, 24, 107—115).—The v.p. of  $\text{O}_2$  has been measured at 37—65° and that of  $\text{N}_2$  at 35—70° abs. The results agree well with the calc. vals.

R. C.

Structure of betaine. E. NORDT and H. G. TRIESCHMANN (Z. ges. Naturwiss., 1935, 1, 197—198; cf. this vol., 436).—The approx. heats of sublimation of the betaines of  $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  and sulphanilic acid are 24—44 and 12—20 kg.-cal., respectively, showing the mols. to be heteropolar.

H. J. E.

Volume coefficient of expansion of deuterium. J. B. M. COPPOCK (Trans. Faraday Soc., 1935, 31, 913—914).—Within the limits of experimental error (1 in 4000)  $\alpha_p$  for  $\text{D}_2$  is identical with the val. for  $\text{H}_2$ .

J. W. S.

Approximate determination of the critical constants of unassociated substances. A. FERGUSON and S. J. KENNEDY (Trans. Faraday Soc., 1935, 31, 1000—1003).—Simple relations are developed to assist in the approx. calculation of crit. data from available data.

E. S. H.

Real gases according to the thermodynamic equation of state. VII. Boyle's law for helium. W. JACYNA (Z. Physik, 1935, 95, 409—414).—The positions of Amagat's minima are discussed.

A. B. D. C.

Equation of state of liquids. Negative internal pressure at high temperatures. P. WEISS (Compt. rend., 1935, 200, 1700—1702).—Theoretical. At a sufficiently high temp. the internal pressure is shown to become negative.

H. J. E.

Rotational entropy of non-rigid polyatomic molecules. M. L. EIDINOFF and J. G. ASTON (J. Chem. Physics, 1935, 3, 379—383).—Theoretical.

H. J. E.

Thermal conductivity of quartz at low temperatures. W. J. DE HAAS and T. BIERMASZ (Physica, 1935, 2, 673—682).—Measurements parallel to the crystal axis are recorded at 90—2.7° abs. The thermal resistance rises rapidly below 10° abs. The vals. at low temp. were increased by first heating at 340° and 570°.

H. J. E.

Viscosity of liquid nitrogen, carbon monoxide, argon, and oxygen, and its dependence on temperature. N. S. RUDENKO and L. V. SCHUBNIKOV (Physikal. Z. Sovietunion, 1934, 6, 470—477).—Data for the m.p.—b.p. ranges are recorded.

CH. ABS. (e)

Viscosity of sulphuric acid and its chlorides. G. P. LUCHINSKI (J. Phys. Chem. U.S.S.R., 1934, 5, 848—853).—Vals. of  $\eta$  as a function of temp. are given for  $\text{H}_2\text{SO}_4$  by  $\eta_t = 0.001236/(v_t - 0.5411)$ , for  $\text{SO}_2\text{Cl}_2$  by  $\eta_t = 0.000759/(v_t - 0.5114)$ , and for  $\text{ClSO}_3\text{H}$  by  $\eta_t = 0.000698/(v_t - 0.5440)$ ,  $v$  being the sp. vol. The limiting  $v$  at low temp. is given by  $\omega = pM - qM^2$ , where  $p = 0.010135$ ,  $q = 0.000047$ , and  $M = \text{mol. wt.}$   $\omega/M$  for  $\text{ClSO}_3\text{H}$  is the arithmetic mean of  $\omega/M$  for  $\text{H}_2\text{SO}_4$  and  $\text{SO}_2\text{Cl}_2$ .

CH. ABS. (e)



**Viscosity and heat conduction according to the geometrical weight method compared with other treatments.** W. S. KIMBALL (Phil. Mag., 1935, [vii], 20, 355—390).—Theoretical. The mathematical treatment of Chapman and Enskog is shown to be inadequate for the problem of viscosity and heat-conductivity distribution. A. J. M.

**Logarithmic increments of fluidity.** R. LAUTIE (Bull. Soc. chim., 1935, [v], 2, 1467—1470).—The log. of fluidity is an additive function. Consts. assigned to C, H, and to various rings are used to calculate the fluidities of certain hydrocarbons. Anomalies between the calc. and experimentally determined vals. for higher cyclanes are discussed. T. G. P.

**Dispersing and condensing tendencies in a viscous, compressible gas.** G. STROMBERG (Astrophys. J., 1935, 81, 474—478).—Certain conditions for general and local expansion and condensation in a viscous, compressible gas have been formulated. L. S. T.

**Complex viscosity.** A. GEMANT (Naturwiss., 1935, 23, 406—407).—The increase of damping with frequency, in so far as it affects the theory of dipole losses due to mol. rotation, and of sound waves in solids, may be explained by an extension of the theory applied to liquids by Hencky, depending on Maxwell's conception of relaxing elasticity. A. J. M.

**Physical properties of surfaces. I. Kinetic friction.** W. G. BEARE and F. P. BOWDEN (Phil. Trans., 1935, A, 234, 329—354).—Measurements of kinetic friction, using a modified Hardy apparatus, showed that for highly polished unlubricated surfaces of mild steel, Ni, and glass the coeff. of kinetic friction  $\mu_K$  is independent of load, area of contact, and velocity; contaminating films give rise to apparent deviations from these results. For lubricated surfaces a transition from "fluid" to "boundary" lubrication is shown, and in the latter state  $\mu_K$  is independent of velocity and area of contact. With some lubricants (notably octyl alcohol on steel)  $\mu_K$  decreases with increasing load, with others it is const.;  $\mu_K$ -load is not connected with viscosity of the lubricant. No latent period was found for kinetic friction. The effect of chemical composition on  $\mu_K$  was investigated for homologous series of hydrocarbons, alcohols, and acids. N. M. B.

**X-Ray examination of barium-aluminium alloys.** K. R. ANDREAS and E. ALBERT (Z. Metallk., 1935, 27, 126—128).—No solid solutions exist and only one compound,  $\text{Al}_4\text{Ba}$ , is formed; this has a body-centred tetragonal lattice,  $a$  4.53,  $c$  11.14 Å. A. R. P.

**Optical constants of the copper-nickel alloys.** H. LOWERY, J. BOR, and H. WILKINSON (Phil. Mag., 1935, [vii], 20, 390—410).—Vals. of  $n$ , absorption coeff., and reflexion coeff. for the complete range of alloys have been determined for  $\lambda$  5780, 5461, and 4358 Å. The specimens were prepared by a method of polishing which gives a very thin flowed layer. The various property-composition curves are continuous, but not linear. A. J. M.

**Structure of nickel-cobalt alloys.** W. BRONIEWSKI and W. PIETREK (Compt. rend., 1935, 201, 206—208; cf. A., 1933, 771).—The variation of the electrical conductivity, thermoelectric properties, Curie points, expansion coeffs., hardness, and magnetic properties of alloys affords no evidence of compound formation. The alloys with <75% Co are solid solutions of  $\gamma$ -Co in  $\alpha$ -Ni, and those with >75% Co solutions of  $\alpha$ -Ni in Co. H. J. E.

**Equilibrium diagrams of binary alloys of tin.** E. S. HEDGES and C. E. HOMER (Tech. Publ. Int. Tin Res. Dev. Counc., B, No. 2, 90 pp.).—A compilation of equilibrium diagrams of binary systems containing Sn with Al, Sb, As, Ba, Bi, Cd, Ca, Ce, Cr, Co, Cu, Ga, Au, I, Fe, La, Pb, Li, Mg, Mn, Hg, Ni, P, Pt, K, Se, Si, Ag, Na, Sr, S, Te, Tl, and Zn, respectively, with notes on the transformations occurring in each system, and a discussion of the interpretation of the diagrams. E. S. H.

**Kinetics and mechanism of the allotropic transformation in the Pd-Cu system.** (X-Ray investigation with single crystals containing 40—50 at.-% of palladium.) L. GRAF (Physikal. Z., 1935, 36, 489—498).—The transition of the  $\alpha$ -phase (stable at room temp.) of Pd-Cu alloys containing 40—50 at.-% Pd into the  $\beta$ -phase (stable at temp. >600°) has been investigated by the X-ray method. It is a two-phase transition. The transition point is the higher, and the transition velocity the smaller, the higher is the Pd content, and for single crystals < for polycryst. specimens. The transition starts at points of instability in the crystal, e.g., on the surface, at nuclear boundaries, or where there has been plastic deformation. Previous heat-treatment of the alloy has no effect on the kinetics of the transition. There are certain exact geometrical relationships between the cryst. forms of the two phases.  $[311]_\alpha$  is parallel to  $[100]_\beta$ , and  $(001)_\alpha$  is parallel to  $(113)_\beta$ . This suggests that the breakdown of the  $\beta$ -crystal starts from quite definite energy-labile planes, the atoms set free arranging themselves in definite positions with respect to the  $\beta$ -crystal. A. J. M.

**Cubic sodium tungsten-bronzes.** G. HÄGG (Z. physikal. Chem., 1935, B, 29, 192—204).—These have the composition  $\text{Na}_x\text{WO}_3$ , where  $x=0.3-1$ , and all their lattices are of the perovskite type. When  $x=1$  the unit cell contains 1  $\text{NaWO}_3$  mol.,  $a \approx 3.850$  Å., and the colour is yellow. As  $x$  falls the colour changes through red to violet, being deep bluish-violet when  $x \approx 0.3$ , and  $a$  falls steadily, but the original W-O lattice is retained. The deepening in colour is due to progressive oxidation of  $\text{W}^{\text{V}}$  to  $\text{W}^{\text{VI}}$  ions. This is compensated by a fall in the no. of  $\text{Na}^+$  ions, an increasing no. of  $\text{Na}^+$  ion positions in the lattice being left empty. The colours are surface colours, not body colours. At 20—350° the bronzes are electronic semi-conductors with high conductivity and small temp. coeff. Tetragonal W-bronzes contain less Na than the cubic bronzes so far examined. R. C.

**X-Ray analysis of binary metallic alloys at higher temperatures.** G. F. KOSOLAPOV and A. K. TRAPEZNIKOV (J. Tech. Phys. U.S.S.R., 1934, 4, 1622—1624).—A 7:3 Cu-Pb alloy at 320° gave both



Cu and Pb lines, but at 340° only Cu lines. Those of Pb reappeared on cooling. CH. ABS. (e)

**Equilibrium relations in the copper corner of the ternary system copper-tin-beryllium.** E. S. ROWLAND and C. UPTHEGROVE (Amer. Inst. Min. Met. Eng., Inst. Met. Div., 1935, Tech. Publ. 613, 26 pp.).—Data based on thermal analysis, X-ray studies, and quenching experiments are given for Cu-Sn-Be alloys ( $\geq 32\%$  Sn,  $\geq 1\%$  Be). CH. ABS. (e).

**X-Ray examination of  $\alpha$ -iron magnet alloys.** R. GLOCKER, H. PFISTER, and P. WIEST (Arch. Eisenhüttenw., 1934—1935, 8, 561—563).—The effect of heat-treatment on the X-ray patterns of Fe alloys containing (a) Al 12 and Ni 30% and (b) Al 10, Ni 22.5, and Co 13% has been determined and the results correlated with the changes in coercivity ( $C$ ). No line-broadening or change in lattice parameter ( $a$ ) occurs up to the point at which max.  $C$  is obtained; only very prolonged annealing at high temp., by which  $C$  is reduced to a very low val., causes any change in  $a$ . At still higher temp. a phase with a  $\gamma$ -Fe lattice is pptd. Hence the characteristic magnetic properties of these alloys cannot be ascribed to a favourable particle size of the pptd. phase; the optimum magnetic properties are obtained when the alloy is in a similar condition to that in which duralumin shows its max. hardness, i.e., when the new phase is ready to be pptd. but before its pptn. can be detected by X-ray or micrographic examination. A. R. P.

**System iron-cobalt-tin.** W. KÖSTER and W. GELLER (Arch. Eisenhüttenw., 1934—1935, 8, 557—560).—The system has been investigated by thermal and micrographic methods up to 40% Sn. The compounds  $\text{Fe}_2\text{Sn}$  and  $\text{Co}_2\text{Sn}$  form a continuous series of solid solutions ( $\delta$ ). The peritectic equilibrium  $\alpha + \text{liquid} \rightleftharpoons \text{Fe}_2\text{Sn}$  is displaced to higher temp. by addition of Co and merges with the  $\alpha + \text{liquid} \rightleftharpoons \gamma$  equilibrium of the Fe-Co system, the temp. of which falls rapidly with addition of Sn, and with the equilibrium  $\text{liquid} \rightleftharpoons \gamma + \text{CoSn}_2$ , the temp. of which falls only slightly with addition of Fe, to form the 4-phase equilibrium:  $\text{liquid} + \gamma \rightleftharpoons \alpha + \delta$ . The solubility of  $\delta$  in the  $\alpha$ - and  $\gamma$ -phases decreases with fall in temp. and these alloys can therefore be pptn.-hardened. Hardness and coercivity vals. for some alloys with 15 and 20% Co are tabulated and some characteristic microstructures are shown. A. R. P.

**Induction period of the austenite transformation.** E. SCHEIL (Arch. Eisenhüttenw., 1934—1935, 8, 565—567).—The degree to which a transformation can be suppressed depends on the time that elapses before nuclei of the new phase form. This induction period can be calc. from the relation between the transformation temp. and the rate of cooling; for the austenite transformation the relation between induction period and transformation temp. passes through a min. the position of which has not yet been satisfactorily determined. A diagram has been constructed showing the relation between induction period, transformation temp., and the C content of steels based on the work of Sato (A., 1931, 557); this consists of three zones: ferrite, cementite, and pearlite. The formation of a pearlite nucleus in the

pearlite zone takes place more readily than that of a ferrite or cementite nucleus, and the influence of already formed crystals of these constituents is small, being greatly exceeded by the influence of the C content of the austenite. The inoculating effect of various substances on ferrite decreases in the order: sulphides, austenite grain boundaries, oxides.

A. R. P.

**Chemical stability of metallic solid solutions.** V. V. SKORCHELETTI and B. M. IDELCHIK (Metallurg, 1934, 9, No. 2, 30—43; No. 3, 27—38).—The dissolution of Mg-Cd alloys in dil.  $\text{H}_2\text{SO}_4$ , NaCl, and aq.  $\text{NH}_3$  has been studied. At 10° there is a sharp reaction limit at 25 mol.-% and a less sharp limit at 12.5 mol.-% Cd. At 25° these limits lose their sharpness, owing to the diffusion of Cd atoms above 20°. When the Mg atoms are dissolved from the Cd-rich planes the holes left are large enough for  $\text{H}^+$  to pass, but not for  $\text{SO}_4^{--}$ . It is inferred that the attack must be due to  $\text{SO}_4^{--}$ . With Ni-Cu alloys and aq.  $\text{NH}_3$  there are reaction limits at 12.5, 25, and 50 mol.-% Ni; no such limits are observed with  $\text{S}_2\text{Cl}_2$ . CH. ABS. (e)

**Thermo-electric forces of some alloys at 2.5—17.5° abs.** W. H. KEESOM and C. J. MATTHIJS (Physica, 1935, 2, 623—632; cf. A., 1932, 683).—Data are recorded for Ag with 0.91 at.-% Au, and for Au with small additions of Fe, Co, Ni, Mn, and Cr. H. J. E.

**X-Ray study of the inter-diffusion of copper and zinc.** E. A. OWEN and L. PICKUP (Proc. Roy. Soc., 1935, A, 149, 282—298).—With ungraded particles, Cu-Zn alloys can be prepared in powder form by the inter-diffusion of filings at temp.  $< \text{m.p.}$  of Cu but  $>$  that of Zn. The photographs show, in addition to the  $\alpha$ -phase, the production and disappearance of the  $\beta$ -phase from its reflexion lines. The  $\gamma$ -phase is not revealed. The rate of diffusion is not affected when the particles are exposed to the atm. for short intervals of time. Inter-diffusion takes place more readily between unannealed than between annealed particles. With graded particles the amount of inter-diffusion in a given time is the greater the smaller is the size or the lower the grade of the particle. A linear relation exists between the parameter val. and the grade val. for a given time of inter-diffusion. L. L. B.

**Molecular volumes of electrolytes in concentrated solutions.** B. PESCE (Gazzetta, 1935, 65, 448—452).—The variation of the mol. vol. with the concn. has been studied for solutions of  $\text{Sr}(\text{ClO}_4)_2$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Cu}(\text{NO}_3)_2$ , and  $\text{Na}_2\text{Cr}_2\text{O}_7$ . Deviations from linearity are observed in some cases. O. J. W.

**Viscosity formula for binary mixtures, the association degrees of constituents being taken into consideration.** T. ISHIKAWA (Bull. Chem. Soc. Japan, 1935, 10, 248—252; cf. this vol., 817).—The author's formula (A., 1934, 723) has been applied successfully to the data for molten  $\text{C}_{10}\text{H}_8$  and molten  $\text{Ph}_2$ . When it is applied to molten KCl good agreement is also found. Extrapolation of the formula to temp.  $< \text{m.p.}$  suggests differences between electrolytes and non-electrolytes. W. R. A.



**Influence of sexatomic rings on the viscosity of solutions of polymerides with filiform molecules.** S. BEZZI (Atti R. Accad. Lincei, 1935, [vi], 21, 372—380).—Solutions of various polymerides,  $(C_6H_4 \cdot CH_2)_n$ , obtained by condensing  $CH_2PhCl$  under different conditions, have been examined. The results indicate that hydrocarbons with aromatic nuclei in the chain have the same viscosity as paraffins of equal length, and that the high vals. shown by cellulose must be due to some other cause.

T. H. P.

**Molecular association and polarisation of ethyl alcohol in various solvents.** P. MORTIER (Bull. Acad. roy. Belg., 1935, [v], 21, 594—605).—Polarisation—composition curves for binary mixtures of EtOH with  $C_6H_6$ ,  $CCl_4$ ,  $C_6H_{14}$ ,  $C_7H_{16}$ , and  $CS_2$  agree with the theory of Wolf and Herold (this vol., 24).

D. R. D.

**B.p. of the constant-boiling mixture HCl-H<sub>2</sub>O.** W. E. CADBURY, jun. (J. Chem. Educ., 1935, 12, 292).—A crit. examination shows that the val. 110° usually quoted should be replaced by 108.584°/760 mm.

L. S. T.

**System pyridine-acetic acid. IV.** B.p. L. E. SWEARINGEN and R. F. ROSS (J. Physical Chem., 1935, 39, 821—827).—B.p. and  $d$  vals. are recorded. The max. b.-p. mixture at 760 mm. contains 58.4 mol.-% AcOH (b.p. 138.35°), but its composition varies with pressure. No complexes are indicated by the b.p.-composition curve.

J. W. S.

**Properties of ternary heterogeneous mixtures.** P. MONDAIN-MONVAL (Bull. Soc. chim., 1935, [v], 2, 1106—1118).— $n_D^{20}$  and  $d_4^{20}$  have been determined for mixtures of EtOH, *iso*-C<sub>5</sub>H<sub>11</sub>OH, and H<sub>2</sub>O in the region of the crit. point, at which, contrary to Brun (cf. A., 1934, 357), no irregularities occur.

R. S. B.

**Intermetallic solid solutions.** E. R. JETTE (Trans. Amer. Soc. Min. Met. Eng., Inst. Met. Div., 1934, 111, 53—74).—The conditions which must be fulfilled by solute and solvent atoms in solid solution if Vegard's law holds are identical with those which are required by Raoult's law for liquid solutions. The results of a no. of accurate determinations of lattice consts. for intermetallic systems in which a range of solid solutions exist show that positive and negative deviations from Vegard's law occur.

W. P. R.

**Detection of dilute solid solution formation with the iron oxides by means of thermomagnetic analysis.** A. MICHEL and A. GIRARD (Compt. rend., 1935, 201, 64—65).—The solid solution of Fe<sub>3</sub>O<sub>4</sub> in rhombohedral Fe<sub>2</sub>O<sub>3</sub> shows a greatly increased susceptibility, although the X-ray diagram and Curie point of the Fe<sub>2</sub>O<sub>3</sub> are unchanged by the solute.

H. J. E.

**Influence of the addition of salts on the temperature of [complete] miscibility in the system water-phenol.** A. BANCHETTI (Atti Soc. Toscana Sci. Nat., 1935, 44, 1—7).—The temp. is raised by addition of KCl. Over the concn. range 0.0004—0.06 mols. per 1000 g.,  $t = Ac^B$ ; if  $c > 0.02$ ,  $t = a\sqrt{c} + b$ , where  $t$  = temp. elevation,  $c$  = concn. of KCl, and  $a$ ,  $b$ ,  $A$ , and  $B$  are consts.

D. R. D.

**Solubility of noble gases in aqueous salt solutions at 25°.** G. ÅKERLÖF (J. Amer. Chem. Soc., 1935, 57, 1196—1201).—The solubility of He and A in several aq. salt solutions has been determined. The salting-out consts. are of the same order of magnitude as those for other non-electrolytes.

E. S. H.

**Transition of gas from the dissolved to the dispersed state.** N. N. ANDREEV and L. E. KULIKOVA (J. Gen. Chem. Russ., 1935, 5, 366—370).—The relation of the degree of dispersion of bubbles of gas liberated from solutions by reducing the pressure to the solubility of the gas has been determined.

R. T.

**Dependence of mist absorption by liquids on the bubble size.** I. H. REMY and W. SEEMANN (Kolloid-Z., 1935, 72, 3—12).—The absorption of SO<sub>2</sub> mists by Et<sub>2</sub>O, MeOH, EtOH, H<sub>2</sub>O, 10% aq. AgNO<sub>3</sub>, 5% and 20% KOH, and glycerol, respectively, has been investigated. For a given velocity of streaming the absorption decreases as the size of the bubbles carrying the mist increases. The pure solvents are better absorbers than the solutions. The absorption varies almost linearly with the reciprocal of streaming velocity over a wide range, but deviations occur when the velocity is low. A method for determining the no. of bubbles passing, when these exceed a rate of 2000 per min., is described.

E. S. H.

**Heptane and its solutions. VI. Solubility of halogens in heptane.** J. SEMB (J. Amer. Pharm. Assoc., 1935, 24, 547—553).—The solubilities of Cl<sub>2</sub>, Br, and I in C<sub>7</sub>H<sub>16</sub> have been determined from —23° to 85°, —67° to —12°, and —21° to 78°, respectively. Cl<sub>2</sub> and Br react with the solvent to a variable extent, HCl and HBr probably being catalysts. Reaction of the solutions with various metals is described.

R. S. C.

**Absorption of hydrogen chloride into various organic liquids and the calculation of the heat of absorption. II.** S. HAMAI (Bull. Chem. Soc. Japan, 1935, 10, 207—211; cf. this vol., 441).—The absorption of HCl by CHCl<sub>3</sub>-CH<sub>2</sub>Cl and by C<sub>2</sub>HCl<sub>5</sub> at 12°, 15°, and 20° and the respective heats of absorption have been determined. Solubilities  $\propto$  total bond energies of the solvent.

W. R. A.

**Determination of solubility of ethylene, propylene, and butylene in certain solvents at —20° to 40°, at pressures less than atmospheric.** V. V. A. KIREEV, S. I. KAPLAN, and M. A. ROMANTSCHUK (J. Gen. Chem. Russ., 1935, 5, 444—449).—Solubility data are recorded for xylene, cracking benzene, kerosene, C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>, crude C<sub>6</sub>H<sub>6</sub>, and heavy solvent naphtha at —20° to 40°, and at 50—760 mm.

R. T.

**Solubility of non-electrolytes. II. Influence of polar group on the free energy of hydration of aliphatic compounds.** J. A. V. BUTLER and C. N. RAMCHANDANI (J.C.S., 1935, 952—955; cf. this vol., 441).—Partial pressures of NH<sub>3</sub>Et, NH<sub>3</sub>Pr, NH<sub>3</sub>Bu, EtCO<sub>2</sub>H, PrCO<sub>2</sub>H, EtCN, PrCN, MeOAc, EtOAc, (CH<sub>2</sub>OH)<sub>2</sub>, and glycerol over their dil. aq. solutions have been determined and the free energy of hydration,  $F$ , calc. Vals. of  $F$  for ethers, hydro-



carbons,  $\text{COMe}_2$ ,  $\text{AcOH}$ , and  $\text{PrOAc}$  are calc. from existing data.  $F$  for simple compounds is approx. an additive function of the groups present, and is represented by  $F = 0.5n \cdot \gamma_{A-W} - \sum a\gamma_{A-W} + 8600$ , where  $n$  is the no. of  $\text{H}_2\text{O}$  mols. on the surface of the cavity containing the solute mol. and  $a$  the no. of  $\text{H}_2\text{O}$  mols. in contact with group  $A$ . Vals. are derived for the interaction consts.,  $\gamma_{A-W}$ , between various groups and the  $\text{H}_2\text{O}$  mol. The effects of successive OH groups are not additive.

J. G. A. G.

**Periodicity in the series of saturated fatty acids.** [Solubility.] A. DE KUTHY (J. Chim. phys., 1935, 32, 406—409).—The solubility of digitoxin, cholesterol,  $\text{Ca}_3(\text{PO}_4)_2$ , and  $\text{CaC}_2\text{O}_4$  in  $2N$  aq. solutions of Na salts of the fatty acids varies periodically as the series is ascended. Salts with an odd no. of C atoms afford solubilities > those afforded by contiguous members with an even no.

J. G. A. G.

**Precipitation colorimetry. Effect of ammonium chloride on solubility of  $\text{ZnHg}(\text{SCN})_4$  and of  $(\text{Co,Zn})\text{Hg}(\text{SCN})_4$ .** B. V. J. CUVELIER (Z. anal. Chem., 1935, 102, 16—20).—The solubility of  $\text{ZnHg}(\text{SCN})_4$  has been determined by a colorimetric method. The solubility of  $\text{ZnHg}(\text{SCN})_4$  is increased in presence of  $\text{NH}_4\text{Cl}$ ; the latter must not be present when  $\text{Na}_2\text{Hg}(\text{SCN})_4$  is used for the determination of Zn.

S. J. G.

**Distribution of saturated aliphatic monocarboxylic acids between two contiguous liquid phases.** N. A. DE KOLOSOVSKI, A. BEKTUROV, and F. S. KULIKOV (J. Gen. Chem. Russ., 1935, 5, 319—326).—Data are recorded for the systems  $\text{H}_2\text{O}$ - $\text{PhNO}_2$ - $\text{HCO}_2\text{H}$  and  $-\text{AcOH}$ ;  $\text{H}_2\text{O}$ -*iso*- $\text{C}_5\text{H}_{11}$ - $\text{OH}$ - $\text{EtCO}_2\text{H}$ ,  $-\text{PrCO}_2\text{H}$ , and  $-\text{Bu}^i\text{CO}_2\text{H}$ ;  $\text{H}_2\text{O}$ - $\text{Bu}^i\text{CO}_2\text{H}$ - $\text{CCl}_4$  and  $-\text{EtBr}$ , at  $25^\circ$ .

R. T.

**Mechanism of electrodiffusion of hydrogen through palladium.** N. I. KOBOSEV and V. V. MONBLANOVA (Acta Physicochim. U.R.S.S., 1934, 1, 611—650).—In the electrodiffusion of H into various gases ( $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{C}_6\text{H}_6$ , etc.) on the other side of the Pd cathode, the following stages are considered: (a) adsorption of H on the Pd surface (polarisation surface), (b) occlusion of the adsorbed H atoms in the inner layers of the metal, (c) transport of occluded atoms through the metal, and (d) the reverse processes of (b) and (a) at the surface of the Pd in contact with the diffusion medium (diffusion surface). The rate of diffusion of H under various conditions has been measured experimentally. The main conclusions are: (1) diffusion is independent of the physical properties of the diffusion medium; (2) poisoning of the polarisation surface accelerates, whereas poisoning of the diffusion surface retards, diffusion; (3) electrolytes, especially KCl and KOH, in the solution on the polarisation side accelerate diffusion; (4) diffusion takes place through the inter-cryst. spaces and the edges of the crystals form the diffusion centres.

O. J. W.

**Ionisation of hydrogen in contact with platinum, copper, and nickel.** C. Y. MENG, P. A. ANDERSON, and Y. M. HSIEH (J. Chinese Chem. Soc., 1935, 3, 103—114; cf. J.C.S., 1922, 121, 1153).—

The ionisation current  $i$  obtained when  $\text{H}_2$  is passed over Pt, Cu, and Ni and between Al electrodes has been measured.  $i$  increases rapidly with rise of temp. It is inferred that the activity of H desorbed from Pt is not due to ionisation.

R. S.

**Adsorption of hydrogen by palladium in presence and absence of water.** M. I. TEMKIN and A. N. BAKH (J. Phys. Chem. U.S.S.R., 1934, 5, 809—811).—Neither  $\text{H}_2\text{O}$  nor  $\text{O}_2$  has any effect on the rate or amount of  $\text{H}_2$  adsorbed by Pd or Pd-black at  $15$ — $20^\circ$ . The total adsorption is 67.5 c.c. per g.

CH. ABS. (e)

**Adsorption of hydrogen by supported copper poisoned with carbon monoxide.** C. W. GRIFFIN (J. Amer. Chem. Soc., 1935, 57, 1206—1208).—A very small quantity of CO causes an increase in adsorption of  $\text{H}_2$  up to 1 atm. With greater amounts of CO the adsorption of  $\text{H}_2$  increases at low pressure and decreases at higher pressures. By using supported Cu the secondary factors of sorption are eliminated.

E. S. H.

**Adsorption of oxygen and the catalysis of hydrogen peroxide by platinum.** V. A. ROTHER and M. G. LEPERSON (Ber. Ukrain. wiss. Forsch.-Inst. physikal. Chem., 1934, 4, 41—48).—Most of the O adsorbed by Pt in anode polarisation and all the H adsorbed by Pt in cathode polarisation reacts with  $\text{H}_2\text{O}_2$ . In the electrolysis of dil.  $\text{H}_2\text{SO}_4$  there is no sorption of electrolytic gas at either electrode if a sufficient  $[\text{H}_2\text{O}_2]$  is maintained (anode 0.5%, cathode 1.8% of  $\text{H}_2\text{O}_2$ ). Cathodic polarisation increases the catalytic activity of Pt in the decomp. of  $\text{H}_2\text{O}_2$ . Anodic polarisation lowers it. The activity is const. if electrolysis occurs in presence of  $\text{H}_2\text{O}_2$ .

CH. ABS. (e)

**Sorption of water vapour from a current of air by inorganic gels.** E. V. ALEXEEVSKI and F. J. RATSCHINSKI (J. Gen. Chem. Russ., 1935, 5, 299—306).— $\text{Al}(\text{OH})_3$  gel is the best adsorbent for  $\text{H}_2\text{O}$  at low (0—3 mm. pressure), and  $\text{SiO}_2$  gel at higher, concns.  $\text{Fe}(\text{OH})_3$  gel is at all pressures an inferior adsorbent.

R. T.

**Adsorption of dilute organic vapours by active charcoal and their desorption in pure air.** A. AKERMANN (Compt. rend., 1935, 201, 210—212).—Data are recorded for a no. of org. substances. Factors controlling adsorption and the retention of the adsorbate are discussed.

H. J. E.

**Adsorption by wood charcoal in solutions and gases.** H. FISCHER (Kolloid-Beih., 1935, 42, 125—183).—Adsorption velocity and equilibrium have been determined with 11 kinds of C in aq. succinic acid, I in aq. KI, I in EtOH, and methylene-blue in  $\text{H}_2\text{O}$ . The samples of C can be divided into three groups according to their adsorptive power and wettability. The adsorptive power of the samples is in the same order for the above solutions, and also for  $\text{SO}_2$ . Adsorption velocity increases as the particle size of the adsorbent is decreased. The adsorption velocity of  $\text{C}_2\text{H}_4$  and  $\text{CO}_2$  is > with solutions, and the order of adsorptive power of the different kinds of C is different. The general phenomena of adsorption of solutes and gases are the same.

E. S. H.



**Chemisorption on charcoal.** VI.  $p_H$  of charcoal suspensions. A. KING (J.C.S., 1935, 889—894).—The  $p_H$  vals. of aq. suspensions of sucrose-C activated in  $O_2$  increase linearly with rise of temp.,  $t$ , of activation, corresponding with the transition from an acidic to a basic condition. The  $p_H$  decreases at  $t > 900^\circ$  and is slightly dependent on the surface area of the C. Activation equilibrium is rapidly established at low  $t$ , but several hr. are required at the higher  $t$ . The effects are reversible, and C activated at  $t_2$  when reactivated at  $t_1$  affords the  $p_H$  characteristic of  $t_1$ . The forms of C are stable in vac., but exposure to air decreases the  $p_H$  given by the basic type. Similar results are shown by graphite and by commercial animal (I) and vegetable (II) C, and also by activating with  $CO_2$  at higher  $t$ . The adsorption of  $EtCO_2H$  and  $NaOH$  by (I) and (II) varies with  $p_H$  in the manner predicted. The interpretation of the phenomena is discussed.

J. G. A. G.

**Influence of certain physical and chemical factors on the activity of charcoal.** VI. Influence of carriers on the adsorptive properties of charcoal. E. V. ALEXEEVSKI and T. G. PLATSCHEV (J. Gen. Chem. Russ., 1935, 5, 294—298).—The adsorptive capacity of C (from sucrose, starch, albumin, and blood) for  $C_6H_6$  vapour is increased when the C is formed by heating ceramic rings or spheres (kaolin 15, diatomite 55, clay 15, wood-C 15%) saturated with aq. solutions of the source of C, when the porosity of the carrier  $< 70\%$ . R. T.

**Sugar charcoal.** I. Grain structure of sugar charcoal. II. Sugar charcoal as irreversible colloid. B. L. VANZETTI (Rend. Fac. Sci. Cagliari, 1933, 3, 141—142, 142—144; Chem. Zentr., 1935, i, 942).—The grain structure of charcoal produced by the action of  $H_2SO_4$  on carbohydrates is detectable ultramicroscopically after progressive replacement of  $H_2O$  by  $EtOH$ ,  $PhMe$ , and paraffin.

II. After dehydration in vac. at  $120^\circ$ , only 7.7% of the original  $H_2O$  was taken up again. J. S. A.

**Examination of positively- and negatively-charged carbon surfaces by adsorption of thorium-B.** H. R. KRUYT and T. KRUYT (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 570—577).—Th-B in acid solution (as Th-B'') is far more strongly adsorbed by active C with a negatively-charged surface (A., 1931, 796) than by positively-charged C. The reverse is true in alkaline solution (Th-B as Th- $BO_2''$ ). D. R. D.

**Chemical reactions of water adsorbed on glass.** H. E. BENT and G. J. LESNICK (J. Amer. Chem. Soc., 1935, 57, 1246—1250).—The amount of  $H_2O$  has been measured by the discharge of the red colour of  $CPh_3Na$  (I) in  $Et_2O$ . The results show that the amount of  $H_2O$ ,  $n$ , removed by (I), expressed as thickness of a layer in mols., is given by  $n = 5(0.25 \times \log_{10} t + 1)$ , where  $t$  is the time in hr. during which the glass has been in contact with (I). The v.p. of  $H_2O$  in equilibrium with (I) is  $< 10^{-12}$  mm., and probably of the order of  $10^{-26}$  mm. E. S. H.

**Loss of hydrogen atoms on water-poisoned glass surfaces.** W. STEINER (Trans. Faraday Soc.,

1935, 31, 962—966).—From published results (cf. this vol., 587) the calc. adhesion coeff. of H on a glass surface poisoned by adding 2.3—3.5% of  $H_2O$  vapour to the flowing mixture of H and  $H_2$  is  $2.6 \times 10^{-6}$ — $9 \times 10^{-6}$ . E. S. H.

**Adsorption of organic substances at crystal surfaces.** III. Adsorption of sodium laurate by barium sulphate. N. A. HELD and K. N. SAMOCHVALOV (Kolloid-Z., 1935, 72, 13—17; cf. A., 1934, 359).—The sp. surface of  $BaSO_4$  powder has been determined (1) by microscopical measurement, and (2) by adsorption measurements with Na laurate in  $H_2O$  and lauric acid in  $C_6H_6$ . Comparison of the results shows that Na laurate is absorbed by  $BaSO_4$  in  $H_2O$  as a bimol. film. The stabilisation of  $BaSO_4$  and flotation phenomena are explained by assuming that the second mol. layer has its polar end turned towards the solution. E. S. H.

**Transference of surface changes inside crystal systems.** IV. D. BALAREV [with K. ANDREEV, E. ZANKOVA, and P. DAMOVA] (Kolloid-Z., 1935, 72, 25—26; A., 1934, 485).—The addition of small amounts of  $CaFe_2O_4$ ,  $CaTiO_3$ ,  $CaMoO_4$ ,  $CaZnO_2$ , or  $CaCdO_2$  lowers the decomp. temp. of  $CaCO_3$  throughout the whole system. E. S. H.

**Exchange adsorption of ions on colloidal arsenic trisulphide.** V. A. KARGIN and H. B. KLIMOVITZKAJA (Acta Physicochim. U.R.S.S., 1935, 1, 729—740).—The Ba, Ca, Mg, and Cl adsorbed in the coagulation of  $As_2S_3$  sols by 0.2N- $BaCl_2$ ,  $-CaCl_2$ , and  $-MgCl_2$ , and the acid content of the filtrate have been determined gravimetrically and potentiometrically, respectively. Adsorption of Cl is very small. There is no equivalence in the exchange adsorption, the quantity of strong acid in the filtrate being  $>$  the adsorbed cation. The filtrate contains  $H_3AsO_3$ , initially present in the intermicellar liquid of the  $As_2S_3$  sol, and acting as a stabiliser.  $H_2S$  is not responsible for stabilisation. H. J. E.

**Adsorptive property of silica gel.** I. Chemical activity of residual water in activated silica gel. M. R. A. RAO and B. S. RAO. II. Adsorptive properties of silica gel containing residual hydrogen chloride. III. Volume changes produced on displacement of adsorbed liquids in silica gel by water. IV. Liberation of air from silica gel capillaries during adsorption of liquid. V. Specific gravity of silica gel under various liquids. M. R. A. RAO (J. Indian Chem. Soc., 1935, 12, 322—325, 326—330, 331—335, 336—339, 340—342).—I.  $CCl_4$  vapour reacts with the residual  $H_2O$  in activated  $SiO_2$  gel. The reaction is perceptible at  $110^\circ$  and fairly rapid at  $300^\circ$ , forming  $COCl_2$  and  $HCl$ . By this reaction all the residual  $H_2O$  can be removed; the resulting gel retains  $HCl$  very firmly.

II. The adsorptive capacity of the gel for  $CCl_4$  and its selective adsorption from a mixture of  $EtOH$  and  $C_6H_6$  have been determined. The  $HCl$  gel takes up less liquid, but the selectivity is enhanced.

III. The vol. changes caused by displacement of adsorbed  $C_6H_6$ ,  $PhMe$ ,  $CCl_4$ ,  $PhNO_2$ , or  $NH_2Ph$  by  $H_2O$  have been determined. Selective adsorption of  $C_6H_6$  from a mixture with  $CCl_4$  has been observed.



IV. Measurement of the vol. of air liberated when  $\text{H}_2\text{O}$  wets  $\text{SiO}_2$  gel shows that the air has a pressure of 2 atm. in the gel space.

V. The apparent sp. gr. varies with the liquid in which  $\text{SiO}_2$  gel is immersed. It is assumed that the liquids vary in their power of penetrating into the capillaries present in the gel. E. S. H.

**Selective adsorption and its significance. I. Nature of selective adsorption.** M. R. A. RAO (J. Indian Chem. Soc., 1935, 12, 345—355).—Selective adsorption by  $\text{SiO}_2$  gel in the mixtures  $\text{EtOH}-\text{C}_6\text{H}_6$ ,  $\text{EtOH}-\text{CCl}_4$ ,  $\text{C}_6\text{H}_6$ — and  $\text{C}_5\text{H}_5\text{N}$ -heptane has been investigated. Assuming that the liquid held in the capillaries of the gel is identical in composition with the bulk liquid, whilst that adsorbed at the gel surface is responsible for the selectivity, a method of calculating the true adsorption of each constituent has been developed. E. S. H.

**Adsorption of aluminium hydroxide by kieselguhr.** E. C. C. BALY and W. P. PEPPER (Nature, 1935, 136, 28).—The curve obtained when the adsorption of  $\text{Al}(\text{OH})_3$  is plotted against the electrokinetic potential ( $\zeta$ ) of the preps. in 0.1N-AcOH indicates that  $\text{Al}(\text{OH})_3$  is first adsorbed as a unimol. layer by the kieselguhr surface and when this layer is completed the  $\zeta$  val. is 75.4 mv. When a second unimol. layer is deposited  $\zeta$  falls to 61.2 mv. and this layer has the same properties as the unadsorbed surface. The enhanced  $\zeta$  val. of the first layer indicates that the mols. in the adsorbed unimol. layer must be activated in some way. L. S. T.

**Selective adsorption from soap solutions.** H. A. NEVILLE and M. HARRIS (Amer. Dye stuff Rep., 1935, 24, 312—314, and J. Res. Nat. Bur. Stand., 1935, 14, 765—770).—In the production and removal of foam from a neutral 0.25% aq. solution of pure olive oil soap ( $p_H$  10.0) by a current of air the residual liquor becomes more alkaline ( $p_H$  10.5) and less conc. (0.08% soap), whilst the condensed foam becomes more acid ( $p_H$  9.6) and more conc. (1.13% soap) and is turbid until the addition of alkali. These changes are due to the formation of an acid soap at the air-solution interface. The composition of the foam is const. during its continuous removal from olive oil soap. Similar changes occur when  $\text{Na}_2\text{CO}_3$  is present in the soap, but the foam is less stable due to repression of hydrolysis. When various substances are added to olive oil soap followed by filtration the residual liquor increases in alkalinity ( $p_H$  10.1—10.4) with lampblack, paraffin, and olive oil (0.33% free fatty acid), and decreases in alkalinity ( $p_H$  9.2) with fuller's earth, cotton, silk, and wool. The last two show pronounced selective adsorption of alkali, but cotton adsorbs equal but relatively small amounts of alkali and fatty acid. Silk adsorbs the greatest amount of alkali, as might be anticipated from its low isoelectric point ( $p_H$  2.5). Olive oil soap becomes immediately turbid when in contact with silk and wool, but remains clear for 24 hr. with cotton. A. J. H.

**Equation of state of monolayers.** J. S. MRCHELL (Trans. Faraday Soc., 1935, 31, 980—986).—Theoretical. The equation of state of an imperfect

gas film is obtained and a method of correlating the surface potential with the deviation from the perfect gas laws is suggested. E. S. H.

**Interaction of atoms and molecules with solid surfaces. I. Activation of adsorbed atoms to higher vibrational states.** J. E. LENNARD-JONES and C. STRACHAN. II. Evaporation of adsorbed atoms. C. STRACHAN (Proc. Roy. Soc., 1935, A, 150, 442—455, 456—464).—I. Mathematical. Formulae are found for the mean interval between successive excitations from the state of lowest vibrational energy to various excited states, and for the mean time during which the atom remains in an excited state. This time is of the order of a few periods of the vibrating atom. The results are applied to the theory of surface migration.

II. The theory is extended to calculate the probabilities of evaporation of atoms or mols. from surfaces. A formula is derived for the interval of time that an atom (or mol.) remains in the adsorbed condition. The theory is applied to the evaporation of  $\text{H}_2$ , HD, and  $\text{D}_2$  from a metal, and it is shown that over a wide temp. range the average length of time spent by HD on Cu is 4—6 times that of  $\text{H}_2$ , whilst that spent by  $\text{D}_2$  is about 20 times that of  $\text{H}_2$ . L. L. B.

**Interfacial tension between two liquids.** D. G. DERVICHIAN (Compt. rend., 1935, 201, 333—334).—Relationships between the interfacial tension of two liquids and their cohesive forces and mutual affinity are discussed. J. W. S.

**Temperature coefficients of surface tension and thermal expansion.** T. S. WHEELER (Current Sci., 1935, 3, 550).—The constancy of the ratio of these coeffs. follows from the observed validity of the parachor law. A. B. D. C.

**Temperature coefficients of surface tension and thermal expansion.** L. SIBAIYA (Current Sci., 1935, 3, 550—551).—The parachor law (cf. preceding abstract) gives the ratio of these coeffs. as 4, and observed vals. are quoted for various liquids including org. compounds and elements.  $\text{C}_6\text{H}_{12}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{O}$ , Hg, and  $\text{H}_2$  do not behave as normal liquids. A. B. D. C.

**Change in the surface tension of a solution of methyl acetate due to hydrolysis.** B. H. HANDORF and E. R. WASHBURN (J. Amer. Chem. Soc., 1935, 57, 1201—1203).—In the hydrolysis of 2M-MeOAc the surface tension, measured by the ring method, varies linearly with the amount of change determined by titration with  $\text{Ba}(\text{OH})_2$ .

E. S. H.

**Formation of multimolecular layers on the partition surface mercury-solution.** A. FRUMKIN, A. GORODETZKAJA, and P. CHUGUNOV (Acta Physicochim. U.R.S.S., 1934, 1, 12—21).—At 25° decioic acid and PhOH lower the surface tension of the Hg-solution boundary layer (using a capillary electrometer method). They are adsorbed in conc. solution giving layers with an average thickness of 2 mols., but actually consisting of "islands" of termol. layers in the general unimol. layer. These effects are not observed at the air-solution interface.

CH. ABS. (e)



**Interfacial tensions between solutions of palmitic acid in benzene and aqueous solutions of sodium salts.** L. GAY and M. CERVEAU (*J. Chim. phys.*, 1935, **32**, 371—384; cf. A., 1932, 1200).—Dissolved NaCl, Na<sub>2</sub>SO<sub>4</sub>, NaNO<sub>3</sub>, Na<sub>2</sub>CrO<sub>4</sub>, and Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> have only very slight effects on the interfacial tension,  $\gamma$ , between H<sub>2</sub>O and 1% palmitic acid in C<sub>6</sub>H<sub>6</sub> at 20°, but with increasing concn. of Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>, and NaOAc,  $\gamma$  decreases slowly to the Adam point and then decreases more rapidly. The data obtained with aq. NaOH alone and in presence of Na salts of strong acids suggest that Na palmitate is responsible for the interface effect. The discrepancies observed with Na salts of weak acids are attributed to dissolution of these salts in the interfacial soap film. J. G. A. G.

**Surfaces of separation. Saponification at interfaces.** J. WAJZER (*J. Chim. phys.*, 1935, **32**, 429—430).—The interfacial tension between arachis oil containing 1% of oleic acid and aq. NaOH decreases with increasing [NaOH]. It is inferred that the interface is occupied by a unimol. layer of Na oleate in the expanded (gaseous) state. J. G. A. G.

**Rigidity with which two solid phases adhere along their interface.** V. P. KONSTANTINOVA (*Acta Physicochim. U.R.S.S.*, 1934, **1**, 286—295; cf. A., 1933, 900).—The effect of unimol. layers of alcohols, acids, and amines on the adherence at quartz-paraffin and calcite-paraffin interfaces has been studied. In homologous series the effect increases with the mol. wt. of the "mol. solder." The mol. solder increases the solidity of thin films of paraffin, probably by sp. conditioning of the crystallisation. J. W. S.

**Heat of wetting. II. Influence of adsorbed air on the heat of wetting.** A. DUMANSKI and M. V. TSCHAPEK (*Kolloid-Z.*, 1935, **72**, 55—58; cf. this vol., 930).—The heat of wetting of peat, soil, SiO<sub>2</sub> gel, and charcoal by H<sub>2</sub>O and C<sub>6</sub>H<sub>6</sub> is increased when adsorbed air is first removed by evacuation. The difference between the vals. determined in air and in vac. is taken as a measure of the heat of adsorption of air. E. S. H.

**Infiltration method for the investigation of the wetting power of mineral dispersoids. Comparative wetting powers of corundum powders.** Z. V. VOLKOVA (*Acta Physicochim. U.R.S.S.*, 1934, **1**, 247—255).—An apparatus is described for measuring the velocity of penetration of liquids into dispersoids and for the saturation of powders with large hysteretic wetting angles. Results for the penetration of H<sub>2</sub>O and PhMe into corundum powders are recorded and discussed. J. W. S.

**Mechanism of flotation. Rôle of highly disperse powder in the flotation process.** Z. V. VOLKOVA and A. V. SAPOROSHEZ (*Kolloid-Z.*, 1935, **72**, 82—86).—In the flotation of S, talc, BaSO<sub>4</sub>, and CaCO<sub>3</sub> powders in H<sub>2</sub>O containing a little iso-amyl alcohol it is shown that no adsorption of the alcohol occurs at the surface of the particles and no increase in coagulation occurs. The finely powdered substances stabilise the air-liquid dispersion, although coarser particles do not. The

fine particles play a part in aiding the flotation of the larger particles. E. S. H.

**Insolubility of thin films of albumin.** H. DEVAUX (*Compt. rend.*, 1935, **201**, 109—111; cf. this vol., 161).—A thin oriented film of albumin, which is capable of considerable expansion or compression, forms on the surface. When removed from the solution and dried, the film is insol. if again treated with H<sub>2</sub>O. H. J. E.

**Albumin membranes: their rigidity, elasticity, and insolubility.** H. DEVAUX (*Compt. rend. Soc. Biol.*, 1935, **119**, 1124—1125).—A unimol. film of albumin forms on the surface of its solutions: it behaves as a solid membrane, perfectly elastic, and has a solubility  $< 10^{-8}$ . R. N. C.

**Significance of structure of a membrane for its selective permeability.** W. WILBRANDT (*J. Gen. Physiol.*, 1935, **18**, 933—965).—The pore and solubility theories advanced to explain selective ion permeabilities of membranes may be reconciled if the arrangement of the dipoles of the membrane mols. is considered. The behaviour of collodion membranes under various conditions is explained. Membranes of Cellophane and ethylcellulose are negatively, and those of cellulose acetate positively, charged. Membranes of collodion impregnated with basic dyes or alkaloids become more permeable to anions than to cations, in contrast to ordinary collodion membranes. A combination of these two types of membranes gives an asymmetric membrane giving a high potential between two identical electrolyte solutions. F. A. A.

**Electrical transport through phase boundaries. System II: glass-molten metal (mercury). System III: glass-molten salt (silver nitrate).** E. MANEGOLD and C. STÜBER (*Z. physikal. Chem.*, 1935, **173**, 321—344; cf. this vol., 705).—Changes produced by a d.c. in the anode surface of a heated glass diaphragm coated on both sides with Hg or molten AgNO<sub>3</sub> have been examined chemically and under the microscope, and their influence on the electrical properties of the diaphragm has been measured. Transport occurs either with or without the wandering of material particles. To the former class belong the systems glass-Na vapour, -molten AgNO<sub>3</sub>, -K vapour, -H<sub>2</sub>, and -N<sub>2</sub>, and to the latter glass-He, -O<sub>2</sub>, -CO<sub>2</sub>, and -Hg. The conditions necessary for the processes are discussed, and mechanisms are suggested. T. G. P.

**Colloidal ultra-filter containing hydrated silica.** G. A. BLANC (*Atti R. Accad. Lincei*, 1935, [vi], **21**, 296—301; cf. A., 1931, 1253).—Negatively-charged colloidal Au passes through the filter without adsorption, whereas positively-charged Au does so only if protected by addition of gum arabic. The adsorbed Au can be washed out by means of 1% aq. Na<sub>2</sub>CO<sub>3</sub> (which dissolves the surface layer of the SiO<sub>2</sub>), the particle size undergoing no change in the process. D. R. D.

**Heats of dilution and osmotic pressures of non-electrolyte solutions.** C. FRENZEL, R. BURIAN, and O. HAAS (*Z. Elektrochem.*, 1935, **41**, 419—429).—The sp. heats of aq. sucrose, glue, and CO(NH<sub>2</sub>)<sub>2</sub>



solutions have been determined over a range of concn. and temp., and the temp. coeffs. of the mol. differential heats of dilution calc. therefrom. Neglect of the heat of dilution may lead to an error of 10% in the calculation of osmotic pressure. E. S. H.

**Increase in the rotatory power of mannitol in water by means of zirconium salts.** (MLLE.) M. FALINSKI (Compt. rend., 1935, 201, 69—71).—Addition of aq.  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (I) to mannitol produced a large increase in the rotatory power. With low  $[\text{Zr}]$  at room temp. an equilibrium val. is not reached until after several months. The solutions with 20—50% of (I) show a large increase in  $\eta$  and are colloidal. H. J. E.

**Physico-chemical properties of picric acid with varying  $p_{\text{H}}$ .** J. MOLNAR (Compt. rend., 1935, 201, 59—62).—At const.  $p_{\text{H}}$ , Beer's law holds for concns. of 5—40 mg. of picric acid (I) per litre, and for  $\lambda$  2200—4900 Å. Variations of the absorption spectrum and solubility with  $p_{\text{H}}$  are recorded. At high  $p_{\text{H}}$  (I) is negatively charged, but in HCl and  $\text{H}_2\text{SO}_4$  it becomes positive at the  $p_{\text{H}}$  at which the min. solubility occurs in the same acid. Seven mol. modifications are suggested to account for these results. H. J. E.

**Temperature variation, of the viscosity of aqueous solutions of strong electrolytes.** W. J. SULSTON (Proc. Physical Soc., 1935, 47, 657—666).—Accurate data for KCl and  $\text{K}_2\text{SO}_4$  over the temp. range 18—85° are recorded. The results agree with the Debye-Hückel theory. N. M. B.

**Determination of hydration of magnesium chloride ions.** F. BOURION and E. ROUYER (Compt. rend., 1935, 201, 65—67; cf. A., 1934, 728).—Hydration decreases in the order  $\text{MgCl}_2 > \text{CaCl}_2 > \text{SrCl}_2 > \text{BaCl}_2$ . H. J. E.

**Metastructures of matter.** Wo. OSTWALD (Kolloid-Beih., 1935, 42, 109—124).—A lecture on the colloidal state. E. S. H.

**Somatoids.** I. K. HUBER (Helv. Chim. Acta, 1935, 18, 858—891).—A summary of published work on the non-crystallographic morphology of inorg. substances. E. S. H.

**Use of colloidal cobaltinitroso- $\beta$ -naphthol in a general chemistry experiment.** G. H. DAMON (J. Chem. Educ., 1935, 12, 193—195).—Colloidal cobaltinitroso- $\beta$ -naphthol (prep. described) provides an excellent sol for the elementary study of colloids. Coagulation experiments with  $\text{Na}_2\text{SO}_4$ ,  $\text{BaCl}_2$ ,  $\text{Fe}_2\text{O}_3$  sol, and  $\text{As}_2\text{S}_3$  sol show that it is positively charged. Flocculation vals. in millimols. per litre are HCl 9.0, NaCl 6.0, NaBr 5.5,  $\text{NaNO}_3$  4.8,  $\text{H}_2\text{SO}_4$  1.6,  $\text{Na}_2\text{SO}_4$  1.0,  $\text{K}_2\text{CO}_3$  2.0,  $\text{Na}_2\text{HPO}_4$  1.6,  $\text{Na}_2\text{HAsO}_4$  2.0,  $\text{Na}_3\text{PO}_4$  1.2. Gelatin has a marked protective action on the colloid.  $\text{Na}_2\text{SO}_4$  and AcOH, respectively, are recommended in place of  $\text{NH}_4\text{Cl}$  and HCl in determining Co by means of nitroso- $\beta$ -naphthol. L. S. T.

**Method of comparing magnitudes of molecules and colloidal micelles.** A. BOUTARIC (Ann. Soc. Sci. Bruxelles, 1935, 55, B, 101—106).—Equal masses of the same adsorbent were introduced into solutions of Na oleate (I) and, after equilibrium, the

surface tension was measured. The mol. cross-section of (I) can be determined and hence the total surface of adsorbent. Similar experiments have been made with colloidal solutions instead of (I). Modification in the degree of association of the solution can be followed and the micellar magnitudes at various stages can be compared. The mathematical theory is discussed. W. R. A.

**Consolidation of charged clay particles.** M. BIOT (Ann. Soc. Sci. Bruxelles, 1935, 55, B, 110—113).—Theoretical. W. R. A.

**Integrability of non-linear equations [in the theories] of heat [transfer] and of the consolidation of clay sediments.** M. BIOT (Ann. Soc. Sci. Bruxelles, 1935, 55, B, 106—109).—Mathematical. W. R. A.

(A) Study of degree of dispersion of dyes by the diffusion method. (B) Adsorption of dyes of varying degrees of dispersion. N. S. SCHEINKER (J. Phys. Chem. U.S.S.R., 1933, 4, 860—864, 865—870).—(A) The coeff. of diffusion of dyes dissolved in various  $\text{H}_2\text{O}$ -EtOH solutions has been measured by the Quast-Ostwald method. The radii of the methylene-blue particles varied from  $0.39 \times 10^{-7}$  cm. in  $\text{H}_2\text{O}$  to  $0.21 \times 10^{-7}$  cm. in 70% EtOH, that of crystal-violet from  $0.57$  to  $0.26 \times 10^{-7}$  cm., and that of neutral-blue from  $2.4$  to  $0.34 \times 10^{-7}$  cm. Aggregation occurs in the  $\text{H}_2\text{O}$  solutions (max. for neutral-blue).

(B) For dyes dissolved in  $\text{H}_2\text{O}$  in the mol. dispersed form, adsorption on glass is unimol. If the dye mols. are aggregated, the adsorbed layer is unimicellar. Methylene-blue B extra showed the first type of adsorption, and neutral-blue and crystal-violet the second (2.18 and 1.6 mols. per micelle, respectively). CH. ABS. (e)

**Diffusion of compounds of high mol. wt. and related compounds.** I. Glucose penta-acetate, cellobiose acetate, and quinol in organic fluids. II. Calculation of molecular size. III. Measurements in cellulose nitrate solution. M. TANIGUCHI and I. SAKURADA (J. Soc. Chem. Ind. Japan, 1935, 38, 241—245B, 245—246B, 246—248B).—I. Diffusion coeffs. (D) have been determined for glucose penta-acetate (I), cellobiose acetate (II), and quinol (III) at 20° in org. solvents. D varies slightly from layer to layer, as in the case of a colloidal solution. It follows that the explanation given for colloids (cf. A., 1934, 483), viz., polydispersion, is incorrect, since the above solutions are mol. D increases with concn. except for (I) in MeOAc and  $\text{C}_5\text{H}_5\text{N}$ , and (III) in  $\text{H}_2\text{O}$ , but becomes approx. const. above a certain concn.

II. Vals. of the mol. radius calc. by the Einstein and Sutherland formulæ, respectively, are (I) 4.26 and 6.39, (II) 4.96 and 7.44, and (III) 2.91 and 4.36 Å. It is almost independent of the solvent, and the vals. given for (I) by Einstein's formula are close to those calc. from  $d$ , and from  $\eta$  (cf. A., 1933, 670). It follows that solvation is small.

III. D is unaffected by dissolving in the org. solvent approx. 0.1—0.2% of cellulose nitrate (IV), in spite of the large increase in  $\eta$ , owing to the enmeshing of solvent by (IV). D for (I) in  $\text{COMe}_2$  + (IV) does not



vary from layer to layer, and becomes const. at a concn. much < in pure  $\text{COMe}_2$ . R. S. B.

**Nature of the nucleus in hygroscopic droplets.** J. H. COSTE and H. L. WRIGHT (Phil. Mag., 1935, [vii], 20, 209—234).—Nuclei for the condensation of moisture are produced in air, previously freed from nuclei,  $\text{SO}_2$ , and other acid gases, by heating, irrespective of the source of heat. Since nuclei are produced when Pt foil is electrically heated in air, they probably consist of droplets of  $\text{HNO}_3$  formed from atm.  $\text{N}_2$  and  $\text{O}_2$ .  $\text{HNO}_3$  can exist in air both as a gas and as a liquid. The latter acts as a source of nuclei and can be detected in air collected after various combustions. Results of spraying various liquids into air show that fuming  $\text{H}_2\text{SO}_4$  and sea- $\text{H}_2\text{O}$  produce many nuclei. Many nuclei are also formed when fuels containing S (coal gas, and  $\text{CS}_2 + \text{EtOH}$ ) are burnt.  $\text{H}_2\text{SO}_4$  produced by the oxidation of  $\text{SO}_2$  in air may therefore be one of the nucleus-forming substances in ordinary air. A. J. M.

**Mechanism of division of small liquid systems which are the seats of physicochemical reactions.** N. RASHEVSKY (Physics, 1934, 5, 374—379; cf. A., 1932, 294).—The mechanism of division of small liquid drops has been studied from the kinetic viewpoint. Crit. sizes calc. by this method agree with thermodynamic computations. CH. ABS. (c)

**Mol. wt. of linear macromolecules by ultracentrifugal analysis. III. Mol. wt. analysis of mixtures by sedimentation equilibrium in the Svedberg ultracentrifuge.** W. D. LANSING and E. O. KRAEMER (J. Amer. Chem. Soc., 1935, 57, 1369—1377; cf. this vol., 688).—Three types of average mol. wt. are distinguished, viz., "no.-average" (deduced from usual physico-chemical methods), "wt.-average" (Staudinger's viscosity method), and "z-average" (ultracentrifuge data). These can all be calc. from data on sedimentation equilibrium. The methods used are now applied to Krishnamurti and Svedberg's data (A., 1930, 1198) for gelatin. The significance of the results in connexion with other macromol. substances is discussed. H. B.

**Preparations of emulsions and colloidal solutions by ultra-sonic waves.** S. N. RSCHEVKIN and E. P. OSTROVSKI (Acta Physicochim. U.R.S.S., 1935, 1, 741—744).—With a frequency of  $4 \times 10^5$  Hertz, obtained by means of a quartz-plate oscillator, emulsions of Hg, Sn, Bi, Cu, Ag, S, paraffin, and various oils in  $\text{H}_2\text{O}$  have been obtained. Conductivity measurements for the Hg emulsions are recorded. H. J. E.

**Mode of formation and composition of colloidal and precipitated copper sulphides.** E. SAUER and D. STEINER (Kolloid-Z., 1935, 72, 41—46).—Under certain conditions of concn. etc.,  $\text{H}_2\text{S}$  gives a sol of  $\text{Cu}_2\text{S}$  with  $\text{Cu}^{\text{I}}$  salts; with  $\text{Cu}^{\text{II}}$  salts under similar conditions a mixture of  $\text{Cu}_2\text{S}$  and S in colloidal form is obtained, which on warming changes to  $\text{CuS}$ . E. S. H.

**Formation and properties of acidoid gold sols with charging mixed complexes.** W. PAULI, E. RUSSE, and E. BRUNNER (Kolloid-Z., 1935, 72, 26—35).—Au sols prepared by electro-dispersion in

HCl are stable to boiling and are stabilised by the charging complex  $[\text{Au}^{\text{I}}\text{Cl}_2]\text{H}$ . Progressive electro-decantation converts them into sols which are not stable to boiling and are charged by the complex  $[\text{Au}^{\text{I}}(\text{OH})\text{Cl}]\text{H}$ . The more stable sol is re-formed by adding HCl in accordance with the equilibrium  $[\text{Au}^{\text{I}}(\text{OH})\text{Cl}]\text{H} + \text{HCl} \rightleftharpoons [\text{Au}^{\text{I}}\text{Cl}_2]\text{H} + \text{H}_2\text{O}$ . Similar relations have been observed in Au sols prepared by reduction of  $\text{HAuCl}_4$  with P or  $\text{H}_2$  in presence of  $\text{K}_2\text{CO}_3$ . E. S. H.

**Dissolution of titanite hydroxide in hydrogen peroxide.** S. KATZOFF and R. ROSEMAN (J. Amer. Chem. Soc., 1935, 57, 1384).—Freshly pptd. and washed  $\text{Ti}(\text{OH})_4$  dissolves in  $\text{H}_2\text{O}_2$  giving a colloidal sol, which is pptd. by electrolytes. Gels can be formed by evaporating the sols and cooling. E. S. H.

**Electrical conductivity of colloidal solutions.** J. J. BIKERMAN (J. Chim. phys., 1935, 32, 460—465; cf. this vol., 700).—The equation derived from the diffuse double layer theory shows that the fraction of the observed conductivity of aq. sols which is due to micelles is, in general, negligible when  $\kappa$  is  $> 10^{-5}$  ohm $^{-1}$  cm. $^{-1}$ . J. G. A. G.

**Preparation of colloidal ferric hydroxide solutions with the aid of tetra-alkylammonium hydroxides containing several vicinal hydroxyl groups in one alkyl residue.** W. TRAUBE and K. E. STUMPF (Ber., 1935, 68, [B], 1394—1398).—Solutions of trimethyl- $\beta$ - $\gamma$ -dihydroxypropylammonium hydroxide dissolve  $\text{Fe}(\text{OH})_3$  in large amount which increases with the concn. of the alkali solution. The greater amount of  $\text{Fe}(\text{OH})_3$  is present as colloid, only a small portion being in complex union. The amount of  $\text{Fe}(\text{OH})_3$  dissolved depends on its previous history. Treatment of the solutions with  $\text{BaCl}_2$  or  $\text{BaSO}_4$  causes pptn. of all the colloiddally dissolved  $\text{Fe}(\text{OH})_3$ . Similar solvent power is shown by  $\beta$ - $\delta$ -tetrahydroxy-*n*-hexyleneditrimethylammonium hydroxide. The presence of the  $\text{NH}_4$  base does not appear to hinder the formation of  $\text{Fe}^{\text{III}}$ -mannitol complexes but, unexpectedly, the colloidal  $\text{Fe}(\text{OH})_3$  thus prepared appears to react more slowly than that obtained by other methods. Sorbitol behaves similarly to mannitol but somewhat more rapidly. H. W.

**Viscometric investigation of structure formation in  $\text{Fe}(\text{OH})_3$  sols. II. Influence of warming.** A. RABINERSON (Acta Physicochim. U.R.S.S., 1934, 1, 256—265).—Viscosity-pressure curves for a sol containing 10.07 g. of  $\text{Fe}_2\text{O}_3$  per 100 c.c. show that the viscosity increases with lapse of time, this change being accelerated by heating to 55—60°. Further heating to 70—72° yields a jelly; this on shaking yields a thick sol which on keeping returns partially to the thixotropic state. This effect is increased after frequent warming. The phenomena are explained by the diminution in  $[\text{Fe}^{\text{III}}]$  in the solution due to hydrolysis on warming, modifying the adsorption equilibrium with ions on the particles and leading to partial coagulation, these processes being partially reversible at lower temp. J. W. S.

**Anomalous variations of viscosity during the coagulation of positive ferric oxide sol by col-**



**loidal arsenious sulphide sol.** S. S. JOSHI and K. P. N. PANNIKAR (J. Chim. phys., 1935, 32, 455—459).—Large and irregular changes of viscosity occur during the coagulation of colloidal  $\text{Fe}(\text{OH})_3$  (1.5 g.  $\text{Fe}_2\text{O}_3$  per litre) by colloidal  $\text{As}_2\text{S}_3$  at various dilutions (cf. A., 1934, 597). J. G. A. G.

**Influence of concentration and age on some colloidal properties of ferric chloride solutions.** H. L. ELLISON and F. HAZEL (J. Physical Chem., 1935, 39, 829—835).—The no. of nuclei initially present in 0.1—0.001M- $\text{FeCl}_3$  solutions increases with increasing concn. On ageing the no. of colloidal particles increases in a stepwise manner with abrupt discontinuities. The increase in  $[\text{H}^+]$  during ageing is approx.  $\propto$  the increase in no. of particles. The electrophoretic velocity decreases with ageing. The no. of particles produced in the high-temp. hydrolysis product depends on the no. of particles in the initial solution. J. W. S.

**Investigation of solvation and aggregation.** N. S. SCHEINKER, R. E. NEUMANN, and G. A. SCHIROV (Acta Physicochim. U.R.S.S., 1935, 1, 795—804).—Diffusion observations show that addition of  $\text{C}_6\text{H}_6$  to an EtOH solution of Et-violet causes first a decrease in the size of colloidal particles due to desolvation, and then an increase, due to aggregation. With MeOH solutions an increase only is observed, the particles being aggregated but not solvated. The behaviour in EtOH- $\text{H}_2\text{O}$  mixtures resembles that in EtOH. The solvation in EtOH corresponds with a unimol. layer of solute. H. J. E.

**Theory of coagulation.** N. FUCHS (Z. physikal. Chem., 1935, 173, 387).—A correction (cf. this vol., 164). T. G. P.

**Kinetics of coagulation of colloidal gold.** K. JABEŁCZYŃSKI and W. KOSCHANY (Rocz. Chem., 1935, 15, 283—289).—A spectrophotometric study of Au sols indicates that the dimensions of the particles do not vary during 21 days of observation, but their negative charge increases. Different samples of identically prepared Au sols exhibit different initial rotations. The spectrophotometric method is not applicable to quant. study of sols which change colour with time. R. T.

**Spontaneous formation of ordered aggregates in sols containing non-spherical particles.** W. HELLER (Compt. rend., 1935, 200, 2082—2084).—By the mechanical coagulation of  $\text{Fe}(\text{OH})_3$  sols under conditions such that coagulation is difficult, a small no. of aggregates is formed which show anisotropy. These are not formed in presence of electrolyte. H. J. E.

**Structure viscosity of solutions of highly polymerised substances.** J. COUMOU (Chem. Weekblad, 1935, 32, 426—429).—Solutions of gelatin, starch (if not heated for too long a period), dextrin, carobin, gum tragacanth, linseed, and pectin in  $\text{H}_2\text{O}$ , lichenin in dil. alkali, and polystyrene in tetrahydronaphthalene show structure viscosity (change in  $\eta$  with rate of flow). Solutions of sucrose, glucose, gum arabic, and gum acajou in water and of PhOH- and cresol- $\text{CH}_2\text{O}$  resins in  $\text{COMe}_2$  or EtOH do not show this effect. The difference is attributed to the

long-chain structure of the former and relatively compact form of the mols. of the latter. D. R. D.

**Reaction [between] metal hydroxide solution [and] cellulose fibre. II. X-Ray investigation of the reversibility of the lattice transformation in sodium-cellulose.** W. SCHRAMEK and H. GÖRG (Kolloid-Beih., 1935, 42, 302—330; cf. this vol., 29).—Equilibrium in the system cellulose-NaOH has been studied by X-ray examination. The phase rule is not applicable. Five kinds of Na-cellulose have been recognised, and the conditions of inter-conversion determined. Na-cellulose I is assigned the mol. ratio  $2\text{C}_6 : 1\text{NaOH}$ . E. S. H.

**Relative precipitating effect of alcohols on organosols.** B. YAMAGUCHI (Kolloid-Z., 1935, 72, 51—55).—The pptg. effect of a series of homologous aliphatic alcohols on solutions of cellulose acetate in  $\text{COMe}_2$  and of polystyrene in  $\text{C}_6\text{H}_6$  or PhCl increases with increasing mol. polarisation ( $P$ ) of the alcohol, but with polystyrene in EtOAc the pptg. effect is independent of the alcohol. The general relation is expressed by  $a - 1/(P - 36.8)^n = k$ , where  $n$  and  $k$  are consts. characteristic of the sol. The relation between the pptn. curve and the solvation of the solute is discussed. E. S. H.

**Influence of alcohols on structure formation in ferric hydroxide sols.** A. RABINERSON (Kolloid-Z., 1935, 72, 58—62).—Addition of about 40% of EtOH to conc.  $\text{Fe}(\text{OH})_3$  sols causes a great increase of  $\eta$  and, eventually, solidification. Small amounts of EtOH have no appreciable effect.  $(\text{CH}_2\text{OH})_2$  (I) and glycerol (II) do not behave like EtOH, although they have a dehydrating action. Conc. sols of  $\text{Fe}(\text{OH})_3$  in (I) or (II) can be prepared by direct dispersion, but not in EtOH, which gives a coarse dispersion. E. S. H.

**Chemical reactions between colloids. I. Copper and sulphur.** E. SAUER and D. STEINER (Kolloid-Z., 1935, 72, 35—40).—Sols of Cu and S, prepared in different ways, react to form  $\text{Cu}_2\text{S}$ , which later reacts with more S, forming CuS. The participation of electrolytes in the chemical change was excluded. E. S. H.

**Thixotropy in suspensions of coarsely disperse aluminium compounds.** T. HENNIG (Kolloid-Z., 1935, 72, 63—66).—The thixotropic properties of Al formate and acetate and Ca and Mg aluminates are described. The terms negative and positive thixotropy, according to whether the change is in the direction of forming solid or liquid, are introduced. E. S. H.

**Structure viscosity and thixotropic properties of cellulose ester solutions. I. Dependence of structure viscosity and thixotropic properties of alcohol-ether solutions of cellulose nitrate on specific viscosity.** S. ROGOVIN and V. IVANOVA (Kolloid-Z., 1935, 72, 86—92).—Structure viscosity generally increases with increasing sp. viscosity, especially in conc. solutions, but several contrary results in solutions containing large amounts of degradation products are noted. There is no direct relation between thixotropy and sp. viscosity. E. S. H.



**Amorphous and crystalline oxide hydrates and oxides.** XXII. Hydroxide gels and oxide hydrate gels, and their amphoteric properties. A. KRAUSE (Kolloid-Z., 1935, 72, 18—25; cf. this vol., 946).—A discussion of published work.

E. S. H.

**$p_H$  measurements in gelatin solutions.** I. PETROV and A. PASINSKI (J. Appl. Chem. Russ., 1935, 8, 165—171; cf. A., 1932, 700).—The  $p_H$  of buffered gelatin solutions can be reproduced with an accuracy of  $\pm 0.05$  potentiometrically (H, quinhydrone, glass electrodes), and  $\pm 0.1$  colorimetrically with Michaelis' and with Clarke and Lubs' indicators. In unbuffered solutions the corresponding vals. are  $\pm 0.15$  for purified, and  $-0.25$  and  $-0.50$  for impure, gelatin.

R. T.

**Response of electrolytes in gelatin to an applied electric field.** (MLLE.) S. VEIL (J. Chim. phys., 1935, 32, 429).—For a p.d.  $\ll$  that required to cause decomp. the applied field gives rise to a periodic distribution of electrolyte in a layer of gelatin spread on glass, suggesting the existence of zones of unequal rates of diffusion.

J. G. A. G.

**Residual water in activated silica gel.** S. S. KISTLER and K. KEARBY (Acta Physicochim. U.R.S.S., 1934, 1, 354—364).—By treatment with  $\text{SiCl}_4$ , about 94% of the residual  $\text{H}_2\text{O}$  can be removed from  $\text{SiO}_2$  gel below  $350^\circ$  without reducing its activity seriously, indicating that most of the  $\text{H}_2\text{O}$  is within reach of the surface. Adsorption activity, as measured by heat of wetting, is almost independent of  $\text{H}_2\text{O}$  content. Approx. free energies of reaction of  $\text{SiCl}_4$ ,  $\text{BCl}_3$ ,  $\text{TiCl}_4$ ,  $\text{SnCl}_4$ , and  $\text{AlCl}_3$  with  $\text{H}_2\text{O}$  are calc.

J. W. S.

**Structure of silica gel.** M. V. POLJAKOV, P. M. STADNIK, M. V. PARITZKI, and I. M. MALKIN (Ber. Ukrain. wiss. Forsch. physikal. Chem., 1935, 4, 71—73).—The activity of  $\text{SiO}_2$  gel prepared in presence of  $\text{C}_6\text{H}_6$ ,  $\text{PhMe}$ , xylene,  $\text{C}_{10}\text{H}_8$ , and S has been determined. Vals. for  $\text{C}_6\text{H}_6$ ,  $\text{PhMe}$ , and xylene are  $\propto$  their mol. wts.

R. S.

**Gelatinisation and polymerisation. Explanation of a case of thixotropy.** B. A. TALMUD and D. L. TALMUD (Acta. Physicochim. U.R.S.S., 1934, 1, 282—285).—The formation of thixotropic gels from non-aq. Ba malonate sols is attributed to rearrangement of the mols. into chains, each Ba atom being linked to two  $\text{CO}_2$  groups of different malonate mols.

J. W. S.

**Hydrophilic colloids.** I. Calorimetric investigation of the hydration of hydrophilic colloids in ethyl alcohol-water mixture and in ethyl alcohol-ether-water mixture. M. V. TSCHAPEK (Kolloid-Z., 1935, 72, 46—50).—Experiments with agar, potato starch, peat, and gelatin show that the hydration is not reduced by EtOH until  $> 80\%$  is present. Throughout the ternary liquid mixture the hydration is always  $>$  half that in  $\text{H}_2\text{O}$ . Addition of  $\text{Et}_2\text{O}$  increases the hydration, apparently by removing some of the EtOH.

E. S. H.

**Storage of polonium solutions.** C. ROSENBLUM and E. W. KAISER (J. Physical Chem., 1935, 39, 797—

801).—The storage of Po solutions in paraffin-coated glass vessels decreases the formation of colloids.

J. W. S.

**Influence of salts on the potential and charge of inert and protein surfaces.** H. A. ABRAMSON (J. Physical Chem., 1935, 39, 749—760).—The electrokinetic potential ( $\zeta$ ) and density of surface charge ( $\sigma$ ) of colloids in aq. salt solutions of various concns. (c) have been calc. from mobility measurements. The  $\zeta$ -c curves for graphite, quartz, collodion, cellulose, and paraffin oil in solutions for which the sign of  $\sigma$  is not reversed show max. for about  $10^{-5}M$  solutions, but the  $\sigma$ -c curves follow a simple form resembling a typical adsorption curve, with an initial steep slope and reaching saturation at about  $0.01M$ . The  $\zeta$ -c curves for proteins are in agreement with the view that the net charge on the protein surface depends primarily on the  $p_H$  and that  $\zeta$  in dil. solution depends on the thickness of the electrical double layer.

J. W. S.

**Electrokinetic potential and the stability of colloids.** H. MUELLER (J. Physical Chem., 1935, 39, 743—747).—The electrostatic forces of the double layer on hydrophobic colloid particles are sufficient to account for the existence of a stable protective layer of  $\text{H}_2\text{O}$  mols. The theory indicates that the stability of such colloids should decrease rapidly at temp.  $> 80^\circ$ .

J. W. S.

**Cataphoresis of particles of the fatty acids and related compounds.** T. ALTY and O. JOHNSON (Phil. Mag., 1935, [vii], 20, 129—145).—The mobility of particles of fatty acids and other related compounds in  $\text{H}_2\text{O}$  and in aq. HCl depends on the nature of the  $\text{H}_2\text{O}$ -sol. group and on the length of the hydrocarbon chain. For const. chain length the mobility follows the order  $\text{CO}\cdot\text{NH}_2 > \text{CO}_2\text{H} > \text{CH}_2\cdot\text{OH}$ , whilst in the series of acids the mobility decreases with increasing length of the chain. The mobility is increased by a double linking near the middle of the chain. The mobilities decrease with increasing  $[\text{H}^+]$  of the solution.

J. W. S.

**Cataphoresis of Chinese ink in water containing deuterium oxide.** T. TERADA and R. YAMAMOTO (Proc. Imp. Acad. Tokyo, 1935, 11, 214—215).—Differences from the behaviour in ordinary  $\text{H}_2\text{O}$  are attributed to substitution of D for H in the  $\text{NH}_2$  groups of the gelatin protecting the ink.

C. W. G.

**Thermodynamical treatment of base-exchange equilibria. Real solid solutions of two zeolite components.** J. KIELLAND (Tidsskr. Kjemi, 1935, 15, 74—76).—Theoretical.

E. S. H.

**Thermodynamics of base-exchange equilibria of some different kinds of clays.** J. KIELLAND (J.S.C.I., 1935, 54, 232—234T).—A thermodynamic method of treating base-exchange equilibria is given which takes account of the activity coeffs. of the zeolitic components. The method is shown to give const.  $K_a$  vals. Free energies for various components are calc. In exchange reactions with H- and Tl-clays, the occurrence of the compound  $2\text{HZ}, \text{TlZ}$  is indicated.

**Reciprocity theorem in colloid optics.** R. S. KRISHNAN (Proc. Indian Acad. Sci., 1935, 1, A, 782—788).—A previous algebraic relation (cf. this vol.,



821) is deduced from the Helmholtz-Rayleigh principle of reciprocity and supported by experimental evidence. N. M. B.

Possible determination of state of degeneracy of a gas. M. SATÔ (Sci. Rep. Tôhoku, 1935, 24, 26—29).—For the Brownian motion in a degenerate gas, the motion deduced for  $A < 1$  by means of the Bose-Einstein statistics is  $<$  that derived by the classical theory. R. C.

Intensity parameter and stable thermodynamic equilibrium. T. EHRENFEST-AFANASSJEVA and G. L. DE HAAS-LORENTZ (Physica, 1935, 200, 743—752).—Theoretical. H. J. E.

Mass action. N. A. BRUNT (Chem. Weekblad, 1935, 32, 446—448). I. M. KOLTHOFF (*ibid.*, 448—449).—Polemical (cf. this vol., 702). D. R. D.

Formulation of the law of mass action in homogeneous and heterogeneous systems with particular regard to metallurgical equilibria. A. SKAPSKI (Bull. Acad. Polonaise, 1935, A, 174—188).—Theoretical. J. W. S.

Equilibrium and heat of the reaction  $C_2H_4 + H_2 = C_2H_6$ . E. TELLER and B. TOPLEY (J.C.S., 1935, 876—885; cf. A., 1934, 254).—The most trustworthy val. of the equilibrium const. is  $\log_{10} K_{P(atm.)} = 1.613$  at 863° abs. Within the limits of spectroscopic and sp. heat data, assumptions relating to the potential energy of the restricted rotation of Me in  $C_2H_6$  and also to the frequencies of  $C_2H_4$  and  $C_2H_6$  not fixed spectroscopically lead from  $K_P$  to  $-\Delta H_{298} = 31,050 \pm 300$  g.-cal. per mol. The thermodynamic evaluation of  $-\Delta H_{298}$  from the temp. coeff. of  $K_P$  is less trustworthy. The max. and the probable errors in the statistical mechanical vals. are  $\pm 600$  and  $\pm 300$  g.-cal., respectively, and the origin of the discrepancy between the experimental (cf. this vol., 304) and the calc. vals. of  $-\Delta H_{298}$  is obscure. The heat of reaction at 0° abs. is  $-\Delta E_0 = 29,420 \pm 100$  g.-cal. per mol. J. G. A. G.

Solvation and equation of state of dissolved substances. M. AF HALLSTRÖM (Suomen Kem., 1935, 8, A, 53—57).—The influence of solvation on the mol. wt. ( $M$ ) calc. from the f.p. is given by  $M = M_0(1 - Sc)$ , where  $M_0$  = theoretical mol. wt.,  $S$  = solvated solvent in kg., and  $c$  = wt. concn. This leads to an equation of state of the same form as that used by Sackur,  $p(v - b) = RT$  (cf. A., 1910, ii, 273). The degree of hydration is calc. from the consts.  $b$  given by Sackur, and also from the quantities of solvent in isotonic solutions. The vals. obtained agree with those calc. by Tammann from hydration pressure and Öholm (A., 1912, ii, 564) from diffusion. In solvents other than  $H_2O$  a term must be included in the equation of state to allow for mol. attraction. R. S. B.

Electrolytic dissociation of heavy water. E. ABEL, E. BRATU, and O. REDLICH (Z. physikal. Chem., 1935, 173, 353—364; cf. A., 1934, 1173).—The e.m.f. of the cells  $D_2[DCl(0.1M)|AgCl|Ag]$  and  $D_2[NaOD(0.1M) + NaCl(0.1M)|AgCl|Ag]$  have been measured. The ratio of the dissociation consts.  $D_2O : H_2O$  is 0.16 at 21°. The product of the different "hydrogen-ion" and "hydroxyl-ion" concns. is

strictly dependent on the stoichiometric isotopic composition, and is the same for acid or alkali in the same water. This product plays a similar rôle for mixtures of  $D_2O$  and  $H_2O$  as does the dissociation const. in pure  $H_2O$ . For  $D_2$  in  $D_2O$   ${}_0E_h = -0.0034$  volt; for Ag, AgCl,  $Cl^-$  in  $D_2O$   ${}_0E_h = -0.218(7)$  volt. DCl is less sol. in  $D_2O$  than HCl in  $H_2O$  in the ratio 0.62 : 1. T. G. P.

Influence of substituents on the dissociation constants of carboxylic acids. J. F. J. DIPPEY and H. B. WATSON (Chem. and Ind., 1935, 735—737).—The relation between the dissociation const. of substituted acetic acids and the dipole moment of the substituent (cf. A., 1933, 890) has been applied to substituted phenylacetic acids. Deviations from the relation are discussed. R. S.

Dissociation constants of organic acids. XII. New buffer: phenylacetic acid-sodium phenylacetate. W. L. GERMAN and A. I. VOGEL (J.C.S., 1935, 912—914).—Measurements of  $p_H$  have been made with the quinhydrone electrode at 25°. The H electrode affords unsteady and drifting potentials owing to the catalytic reduction of  $CH_2Ph \cdot CO_2H$  to cyclohexylacetic acid. The buffer solutions cover the range  $p_H$  3.16—4.66 and lead to  $K_a = 4.89 \times 10^{-5}$ , in good agreement with other vals. J. G. A. G.

Electrometric titration curves of dibasic acids. V. Dissociation constants of cyclopentanedicarboxylic acids [at 25°]. Attempted check on methods proposed for calculating mol. dimensions. C. K. INGOLD and H. G. G. MOHRHENN (J.C.S., 1935, 949—952).—The first and second dissociation consts.,  $K_1 \times 10^5$  and  $K_2 \times 10^6$ , of the isomerides are: *cis*-1 : 2-, 3.7, 0.27; *trans*-1 : 2-, 11, 1.4; *cis*-1 : 3-, 5.5, 3.1; *trans*-1 : 3-, 4.8, 3.8, respectively. The extended equation (A., 1931, 1126) gives vals. for the distances between the charges of the bivalent anions in closer agreement with the requirements of the mol. models than the vals. calc. from Bjerrum's original equation. J. G. A. G.

Classical dissociation constant of benzoic acid in various salt solutions. L. C. RIESCH and M. KILPATRICK (J. Physical Chem., 1935, 39, 891—899).—The classical dissociation const. of BzOH has been determined in solutions of LiCl, NaCl, KCl,  $LiNO_3$ ,  $NaNO_3$ ,  $KNO_3$ ,  $NaClO_4$ ,  $PhSO_3Na$ , and  $p\text{-}C_6H_4Me \cdot SO_3Na$ . The mean activity coeffs. of OBz ions are calc. from the activity coeff. of mol. BzOH and the thermodynamic dissociation const. J. W. S.

Rôle of *o*-substitution in the ionisation of organic acids and bases. A. W. WALDE (J. Physical Chem., 1935, 39, 885—889).—The increase in acidity of *o*-substituted BzOH and  $NH_2Ph$  is attributed to the restriction of the free rotation of the  $CO_2H$  or  $NH_2$ . J. W. S.

Solubilities, apparent dissociation constants, and thermodynamic data of dihalogenated tyrosine compounds. P. S. WINNER and C. L. A. SCHMIDT (J. Gen. Physiol., 1935, 18, 889—903).—The solubilities and differential heats of solution of *d*-, *dl*-, di-iodo-*dl*-, dibromo-*l*-, (I), and dichloro-*l*-tyrosine (II) are given. There is evidence that



*dl*-tyrosine is a compound. From solubility determinations at 25° and 40° at different  $p_H$  the apparent acid and basic dissociation consts., and the apparent heats of ionisation, of (I) and (II) are calc.

F. A. A.

**Reaction of malonic acid with metallic bases.** C. W. DAVIES (J.C.S., 1935, 910—912).—Anomalies of Cu malonate and Cu H malonate solutions are explained by the low dissociation consts.,  $K$ , of the salts and there is no reason for inferring the presence of colloidal basic aggregates (cf. this vol., 449). The Cu salts of disubstituted malonic acids are largely hydrolysed, and the recorded vals. of  $K$  (A., 1931, 1126) are therefore uncertain.  $K$  for the reaction  $\text{CuOH}^+ \rightleftharpoons \text{Cu}^{2+} + \text{OH}^-$  is  $3 \times 10^{-8}$ , approx.

J. G. A. G.

**Activity coefficients of the alkali bromides and iodides in aqueous solution from vapour-pressure measurements.** R. A. ROBINSON (J. Amer. Chem. Soc., 1935, 57, 1161—1165).—The concns. of solutions of LiBr, NaBr, KBr, RbBr, CsBr, NaI, KI, RbI, and CsI which are isopiestic with KCl solutions of known concn. at 25° have been measured. Activity coeffs. of the above salts have been calc. at concns. from 0.1M to 4M. The results agree satisfactorily with those from e.m.f. and f.-p. data.

E. S. H.

**Activity coefficients of alkali nitrates, acetates, and *p*-toluenesulphonates in aqueous solution from vapour-pressure measurements.** R. A. ROBINSON (J. Amer. Chem. Soc., 1935, 57, 1165—1168; cf. preceding abstract).—The activity coeffs. have been calc. from determinations of the concns. of aq. alkali nitrates, acetates, and *p*-toluenesulphonates which are isopiestic with KCl solutions of known concn. at 25°. The results agree with those obtained from f.-p. data.

E. S. H.

**Liquid ammonia as a solvent. IV. Activities of ammonium nitrate, iodide, bromide, and chloride at 25°.** W. E. LARSEN and H. HUNT (J. Physical Chem., 1935, 39, 877—883).—Vals. of the relative mean ionic activity coeffs. are calc. from the v.p. of solutions of these salts in liquid  $\text{NH}_3$ . It is suggested that deviations from Raoult's law are due to partial association of the solutes and solvation of the ions.

J. W. S.

**Activity of ammonium ions in liquid ammonia.** V. A. PLESKOV and A. M. MONOSSOHN (Acta Physicochim. U.R.S.S., 1935, 1, 713—728; cf. A., 1934, 1309).—The activities of  $\text{NH}_4\text{NO}_3$  (0.0001—1.0N) and  $\text{NH}_4\text{Cl}$  (0.005—0.5N) in liquid  $\text{NH}_3$  have been measured with the H electrode at -50°. A discrepancy exists with vals. from conductivity measurements. The Debye-Hückel theory is unsatisfactory in this case. The dissociation const. of  $\text{NH}_3$  at -50°, determined potentiometrically, is  $1.9 \times 10^{-33}$ . Results of Zintl and Neumayr and of Fredenhagen (A., 1930, 297, 537) are criticised.

H. J. E.

**Complexes of aromatic nitro-compounds with acids.** B. V. TRONOV and L. P. KULEV (J. Gen. Chem. Russ., 1935, 5, 401—412).—Measurements of the e.m.f. obtained on immersing a Na electrode in  $\text{C}_6\text{H}_5$  solutions of  $\text{PhNO}_2$ ,  $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$ , or  $1\text{-C}_{10}\text{H}_7\text{-NO}_2$  and  $\text{AcOH}$ ,  $\text{EtCO}_2\text{H}$ ,  $\text{Pr}^n\text{CO}_2\text{H}$ ,  $\text{Pr}^i\text{CO}_2\text{H}$ ,

or  $\text{Bu}^i\text{CO}_2\text{H}$  indicate potential max. corresponding with complexes of 1 mol. of  $\text{NO}_2$ -compound with 1—2 mols. of acid. The e.m.f. of systems containing  $\text{AcOH}$  is greatly increased by adding 1% of  $\text{H}_2\text{O}$ .

R. T.

**System calcium nitrite-water.** J. BUREAU (Compt. rend., 1935, 201, 67—69).—Data obtained by thermal analysis and solubility methods are recorded. The hydrates  $\text{Ca}(\text{NO}_2)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Ca}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$  are formed.

H. J. E.

**System bismuth iodide-ammonium iodide.** (MLLE.) M. L. DELWAULLE (Compt. rend., 1935, 201, 341—344).—This system has been investigated at 11°, 35°, and 50°, the existence of  $\text{BiI}_3 \cdot \text{NH}_4\text{I} \cdot 2\text{H}_2\text{O}$  and  $\text{BiI}_3 \cdot 4\text{NH}_4\text{I} \cdot 3\text{H}_2\text{O}$  being confirmed and a further compound  $\text{BiI}_3 \cdot 2\text{NH}_4\text{I} \cdot 2\text{H}_2\text{O}$  identified.

J. W. S.

**Equilibrium diagram of system barium fluoride-magnesium fluoride.** M. OKAMOTO and U. NISIOKA (Sci. Rep. Tôhoku, 1935, 24, 141—149; cf. A., 1933, 782).—The compound  $\text{BaF}_2 \cdot 2\text{MgF}_2$  is formed at 930° in accordance with  $\text{MgF}_2 + \text{melt} \rightleftharpoons \text{BaF}_2 \cdot 2\text{MgF}_2$ .

R. C.

**System  $\text{MnO} \cdot \text{SiO}_2$ -FeS.** A. S. GINZBERG, B. P. SELIVANOV, and S. I. NIKOLISKI (Soob. Vsesoy. Inst. Met., 1931, No. 8, 25—29).—A m.-p. diagram is given.

CH. ABS. (e)

**Thermodynamics of the binary system: *p*-cresol-benzoic acid.** G. CHAPAS (J. Chim. phys., 1935, 32, 466—468).—The liquid probably consists of double mols. of each component (cf. this vol., 35).

J. G. A. G.

**Purification and physical properties of organic compounds. IX. Some binary freezing-point diagrams and a study of their ideality.** E. L. SKAU (J. Physical Chem., 1935, 39, 761—767; cf. A., 1930, 543).—The system  $\text{NH}_2\text{Bz}-m\text{-OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$  shows a eutectic point at 42.1° with 56.6 mol.-% of  $m\text{-OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ . The system acenaphthene- $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$  has two eutectics at 68.7° and 66.5° with 36 and 68 mol.-% of  $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$ , respectively. An equimol. compound, m.p. 71.9°, is formed.  $\beta\text{-C}_{10}\text{H}_7 \cdot \text{NH}_2$  and  $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$  also form a compound. The greatest deviations from ideality occur with the first mixture and it is suggested that a compound does form but that conditions are such that it does not crystallise. The m.p. obtained are generally > those given by other authors.

J. W. S.

**System antimony iodide-ammonium iodide-water.** F. FRANÇOIS (Compt. rend., 1935, 201, 215—216).—Solubility data at 11°, 20°, 35°, 50°, and 75° are recorded. The compound  $\text{SbI}_3 \cdot 4\text{NH}_4\text{I} \cdot 3\text{H}_2\text{O}$  is formed below 75°.  $\text{SbI}_3 \cdot 2\text{NH}_4\text{I} \cdot 2\text{H}_2\text{O}$  and an unidentified orange-red compound, stable below approx. 20°, have also been observed.

H. J. E.

**System iron-phosphorus-oxygen.** H. WENTRUP (Arch. Eisenhüttenw., 1935—1936, 9, 57—60).—The system  $\text{Fe}_2\text{O}_3\text{-P}_2\text{O}_5$  has been examined by thermal and micrographic methods in the range 30—50.6% Fe;  $\text{FePO}_4$  (I) melts without decomp. at 1240° and  $\text{Fe}_4(\text{P}_2\text{O}_7)_3$  (II) at 1270°. (I) and (II) form a eutectic with 34.6% Fe at 964° and (I) also forms a eutectic at 42.6% Fe and 968° with the compound  $2\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$ .



(III) formed by a peritectic reaction between  $\text{Fe}_2\text{O}_3$  and (I) at  $1095^\circ$ . (I) exists in three forms, the  $\gamma$ -form crystallising in grey transparent crystals from the melt and changing at  $889^\circ$  into the grey  $\beta$ -form, which changes at  $784^\circ$  into white needles of the  $\alpha$ -form. (II) exists in two forms with a transformation point at  $865^\circ$  and (III) also exists in two forms, the grey  $\alpha$  being converted into lighter-coloured  $\beta$  at  $869^\circ$ . There appears to be no solid solution range in the system. The system  $\text{FeO}-\text{P}_2\text{O}_5$  has been examined in the range 46.9–59.8% Fe;  $3\text{FeO} \cdot \text{P}_2\text{O}_5$  (IV) exists in two forms, the grey  $\alpha$  being converted at  $942^\circ$  into white rhombic crystals of  $\beta$  which melt without decomp. at  $1238^\circ$  and form with FeO a eutectic at  $1008^\circ$  and 53.9% Fe. (IV) and (II) appear to form a quasibinary system with a eutectic at about  $1040^\circ$  and 38.7% Fe. Characteristic microstructures of mixtures in the above systems are shown.

A. R. P.

**Ferric oxide and aqueous sulphuric acid at  $25^\circ$ .** W. H. BASKERVILLE and F. K. CAMERON (J. Physical Chem., 1935, 39, 769–779).—Dissolution of  $\text{Fe}_2\text{O}_3$ , hydrated  $\text{Fe}_2\text{O}_3$ , or basic  $\text{Fe}^{\text{III}}$  sulphates in aq.  $\text{H}_2\text{SO}_4$  is slow and its rate depends on the composition, physical properties, and previous history of the solid. Equilibrium is reached the more slowly the more conc. is the acid. The solubility of  $\text{Fe}_2\text{O}_3 \propto$  the  $[\text{SO}_3]$  up to a max. val. of 20.5% with 26.4 g. of  $\text{SO}_3$  per 100 g. of solution, but decreases at higher  $[\text{SO}_3]$ . Below this  $[\text{SO}_3]$  the solids in equilibrium with the solutions form a continuous series of solid solutions, but at higher  $[\text{SO}_3]$  the following solid phases have been identified:  $\text{Fe}_2\text{O}_3 \cdot 2.5\text{SO}_3 \cdot 7\text{H}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 9\text{H}_2\text{O}$ , and  $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ . The solutions in equilibrium with  $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 8\text{H}_2\text{O}$  are unstable. There are no congruent points in this system.

J. W. S.

**Thermal equilibria in ternary systems. VI. Phenacetin-antipyrine-menthol. VII. Phenacetin-urethane-menthol. VIII. Resorcinol-pyrocatechol-quinol.** K. HRYNAKOWSKI and F. ADAMIANIS (Rocz. Chem., 1935, 15, 311–317, 318–324, 325–330).—VI. Compounds are not formed. The eutectic, f.p.  $31.0^\circ$ , contains antipyrine 16, phenacetin 1.5, and menthol 82.5%.

VII. The eutectic, f.p.  $24.8^\circ$ , contains phenacetin 2, menthol 72, and urethane 26%.

VIII. The eutectic, f.p.  $58.7^\circ$ , contains quinol 15, resorcinol 49, and pyrocatechol 36%. R. T.

**Double decomposition in the absence of a solvent. XXVII. Complex mutual systems of a higher order.** A. G. BERGMAN (J. Gen. Chem. Russ., 1935, 5, 432–437).—Possible methods of study of systems of 6 or more salts are considered. R. T.

**Heats of formation of certain sulphides.** H. ZEUNER and W. A. ROTH (Z. physikal. Chem., 1935, 173, 365–382).—The heats of formation of  $\text{FeS}$  and  $\text{Ag}_2\text{S}$  have been determined by synthesis in a calorimeter, and of  $\text{PbS}$  by pptn. of dil. aq.  $\text{Pb}(\text{NO}_3)_2$  with aq.  $\text{H}_2\text{S}$ . At  $20^\circ$ ,  $\text{Fe}(\alpha) + \text{S}(\text{rhomb.}) = \text{FeS} + 22.8 \text{ kg.-cal.}$ ,  $2\text{Ag} + \text{S}(\text{rhomb.}) = \text{Ag}_2\text{S} + 6.6 \text{ kg.-cal.}$ ,  $\text{Pb} + \text{S}(\text{rhomb.}) = \text{PbS} + 23.1 \text{ kg.-cal.}$  The heat of dissolution of  $\text{PbCl}_2$  has also been determined.

T. G. P.

**Transition point and thermodynamic values of silver sulphide.** G. KIMURA (Sci. Rep. Tôhoku, 1935, 24, 77–90).—The rhombic changes to the cubic form at  $175\text{--}176^\circ$ , the vol. increasing by 0.00065 c.c. per g. From the e.m.f. of the cell  $\text{H}_2(p)|\text{HCl}(m)|\text{HCl}(m), \text{H}_2\text{S}(p), \text{Ag}_2\text{S}|\text{Ag}$  the vals.  $\Delta F_{298} = -9542$  and  $\Delta H_{298} = -7512 \text{ g.-cal.}$  are obtained for  $2\text{Ag} + \text{S}(\text{rhomb.}) = \text{Ag}_2\text{S}$  (cf. A., 1934, 148).

R. C.

**Transference numbers of aqueous solutions of some electrolytes at  $25^\circ$  by the moving boundary method.** L. G. LONGSWORTH (J. Amer. Chem. Soc., 1935, 57, 1185–1191).—Data for aq.  $\text{KBr}$ ,  $\text{KI}$ ,  $\text{KNO}_3$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NaOAc}$ ,  $\text{CaCl}_2$ , and  $\text{Na}_2\text{SO}_4$  over the concn. range 0.01–0.2N are recorded. E. S. H.

**Conductivity of silver, thallium, magnesium, and alkaline-earth metal hydroxides in aqueous solution.** M. HŁASKO and A. SALITÓWNA (Rocz. Chem., 1935, 15, 273–282).—Direct measurements indicate that  $\lambda_\infty$  is attained in  $2 \times 10^{-8}\text{N-Ca}(\text{OH})_2$ ,  $5 \times 10^{-8}\text{N-Sr}(\text{OH})_2$ ,  $1 \times 10^{-7}\text{N-Ba}(\text{OH})_2$ , and  $2 \times 10^{-6}\text{N-TlOH}$ ; these vals. differ by  $> 0.2\%$  from those calc. from Kohlrausch's equation.  $\lambda_\infty$  cannot be measured directly for  $\text{AgOH}$  and  $\text{Mg}(\text{OH})_2$ , although very approx. vals. are obtained. The cationic mobilities are:  $\text{Mg}^{++} 56$ ,  $\text{Ca}^{++} 60.1$ ,  $\text{Sr}^{++} 60.3$ ,  $\text{Ba}^{++} 65.05$ ,  $\text{Ag}^+ 63.3$ ,  $\text{Tl}^+ 78.7$ . The measured conductivity coeffs. ( $f_\mu$ ) differ by  $> 1\%$  from those calc. from Onsager's equation, except for  $\text{AgOH}$  and  $\text{Mg}(\text{OH})_2$ , which are not completely ionised even at very high dilutions. The vals. of  $f_\mu$  for a no. of hydroxides rise in the order  $\text{NH}_4 < \text{Ag} < \text{Mg} < \text{Ca} < \text{Sr} < \text{Ba} < \text{Tl} < \text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$ .

R. T.

**Conductance of potassium chloride and of hydrochloric-deuterochloric acid in  $\text{H}_2\text{O}-\text{D}_2\text{O}$  mixtures. Viscosity of  $\text{H}_2\text{O}-\text{D}_2\text{O}$ .** W. N. BAKER and V. K. LA MER (J. Chem. Physics, 1935, 3, 406–410).—Conductivity measurements for 0.01N-KCl and  $\text{HCl-DCl}$  in  $\text{H}_2\text{O}-\text{D}_2\text{O}$  mixtures and of  $\eta$  for  $\text{H}_2\text{O}-\text{D}_2\text{O}$  mixtures at  $25^\circ$  are recorded. The  $\eta$  of  $\text{D}_2\text{O}$  is 23%  $>$ , the conductance of KCl in  $\text{D}_2\text{O}$  17%  $<$ , and that of  $\text{DCl}$  in  $\text{D}_2\text{O}$  26%  $<$ , corresponding vals. in  $\text{H}_2\text{O}$ . The  $\eta$  and conductance of KCl solutions and of  $\text{HCl-DCl}$  solutions show max. deviations of 0.4, 0.8, and 5.4% from linearity. The decreased conductance of KCl in  $\text{D}_2\text{O}$  is due mainly to the increased  $\eta$  of the solvent. H. J. E.

**Electrical conductivity of glass-like alkali borates.** B. I. MARKIN and R. L. MÜLLER (Acta Physicochim. U.R.S.S., 1934, 1, 266–281; cf. A., 1930, 1511).—The conductivities of glasses composed of  $\text{B}_2\text{O}_3$  and  $\text{Li}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{Rb}_2\text{O}$ , or  $\text{Cs}_2\text{O}$  follow the law  $\log k = -A/T + B$ , excepting at low alkali concn. where the curves show breaks near the crit. softening point. At low alkali concn. the mol. conductivity remains almost const., but with increasing concn. a min. is first reached followed by a sharp rise. The min. is most marked with  $\text{K}_2\text{O}$ . Empirical relations between the const. for the various alkalis are evolved. The mobilities of the alkali metal ions decrease with increasing mol. wt. of the ion.

J. W. S.

**Influence of temperature on the electrical conductivity of saccharin solutions.** A. IMBESI and V. DE ANGELIS (Annali Chim. Appl., 1935, 25,



254—262).—In the variation of degree of ionisation and dissociation const. with temp. and concn., saccharin behaves similarly to aliphatic and aromatic carboxylic acids. T. H. P.

**Magnetic fields and electrolytic conductors.** K. KRISHNAMURTI (Current Sci., 1935, 3, 351—352).—The decrease in the current on application of a magnetic field normal to the current has been studied by following the movements of streams of fine gas bubbles. A. B. D. C.

**Contact cells and their short-circuiting.** (Mlle.) S. VEIL (Compt. rend., 1935, 200, 2013—2015; cf. A., 1932, 226; this vol., 822).—A general discussion of e.m.f. phenomena in conducting gels. H. J. E.

**Ammonia gas electrode.** V. FINKELSTEIN, M. SCHELUDKO, and A. TERESCHTSCHENKO (Acta Physicochim. U.R.S.S., 1935, 1, 805—816).—E.m.f. measurements are recorded for the cells  $\text{Pt}|\text{NH}_3|\text{aq. NH}_4\text{NO}_3|\text{aq. KNO}_3|\text{aq. NH}_4\text{NO}_3|\text{Pt}|\text{O}_2$  and  $\text{Pt}|\text{NH}_3|\text{aq. NH}_4\text{NO}_3|\text{aq. KNO}_3|\text{N-aq. KCl}+\text{Hg}_2\text{Cl}_2|\text{Hg}$ ; the vals. agree with those calc. from thermochemical data. The potential of the  $\text{NH}_3$  gas electrode  $\Pi_{\text{NH}_3} \rightarrow \text{NO}_3 = -0.17 \pm 0.01$  volt. H. J. E.

**Argentate salts in acid solution. II. Oxidation state of argentate salts.** A. A. NOYES, K. S. PITZER, and C. L. DUNN. **III. Oxidation potential of argentous-argentate salts in nitric acid solution.** A. A. NOYES and A. KOSSIAKOFF (J. Amer. Chem. Soc., 1935, 57, 1229—1237, 1238—1242).—II. Chemical and magnetic methods of examination confirm that the substance produced by oxidising  $\text{AgNO}_3$  in  $\text{HNO}_3$  solution with  $\text{O}_3$  contains  $\text{Ag}^{++}$ , but not  $\text{Ag}^{+++}$ .

**III.** The oxidation potential determined by e.m.f. measurements is  $1.914 \pm 0.002$  volts, and it remains const. when  $[\text{Ag}^{++}]:[\text{Ag}^+]$  is varied 2-fold and over the  $[\text{HNO}_3]$  range 1—4*N*. Further evidence is adduced that the oxidation product consists almost entirely of  $\text{Ag}^{++}$ . E. S. H.

**Relations between oxidation-reduction potentials and acidity potentials in organic derivatives of arsenic acid.** H. ERLENMEYER and E. WILLI (Helv. Chim. Acta, 1935, 18, 733—740).—In the series of acids represented by  $\text{C}_6\text{H}_4\text{X}\cdot\text{AsO}_3\text{H}_2$ , where  $\text{X}=\text{NH}_2$ , Me, Cl, or  $\text{NO}_2$ , the oxidation-reduction potential is practically const., but there are considerable differences in acidity potential. E. S. H.

**Polarographic studies with the dropping mercury cathode. XLVIII. Overpotential in heavy water.** J. HEYROVSKÝ and O. H. MÜLLER. **XLIX. Electro-reduction and determination of bromates and iodates.** A. RYLICH (Coll. Czech. Chem. Comm., 1935, 7, 281—287, 288—298).—XLVIII. Solutions of HCl, TiCl<sub>3</sub>, and KCl in 3—99.2%  $\text{D}_2\text{O}$  have been studied polarographically with a dropping Hg cathode. Compared with  $\text{H}_2\text{O}$  solutions no differences are found in the  $b \log i$  term of the over-voltage relation, in current oscillations due to the change of surface of the Hg drops, in the catalytic lowering of the overpotential due to a trace of quinine, in the currents due to deposition of alkali metals,

in the reduction of atm.  $\text{O}_2$ , in the depolarising action of  $\text{OH}^+$ , or in the electro-reduction of maleic acid. The inflexion points, characterising the process of electro-reduction, are 20—25 mv. more negative for dil. HCl solutions in 99.2%  $\text{D}_2\text{O}$  than for the same concn. in  $\text{H}_2\text{O}$ .

**XLIX.** Vals. for the reduction potentials of  $\text{IO}_3^-$  and  $\text{BrO}_3^-$  have been determined in presence of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{++}$ ,  $\text{Sr}^{++}$ ,  $\text{Ba}^{++}$ , and  $\text{La}^{+++}$ . They vary with the cation valency in the same way as for  $\text{NO}_2^-$  and  $\text{NO}_3^-$ . The process of electro-reduction is  $\text{IO}_3^- + 6\text{H}^+ + 6\text{e}^- = \text{I}^- + 3\text{H}_2\text{O}$ .  $\text{ClO}_3^-$  and  $\text{ClO}_4^-$  are not reducible at the dropping Hg cathode. The reducibility of  $\text{IO}_3^-$ ,  $\text{BrO}_3^-$ , and  $\text{ClO}_3^-$  is given by their order of deformability. Simultaneous polarographic determination of  $\text{IO}_3^-$  and  $\text{BrO}_3^-$  is very sensitive,  $\text{IO}_3^-$  being determinable with any excess of  $\text{BrO}_3^-$  and  $\text{ClO}_3^-$ , and  $\text{BrO}_3^-$  with any excess of  $\text{ClO}_3^-$ .  $\text{IO}_3^-$ ,  $\text{BrO}_3^-$ , and  $\text{NO}_3^-$  are simultaneously determinable. H. J. E.

**Maxima of the polarisation curve of mercury cathodes.** A. FRUMKIN and B. BRUNS (Acta Physicochim. U.R.S.S., 1934, 1, 232—246).—Previous theories are discussed and considered as unsatisfactory. It is suggested that the charge and discharge of the double layer and disturbances in the neighbourhood of the cathode, occasioned by local differences in the surface potential, are the primary factors in the polarisation phenomena. J. W. S.

**Polarisation capacity and constitution of the conducting layer at the electrode.** N. THON (J. Chim. phys., 1935, 32, 430—431).—With 0.5*M*- $\text{Hg}_2(\text{NO}_3)_2$ , the apparent capacity of the Hg electrode  $\sim 1/(\text{frequency})^2$ , which is incompatible with the Warburg-Krüger theory. An electrode model for a.c. consistent with the results consists of a capacity and a resistance in parallel. J. G. A. G.

**Influence of the electrode surface on anodic processes.** O. J. WALKER and J. WEISS (Trans. Faraday Soc., 1935, 31, 1011—1017).—The phenomena observed by Glasstone and Hickling (cf. this vol., 176) on the addition of certain salts in the anodic oxidation of  $\text{S}_2\text{O}_3^{--}$ ,  $\text{SO}_3^{--}$ , and  $\text{OAc}^-$  is traced to a change in the anode surface through the formation of oxide layers. The mechanism of evolution of  $\text{O}_2$  at the anode and of the anodic oxidation of inorg. and org. ions and mols. is discussed. E. S. H.

**Oxygen overvoltage in the electrolysis of liquid mixtures of  $\text{KNO}_3$ - $\text{NaNO}_3$ - $\text{LiNO}_3$ .** S. KARPATSCHEV and V. PATZUG (Z. physikal. Chem., 1935, 173, 383—387).—The anode overvoltages in eutectic mixtures have been measured. T. G. P.

**Theory of passivity phenomena. XXVII. Time phenomena in the anodic polarisation at smooth platinum in 2*N*-sulphuric acid.** W. J. MÜLLER and O. HERING (Monatsh., 1935, 66, 35—56).—An arrangement is described for measuring both the current-time and potential-time curves in the anodic polarisation of smooth Pt in 2*N*- $\text{H}_2\text{SO}_4$ . For the range 1.8—3.5 volts the two curves are similar. The ratio of initial current (after 0.005 sec.) to final current (after 20 min.) depends largely on the applied



potential, but the amount of current which passes during the period of the initial rapid decrease is practically const. (about  $18 \times 10^{-4}$  coulomb). Up to potentials of 2 volts the main process in the anodic polarisation consists in the dissolution of Pt in the pores of the metal. During this stage the current falls rapidly. Above 2 volts  $O_2$  evolution commences.

O. J. W.

**Electrolysis of sodium chloride in liquid ammonia.** I. E. I. ACHUMOV and B. B. VASILIEV (J. Gen. Chem. Russ., 1935, 5, 334—342).—The conductivity of solutions of NaCl in liquid  $NH_3$  rises with the [NaCl]; the decomp. potential of NaCl is 3.54 volts. Electrolysis with a diaphragm leads to production of  $NH_4Cl$  in the anode, and of  $NaNH_2$  in the cathode, section.

R. T.

**Formation of alloys from galvanic elements.** V. A. PLOTNIKOV and D. P. ZOSIMOVITSCH (J. Gen. Chem. Russ., 1935, 5, 327—333).—On closing the circuit between two electrodes immersed in a fused salt, or in its aq. solution, the baser metal is deposited on the nobler one, yielding an alloy. The e.m.f. of the cell  $Zn[fused\ ZnCl_2]Cu$  changes with time to that of  $Zn[fused\ ZnCl_2]_{\beta}$ -brass. A deposit of brass forms on the Pt electrode of a Daniell cell containing  $CuSO_4$  and  $ZnSO_4$ .

R. T.

**Determination of the mechanism of chemical reactions.** M. BODENSTEIN (Helv. Chim. Acta, 1935, 18, 743—759).—A lecture.

E. S. H.

**Kinetics of polymerisation processes.** G. GEE and E. K. RIDEAL (Trans. Faraday Soc., 1935, 31, 969—979).—Theoretical. A steric factor provides a sufficient mechanism for chain termination. Induction periods, points of max. reaction, and variations of chain length are discussed.

E. S. H.

**Calculation of energy loss in combustion.** J. VILLEY (Compt. rend., 1935, 200, 1921—1923).—Theoretical. A thermodynamical treatment.

H. J. E.

**Ignition temperatures of gases.**—See B., 1935, 660.

**Thermal decomposition of ozone.** H. J. SCHUMACHER (Proc. Roy. Soc., 1935, A, 150, 220—223).—Polemical. If the reaction scheme given by Ritchie (this vol., 39) were correct, the kinetics of the thermal decomp. would be identical with those of the photochemical decomp.; this is not the case, and it is concluded that his mechanism is incorrect. The high velocities obtained by Ritchie indicate that he was measuring the catalytic, not the homogeneous, decomp. of  $O_3$ .

L. L. B.

**Mechanism of hydrogen-oxygen explosions.** M. V. POLJAKOV, I. I. MALKIN, and V. A. ALEXANDROVITSCH (Acta Physicochim. U.R.S.S., 1935, 1, 821—832).—Data are recorded for the dependence of the  $H_2O_2$  yield in  $H_2-O_2$  explosions initiated by a Pt wire (the reaction vessel being dipped in liquid air) on the vessel dimensions and pressure.  $O_3$  was also detected. Increase in total pressure or in vessel dimensions lowers the  $H_2O_2$  yield. Increase in the  $H_2$  pressure raises it. Increase in the  $O_2$  raises the

$O_3$ . The reaction mechanism is discussed. The chain mechanism probably changes with the conditions.

H. J. E.

**Detonation in gas mixtures. II. Influence of pressure on the velocity of a detonation wave.** A. SOKOLIK and K. SCHTSHOLKIN (Acta Physicochim. U.R.S.S., 1934, 1, 311—317).—The velocities of detonation waves in  $2H_2+O_2$ ,  $CH_4+2O_2$ ,  $CH_4+O_2$ , and  $H_2+Cl_2$  mixtures have been determined between atm. pressure and the min. explosion pressure. The val. changes with initial pressure for  $2H_2+O_2$  and  $CH_4+2O_2$  mixture in the direction indicated by Jouguet's theory, whereas the velocity is independent of initial pressure for  $H_2+Cl_2$ . The results are in accord with the theory that dissociation occurring in the wave front causes the change in the velocity of detonation with pressure.

J. W. S.

**Combustion of  $H_2+O_2$  at room temperature in the presence of oxygen atoms.** A. NALBANDJAN (Acta Physicochim. U.R.S.S., 1934, 1, 305—310).—An arrangement for introducing a  $H_2+O_2$  mixture into a reaction vessel 0.07 sec. after switching off a discharge in the vessel is described. Contrary to previous data, the length of the reaction chain (calc. from the no. of O atoms present on introduction of the gases) is about 70, and reaction is complete in 0.1 sec. These observations are explained by assuming that when there is a large no. of initial centres the chains interact, thus increasing chain length.

J. W. S.

**Explosion regions at reduced pressure. I. Pressure limits in the system  $H_2-O_2-N_2$ .** J. DROP (Rec. trav. chim., 1935, 54, 671—679).—The explosion limits were determined for a series of  $[H_2-O_2]-N_2$  mixtures, in which the  $H_2:O_2$  ratio varied from 25:75 to 80:20, whilst for each  $H_2:O_2$  ratio the  $N_2$  ranged from 0 to 60%. Pressure throughout was 60 cm. The results agreed with those deduced theoretically, from the law of mass action, by van Heinigen (Diss., Leyden, 1934), the explosion limits being represented by the surface  $q=Kp^2x(1-x-y)$  where  $q$  is the reaction rate just yielding explosion,  $K$  is a const.,  $p$  is the pressure, and  $x$ ,  $1-x$ , and  $y$  are the concns. of  $H_2$ ,  $O_2$ , and  $N_2$ , respectively.

S. J. G.

**Experimental determination and theoretical calculation of flame temperatures and explosion pressures.** B. LEWIS and G. VON ELBE (Phil. Mag., 1935, [vii], 20, 44—65).—Anomalies between theoretical flame temp. calc. from band spectra and experimental vals. are discussed and attributed to effects such as time dependency of sp. heats and radiation losses. The results and conclusions of David and others (A., 1930, 865; 1932, 25; 1934, 258, 1073) are criticised.

J. W. S.

**Flame temperatures and explosion pressures.** W. T. DAVID (Phil. Mag., 1935, [vii], 20, 65—68).—Polemical against Lewis and von Elbe (cf. preceding abstract).

J. W. S.

**Kinetics of carbon monoxide combustion. II. Heat of activation with respect to different catalysts.** V. FINKELSHTEIN, I. CHRISMAN, and M. RUBANIK (Ber. Ukrain. wiss. Forsch.-Inst. physik.



Chem., 1934, 4, 19—27; cf. A., 1929, 515).—For oxidation of CO on  $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{ZnO}$ , porcelain,  $\text{Al}_2\text{O}_3$ ,  $\text{CuO}$ , pyrolusite, and  $\text{MnO}_2$ , the heats of activation were respectively 29.1, 25.2, 26.1, 24.9, 24.9, 22.0, 8.3, and 10.7 kg.-cal. The reaction, especially with the weaker catalysts, is initially third order, but is later retarded owing to poisoning by  $\text{CO}_2$ . The mechanism is firstly an activation of adsorbed  $\text{O}_2$ , followed by a three-body collision on the catalyst surface:  $\text{O}_2 + 2\text{CO} = 2\text{CO}_2$ . For more active catalysts intermediate higher oxides may be formed.

CH. ABS. (e)

**Explosions of carbon disulphide-nitric oxide mixtures and their practical applications.** J. A. M. VAN LIEMPT (Chem. Weekblad, 1934, 31, 706—708).—There is a crit. point for the mixtures at 3.5 cm. pressure and a mol. ratio ( $\text{CS}_2:\text{NO}$ ) of 1:2.3. The max. light output ( $I \times t$ ) at a given pressure is obtained with a ratio between 1:2.25 and 1:2.75, and varies with the square of the pressure. The reaction is  $5\text{CS}_2 + 10.8\text{NO} \rightarrow 5.4\text{N}_2 + 2.6\text{CO} + 2.4\text{CO}_2 + 1.7\text{SO}_2 + 8.3\text{S} + 784 \text{ kg.-cal.}$  At 11 cm. the light output is 16.7% of the theoretical, and at 70 cm. 41.5%. The spectrum of the radiation is continuous between 3200 and 6300 Å., with the max. intensity between 3700 and 4200 Å. For photography with panchromatic plates, Na, Ca, Ba, and Sr salts should be used to raise the intensity at the longer  $\lambda$ . Experiments on the speed of the reaction, and its practical significance, are described.

H. F. G.

**Explosion ranges.** W. P. JORISSEN (Chem. Weekblad, 1934, 31, 694—699).—The rates of reaction and reaction limits for various binary and ternary mixtures of gases and solids (e.g., Fe and S, Fe, Mg, and S) are given and discussed.

H. F. G.

**Explosive reactions between combustible gases and nitrous and nitric oxides.** M. J. VAN DER WAL (Chem. Weekblad, 1934, 31, 708—711).—The explosion limits in the systems  $\text{CH}_4\text{-NO}$ ,  $\text{CH}_4\text{-N}_2\text{O}$ ,  $\text{CH}_4\text{-NO-N}_2\text{O}$ ,  $\text{CO-N}_2\text{O}$ ,  $\text{CH}_4\text{-CO-N}_2\text{O}$ ,  $\text{CO-N}_2\text{O-NO}$ ,  $\text{H}_2\text{-N}_2\text{O}$ ,  $\text{H}_2\text{-N}_2\text{O-NO}$ , and  $\text{H}_2\text{-CO-N}_2\text{O}$  have been determined. No closed explosion region could be found for ternary gas mixtures, but the model for the quaternary system  $\text{H}_2\text{-CO-NO-N}_2\text{O}$ , derived from the three three-component systems, appears to contain a closed explosion range.

H. F. G.

**Theory of combustion of hydrocarbons.** R. G. W. NORRISH (Proc. Roy. Soc., 1935, A, 150, 36—57).—The slow and explosive combustion of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ , and olefines in general can be described by representing the reaction in terms of an atom-chain mechanism involving alternately O and free radicals. At low temp. (300—500°) the chains start at the surface from O generated from traces of aldehyde initially formed on the surface during the induction period:  $\text{R}\cdot\text{CHO} + \text{O}_2 \rightarrow \text{R}\cdot\text{CO}_2\text{H} + \text{O}$ . At high temp. free radicals may be directly generated from hydrocarbons (e.g.,  $\text{CH}_2$  from  $\text{CH}_4$  at 800°) and these may form chains directly. The propagation of the  $\text{CH}_4$  chain may be represented by the alternating reactions:  $\text{O} + \text{CH}_4 = \text{CH}_2 + \text{H}_2\text{O}$ ;  $\text{CH}_2 + \text{O}_2 = \text{CH}_2\text{O} + \text{O}$ . Branching may also occur through  $\text{CH}_2\text{O} + \text{O}_2 = \text{HCO}_2\text{H} + \text{O}$ . The chains end at the wall or by ternary

collision, e.g.,  $\text{X} + \text{CH}_4 + \text{O} \rightarrow \text{X}' + \text{MeOH}$ . This is the origin of MeOH in combustions at high pressures. This hypothesis affords an explanation of the varied kinetic and analytical data of the oxidation of hydrocarbons.

L. L. B.

**Rate of combustion of pentane[oxygen] mixtures.** N. N. GUSEV and M. B. NEUMAN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 377—382).—Mean velocities of flame propagation in pentane- $\text{O}_2$  mixtures ignited by an electric spark have been determined. At a given initial pressure and temp., velocity  $\propto$  composition, and within a narrow pressure range there are two velocity max., which were also found with other air-hydrocarbon mixtures, in accord with the semi-quant. theory outlined.

T. G. P.

**Pyrogenetic reactions of condensation of hydrocarbons. II. Kinetics of polymerisation and decomposition of ethylene. III. Kinetics and mechanism of polymerisation of propylene. IV. Kinetics of polymerisation of butylenes and amylenes.** M. V. KRAUZE, M. S. NEMTZOV, and E. A. SOSKINA (J. Gen. Chem. Russ., 1935, 5, 343—355, 356—360, 382—387).—II. A detailed account of work already noted (A., 1934, 736). The products are chiefly unsaturated aliphatic hydrocarbons, together with *iso*-paraffins; aromatic, naphthenic, and cyclohexene hydrocarbons are absent. The reactions  $\text{CH}_4 + \text{C} + 28,200 \text{ g.-cal.} \leftarrow \text{C}_2\text{H}_4 \rightarrow 2\text{C} + 2\text{H}_2 + 8600 \text{ g.-cal.}$  take place under the conditions of cracking of liquid hydrocarbons.

III (see *ibid.*, 1179). The products are chiefly olefines and saturated aliphatic hydrocarbons; gaseous olefines ( $\text{C}_2\text{H}_4$  and butenes) and cyclic hydrocarbons are not formed.

IV. The results (*loc. cit.*) indicate that substitution of one H per C of  $\text{C}_2\text{H}_4$  retards reaction, owing to steric hindrance, whilst substitution of both H modifies the energetic character of the mol., raising its activation energy.

R. T.

**Kinetics of the thermal decomposition of methylamine.** H. J. EMELEUS and L. J. JOLLEY (J.C.S., 1935, 929—935; cf. this vol., 172).—The decomp. of 375—33 mm. of  $\text{NH}_2\text{Me}$  at 540—670° consists mainly of (a)  $\text{NH}_2\text{Me} \rightarrow \text{HCN} + 2\text{H}_2$  and (b)  $\text{NH}_2\text{Me} + \text{H}_2 \rightarrow \text{CH}_4 + \text{NH}_3$ . (a) is largely homogeneous with an energy of activation 58,000 g.-cal., and is unimol. at pressures as low as 33 mm., corresponding with  $\pm 13$  degrees of freedom being involved in the activation process. (b) is heterogeneous and the yield of  $\text{CH}_4$  is increased by lowering the temp. and by packing the vessel, but is not affected by the products of decomp. or added  $\text{H}_2$ . (a) and (b) are consistent with a chain reaction initiated by  $\text{NH}_2\text{Me} \rightarrow \text{Me} + \text{NH}_2$ .

J. G. A. G.

**Thermal decomposition of diethylamine.** H. A. TAYLOR and C. R. HERMAN (J. Physical Chem., 1935, 39, 803—810).—The rate of increase of pressure during the decomp. of  $\text{NHEt}_2$  at 510—540° indicates a homogeneous reaction with, in the early stages, an energy of activation of 49,000 g.-cal. per mol. Analysis of the intermediate products indicates that the decomp. involves the formation and subsequent decomp. of  $(\text{NHEt})_2$  and  $\text{C}_4\text{H}_{10}$ .

J. W. S.



**Polymerisation and hydrogenation of acetylene.** H. A. TAYLOR and A. VAN HOOK (J. Physical Chem., 1935, 39, 811—819).—The principal processes in the homogeneous thermal polymerisation of  $C_2H_2$  and the hydrogenation of  $C_2H_2$  at 495—535° are bimol., with energies of activation of 40,500 and 42,000 g.-cal. per mol., respectively. The efficiency of collisions between activated mols. is high. J. W. S.

**Chlorination of propane. I. Homogeneous reaction.** S. YUSTER and L. H. REYERSON (J. Physical Chem., 1935, 39, 859—875).—The homogeneous reaction between  $C_3H_8$  and  $Cl_2$  at 100—300° is a chain reaction, and a chain mechanism is suggested which accounts for the results obtained. Chains are stopped by the walls of the reaction vessel and to a smaller extent are initiated by them, but the walls become poisoned at high  $[Cl_2]$ . High rates of flow and high  $[Cl_2]$  favour explosions. The heat of activation calc. from the temp. coeff. and from the collision efficiency is about 20,000 g.-cal. per mol. J. W. S.

**Velocity of reaction of sodium atoms with chloro-, bromo-, and iodo-benzene.** F. FAIRBROTHER and E. WARHURST (Trans. Faraday Soc., 1935, 31, 987—998).—The rates of reaction of PhCl, PhBr, and PhI with Na vapour, determined by the "life-period" method, are of the same order as in the aliphatic series. The effect of the change of halogen atom is also similar in the two series. E. S. H.

**Kinetic derivation of the mass action expression.** H. G. DEMING (J. Chem. Educ., 1935, 12, 195). L. S. T.

**Velocity of oxidation of sodium arsenite by atmospheric oxygen under pressure.** V. S. MALINOVSKI and E. P. LOPATINA (J. Appl. Chem. Russ., 1935, 8, 425—428).—The reaction of oxidation of  $NaAsO_2$  by atm.  $O_2$  at 100—250°, under pressure, is one of the first order. R. T.

**Velocity of formation of an amorphous precipitate of sulphur in a certain simple case.** W. JACEK (Rocz. Chem., 1935, 15, 258—272).—The velocity of formation of a ppt. of S from aq.  $Na_2S_2O_3$  or KCNS is expressed by  $dx/dt = Kx^{5/3}(1-x)/(x+k_1)$ , where  $x = (r/r_0)^3$ ,  $r$  and  $r_0$  are the radii of the particles at time  $t$ , and after completion of the process,  $K = h_0/3r_0$ ,  $h_0$  is the increase in the radius of the particles in unit time during the initial stages of the process, and  $k_1$  is a const. R. T.

**Oxidation of stannous sulphate by oxygen.** D. STEPANOV and F. MARSCHAK (J. Gen. Chem. Russ., 1935, 5, 289—293).—The velocity of oxidation of aq.  $SnSO_4$  by atm.  $O_2$  falls with increasing  $[H_2SO_4]$ ; the reaction in no case proceeds to completion. Oxidation is inhibited by traces of phenols [ $C_6H_4(OH)_2$ , guaiacol,  $C_{10}H_7OH$ , vanillin,  $C_6H_3(OH)_3$ , PhOH, cresol] or alkaloids (morphine, papaverine), whilst neutral sulphates ( $MgSO_4$ ,  $Na_2SO_4$ ) are without effect. R. T.

**Rate of reaction between ferric and stannous salts in solution.** R. A. ROBINSON and N. H. LAW (Trans. Faraday Soc., 1935, 31, 899—906).—The reaction between  $Fe(ClO_4)_3$  and  $Sn(ClO_4)_2$  is termol. owing to hydrolysis of the  $Fe(ClO_4)_3$ . With  $FeCl_3$  and  $SnCl_2$  in acid or neutral solution a bimol. reaction occurs simultaneously, being accelerated by  $Cl^-$ ,

probably owing to polymerisation of  $FeCl_3$ . The temp. coeff. of the reaction velocity suggests that reaction occurs between one  $Sn^{++}$  ion and one  $Fe_2(OH)_2^{+++}$  ion present in small concn. relative to the total amount of hydrolysed  $FeCl_3$ . J. W. S.

**Variation of reaction velocity with temperature.** J. A. MULLER and (Mlle.) E. PEYTRAL (Bull. Soc. chim., 1935, [v], 2, 1462—1467).—The relationship  $k = \alpha\beta^{-1/T}$ , where  $\alpha$  and  $\beta$  are two parameters which depend on the reaction, is applied to the reaction between salicylic acid and  $Ac_2O$ ,  $H_2C_2O_4$  and  $KMnO_4$  in the presence of  $H_2SO_4$ , and to the saponification of Et lactate. T. G. P.

**Effect of pressure on reactions in solution. I. Sodium ethoxide and ethyl iodide to 3000 kg. per sq. cm. II. Pyridine and ethyl iodide to 8500 kg. per sq. cm.** R. O. GIBSON, E. W. FAWCETT, and M. W. PERRIN (Proc. Roy. Soc., 1935, A, 150, 223—240).—Vals. are given for the velocity coeffs. for the reaction between NaOEt and EtI in EtOH for pressures of 1 and 3000 kg. per sq. cm. at 15—30° in a 0.1M solution, and at 25° with initial concns. of NaOEt of 0.05—0.5M; and for the reaction between  $C_5H_5N$  and EtI in  $COMe_2$  for pressures of 1, 3000, 5000, and 8500 kg. per sq. cm. at 20—60°. A marked difference is found in the effect of pressure on the typical "normal" and "slow" reactions studied. Whilst a pressure of 3000 kg. per sq. cm. increases the velocity coeff. of the normal reaction only 1.6 times, it increases that of the slow reaction 7.2 times. In the normal reaction, only the val. of the "collision term"  $A$  of the Arrhenius equation is increased by pressure, whilst in the slow reaction the vals. of both  $A$  and of the "activation energy"  $E$  are increased by pressure. L. L. B.

**Kinetics of rapid reactions. I.** H. VON HALBAN and H. EISNER (Helv. Chim. Acta, 1935, 18, 724—733).—Using an optical method, preliminary observations have been made with several inorg. oxidation-reduction reactions. The method has been applied to the study of the kinetics of the reaction of  $C_6H_4(NO_2)_2$  with  $NPhMe_2$  or  $NPhEt_2$  in EtOH solution. E. S. H.

**Velocity of absorption of propylene by sulphuric acid.** V. PIGULEVSKI and N. RUDAKOVA (Materials on Cracking, 1933, No. 1, 67—77; cf. A., 1930, 549).—Absorption of  $C_3H_6$  by  $H_2SO_4$  follows the law for unimol. reactions. The amount absorbed by unit surface in unit time  $\propto$  the partial pressure of  $C_3H_6$ , and is independent of its vol. The absorption is an autocatalytic process. Vals. of the velocity coeff. at 5—25° were determined for 75—88% acid. CH. ABS. (e)

**Velocity of decomposition of diazo-compounds in water. XVII.** E. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1935, 38, 275—280B; cf. this vol., 173).—Sunlight increases the velocity coeff. ( $k$ ) of decomp. of  $1-C_{10}H_7N_2Cl$ . Results on the naphthalenediazo-compounds are collated and discussed. The order of the reaction is 0 or 1 according as the diazo-compound is pptd. or dissolved. Temp. coeffs.,  $k$ , temp. of diazotisation, and the influence of sunlight and added substances are compared. R. S. B.



**Oxidation of quinol solutions. III. Effect of alkali salts and metallic hydroxides.** A. SAINT-MAXEN (J. Chim. phys., 1935, 32, 410—428).—Details of earlier work (A., 1930, 1128; 1932, 578) are given. The log. of the initial rate of oxidation of quinol (I) in a given type of buffer solution increases linearly with increasing  $p_H$  and is independent of [salt], but in borate buffers is  $>$  in phosphate buffers of equal  $p_H$ . Carbonate buffers give similar results. The oxidation catalysed by alkalis and  $Mg(OH)_2$  is interpreted in terms of sol. compounds formed with (I). The rate of oxidation induced by equiv. proportions of  $La(OH)_3 > Y(OH)_3 > Ni(OH)_2$ , prepared by hydrolysing the acetates, increases during re-hydration and decreases during the subsequent coagulation of the hydroxide. These hydroxides do not form compounds with (I) and are insol. in aq. (I) and probably catalyse the fixation of  $O_2$  on the acceptor, (I). Equiv. amounts of KOH and  $Ni(OH)_2$  have approx. equal catalytic effects.

J. G. A. G.

**Physicochemical study of the reducing action of glucose.** W. B. WOOD, jun. (J. Biol. Chem., 1935, 110, 219—232).—A potentiometric method for studying the irreversible oxidation of glucose (I) by  $Fe(CN)_6'''$  (II) is described. Decreasing the  $p_H$ , lowering the temp., or increasing the salt content slows down the reaction rate but increases the final amount of (II) reduced. The final amount of (II) reduced  $\propto$  the concn. of (I) (within the limits of blood-sugar determinations), but the time for complete reaction also increases with the (I) concn. An increase in the (II) concn. slightly increases the final amount of (II) reduced. There is a great similarity in the oxidising action of  $Cu^{++}$  and (II) in alkaline solution. As changes in  $p_H$  affect reduction of (II) by (I) and fermented blood filtrate to about the same extent, it is concluded that there is no optimum  $p_H$  at which the non-(I) reducing substances exert a min. effect. An enhancement by NaCN of the reducing action of (I) accounts for the lower, and more accurate, blood-sugar vals. obtained by the Folin microcolorimetric method.

E. A. H. R.

**Isomerisation of cyanogenic heterosides. V.** PLOUVIER (Compt. rend., 1935, 200, 1985—1987).—The rates of isomerisation of amygdalin and of amygdonitrileglucoside (I) are increased by rise in temp. and in  $p_H$ . (I) is isomerised to prulaurasin (II). Both have been isolated from the leaves of *Photinia serrulata* (A., 1912, ii, 675), but the (II) may be due to isomerisation of (I) during the extraction process.

H. G. M.

**Rates of racemisation of acids of the type  $CHRR'CO_2H$ .** B. K. MENON and D. H. PEACOCK (J. Indian Chem. Soc., 1935, 12, 268—272).—The rates of racemisation of six acids of the above type have been measured, in which R and R' are, respectively:  $Bu^a$ ,  $CH_2Ph$ ;  $Bu^a$ ,  $p-C_6H_4Br-CH_2$ ;  $CH_2Ph$ ,  $p-C_6H_4Br-CH_2$ ;  $CH_2Ph$ ,  $m-C_6H_4Br-CH_2$ ;  $CH_2Ph$ ,  $p-C_6H_4Cl-CH_2$ , and  $CH_2Ph$ ,  $m-C_6H_4Cl-CH_2$ . Replacement of  $Bu^a$  by  $CH_2Ph$  or  $p-C_6H_4Br-CH_2$  greatly increases the rate of racemisation. With the *m*-substituted acids the Br-acid racemises faster than the Cl-acid, but with the *p*-substituted acids

the rates are equal for Cl- and Br-derivatives. The results are discussed.

O. J. W.

**Salt activation. I. Influence of neutral salts on the enzymic hydrolysis of starch.**—See this vol., 1162.

**Kinetics of the decomposition process and the problem of chains in the solid phase.** S. M. MOSKOVITSCH (Uspekhi Khim., 1934, 3, 752—760).—A discussion. Chain mechanisms in solids differ from those in a homogeneous gas phase because chains can be broken on the phase boundaries, and because of anisotropic properties of the crystals.

CH. Abs. (e)

**Thermal dissociation of silver nitrite.** M. CENTNERSZWER and T. CHĘCIŃSKI (Bull. Acad. Polonaise, 1935, A, 156—165).—In a vac. or at low pressure the dissociation of  $AgNO_2$  follows the equation  $AgNO_2 \rightleftharpoons Ag + NO_2$ , but at higher pressure it is a reversible reaction:  $2AgNO_2 \rightleftharpoons Ag + AgNO_3 + NO$ . The dissociation pressures above 150 mm. follow the Nernst equation  $\log p = (15365.6/4-571T) + 1.75 \log T + 3.716$ .

J. W. S.

**Kinetics of the thermal dissociation of silver nitrite.** M. BLUMENTHAL and T. CHĘCIŃSKI (Bull. Acad. Polonaise, 1935, A, 166—173; cf. preceding abstract).—The thermal decomp. of  $AgNO_2$  occurs in two stages, viz.,  $AgNO_2 = Ag + NO_2$  and  $NO_2 + AgNO_2 = AgNO_3 + NO$ , the velocity of each reaction being dependent on pressure. In a vac. the reaction is of the first order, and at atm. pressure of the second order. Rise in temp. diminishes the order of the reaction. An induction period is observed near the equilibrium state.

J. W. S.

**Kinetics of decomposition of sodium mercurisulphide by water.** A. LOTTERMOSER and E. HAENEL (Abh. nat. Ges. Isis, Festschr., 1934, 195—203; Chem. Zentr., 1935, i, 1026—1027).—The rate of decolorisation of Na mercurisulphide (I) solutions was followed photometrically; it is compounded of the rate of decomp. of (I) and the rate of separation of HgS, and is independent of the concn. of (I),  $\propto$  the amount of  $H_2O$  and of neutral salts, and  $\propto 1/[Na_2S]$ .

J. S. A.

**Rate of dissolution of zinc in acids.** C. V. KING and M. SCHACK (J. Amer. Chem. Soc., 1935, 57, 1212—1217).—The rate of dissolution of rotating Zn cylinders in dil. AcOH  $\propto$  the peripheral velocity up to 163,000 cm. per min. In presence of  $KNO_3$  the rate is at first nearly  $\propto [AcOH]$  and almost independent of  $[KNO_3]$ . In presence of  $p-OH-C_6H_4-NO_2$ , benzoquinone, or  $H_2O_2$  the rate increases with the concn. of oxidising agent and is nearly independent of  $[AcOH]$ . NaCl accelerates the rate at low concn. but retards it at higher concn.; NaOAc has a retarding effect throughout.

E. S. H.

**Kinetics of anode film formation on metals.** L. J. KURTZ (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 383—389).—The formation and nature of AgCl and AgBr films deposited on a Ag anode by the electrolysis of KCl and KBr solutions have been studied through the polarisation curve of the electrode, the conductivity of the films, and their appearance under the microscope. Deposition begins in isolated islets



which spread until the surface is covered at a definite mean film thickness, which decreases with increasing c.d., as does the size of the crystals deposited and the sp. resistivity of the film. There is an unexplained discontinuity in the polarisation curve. T. G. P.

**Corrosion of aluminium by sodium hydroxide.** Y. K. HENG and Y. TA (Compt. rend., 1935, 200, 2153—2155; cf. A., 1933, 240).—Corrosion by NaOH was measured in presence of Na tartrate by determining the  $\alpha$  of the Na aluminotartrate produced. Preliminary data are given for the rate of corrosion of Al specimens of varying purity and for Al alloys.

H. J. E.

**Catalytic and induced reactions in micro-chemistry.** I. M. KOLTHOFF and R. S. LIVINGSTON (Ind. Eng. Chem. [Anal.], 1935, 7, 209—213).—Mainly a discussion. Observations on the catalytic influence of Ag on the reduction of  $Mn^{III}$  and of Hg on the reduction of  $As^V$  are recorded. E. S. H.

**Polymerisation of ethylene induced by methyl radicals.** O. K. RICE and D. V. SICKMAN (J. Amer. Chem. Soc., 1935, 57, 1384—1385).— $C_2H_4$  is rapidly polymerised at about  $300^\circ$  by small amounts of azomethane (I). Under the conditions studied the initial rate depends on  $\sqrt{p}$  of (I) and  $p^{3/2}$  of  $C_2H_4$ ;  $k$  is 3.0 and  $6.5 \times 10^{-6}$  mm.<sup>-1</sup> sec.<sup>-1</sup> at  $290^\circ$  and  $310^\circ$ , respectively. A chain decomp. is also set up in EtCHO (II) and isobutane by (I); the use of 6.5% of (I) leads to 60—70% decomp. of (II), showing that the reaction is not a "degenerate explosion" (Semenov, this vol., 451). H. B.

**Enzyme catalysis of the exchange of deuterium with water.** G. H. BOTTOMLEY, B. CAVANAGH, and M. POLANYI (Nature, 1935, 136, 103—104; cf. A., 1934, 738).—The first-order velocity coeff. is inversely  $\propto$  the square root of the pressure of the hydrogen. The reaction takes place in two stages,  $HD + 2B \rightleftharpoons HB + DB$  and  $DB + H_2O \rightarrow HB + DHO$ , where  $B$  represents a catalytic centre. During the reaction the no. of living bacteria (*B. acidi lactici*) diminishes rapidly without affecting the catalytic power. L. S. T.

**Influence of small amounts of agar-agar and gelatin on the KG [crystallisation velocity] of cathode deposits of silver.** A. GLAZUNOV, J. TEINDL, and J. HALÍK (Chem. Listy, 1935, 29, 117—118, 131—133).—The velocity of crystallisation (linear) of Ag at the cathode during electrolysis of  $AgNO_3$  is reduced by presence of 0.03—0.15% of agar or gelatin in the electrolyte; the effect is not due to viscosity changes. The colloids are present in small amount in the deposit, either in the residual electrolyte between the crystallites, or in the crystal lattice.

R. T.

**Reactions between oxalic and permanganic acids in presence of dilute sulphuric acid, and the velocities of these reactions.** J. A. MÜLLER and (MLLE.) E. PEYTRAL (Bull. Soc. chim., 1935, [v], 2, 1457—1462).—The nature and velocities of the intermediate reactions occurring in the autocatalytic oxidation of  $H_2C_2O_4$  by  $KMnO_4$  in presence of  $H_2SO_4$  have been studied. T. G. P.

**Catalytic decomposition of formic acid in presence of selenic acid.** R. DOLIQUE (Bull. Soc. chim., 1935, [v], 2, 1489—1491).— $H_2SeO_4$  catalyses the decomp. of  $HCO_2H$  into CO and  $H_2O$ ,  $CO_2$  appearing only towards the end of the reaction, or when the  $H_2SeO_4$  is in excess. T. G. P.

**Intermediate stages of aldehyde oxidation.**

**I. Catalytic action of manganese catalyst in the various stages of the process of acetaldehyde oxidation.** M. J. KAGAN and G. D. LUBARSKY.

**II. Kinetics of the interaction between peracetic acid and the aldehydes.** G. D. LUBARSKY and M. J. KAGAN (J. Physical Chem., 1935, 39, 837—846, 847—857).—I. The oxidation of MeCHO by  $O_2$  in AcOH solution in presence of  $Mn^{II}$  salts proceeds rapidly after production of the dark brown  $Mn(OAc)_3$  (through action of  $AcO_2H$  on  $Mn^{II}$ ) which acts as a catalyst. Presence of  $H_2O$  increases the induction period, owing to decomp. of the catalyst, and in absence of  $H_2O$  the induction period can be eliminated by addition of a  $Mn^{III}$  salt. It is suggested that the catalyst may hasten the decomp. of an intermediate peroxide produced by addition of  $AcO_2H$  to MeCHO, as well as decompose  $AcO_2H$  to yield active O which can oxidise MeCHO directly.  $AcO_2H$  is decomposed vigorously and exothermically by  $Mn^{III}$  in AcOH, yielding mainly  $CO_2$ , and only slowly in  $H_2O$ , yielding mainly  $O_2$ . The latter process is a first-order reaction with an energy of activation of about 12,000 g.-cal. per mol.

**II. The reaction between  $AcO_2H$  and MeCHO in AcOH,  $C_6H_6$ ,  $PhNO_2$ ,  $CHCl_3$  or PhMe at  $10-30^\circ$  has an energy of activation of 15,400—16,300 g.-cal. per mol. It follows a second-order equation but there is a short initial period of rapid decrease of  $[MeCHO]$ , attributed to the formation of an intermediate compound, probably  $OH \cdot CHMe \cdot O \cdot O \cdot COMe$ , which exists in equilibrium with the reactants and decomposes relatively slowly. This intermediate compound separates on carrying out the reaction at  $-40^\circ$  to  $-60^\circ$ , the energy of activation of this stage of the reaction being 7000 g.-cal. per mol. Its decomp. is unimol. The behaviour of  $Bu^sCHO$  is similar to that of MeCHO. J. W. S.**

**Benzoin reaction. II. Negative catalysis.**

D. R. NADKARNI and S. M. MEHTA. **III. Effect of water.** D. R. NADKARNI (J. Physical Chem., 1935, 39, 901—906, 907—912).—II. KCl, NaCl, KI, and quinol inhibit the benzoin reaction through stopping the heterogeneous reaction, but they do not affect the homogeneous autocatalytic reaction.

**III. Addition of  $H_2O$  to KCN first increases and then decreases its rate of reaction with PhCHO, autocatalysis disappearing gradually. This is attributed to the extraction of  $CN^-$  from solution in the PhCHO. Inhibition of the reaction by KI is less marked in presence of  $H_2O$ . J. W. S.**

**Kinetics of heterogeneous catalysis and of enzyme action.** E. C. C. BALY (Nature, 1935, 136, 146).—Theoretical. Equations are given, and it is suggested that enzyme reactions are of the two-stage activation type. Neither the crit. increment of a heterogeneous reaction nor that of the deactivation of an enzyme system can be determined directly from



measurements of reaction velocity at two different temp. L. S. T.

**Velocity of absorption of unsaturated gases by sulphuric acid in presence of catalysts.** M. B. MARKOVITSCH, V. G. MOOR, and M. I. DEMENTIEVA (Materials on Cracking, 1933, 1, 77—102).—Data are recorded for the effect of numerous substances (e.g., alkali sulphates,  $\text{As}_2\text{O}_3$ , Se,  $\text{COMe}_2$ ,  $\text{C}_5\text{H}_5\text{N}$ ) on the absorption. Ag compounds gave the best results. Some of the salts had a retarding action. Addition of liquids insol. in  $\text{H}_2\text{SO}_4$  increased the rate of physical dissolution of the gases.

CH. ABS. (c)

**Spin-isomerisation of hydrogen in paramagnetic and diamagnetic surfaces.** H. S. TAYLOR and H. DIAMOND (J. Amer. Chem. Soc., 1935, 57, 1251—1256).—Rapid interconversion of ortho- and para- $\text{H}_2$  at low temp. is obtained on surfaces of paramagnetic metals, oxides, and salts. The velocity is reduced by decreasing magnetic susceptibility or adsorptive capacity. Slow conversion at liquid-air temp. on diamagnetic catalysts may be due to paramagnetism of surface atoms or residual low-temp. activated adsorption. A new high-temp. conversion involving an exchange reaction with  $\text{H}_2\text{O}$  has been observed. Sintering of Cu catalysts affects the low-temp. activity for the  $\text{H}_2$  conversion < for the hydrogenation of  $\text{C}_2\text{H}_4$ .

E. S. H.

**Catalytic exchange reaction between deuterium and water.** H. S. TAYLOR and H. DIAMOND (J. Amer. Chem. Soc., 1935, 57, 1256—1259).—Rapid exchange has been observed at high temp. between  $\text{D}_2$  and  $\text{H}_2\text{O}$  retained by catalysts of  $\text{Cr}_2\text{O}_3$ ,  $\text{ZnO}$ ,  $\text{ZnCr}_2\text{O}_4$ ,  $\text{Al}_2\text{O}_3$ , and Pt-asbestos. The reverse reaction between  $\text{H}_2$  and  $\text{D}_2\text{O}$  has also been demonstrated. The variation of reaction velocity with temp. has been approx. determined with  $\text{Cr}_2\text{O}_3$ . The mechanism is discussed.

E. S. H.

**Heterogeneous-homogeneous catalysis. Hydrogen and oxygen in presence of platinum.** III. M. V. POLJAKOV, P. M. STADNIK, and A. T. ELKENBARD (Acta Physicochim. U.R.S.S., 1935, 1, 817—820; cf. this vol., 588).—Interaction of  $\text{H}_2$  and  $\text{O}_2$  on a Pt wire at 400—450° leads to formation of  $\text{H}_2\text{O}_2$ , yield depending in the same manner on the  $\text{H}_2$  pressure as does that in the homogeneous explosive reaction. The mechanism in the two cases is the same, the heterogeneous process initiating homogeneous  $\text{H}_2\text{O}_2$  formation. The no. of active centres, and hence the abs.  $\text{H}_2\text{O}_2$  yield, is much greater in the explosive reaction.

H. J. E.

**Active oxides. LXXXIX. Course of formation of zinc ferrite from zinc oxide and iron oxide.** G. F. HÜTTIG, H. E. TSCHAKERT, and H. KITTEL (Z. anorg. Chem., 1935, 223, 241—250; cf. A., 1934, 850).—The catalytic activity of equimol.  $\text{ZnO} + \text{Fe}_2\text{O}_3$  mixtures for both the  $2\text{CO} + \text{O}_2$  reaction and the  $\text{N}_2\text{O}$  decomp. plotted as a function of the temp. of heating shows two max. The higher corresponds also with the onset of paramagnetism, and with fluorescence different from that of  $\text{ZnO}$ , with a min.  $d$ , and with the threshold of crystallisation of  $\text{ZnFe}_2\text{O}_4$ . The formation of two states of max. catalytic activity

is discussed in relation to the theory of solid reactions. J. S. A.

**Primary decomposition of hydrocarbon vapours on carbon filaments.** L. BELCHETZ and E. K. RIDEAL (J. Amer. Chem. Soc., 1935, 57, 1168—1174).—The primary products of decomp. of  $\text{CH}_4$  at heated C or Pt filaments are  $\text{CH}_2$  and  $\text{H}_2$ .  $\text{CH}_2$  radicals condensing on a cooled surface readily unite to form  $\text{C}_2\text{H}_4$ .  $\text{TeCH}_2$  is readily reduced to  $\text{TeMe}_2$  and  $\text{Te}_2\text{Me}_2$ . The energy of activation for the decomp. of  $\text{CH}_4$  on C is 95 kg.-cal. per mol., and for the decomp. of  $\text{C}_2\text{H}_6$  to  $\text{C}_2\text{H}_4$  on C is 94.6 kg.-cal. per mol. There is no evidence of the formation of Me or the ethylidene radical.

E. S. H.

**Oxidising faculty of nitrogen oxide.** J. BJERRUM and L. MICHAELIS (J. Amer. Chem. Soc., 1935, 57, 1378—1379).—The oxidation of reduction products of dyes by NO in presence of colloidal Pd is described.

E. S. H.

**Effects of fluorides on the thermal synthesis of calcium silicates.** VI. S. NAGAI and Y. KOSAKI (J. Soc. Chem. Ind. Japan, 1935, 38, 229—232B; cf. this vol., 49).—A mixture of  $2\text{CaCO}_3 : \text{SiO}_2$  was heated for 1 hr. at 1000—1400°, and the product analysed by Jander and Hoffmann's method (cf. B., 1933, 270) for free CaO and  $\text{SiO}_2$ ,  $3\text{CaO}.\text{SiO}_2$  (I),  $2\text{CaO}.\text{SiO}_2$  (II),  $3\text{CaO}.\text{SiO}_2$ , and  $\text{CaO}.\text{SiO}_2$ . The ratio of combined CaO to combined  $\text{SiO}_2$  is const. at 1100—1400°, but the % of (II) increases with temp. 1% of  $\text{CaF}_2$  was then added to the same mixture, and the product analysed after heating as before. The % of (I) is greatly increased at 1000—1100° by the addition of  $\text{CaF}_2$ , but the effect falls with rise in temp. owing to decomp. of (I) into (II). The % of (II) and of total silicate is greatly increased by  $\text{CaF}_2$ , approx. 75—80% of which remains unchanged.

R. S. B.

**Effect of fluorides on the thermal synthesis of calcium silicates.** VII. S. NAGAI and Y. KOSAKI (J. Soc. Chem. Ind. Japan, 1935, 38, 294—298B).—Prolonged heating at 1200° of mixtures of  $\text{CaCO}_3$  and  $\text{SiO}_2$  (2 : 1) is not so effective in causing silicate formation as is the addition of 1% of  $\text{CaF}_2$ ; more  $\text{CaF}_2$  is still more effective. At 1300° the yield of  $\text{Ca}_3$  silicate from the mixture  $\text{CaCO}_3 : \text{SiO}_2 = 3$  is 90% when 1% of  $\text{CaF}_2$  is present, and complete combination is not obtainable at a lower temp. A. G.

**Catalytic preparation of hydrochloric acid from chlorine and water.**—See B., 1935, 722.

**Poisoning of molybdenum-zinc catalyst.** G. N. MASLIANSKI and M. S. NEMTZOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 404—408).—The catalytic activity of a mixture of  $\text{MoS}_2$  and  $\text{ZnO}$  in the  $\text{C}_2\text{H}_4$ - $\text{H}_2$  reaction is diminished in the presence of  $\text{O}_2$ . If poisoning occurs below 300°, the activity returns completely after the  $\text{O}_2$  is removed. At 400° poisoning is partly irreversible, and the greater is  $[\text{O}_2]$  in the gas, the lower is the residual activity of the catalyst.  $\text{H}_2\text{O}$  vapour induces similar effects, but the deceleration of the reaction diminishes with rising temperature. Preheating the catalyst to 450° in  $\text{H}_2$  enhances, and the use of  $\text{C}_2\text{H}_4$ -rich mixtures diminishes, the activity of the catalyst. T. G. P.



**Direct oxidation of platinum and the nitriding of metals (Cu, Al, Mg, Zn, Fe, Ni, and W).** P. GRANDADAM (Ann. Chim., 1935, [xi], 4, 83—146).—Pt-black heated at 450° in O<sub>2</sub> at 170 kg. per sq. cm. gives PtO<sub>2</sub>, *d* 10, insol. in mineral acids, which decomposes in air at 380—400° to give Pt, and catalyses the combustion of slightly heated coal gas and the combination of H<sub>2</sub> and O<sub>2</sub> at room temp., and is fully reduced after 1 hr. in H<sub>2</sub> at 90°. Pt-black heated at 430° at 8.25 kg. per sq. cm. gives PtO, *d* 15, little attacked by HCl in absence of air, easily sol. in aqua regia, does not decompose in air below 500°, catalyses instantaneously the combustion of coal gas and H<sub>2</sub> at room temp., and is instantly reduced by H<sub>2</sub> at room temp. with incandescence. PtO<sub>2</sub> is a better reduction catalyst for C:C and C:O than the well-known Pt-blacks; PtO is good for C:C linkings, but less effective for C:O. Pt-black heated between 100° and 200° in O<sub>2</sub> at 150 kg. per sq. cm. becomes three times as active for the reduction of C:C or C:O linkings, and is recommended for laboratory use.

Li combines with N<sub>2</sub> at room temp. by an autocatalytic process. Ni reacts with NH<sub>3</sub> at 530° to give a product of uncertain stoichiometric composition, but the reaction between NiCO<sub>3</sub> and Li<sub>3</sub>N appears to yield the nitride. The sp. electrical conductances and temp. increments have been determined for Al, Fe, Ni, Zn, W, and Mg, which also exhibited an allotropic transition at 280°. By examining the conductivity of a filament heated at various temp. in NH<sub>3</sub>, dissolution and chemical combination were discriminated, the exact temp. at which nitriding commenced was ascertained, and the reversible process of nitriding was followed for each of these metals. The action of Ni and Fe in the synthesis of NH<sub>3</sub> is discussed. T. G. P.

**Reactivity and catalytic activity of solid substances in transition states.** J. A. HEDVALL (Svensk Kem. Tidskr., 1935, 47, 161—188).—A comprehensive review and discussion of previous work bearing on various factors (*e.g.*, changes in magnetic state or in crystal structure) which influence the reaction of solids. H. J. E.

**Kinetics of the catalytic dehydrogenation of methylcyclohexane with a nickel-aluminium oxide catalyst.** A. A. BALANDIN and N. I. SCHUJKIN (Acta Physicochim. U.R.S.S., 1934, 1, 200—211).—The effects of temp. of 200—350° and of the presence of reaction products on the dehydrogenation of methylcyclohexane has been investigated. The energy of activation is 12,300 kg.-cal. per mol. The data are compared with those for cyclohexane and dimethylcyclohexane (*cf.* A., 1933, 234; this vol., 310).

J. W. S.

**Function of carriers in heterogeneous catalysis. IV. Dehydrogenation and hydrogenation of ethyl alcohol on zinc oxide deposited on charcoal.** I. E. ADADUROV and P. Y. KRAINI. V. Decomposition of formic acid on lead oxide deposited on birchwood charcoal. I. E. ADADUROV (J. Phys. Chem. U.S.S.R., 1934, 5, 1132—1138, 1139—1145).—IV. The carrier may alter the magnitude and even the sign of the field of the catalyst. Data for ZnO catalysts are discussed. Easily deformed cations of catalysts are most subject to carrier effects.

V. HCO<sub>2</sub>H decomposes almost 100% into CO<sub>2</sub> and H<sub>2</sub> on pure birch C at 200—350°, or on PbO prepared from Pb(NO<sub>3</sub>)<sub>2</sub> up to 360°. A catalyst prepared by adsorption on the C from 0.01*N*-Pb(NO<sub>3</sub>)<sub>2</sub>, drying, and heating to 360°, gave 100% of CO<sub>2</sub>+H<sub>2</sub> at 200—360°. A similarly treated catalyst prepared from 0.05*N*-Pb(NO<sub>3</sub>)<sub>2</sub> gave at 255°, 75 and 25%, respectively, of CO<sub>2</sub> and CO, at 275°, 50 and 50%, at 305°, 37 and 63%, at 325°, 2 and 98%, and at 350°, 67 and 33%, respectively, of the two gases.

CH. ABS. (e)

**Catalytic reduction reactions.**—See this vol., 1120.

**Physicochemical conditions of the production of potassium persulphate.** V. P. ILJINSKI, A. F. SAGAJDACHNUI, and E. K. HELIGREN (Trans. State Inst. Appl. Chem. U.S.S.R., 1934, 19, 2—12).—Saturated (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> is used. When the solution becomes alkaline, powdered KHSO<sub>4</sub> is added. It reacts with (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> crystallising out. The optimum anode and cathode c.d. are 5 amp. and 1 amp. per sq. cm., respectively (optimum temp. 30°).

CH. ABS. (e)

**Chemical stability of the terminal faces of acicular crystals.** D. W. PEARCE, T. T. QUIRKE, and B. S. HOPKINS (Amer. J. Sci., 1935, [v], 30, 116—120).—In the electrolytic reduction of YbCl<sub>3</sub> in the presence of H<sub>2</sub>SO<sub>4</sub> (A., 1931, 51; 1933, 37) the pptd. YbSO<sub>4</sub> has the form of radiating tufts of acicular crystals, but with slower pptn., with a weaker current and in the presence of more acid, a granular ppt. of spherulites was obtained. The latter is more resistant to acids, probably owing to the lower solubility of the ends of the acicular crystals. It is argued that acicular crystals of various substances are of slower growth than crystals of other habits.

L. J. S.

**Theory and practice of chromium plating.**—See B., 1935, 678.

**Electrolysis of chlorides of nickel and cobalt dissolved in mixtures of water and ethyl alcohol.** C. CHARMETANT (Compt. rend., 1935, 201, 43—45; *cf.* this vol., 456).—For NiCl<sub>2</sub> and CoCl<sub>2</sub> the anodic phenomena resemble those for ZnCl<sub>2</sub>, a large proportion of the Cl oxidising EtOH to MeCHO. At the cathode, for NiCl<sub>2</sub>, Ni oxides are first deposited, and dissolve later owing to diffusion of HCl from the anode. In 0.006*N*-acid pure Ni is deposited, the yield decreasing with time and with increasing c.d. The acid concn. needed to avoid oxide formation increases with the [EtOH]. The Ni yield passes through a min. with 150 g. of EtOH per litre. Co is deposited from an EtOH-H<sub>2</sub>O solution of CoCl<sub>2</sub> even in neutral solution.

H. J. E.

**Electrochemical production of aluminium oxide from aqueous aluminium sulphate.**—See B., 1935, 723.

**[Electrolytic] preparation of mercuric oxide.** See B., 1935, 723.

**Electrodeposition of alloys of copper and tin.**—See B., 1935, 730.

**Electrodeposition of noble-metal alloys.**—See B., 1935, 730.



Electrolytic deposition of cerium from anhydrous organic solvents (i) alone, and (ii) in presence of reducing agents.—See B., 1935, 730.

**Chemical reactions in electrical discharges.**  
**I. Reactions of free atoms. Recombination of oxygen and hydrogen atoms on metal wires.** S. ROGINSKI and A. SCHECHTER (*Acta Physicochim. U.R.S.S.*, 1934, 1, 318—332).—The velocities of recombination of O and of H atoms on heated Pt and Pd filaments have been determined comparatively from the currents required to maintain the filament at a specified temp. The usual method of determination, using a thermometer coated with a catalyst, is untrustworthy, the low thermal conductivity of the catalyst powder generally causing autocatalysis of the recombination. J. W. S.

[Cathodic catalysis in the electrical discharge.]  
**Application to ammonia.** P. JOLIBOIS and F. OLMER (*Compt. rend.*, 1935, 201, 62—64; cf. this vol., 446).—The equilibrium concn. of  $\text{NH}_3$  formed from a  $\text{N}_2\text{—H}_2$  mixture at 1.1—3.5 mm. in the gas near the Pt cathode of a discharge tube varies from 3.3 to 24% with the discharge conditions. Data are recorded for the energy input needed to obtain 1 g. of  $\text{NH}_3$  using cathodes of Fe, Cu, Ni, Cu—Hg, Al, and Pt. The gas circulating in the positive column contains no  $\text{NH}_3$ . The catalysis is attributed to the action in the gas phase of metal particles ejected from the cathode. The same explanation applies to formation of  $\text{NH}_3$  in the spark. H. J. E.

**Photochemical decomposition of hydrogen peroxide in aqueous solution.** G. KORNFELD (*Z. physikal. Chem.*, 1935, B, 29, 205—214).—Following Haber and Weiss (A., 1933, 234) the mechanism of decomp. proposed is:  $\text{H}_2\text{O}_2 + h\nu = 2\text{OH}$ ,  $\text{H}_2\text{O}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2\text{H}$ ,  $\text{H}_2\text{O}_2 + \text{O}_2' = \text{O}_2 + \text{OH}' + \text{OH}$ ,  $\text{OH} + \text{O}_2\text{H} = \text{H}_2\text{O} + \text{O}_2$ . This requires that the rate  $\propto \sqrt{I[\text{H}_2\text{O}_2]}$ , which accords with the experimental data for the reaction in absence of acid (A., 1921, ii, 670). The observed decline in the rate of increase of the velocity with  $[\text{H}_2\text{O}_2]$  at higher concns. in presence of acid is also quantitatively predicted from the above. The retardation by alkali is, however, not fully accounted for. R. C.

**Photochemical oxidation-reduction equilibrium in methylene-blue solutions.** H. VON EULER, H. HELLSTRÖM, and K. BRANDT (*Naturwiss.*, 1935, 23, 486—489).—The photochemical processes in methylene-blue (I)—EtOH and (I)— $\text{Fe}^{II}$ —EtOH systems have been investigated. The quantum efficiency of the reduction of (I) in the first system is considerably  $< 1$ . In the second system, reduction velocity is dependent on  $p_{\text{H}}$ , increasing with increasing acidity to a max. at  $p_{\text{H}}$  3.6. Light favours the formation of the leuco-base (II) in the equilibrium  $\text{H}_2 + (\text{I}) \rightleftharpoons (\text{II})$ . The quantity of (II) in the irradiated substance is not  $\propto$  intensity of absorbed light. A. J. M.

**Fog formation by dyes.** LÜPPO-CRAMER (*Phot. Ind.*, 1934, 32, 974).—Sensitising nuclei are removed with  $\text{H}_2\text{CrO}_4$  after application of the dye. Results vary with the dye used, and apparently depend on a secondary reaction between the dye and the oxidant. CH. ABS. (e)

**Action of various elements and compounds on photographic plate.** II. S. AOYAMA and T. FUKUROI (*Bull. Inst. Phys. Chem. Res. Japan*, 1935, 14, 481—496).—Direct chemical reaction of activated gases on the photographic plate is a more plausible view than emission of radiation when the gases associate. W. R. A.

**Photo-reaction in tropical sunlight.** B. J. MALAVIYA and S. DUTT (*Proc. Acad. Sci. Agra and Oudh*, 1935, 4, 319—329).—The products of the action of intense sunlight on a large no. of org. compounds have been identified. C. W. G.

**Mechanism of the activation of oxygen by irradiated pigments.** II. **Photo-oxidation in the near infra-red.** H. GAFFRON (*Ber.*, 1935, 68, [B], 1409—1411).—Solutions of bacterio-chlorophyll or bacterio-phaeophytin resemble chlorophyll (I) in sensitising ability and are active in the infra-red. A solution of these pigments in  $\text{COMe}_2$  with thiosinamine as acceptor vigorously absorbs  $\text{O}_2$  when exposed to light of  $\lambda < 760 \text{ m}\mu$ . The absorption limit of (I) in the red is therefore certainly not the limit of such photochemical reactions. H. W.

**Exchange reactions with deuterium atoms.** K. H. GEIB and E. W. R. STEACIE (*Z. physikal. Chem.*, 1935, B, 29, 215—224).—At. D enters into exchange reactions with  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , and  $\text{C}_2\text{H}_2$ , the energies of activation being  $12 \pm 1$ ,  $11 \pm 1$ , and  $< 5 \text{ kg.-cal.}$ , respectively. No exchange was observed with  $\text{CH}_4$ ; contrary to Taylor's findings (this vol., 457) the energy of activation of  $\text{CH}_4 + \text{D} = \text{MeD} + \text{H}$  is  $< 11 \text{ kg.-cal.}$  At  $20^\circ$  the reaction with  $\text{H}_2\text{O}$  apparently occurs partly on the wall. R. C.

**Production of light water and determination of the deuterium concentration in normal water.** N. MORITA and T. TITANI (*Bull. Chem. Soc. Japan*, 1935, 10, 257—258).—Light  $\text{H}_2\text{O}$  was prepared from Osaka conductivity water (I) by fractional electrolysis and was  $19.3 \gamma$  lighter than (I). The D : H ratio in (I) is  $1 : 5500 \pm 200$ . W. R. A.

**Distillation and rectification of dilute solutions of volatile substances.** I. **Heavy water.**—See B., 1935, 609.

**Separation of lithium [sulphate] from spodumene by heating with alkali-metal salts.**—See B., 1935, 723.

**Hydrolysis of alkali chlorides.** C. R. JOHNSON (*J. Physical Chem.*, 1935, 39, 791—795).—Carefully purified NaCl and KCl contain  $< 1\text{—}2 \text{ p.p.m.}$  of alkali after fusion in  $\text{N}_2$  under specified conditions. Such fused salts can be weighed in air of low or moderate R.H. without absorbing weighable amounts of  $\text{H}_2\text{O}$ . NaCl hydrolyses  $>$  KCl when fused in moist air. J. W. S.

**Preparation of sodium persilicate.**—See B., 1935, 671.

**Ammine from phenylenediamines and metallic salts.** M. PAPAFIL (*Ann. sci. Univ. Jassy*, 1934, 20, 139—153; cf. A., 1934, 66).—The prep. and properties of the following compounds are described [*Bo*, *Bm*, and *Bp* representing *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ ]:  $\text{CuSO}_4 \cdot \text{Bm}$ ;  $\text{Cu}(\text{NO}_3)_2 \cdot \text{Bm}$ ;  $\text{Cu}(\text{NO}_3)_2 \cdot \text{Bp}$ ;



$\text{CuCl}_2, \text{Bo}, \text{H}_2\text{O}$ ;  $\text{CuCl}_2, \text{Bm}, 2\text{H}_2\text{O}$ ;  $\text{CuCl}_2, \text{Bp}, \text{H}_2\text{O}$ ;  $\text{Co}(\text{NO}_3)_2, 4\text{Bo}$ ;  $\text{Co}(\text{NO}_3)_2, 4\text{Bm}$ ;  $\text{Co}(\text{NO}_3)_2, 2\text{Bp}, \text{H}_2\text{O}$ ;  $\text{CoCl}_2, \text{Bo}$ ;  $\text{CoCl}_2, \text{Bm}$ ;  $\text{NiSO}_4, \text{Bm}, \text{H}_2\text{O}$ ;  $\text{Ni}(\text{NO}_3)_2, 2\text{Bo}$ ;  $\text{Ni}(\text{NO}_3)_2, 4\text{Bm}$ ;  $\text{Ni}(\text{NO}_3)_2, 2\text{Bp}, \text{H}_2\text{O}$ ;  $\text{Ni}(\text{NO}_3)_2, 3\text{Bo}$ ;  $\text{NiCl}_2, 4\text{Bo}$ ;  $\text{NiCl}_2, 2\text{Bm}, \text{H}_2\text{O}$ ;  $\text{NiCl}_2, 2\text{Bp}$ ; and  $\text{CuCl}_2, m\text{-NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2, 2\text{H}_2\text{O}$ . CH. ABS. (e)

**Behaviour of copper on fusion with sodium carbonate and sulphur.** R. HÖLTJE and W. KAHMEN (Z. anorg. Chem., 1935, 223, 234—240).—On fusion of material containing Cu with  $\text{Na}_2\text{CO}_3 + \text{S}$ , and subsequent extraction with  $\text{H}_2\text{O}$ , the Cu dissolved increases with the proportion of S, and is augmented by the presence of Sn. Most is reprecipitated on addition of NaOH,  $\text{Na}_2\text{S}$ ,  $\text{Na}_2\text{SO}_3$ , or KCN, but is best separated by acidifying and then redissolving As, Sb, and Sn with  $\text{Na}_2\text{S} + \text{NaOH} + \text{Na}_2\text{SO}_3$ . A quant. separation of Cu is not possible. J. S. A.

**[Electrolytic] method of studying complexes.** C. DUVAL (Compt. rend., 1935, 200, 2175—2177; cf. this vol., 716).—The double chloride of Cu and Cd has the formula  $\text{Cu}[\text{CdCl}_4]$ . Kainite behaves as a binary electrolyte with the formula  $\text{K}[\text{MgClSO}_4(\text{H}_2\text{O})_3]$ . The complex from AgCl and  $\text{NH}_3$  is  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ . Other applications of the method are briefly indicated. H. J. E.

**Action of water vapour on metallic fluorides.** L. DOMANGE (Compt. rend., 1935, 200, 2180—2182; cf. this vol., 448).— $\text{H}_2\text{O}$  vapour at 200—400° converts AgF into Ag. At 400—650° it converts  $\text{ZnF}_2$  into ZnO (heat of reaction at const. pressure at 525—625° = -25,930 g.-cal.). With  $\text{PbF}_2$  attack was incomplete at 500—750°, a mixture of PbO and  $\text{PbF}_2$  remaining (heat of reaction at const. pressure at 625—725° = -37,200 g.-cal.) H. J. E.

**"Electron transfer" theory applied to the reactions in the (photographic) developing bath.** K. M. PANDALAI (J. Indian Chem. Soc., 1935, 12, 216—219).—The reactions occurring in the developing bath are considered as typical oxidation-reduction processes in which there is a transfer of electrons from the reducing to the oxidising agent. O. J. W.

**Influence of hydrogen ions in the phenomena of reduction and hydrogenation.** A. A. GUNTZ and E. BELTRAN (Compt. rend., 1935, 200, 2011—2013).—In a mechanism suggested for the reduction of  $\text{Ag}_2\text{O}$ ,  $\text{H}^+$  is attracted, and then causes disruption of the mol. by electrostatic repulsion. This will explain the action of an electric field in facilitating the reduction when the oxide is the cathode, and in retarding reduction when the oxide is the anode. H. J. E.

**Argentite salts in acid solution. I. Oxidation and reduction reactions.** A. A. NOYES, J. L. HOARD, and K. S. PITZER (J. Amer. Chem. Soc., 1935, 57, 1221—1229).—Solutions of  $\text{AgNO}_3$  in aq.  $\text{HNO}_3$  are oxidised at room temp. by  $\text{O}_3$ , forming a black, sol.  $\text{Ag}^{\text{II}}$  salt. The reaction ceases before completion, due to reduction of  $\text{Ag}^{\text{II}}$  by  $\text{H}_2\text{O}$  with evolution of  $\text{O}_2$ . At 0° the initial rate of oxidation of  $\text{Ag}^+$  is  $\propto [\text{Ag}^+]$  and  $[\text{O}_3]$  and only slightly affected by  $[\text{HNO}_3]$ . The rate of decomp. of  $\text{Ag}^{\text{II}}$  is approx.  $\propto [\text{Ag}^{\text{II}}]^2$  and inversely  $\propto [\text{Ag}^+]$ , and is greatly diminished by increasing  $[\text{HNO}_3]$ . The temp. coeff. is high. The mechanism is discussed. E. S. H.

**Hydrothermal experiments with gold.** S. P. OGRYZLO (Econ. Geol., 1935, 30, 400—424).—Between 250° and 600°, 20% HCl has no action on Au when passed over it.  $\text{AuCl}_3$  is formed when  $\text{Cl}_2$  and steam are passed over Au, the max. amount being formed at 200°. Volatilisation of  $\text{AuCl}_3$  in  $\text{Cl}_2 + \text{H}_2\text{O}$  begins at 125°, increases rapidly to a max. at 200°, and decreases sharply to practically zero at 400°. Au is sol. in dil. HCl at high temp. (300°) and pressures and the amount dissolved increases with a rise in temp., pressure, and concn. of the acid. More Au is dissolved in presence of air than in that of  $\text{CO}_2$  or  $\text{N}_2$ . Aq. solutions of alkali chlorides under pressure at 200—300° have no appreciable solvent action on Au and aq.  $\text{Na}_2\text{CO}_3$  at 200° under pressure has no action. Au is sol. in HCl solutions of  $\text{FeCl}_3$  at 200° under pressure in absence of  $\text{O}_2$ ; it is pptd. on cooling. Aq.  $\text{Na}_2\text{S}$  dissolves only traces of Au at 175—300° under pressure and none at room temp. Some Au is dissolved by NaSH at room temp. and considerable amounts at 200—300° under pressure. The results show that in nature, Au may be transported either in acid or slightly alkaline aq. solutions and also in the vapour phase as  $\text{AuCl}_3$ . L. S. T.

**Basic magnesium carbonates.** (MME.) L. W. LÉVY (Compt. rend., 1935, 200, 1940—1942).—The compounds  $8\text{MgO} \cdot \text{K}_2\text{O} \cdot 5\text{CO}_2 \cdot 5\text{H}_2\text{O}$  and  $4\text{MgO} \cdot 3\text{CO}_2 \cdot 3\text{H}_2\text{O}$  were prepared by the decomp. of  $\text{MgCO}_3 \cdot \text{K}_2\text{CO}_3 \cdot 4\text{H}_2\text{O}$  in a sealed tube at 100—200° by aq.  $\text{K}_2\text{CO}_3$  or  $\text{KHCO}_3$ . H. J. E.

**Action of carbon dioxide on lime water and of alkali carbonate on calcium salt solutions. II.** O. SPENGLER and G. DORFMÜLLER (Z. Wirts. Zuckerind., 1935, 65, 263—281; cf. A., 1933, 1020).—When  $\text{CO}_2$  reacts with aq. CaO the first product is a sol. hydrated carbonate, which is fairly stable up to 100°, and can be crystallised at 0—2°. E. S. H.

**Wet preparation of calcium chromate.** J. MILBAUER and J. DOŠKAŘ (Chem. Listy, 1935, 29, 113—116).— $\text{CaCrO}_4$  is pptd. by adding 1.6 times the theoretical amount of  $\text{CaCl}_2$  (as a solution of 40—45 g. per 100 c.c. of  $\text{H}_2\text{O}$ ) to saturated aq.  $\text{Na}_2\text{CrO}_4$  at 20°. The product obtained using  $\text{K}_2\text{CrO}_4$  is contaminated with difficultly eliminable  $\text{K}^+$  and  $\text{Cl}^-$ . R. T.

**Mechanism of precipitation processes. XVII.  $\text{Ba}(\text{NO}_3)_2$  and  $\text{H}_2\text{SO}_4$ .** Z. KARAOGLANOV and P. SAGORTSCHEV (Z. anorg. Chem., 1935, 223, 217—221; cf. this vol., 317).—When  $\text{Ba}(\text{NO}_3)_2$  is pptd. by  $\text{H}_2\text{SO}_4$  in presence of  $\text{HNO}_3$ , the ratio of Ba to  $\text{SO}_4$  in the ppt. increases with the total  $[\text{NO}_3^-]$ , up to a max. corresponding with the presence of 38% of  $(\text{BaNO}_3)_2\text{SO}_4$ . Addition of EtOH lowers the ratio by suppressing the ionisation of  $\text{Ba}(\text{NO}_3)_2$ . J. S. A.

**Deposition of artificial radio-elements by electrochemical exchange.** M. HAISSINSKY (Nature, 1935, 136, 141—142).—Radio-Cu (I) (period 10 hr.) has been separated from Zn by the following method. 8—12 g. of neutron-irradiated Zn powder are treated with conc. HCl until 0.2—0.3 g. remains. Practically all the activity is conc. on this residue, which is dissolved separately in conc. HCl and diluted



with 2 vols. of  $\text{H}_2\text{O}$ . Rotation for 30 min. of a Pb plate insulated on one side collects  $>$  half of (I) on the plate. Strong sources of (I) can thus be prepared in very thin layers without co-pptn. L. S. T.

**Preparation of zinc chloride solutions.** A. RAUSCH (Arch. Chem. Farm., 1935, 2, 237—243).—The difference in  $[\text{ZnCl}_2]$  between filtered and unfiltered aq.  $\text{ZnCl}_2$  [containing suspended  $\text{Zn}(\text{OH})\text{Cl}$ ] is  $> 0.02\%$ . R. T.

**Isomeric amines from cyclic diamines and metallic salts.** II. M. PONI (Ann. sci. Univ. Jassy, 1934, 20, 154—172; cf. A., 1934, 66).—The prep. and properties of the following compounds are described  $[\text{T}=\text{C}_5\text{H}_3\text{Me}(\text{NH}_2)_2; \text{N}=\text{C}_{10}\text{H}_6(\text{NH}_2)_2]$ :  $\text{CdBr}_2, (2:4\text{-T}), 2\text{H}_2\text{O}$ ;  $\text{CdBr}_2, (2:4\text{-T})$ ;  $\text{CdBr}_2, (2:5\text{-T})$ ;  $\text{CdI}_2, (2:4\text{-T}), 2\text{H}_2\text{O}$ ;  $\text{CdI}_2, (2:4\text{-T})$ ;  $\text{CdI}_2, (2:5\text{-T})$ ;  $\text{Cd}(\text{NO}_3)_2, 2(3:4\text{-T})$ ;  $\text{Cd}(\text{NO}_3)_2, 2(2:4\text{-T})$ ;  $\text{CuCl}_2, (3:4\text{-T})$ ;  $\text{CuCl}_2, (2:5\text{-T})$ ;  $\text{CuBr}_2, (2:4\text{-T})$ ;  $\text{CuBr}_2, (2:5\text{-T})$ ;  $\text{Cu}(\text{NO}_3)_2, 2(3:4\text{-T})$ ;  $\text{Cu}(\text{NO}_3)_2, (2:4\text{-T})$ ;  $\text{CoCl}_2, 2(3:4\text{-T})$ ;  $\text{CoCl}_2, (2:5\text{-T}), 2\text{H}_2\text{O}$ ;  $\text{CoCl}_2, (2:5\text{-T})$ ;  $\text{CoBr}_2, (2:4\text{-T})$ ;  $\text{NiBr}_2, 3(2:4\text{-T})$ ;  $\text{NiCl}_2, (2:5\text{-T}), 2\text{H}_2\text{O}$ ;  $\text{NiCl}_2, (2:5\text{-T})$ ;  $\text{CdCl}_2, (1:2\text{-N})$ ;  $\text{CdBr}_2, (1:2\text{-N}), 2\text{H}_2\text{O}$ ;  $\text{Cd}(\text{NO}_3)_2, 2(1:8\text{-N})$ ;  $\text{CdBr}_2, (1:2\text{-N}), 2\text{H}_2\text{O}$ ;  $\text{CdBr}_2, (1:2\text{-N})$ ;  $\text{Cu}(\text{NO}_3)_2, 2(1:5\text{-N})$ ;  $\text{CuCl}_2, (1:8\text{-N})$ ;  $\text{CuBr}_2, 2(1:8\text{-N})$ ;  $\text{Cu}(\text{NO}_3)_2, 2(1:8\text{-N})$ ;  $\text{Cu}(\text{NO}_3)_2, 2(2:7\text{-N})$ ;  $\text{NiCl}_2, 2(1:2\text{-N})$ ;  $\text{NiCl}_2, 2(1:8\text{-N})$ ;  $\text{NiBr}_2, 2(1:8\text{-N})$ ;  $\text{Ni}(\text{NO}_3)_2, 3(1:8\text{-N})$ ;  $\text{NiSO}_4, 2(1:8\text{-N})$ ;  $\text{CoCl}_2, 2(1:2\text{-N})$ ;  $\text{CoI}_2, (1:2\text{-N})$ ;  $\text{CoCl}_2, 2(1:8\text{-N})$ ;  $\text{CoBr}_2, 2(1:8\text{-N})$ ;  $\text{CoI}_2, 2(1:8\text{-N})$ ; and  $\text{Co}(\text{NO}_3)_2, 2(1:8\text{-N})$ . CH. ABS. (e)

**Constitution of compounds formed by cyclic diamines and metallic salts.** R. CERNATESCU, (MME.) M. PAPAÏL, and M. PONI (Ann. Sci. Univ. Jassy, 1934, 20, 175—189; cf. preceding abstract).—In  $\text{CdCl}_2, 2(1:8\text{-N})$ ,  $\text{CdBr}_2, 2(1:8\text{-N})$ , and  $\text{CdBr}_2, (1:2\text{-N})$  each mol. of base is replaceable by  $\text{INH}_3$ , and in  $\text{NiSO}_4, 2(1:8\text{-N})$ ,  $\text{CdBr}_2, (1:5\text{-N})$ ,  $\text{CdCl}_2, Bp$  (I),  $\text{CdI}_2, Bp$  (II), and  $\text{Cd}(\text{NO}_3)_2, 2Bp$  (III),  $\text{NiCl}_2, 2Bp$  (IV) [ $Bp=p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ ], and  $\text{CdBr}_2, (2:5\text{-T})$  each mol. of base is replaceable by  $2\text{NH}_3$ . Formula are assigned to (I)—(IV). CH. ABS. (e)

**Mercuriammonium chromate.** S. AUGUSTI (Boll. Chim. farm., 1935, 76, 505—508, 511—513).—The new prep. of  $(\text{Hg}_2\text{N})_2\text{CrO}_4, 2\text{H}_2\text{O}$  from  $(\text{Hg}_2\text{N})\text{NO}_3$  and  $\text{K}_2\text{CrO}_4$ , and from aq.  $\text{NH}_3$  and  $\text{HgCrO}_4$ , is described. The substance reacts with  $\text{Na}_2\text{S}$  to form  $\text{Hg}_2\text{S}$ ,  $\text{NH}_3$ ,  $\text{NaOH}$ , and  $\text{Na}_2\text{CrO}_4$ . With  $\text{KI}$  it gives  $\text{K}_2\text{HgI}_4$  and  $\text{KOH}$ ; with  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{Na}_2\text{Hg}(\text{S}_2\text{O}_3)_2$  and  $\text{NaOH}$ ; with  $\text{HCl}$  and  $\text{KBr}$ ,  $\text{K}_2\text{HgBr}_4$  and  $\text{KCl}$ ; and with  $\text{KCN}$ ,  $\text{K}_2\text{Hg}(\text{CN})_4$  and  $\text{KOH}$ . In each of these reactions  $(\text{NH}_4)_2\text{CrO}_4$  is also formed. E. W. W.

**Orange modification of mercuric iodide.** V. S. GORSKI (Physikal. Z. Sovietunion, 1934, 6, 515).—Orange crystals of  $\text{HgI}_2$  were obtained from  $\text{COMe}_2$  solution at room temp., together with the known red and yellow forms, this being a new metastable modification (tetragonal;  $a$  8.70,  $c$  23.44 Å.; body-centred; space-group  $D_{2h}^{12}$  or  $C_{4h}^{11}$ ). CH. ABS. (e)

**Modification of Carpenter and Elam's method of producing single crystals of aluminium by**

**deformation and annealing.** V. H. STOTT (Trans. Faraday Soc., 1935, 31, 998—1000).—Modified procedure, involving greater extension of the specimen, is recommended. E. S. H.

**"Decaying" [inter]metallic compounds.** G. TAMMANN and A. RÜHENBECK (Z. anorg. Chem., 1935, 223, 288—296).—Numerous alloys and inter-metallic compounds of Al, Ca, Mg, Ce, and Si with moderately base metals (e.g.,  $\text{FeAl}_3$ ,  $\text{AlSb}$ ,  $\text{PbCa}$ ,  $\text{AgCa}$ ,  $\text{SnMg}_2$ ,  $\text{BiCe}$ , but not  $\text{Al}_3\text{Mg}_4$  or  $\text{AuMg}$ ) decompose on exposure to moist air, probably forming hydroxide and free metal. The effect is attributed to the non-formation by such alloys of protective coatings, either of coherent hydroxide (as on Al, Mg, or Al-Mg alloys) or of the nobler metal. J. S. A.

**Rare earths. XLIV. Preparation of anhydrous rare-earth compounds by the action of fused and solid "-onium" salts on the oxides.** J. B. REED [with B. S. HOPKINS and L. F. AUDRETH] (J. Amer. Chem. Soc., 1935, 57, 1159—1160; cf. A., 1934, 373).—Rare-earth oxides react with  $\text{NH}_4\text{Cl}$  or  $\text{NH}_4\text{Br}$  at 200—300°, yielding the corresponding halides. Rare-earth sulphides, prepared by reducing the sulphates with C, react partly with  $\text{NH}_4\text{I}$  at 450—500°. The action of  $\text{NH}_4\text{I}$  on the rare-earth oxide yields basic iodides. E. S. H.

**Complex iodides of bivalent germanium.** T. KARANTASSIS and L. CAPATOS (Compt. rend., 1935, 201, 74—75).—A HI solution of  $\text{Ge}(\text{OH})_2$  when added to solid  $\text{CsCl}_2$  gave a black microcryst. ppt. of the compound  $\text{CsGeI}_3$ , which was readily hydrolysed by  $\text{H}_2\text{O}$ . With aq.  $\text{NMe}_4\text{I}$ ,  $\text{Ge}(\text{OH})_2$  gave the compound  $\text{NMe}_4\text{GeI}_3$ , white needles, and with a solution of cocaine hydrochloride gave white needles of  $\text{GeI}_2, 3(\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}, \text{HI})$  (decomp. in air). H. J. E.

**Reactions of zirconium tetrabromide and thorium tetrabromide with potassium and with potassium amide in liquid ammonia.** R. C. YOUNG (J. Amer. Chem. Soc., 1935, 57, 1195—1196).—A solution of  $\text{ZrBr}_4$  in liquid  $\text{NH}_3$  is reduced by K; further reaction occurs with evolution of  $\text{H}_2$  and formation of  $\text{Zr}(\text{NK})_2, \text{NH}_3$ , which is also formed by the action of excess of  $\text{KNH}_2$  on  $\text{ZrBr}_4$ . Equiv. proportions of  $\text{KNH}_2$  and  $\text{ZrBr}_4$  yield a mixture of  $\text{Zr}(\text{NH})_2$  and  $\text{Zr}(\text{NH})\cdot\text{NK}$ . When  $\text{ThBr}_4$  in liquid  $\text{NH}_3$  is treated with K, the product is  $\text{Th}(\text{NH})\cdot\text{NK}, \text{NH}_3$ . The action of excess of  $\text{KNH}_2$  on  $\text{ThBr}_4$  yields  $\text{Th}(\text{NK})_2, \text{KNH}_2$ . E. S. H.

**Lead acetatobromide.** E. GRILLOT (Compt. rend., 1935, 200, 2177—2179; cf. this vol., 50).—The compound  $\text{PbBr}\cdot\text{OAc}$  was isolated from a solution containing  $\text{PbBr}_2$ ,  $\text{Pb}(\text{OAc})_2$ , and  $\text{AcOH}$ . It hydrolyses to form  $\text{PbBr}\cdot\text{OH}$ . Solubility data are recorded. H. J. E.

**Action of nitrogen on metals. Electric discharge at low pressures.** G. BERRAZ (An. Soc. cient. Santa Fe, 1933, 5, 54—56; Chem. Zentr., 1935, i, 1020).—Cathodic sputtering of Ag and Au in  $\text{N}_2$  at 0.5 mm. is attended with combination of N. With Pb a nitride is formed which evolves  $\text{NH}_3$  with  $\text{H}_2\text{O}$ . J. S. A.



**Preparation and properties of phosphorus nitride.** V. F. POSTNIKOV and L. L. KUZMIN (J. Appl. Chem. Russ., 1935, 8, 429—438).— $P_3N_5$  is obtained in good yield by Stock's method (A., 1903, ii, 207), and is also formed in traces from P and  $N_2$  by the silent electrical discharge, or at  $600^\circ$  (Ni and Pt catalysts).  $P_3N_5$  is conveniently analysed by the Kjeldahl method, being quantitatively converted into  $H_3PO_4$  and  $NH_3$  with  $H_2SO_4$  at the b.p. or with  $H_2O$  at  $\leq 180^\circ$ . The  $P_3N_5$  may be dried in air at  $120^\circ$  without decomp.; at  $800^\circ$  conversion into  $N_2$  and  $P_2O_5$  takes place, whilst in  $N_2$  the products are  $N_2$  and P. Conc.  $HNO_3$  and dil.  $H_2SO_4$  cause only inconsiderable decomp. at the b.p., aq. HCl and aq. alkalis have no effect, whilst fusion with NaOH affords Na phosphate and  $N_2$  or  $NH_3$ . R. T.

**Additive compounds of arsenic [tri]chloride.** E. MONTIGNIE (Bull. Soc. chim., 1935, [v], 2, 1365—1367).— $AsCl_3$  combines with  $C_5H_5N$ ,  $NH_2OH$ ,  $NH_2Ph$ , piperazine,  $(CH_2)_6N_4$ , quinoline, NaCl,  $NH_4Cl$ , and  $CoCl_3$ . No reaction occurs with  $MgCl_2$ ,  $ZnCl_2$ , or  $CrCl_3$ . T. G. P.

**Action of liquid ammonia on tantalum pentachloride.** H. MOUREU and C. HAMBLET (Compt. rend., 1935, 200, 2184—2186).—Interaction of anhyd.  $NH_3$  at its b.p. with  $TaCl_5$ , followed by removal of excess of  $NH_3$  at low temp., yields the compound  $Ta(NH_2)_2Cl_3 \cdot 7NH_3$  together with  $NH_4Cl$ . On heating this product to  $> 170^\circ$   $Ta(NH_2)_2Cl_3$  is formed; this, when heated in  $NH_3$  at  $1100^\circ$ , forms  $TaN$ . Two of the Cl in  $TaCl_5$  are particularly reactive. H. J. E.

**Laboratory preparation of oxygen and of chlorine.** F. C. KRAUSKOFF (J. Chem. Educ., 1935, 12, 293—294).—Details are given for the prep. of  $O_2$  from  $Ca(OCl)_2$  and a Co salt and of  $Cl_2$  from a suspension of bleaching powder or  $Ca(OCl)_2$  and HCl. L. S. T.

**Formation of dithionate by oxidation of sulphurous acid and sulphites.** H. BASSETT and A. J. HENRY (J.C.S., 1935, 914—929).—The hydrolytic decomp. of  $H_2S_2O_6$  (I) is not reversible, and oxidising agents have no action unless conditions are such as to cause hydrolysis.  $Cl_2$ , I, and  $H_2O_2$  oxidise sulphite (II) solutions rapidly, and in acid, but not in neutral or alkaline, solutions traces of (I) are formed. This introduces an error in the iodometric determination of  $SO_2$ .  $O_2$  reacts with (II) by a chain mechanism, and (I) is formed in acid solution only. The proportion of (I) increases with increase of [(II)] and for a given [(II)] there is an optimum acidity. Free  $SO_3''$  is oxidised to  $SO_4''$  and the (I) is produced by oxidation of  $S_2O_5''$ . Methylene-blue inhibiting the atm. oxidation of  $H_2SO_3$  is gradually oxidised, and the inhibition is thus removed. In moist  $O_2$ , alkali pyrosulphites yield a mixture of sulphate and approx. 25% of dithionate (III), and in solution, the ratio of (I) formed to total  $S_2O_5''$  oxidised rises to a const. val. with increasing  $[S_2O_5'']$ .

Of the  $H_2SO_3$  oxidised by  $H_2Cr_2O_7$  and  $HMnO_4$ , approx. 4% and 19%, respectively, is converted into (I) under all conditions of concn. and acidity. The  $SO_2$  mols. in the solution probably form, with the oxid-

ising ions, complexes which subsequently break down, producing  $SO_4''$  and  $S_2O_5''$  in proportions which are a function of the metal forming the complex. Analogous considerations are applied to numerous cases in which metal ions, easily reducible to a lower valency state, or the metal, form complexes with  $SO_3''$  and give similar results. In alkaline solution,  $MnO_4'$  affords no (III), and  $SO_4''$  formation is probably accompanied by the process  $MnO_4' \rightarrow MnO_4'' \rightarrow MnO_4''' \rightarrow MnO_2$ . (III) is not produced during the photol. decomp. of  $H_2SO_3$  to  $H_2SO_4$  and S, but traces are produced during the dark decomp.

Electrolytic formation of (III) probably proceeds by the process  $2SO_3'' \rightarrow (2SO_3' + 2e) \rightarrow S_2O_6'' + 2e$ . There is no evidence from these data for the existence of a sulphurous-sulphonic equilibrium in  $H_2SO_3$  solutions. J. G. A. G.

**Loss of selenium in the reduction of selenites by hydrazine.** V. HOVORKA (Coll. Czech. Chem. Comm., 1935, 7, 273—280; cf. A., 1933, 1102).—The loss of Se, due to  $H_2Se$  formation, in reducing  $H_2SeO_3$  by  $N_2H_4$  in acid media has been determined for a series of acids. With mineral acids the loss is 0.17—0.29%, and with tartaric or citric acid it is 0.07—0.1%. H. J. E.

**Nomenclature of the telluric acids.** M. PATRY (Compt. rend., 1935, 201, 71—73; cf. this vol., 593).—The two acids  $H_2TeO_4$  and  $(H_2TeO_4)_n$  are termed ortho- and meta-, respectively. The val. of  $n$  in aq. solution is approx. 3. The conditions for obtaining the two acids, and their properties, are reviewed. H. J. E.

**Preparation of iodine.** C. E. WHITE (J. Chem. Educ., 1935, 12, 169).—9 ml. of 0.25M-NaIO<sub>3</sub> are mixed with 10 ml. of 0.5M-Na<sub>2</sub>SO<sub>3</sub>. 3 ml. of 2N- $H_2SO_4$  are added and the whole is carefully shaken. L. S. T.

**Intermediate product of long life between iodine and oxalate (ion).** E. ABEL and H. SCHMID (Naturwiss., 1935, 23, 501; cf. A., 1933, 237).—In the photochemical reaction between I and  $C_2O_4''$  an intermediate product of long life, probably  $(O_2C \cdot CO_2)'$  ("oxalato-ion") is produced. This may be connected with the "activated form of  $H_2C_2O_4$ " previously described (A., 1928, 505). A. J. M.

**Decomposition of permanganic acid in certain acid media.** Thermal decomposition of manganese carbonate, and its products. (A) J. KOTRBA. (B) J. CHLOUPEK (Chem. Listy, 1934, 28, 137—140, 140—142).—Criticism and a reply (cf. A., 1933, 919, 1022). R. T.

**Anhydrous ferric orthophosphate.** P. BRASSEUR (Compt. rend., 1935, 200, 2182—2184).— $FePO_4$  was prepared by adding aq.  $(NH_4)_3PO_4$  to aq. Fe alum containing  $NH_3$ , evaporating to dryness, and heating gradually to  $800^\circ$ .  $FePO_4$  is white and micro-cryst. Its magnetic properties were studied. No anhyd. basic phosphates were isolated, mixtures of  $FePO_4$  and  $Fe_2O_3$  being always obtained. H. J. E.

**Reaction of carbon dissolved in liquid iron with oxides.** F. KÖRBER and W. OELSEN (Naturwiss., 1935, 23, 462—465).—The removal of C from liquid Fe by the oxidising action of the oxides of the



slag is not entirely governed by mass action, but by a no. of external phenomena, such as the formation of CO bubbles in the melt. There is delayed formation of these bubbles, giving rise to local superheating. Spontaneous formation of the first CO bubbles rarely occurs in the bulk of the melt or at the surface of contact with the slag, but almost exclusively where the melt comes in contact with the walls of the containing vessel.

A. J. M.

**New group of complex compounds.** Compounds with a complex anion, the central ion of which is a complex cation. I. Complex sulphato- and oxalato-anions with complex cobalt cations as central ions. H. BRINTZINGER and H. OSSWALD (Z. anorg. Chem., 1935, 223, 253—256).—Determination of ionic wts. by electrodialysis in solutions of complex salts in aq.  $K_2SO_4$  and  $K_2C_2O_4$  shows that complex sulphato- and oxalato-ions may be formed, in which the central atom of the usual acido-complex is replaced by a central complex ion. The following such complexes were shown to exist: ( $R=SO_4''$  or  $C_2O_4''$ )  $[[Co(NH_3)_5H_2O]R_4]^{5-}$ ;  $[[Co(NH_3)_4(H_2O)_2]R_4]^{5-}$ ;  $[[Co(NH_3)_4SO_4]R_4]^{7-}$ ;  $[[Co(NH_3)_6](SO_4)_4]^{5-}$ ;  $[[Co(NH_3)_5Cl](SO_4)_4]^{6-}$ ;  $[[Co(NH_3)_4CO_3](SO_4)_4]^{7-}$ . In aq.  $K_2C_2O_4$ ,  $[Co(NH_3)_4CO_3]^-$  forms the anion  $[Co(NH_3)_4(CO_3)(C_2O_4)]^-$ .

J. S. A.

**Recent advances in applied microchemistry.** J. B. NIEDERL (Ind. Eng. Chem. [Anal.], 1935, 7, 214—218).—A review.

E. S. H.

**Role of analytical chemistry in industrial research. II. Microanalysis.** B. L. CLARKE and H. W. HERMANCE (Ind. Eng. Chem. [Anal.], 1935, 7, 218—222).—A review.

E. S. H.

**Material testing by flame analysis.** F. WAIBEL (Z. tech. Physik, 1934, 15, 454—456; Chem. Zentr., 1935, i, 1274).—Flame spectra are more accurate and convenient for quant. spectral analysis than spark spectra.

J. S. A.

**Chromatographic adsorption analysis.** N. A. SØRENSEN (Tidsskr. Kjemi, 1935, 15, 53—55).—A review.

R. P. B.

**Determination of  $p_H$  with the glass electrode.** K. BENNEWITZ and E. KELLNER (Z. anal. Chem., 1935, 102, 1—3).—This method dispenses with the use of an electrometer. The glass electrode and a potentiometer are connected in opposition to a condenser, which is discharged through a mirror galvanometer. The potentiometer is adjusted to give zero galvanometer deflexion. A  $p_H$  accuracy of  $\pm 0.003$  is attainable.

S. J. G.

**Buffer action and reciprocity of the acid-base function.** S. KILPI (Z. physikal. Chem., 1935, 173, 223—236).—In acid-alkali titration with one reactant weak,  $[H']$  or  $[OH']$  at the point of min.  $p_H$  change  $\approx K$  and the point of max.  $p_H$  change practically coincides with the equiv. point if  $Kc \ll 10^{-10}$ , where  $c$  is the concn. of weak reactant. If  $Kc$  is smaller, the points of max. and min.  $p_H$  change approach and coincide when  $Kc = 27K_w$ . If both reactants are weak the point of max. or min. buffer action towards strong acids and strong bases generally coincides with the equiv. point, the buffer action being a min. or max. according as

$K_{HA}K_{BOH}$  is  $>$  or  $<$   $15K_w$ . When the salt of a weak acid or base is titrated with a strong base or acid the change in potential has both a max. and a min. if  $K/c < 1/27$ . In displacement titration the solution of a salt of weak acid (base) behaves like a base (acid) with dissociation const. equal to the hydrolysis const. of the salt.

R. C.

**Use of antimony electrode for  $p_H$  determination and acidimetric titration in aqueous or organic solutions.** E. VELLINGER (Ann. Off. nat. Comb. liq., 1934, 9, 673—701; Chem. Zentr., 1935, i, 1274).—An Sb rod electrode is recommended for acidimetric titrations. Acids insol. in  $H_2O$  may be titrated in EtOH,  $C_5H_{11}OH$ , EtOH+Et<sub>2</sub>O, or EtOH+ $C_6H_6$ . Alcoholic LiCl may be added to increase the conductivity.

J. S. A.

**Direct determination of the absolute water-vapour content of gases.**—See B., 1935, 705.

**Determination of chloride, bromide, and iodide by photometric titration.** S. HIRANO (J. Soc. Chem. Ind. Japan, 1935, 38, 175—177B).— $Cl'$ ,  $Br'$ , and  $I'$  may be titrated photometrically with  $AgNO_3$ , using starch as protective colloid. The light absorption attains a const. val. when pptn. of Ag halide is complete.

J. S. A.

**Determination of bromine in brine.**—See B., 1935, 671.

**Electrometric determination of bromine in the presence of large quantities of chlorine.** G. E. VLADIMIROV and J. A. EPSTEIN (Mikrochem., 1935, 18, 58—65).—The method depends on the separation of NaCl from NaBr by pptn. with  $COMe_2$  and centrifuging, removal of the solvent, and titration of the solution with 0.01N- $AgNO_3$  potentiometrically, the NaCl not pptd. having no effect on the potential jump at the end-point of the NaBr titration. For the analysis of org. materials, e.g., blood, the org. matter is destroyed with fuming  $HNO_3$  and  $AgNO_3$ , the  $AgCl+AgBr$  ppt. washed and decomposed by shaking with Na amalgam, the alkaline solution neutralised with  $H_2SO_4$ , and the  $Na_2SO_4$  pptd. with EtOH before making the  $COMe_2$  separation.

A. R. P.

**Micro-iodometric determinations.** I. M. KORENMAN (Mikrochem., 1935, 17, 361—364).—Titration of  $Na_2SO_3$  and  $SnCl_2$  with aq.  $KIO_3$  gives vals. in agreement with I titrations.

R. S.

**Identification of halides in presence of thiocyanates.** G. B. HEISIG and L. K. HEISIG (Ind. Eng. Chem. [Anal.], 1935, 7, 249—250).—The sensitivity of the test for  $I'$  is greatly increased by adding  $K_2S_2O_8$  to a cold 10-c.c. sample containing 1—2 c.c. of  $CCl_4$ . If aq.  $Na_2CO_3$  is then added and the solution evaporated to dryness the CNS' is destroyed.  $Br'$  is then determined colorimetrically in a  $CCl_4$  extract after adding conc.  $HNO_3$ .  $Cl'$  is determined by  $AgNO_3$  after removing Br by adding  $KMnO_4$  and boiling. By this procedure  $\leq 0.25$  mg.  $I'$ , 0.5 mg.  $Br'$ , and 0.25 mg.  $Cl'$  can be detected in presence of 100 mg. CNS'.

E. S. H.

**Penfield's method for determining fluorine.** O. KALLAUNER and K. KURAŠ (Stavivo, 1933, 65).—The Penfield method is modified: into the vessel



in which decomp. occurs, dehydrated Cu uranate is added to ensure complete binding of  $H_2O$  formed in the reaction. A second V-shaped pipe filled with glass balls is used to keep any  $H_2SO_4$  from the gas stream. 0.02N-KOH is used. The titration is performed in an alcoholic medium in presence of excess of KCl (Mc-red indicator). CH. ABS. (e)

**Determination of small quantities of oxygen in gases.**—See B., 1935, 724.

**Oxidation-reduction indicators. I. Diphenylbenzidinesulphonic acid.** L. A. SARVER and W. VON FISCHER (Ind. Eng. Chem. [Anal.], 1935, 7, 271).—The prep. of diphenylbenzidinesulphonic acid (cf. this vol., 462) is described. The product contains 10  $SO_3H$  groups. A 0.1% aq. solution of the Na salt is recommended as an indicator; when oxidised in 0.5–1.0N- $H_2SO_4$  the pale yellow solution becomes green and finally violet. On reduction the colour changes are reversed. The absorption spectra of the different forms have been determined.

E. S. H.

**Determination of atmospheric ozone by fluorescein.** W. HELLER (Compt. rend., 1935, 200, 1936–1938; cf. Maché, this vol., 836).—A discussion of factors which influence the determination.  $N_2$  and  $O_2$  have no influence, and  $NO$ ,  $NO_2$ , and  $CO_2$  are much less effective in destroying the fluorescence than is  $O_3$ .

H. J. E.

**Potentiometric titration of sulphite and sulphonylate alone and in the presence of hyposulphite.** J. LÖBERING (Z. anal. Chem., 1935, 101, 392–398).— $SO_3''$  and derivatives of  $HSO_3'$  with aldehydes can be titrated potentiometrically with  $K_2Cr_2O_7$  in 2%  $H_2SO_4$  using a Pt indicator electrode, the reaction being  $2HSO_3' + HCrO_4' + H^+ \rightleftharpoons 2SO_4'' + Cr^{++} + 2H_2O$ . Similarly,  $2HSO_2' + HCrO_4' + H^+ \rightleftharpoons Cr^{++} + 2H_2SO_4$ .  $Na_2S_2O_4$  does not interfere unless the solution is heated or the acidity is high. A. R. P.

**Argentometric determination of (A) sodium sulphide and hydrosulphide present together, (B) sodium hydroxide and sulphide in sodium aluminate.**—See B., 1935, 723.

**Conductometric titration of selenates with lead nitrate and with barium chloride.** R. RIPAN-TILICI (Z. anal. Chem., 1935, 102, 28–31).—The aq. selenate solution (approx. 0.05M) is made 40% in EtOH and is then titrated with 0.5M- $Pb(NO_3)_2$ , the conductivity being measured after each addition. Selenic acid can be determined if first made slightly alkaline with KOH, but heavy metal selenates are unsuitable. For titration with 0.5M- $BaCl_2$  the selenate solution must contain 50% of EtOH.

S. J. G.

**Determination of ammoniacal and urea-nitrogen.** J. Y. YEE and R. O. E. DAVIS (Ind. Eng. Chem. [Anal.], 1935, 7, 259–261).—Modifications of the urease method, which enable  $CO(NH_2)_2$  to be determined even in highly-coloured solution, are described.  $NH_3$  is determined by distillation at 40° with NaOH in MeOH under reduced pressure with aeration.

E. S. H.

**Determination of ammonia.** S. ŠKRAMOVSKÝ (Lékárn., 1934, 14, 249–251; Chem. Zentr., 1935,

i, 933).—A modified  $NH_3$  distillation apparatus is described.

J. S. A.

**Colorimetric determination of nitric acid and nitrates.** R. CERNATESCU and E. GHELLER (Z. anal. Chem., 1935, 101, 402–406).—The method depends on the formation of a red colour when the solution (0.5 c.c.) is treated with 4 vols. of conc.  $H_2SO_4$  to which has been added 0.5 g. per 100 c.c. of *m*-diaminophenol hydrochloride.  $Fe^{++}$  and  $Fe^{+++}$  must first be removed by pptn. with NaOH and  $NO_2'$  by treatment with  $CO(NH_2)_2$ .

A. R. P.

**Colorimetric determination of phosphorus in presence of silica, arsenic, iron, and nitrates.** C. ZINZADZE (Ind. Eng. Chem. [Anal.], 1935, 7, 227–230).—Modifications in the Mo-blue method are described. In the  $SnCl_2$  reduction method the use of  $MoO_3$  is recommended in place of  $NH_4MoO_4$ .  $SnCl_2$  may be replaced by *p*-OH- $C_6H_4$ -NHMe,  $H_2SO_4$ , quinol, or aminonaphtholsulphonic acid. E. S. H.

**Colorimetric determination of arsenic in phosphorus-free solutions.** C. ZINZADZE (Ind. Eng. Chem. [Anal.], 1935, 7, 230).—The modifications described for the determination of P (see above) are applicable to As.

E. S. H.

**Use of conductometric titrations with visual observation in microchemical tests: titration of minute amounts of arsenic.** G. JANDER and J. HARMS (Angew. Chem., 1935, 48, 267–271).—Quantities of As of the order of 0.1 mg.— $0.1 \times 10^{-6}$  g. can be rapidly determined by visual conductometric titration with an EtOH solution of I using Pt electrodes and a Wheatstone bridge and galvanometer. Addition of  $NaHCO_3$  is unnecessary and undesirable,  $CO_2$ -free  $H_2O$  must be used when the As is  $1-20 \times 10^{-6}$  g. and A must be passed into the titration vessel when  $< 1 \times 10^{-6}$  g. of As is being titrated. The graphs obtained consist of two straight lines, that obtained after the end-point being horizontal to the axis giving c.c. of I. AsPhO can be determined similarly. The necessary apparatus and its connexions are illustrated.

A. R. P.

**Modified procedure for the arsenic group.** A. T. LINCOLN and E. OLSON (J. Chem. Educ., 1935, 12, 264–265).—The solution of thio-salts in  $(NH_4)_2S_2$  is evaporated until it becomes turbid and then 20 ml. of a saturated solution of  $H_2C_2O_4$  and 5 ml. of 3%  $H_2O$  are added. The solution is boiled for 5 min., diluted to 25 ml., saturated with  $H_2S$ , filtered, and washed. The Sn is confirmed with  $HgCl_2$  after reduction of the oxalate in the filtrate with HCl and Al.  $As_2S_5$  is extracted from the ppt. by treatment with 20 ml. of 0.5N- $(NH_4)_2C_2O_4$  and 4 ml. of 5M aq.  $NH_3$ , repptd. with HCl and  $H_2S$ , and confirmed as the arsenomolybdate.  $Sb_2S_5$  from the residue is boiled with 5 ml. of  $HNO_3$ , diluted with 20 ml. of  $H_2O$ , filtered from S, and repptd. with  $H_2S$ . Determinations of the relative solubilities of the sulphides of As and Sb in the common  $NH_4$  salts show that only ammoniacal  $(NH_4)_2C_2O_4$  dissolves those of As completely and is practically without action on those of Sb. 0.9 mg. of As in  $< 3$  ml. can be readily detected by dilution with 24 ml. of this reagent.

L. S. T.



**Volumetric determination of small amounts of boron in natural solutions.** N. V. TAGEEVA (J. Appl. Chem. Russ., 1935, 8, 528—535).—Thomson's method (J.S.C.I., 1896, 12, 432) serves for the determination of  $\pm 2$  mg. of  $B_2O_3$  (error 0—3%), and Foote's method (A., 1932, 242) of  $\pm 0.7$  mg. (error 1—3%). B may be determined in presence of interfering substances by evaporating the solution (containing 1—15 mg. of  $B_2O_3$ ) to dryness, and distilling the residue with 10 ml. of MeOH and 5 drops of conc.  $H_2SO_4$  (to evolution of  $SO_3$ ). The distillate is hydrolysed with NaOH, the solution evaporated to dryness, the residue dissolved in  $H_2O$ , the solution made acid with HCl, boiled, and  $B_2O_3$  is determined by Foote's method. The error is  $\pm 1.4\%$ . R. T.

**Volumetric determination of boron nitride.** B. ORMONT and A. SAMOILOW (Z. anal. Chem., 1935, 102, 20—24).—0.05—0.1 g. of the BN together with 5—6 times its wt. of KOH are heated at  $250^\circ$  in a porcelain crucible held in a test-tube through which a stream of pure  $H_2$  can be passed. The  $NH_3$  formed is collected in excess of HCl, which is titrated. S. J. G.

**Determination of carbon dioxide in air.**—See B., 1935, 671.

**Direct and indirect determination of cyanates with adsorption indicators.** B. RIPAN-TILICI (Z. anal. Chem., 1935, 102, 32—34).—(a) Direct: 25 c.c. of the approx. 0.01M-CNO' solution are titrated with M-AgNO<sub>3</sub> in presence of 4—5 drops of 0.2% fluorescein solution as adsorption indicator, until a marked red colour appears. 1% accuracy is attainable. (b) Indirect: To the KCNO solution, excess of 0.2M-AgNO<sub>3</sub> is added, and the whole diluted to 50 c.c. After filtration the excess of AgNO<sub>3</sub> is pptd. with excess of 0.4M-KCNS and the excess of the latter titrated with AgNO<sub>3</sub>, using fluorescein as indicator. S. J. G.

**Fractional detection of potassium.** C. N. POTSCHINOK (J. Appl. Chem. Russ., 1935, 8, 524—527).—0.5 ml. of aq.  $CH_2O$  is added to 1 ml. of solution, and 2N-Na<sub>2</sub>CO<sub>3</sub> is added to the appearance of a red coloration with phenolphthalein; the solution is filtered, the filtrate is decolorised with AcOH, and a few drops of aq. Na<sub>3</sub>Co(NO<sub>2</sub>)<sub>6</sub> are added, when a ppt. is obtained in presence of  $\leq 0.6$  mg. of K. Other cations do not interfere. R. T.

**Colorimetric determination of potassium according to Lebermann.** H. RIEHM (Z. Pflanz. Dng., 1935, 39, 309—314).—Modifications of the original method (colorimetric comparison of the solution of cobaltinitrite in HCl) are described and a new process for the prep. of the standard tint is given. 0.03—2.0 mg. of K may be determined with 10% accuracy. A. G. P.

**Determination of small amounts of potassium by means of sodium cobaltinitrite.** H. W. LOHSE (Ind. Eng. Chem. [Anal.], 1935, 7, 272—273).—The composition of the ppt. varies between  $KNa_2[Co(NO_2)_6]$  and  $K_2Na[Co(NO_2)_6]$ , according to the conditions of pptn. E. S. H.

**Drop reaction for caesium and its use in drop colorimetry.** E. S. BURKSER and M. L. KUTSCH-

MENT (Mikrochem., 1935, 18, 18—21).—The solution under test (1 drop) is placed on a filter-paper impregnated with a solution of AuBr<sub>3</sub> and PtBr<sub>3</sub> containing 3% Au and 1.5% Pt; a black spot due to Cs<sub>2</sub>Au<sub>2</sub>PtBr<sub>12</sub> forms in the presence of  $0.25 \times 10^{-6}$  g. of Cs per cu. mm. K, NH<sub>4</sub>, Na, and Li give no reaction and Rb gives a similar reaction only when the Cs solution contains  $> 2\%$  Rb. A. R. P.

**Application of a drop reaction to determination of traces of silver in galenites and in Příbram flotational concentrates.** R. JIRKOVSKÝ (Chem. Listy, 1935, 29, 133—136).—The ignited ore is extracted with HNO<sub>3</sub>, and a drop of extract is added to a layer of collodion containing Feigl's reagent (A., 1928, 1108), when the dimensions and intensity of coloration of the spot produced are approx.  $\propto$  the Ag content. R. T.

**Test-tube method for flame testing.** A. R. CLARK (J. Chem. Educ., 1935, 12, 242—243).—New flame tests for certain of the commoner metals obtained by the test-tube method are described and compared with those obtained by using Pt wire. L. S. T.

**Volumetric micro-determination of calcium (precipitated as picrolonate) with methylene-blue.** A. BOLLIGER (Austral. J. Exp. Biol., 1935, 13, 75—78).—0.05N-Li picrolonate is added in known excess to the neutral solution, Ca picrolonate is removed after 24 hr., and excess of picrolonate in the filtrate is titrated against methylene-blue in presence of CHCl<sub>3</sub> (A., 1934, 1017). F. O. H.

**Volumetric determination of beryllium and silicon in solutions of their complex fluorides.** J. A. TSCHERNICHOV and E. J. GULDINA (Z. anal. Chem., 1935, 101, 406—413).—The neutral solution is treated with a large excess of neutral CaCl<sub>2</sub> solution which decomposes the Na<sub>2</sub>SiF<sub>6</sub> with the formation of HF, which can be titrated (Me-orange) with 0.5N-NaOH (1 c.c.=7.5 mg. of SiO<sub>2</sub>). The solution is then diluted to 250 c.c., again titrated with the same NaOH to a pale pink with phenolphthalein, heated to the b.p., and titrated to a permanent pink (1 c.c.=6.25 mg. BeO). If much Na<sub>2</sub>SiF<sub>6</sub> is present the ppt. obtained in the first step must be removed before making the second titration. A. R. P.

**Determination of magnesium as magnesium ammonium phosphate hexahydrate.** J. P. MEHLIG (J. Chem. Educ., 1935, 12, 288—290).—The determination of Mg by this method gives results which compare favourably with those obtained by the pyrophosphate method. The method is also recommended for the determination of P. L. S. T.

**Experiments with Hahn's reagent.** (A) J. ČERVINKA. (B) A. OKÁČ (Chem. Listy, 1935, 29, 35—37, 148).—(A) Mg cannot be distinguished from Ca, Sr, and Ba by means of 1:2:5:8-tetrahydroxy-anthraquinone (A., 1924, ii, 784). Zn, Al, and Fe<sup>III</sup> interfere with the development of the colour reaction. (B) Specificity was not claimed by Hahn *et al.* R. T.

**Pyrophosphate method for the determination of zinc.** Z. H. PAN and C. H. CHIANG (J. Chinese Chem. Soc., 1935, 3, 118—121).—The decomp.



$\text{ZnNH}_4\text{PO}_4 \rightarrow \text{Zn}_3\text{P}_2\text{O}_7$ , begins at  $350^\circ$  and is complete at  $520^\circ$  in 1.5 hr. R. S.

**Quinaldinic acid as a micro-reagent. III. Determination of zinc in the presence of iron, aluminium, uranium, beryllium, and titanium.** P. RAY and M. K. BOSE (Mikrochem., 1935, 18, 89—91).—The ammoniacal tartrate solution is treated with Na quinaldinate, the excess of  $\text{NH}_3$  removed by blowing air over the solution at  $60^\circ$ , the solution cooled and filtered, and the washed ppt. dried at  $125^\circ$ , and weighed as  $\text{Zn}(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_2 \cdot \text{H}_2\text{O}$ . A. R. P.

**Micro-determination of zinc with anthranilic acid.** C. CIMERMAN and P. WENGER (Mikrochem., 1935, 18, 53—55).—The method of Funk and Ditt (A., 1933, 244) is adapted to microchemical work. A. R. P.

**Determination of zinc in water by means of sodium diethyldithiocarbamate.**—See B., 1935, 752.

**Determination of lead. Removal of bismuth interference in the dithizone method.** C. E. WILLOUGHBY, E. S. WILKINS, jun., and E. O. KRAEMER (Ind. Eng. Chem. [Anal.], 1935, 7, 285—286).—Bi is separated from Pb by extracting a  $\text{HNO}_3$  solution of the metals, adjusted to  $p_H$  2.0, with a solution of dithizone in  $\text{CHCl}_3$ . Pb remains in the aq. phase, whilst Bi forms a  $\text{CHCl}_3$ -sol. org. complex. E. S. H.

**Determination of lead. Modification of the Fischer-Leopoldi method.** O. B. WINTER, H. M. ROBINSON, F. W. LAMB, and E. J. MILLER (Ind. Eng. Chem. [Anal.], 1935, 7, 265—271).—Pb is determined colorimetrically by extraction with a solution of dithizone in  $\text{CHCl}_3$ . The method is sensitive to approx. 0.001 mg. Pb in biological material. With suitable modifications the determination may be made in presence of Bi or  $\text{Sn}^{II}$ , which normally interfere. E. S. H.

**Determination of lead in drinking water.**—See B., 1935, 752.

**Iodometric determination of copper.** J. BŘESKEJ (Z. anal. Chem., 1935, 102, 35—38).—The method is based on the reaction  $2\text{Cu}^{II} + 2\text{S}_2\text{O}_3^{II} + 2\text{SCN}^- = 2\text{CuSCN} + \text{S}_4\text{O}_6^{II}$ . To 10 c.c. of the approx. 0.1N solution of  $\text{Cu}^{II}$ , previously neutralised, excess of 0.1N- $\text{Na}_2\text{S}_2\text{O}_3$  is added together with 10 c.c. of 10% AcOH and 1—2 g. of NaOAc. 3 g. of KI, 10 c.c. of 10% KCNS, and 5 c.c. of starch solution are next added and the excess of  $\text{S}_2\text{O}_3^{II}$  is titrated with 0.1N-I. Any  $\text{Fe}^{II}$  must be previously oxidised with conc.  $\text{HNO}_3$ , the excess of this being removed with  $\text{CO}(\text{NH}_2)_2$ . S. J. G.

**New reagent [thiolbenzthiazole] for gravimetric determination of certain metals. I. Copper.** G. SPACU and M. KURAŠ (Z. anal. Chem., 1935, 102, 24—28).—An excess of a 5% EtOH solution of the reagent is added to a warm aq. solution of the Cu salt. After heating and shaking, the orange-yellow ppt. is washed and dried at  $110$ — $120^\circ$ , then ignited to CuO and weighed as such. The method is applicable in presence of Ni, Co, Zn, Cd, Mn, alkaline-earth and alkali metals, but Bi, Pb, Hg, Ag, Au, and Tl are quantitatively pptd. S. J. G.

**Dimercaptothiodiazole as an analytical reagent.** P. RAY and J. GUPTA (J. Indian Chem. Soc., 1935, 12, 308—317).—1:4-Dithiolthiodiazole forms coloured ppts. with most elements in the  $\text{H}_2\text{S}$  analytical group; by its use  $2 \times 10^{-8}$  g. of Cu and  $1 \times 10^{-7}$  g. of Bi can be identified. Methods for separating Cu from As, Sb, Sn, Mo, W, Fe, Zn, and all metals in or following analytical group III, and for separating Pb from As, Sb, Sn, Mo, and alkaline earths are described. E. S. H.

**Colorimetric determination of aluminium with eriochrome-cyanine. II.** F. ALTEN, B. WANDROWSKI, and E. HILLE (Angew. Chem., 1935, 48, 273—275).—A portion of the substance containing  $10$ — $100 \times 10^{-6}$  g. of Al is heated with conc.  $\text{H}_2\text{SO}_4$  to destroy org. matter and expel halides, the residue is ignited and fused with  $\text{NaKCO}_3$ , the melt dissolved in  $\text{H}_2\text{O}$ , acidified with  $\text{HNO}_3$  and treated with  $(\text{NH}_4)_2\text{MoO}_4$  mixture to ppt.  $\text{P}_2\text{O}_5$ , the Al pptd. by addition of  $\text{UO}_2(\text{OAc})_2$  and aq.  $\text{NH}_3$  (bromothymol-blue), and the ppt. extracted first with aq.  $\text{Na}_2\text{CO}_3$  then with aq. NaOH. The combined extracts are acidified with HCl, treated with 15 c.c. of 0.1% eriochrome-cyanine solution, neutralised with NaOH, and buffered to  $p_H$  6 with  $\text{NaOAc}$ — $\text{NH}_4\text{OAc}$ —AcOH mixture. The extinction coeff. is then determined as usual and the Al content read from a graph constructed from standards prepared in the same way. A. R. P.

**Volumetric determinations in strongly alkaline solutions. II. Titration of manganese with ferricyanide.** O. TOMÍČEK and J. KALNÝ (J. Amer. Chem. Soc., 1935, 57, 1209—1211; cf. this vol., 838).—The influence of glycerol, mannitol,  $(\text{CH}_2\text{OH})_2$ , and tartaric acid on the oxidation of  $\text{Mn}^{II}$  salts by  $\text{K}_3\text{Fe}(\text{CN})_6$  in presence of NaOH has been investigated. Using tartaric acid,  $\text{Mn}^{II}$  can be determined by potentiometric titration by this method in presence of  $\text{Cu}^{II}$ ,  $\text{Zn}^{II}$ ,  $\text{Ni}^{II}$ ,  $\text{Co}^{II}$ ,  $\text{As}^{III}$ ,  $\text{As}^V$ ,  $\text{Sb}^V$ ,  $\text{Fe}^{III}$ ,  $\text{Al}^{III}$ ,  $\text{PO}_4^{III}$ , and  $\text{MoO}_4^{II}$ . E. S. H.

**Volumetric determination of manganese by induced oxidation of  $\text{Mn}^{II}$  salts to  $\text{Mn}^{III}$  metaphosphoric acid [complex].** R. LANG (Z. anal. Chem., 1935, 102, 8—16).—The chloride-free  $\text{Mn}^{II}$  solution containing definite quantities of  $\text{H}_2\text{SO}_4$  or of NO-free  $\text{HNO}_3$  is treated with sufficient dil.  $\text{HPO}_3$ . 3 drops of  $\text{NHPh}_2$  indicator (1% solution in syrupy  $\text{H}_3\text{PO}_4$ ) are added, then excess of  $\text{K}_2\text{Cr}_2\text{O}_7$ , followed by excess of arsenite solution. The Mn, now in the  $\text{Mn}^{III}$  condition, is titrated with 0.1N- $\text{FeSO}_4$  until the solution becomes grass-green. Small quantities of NaCl, of Mg, Ca, Al, Ni, Co, Pb, Cu, and Ti do not interfere. In presence of Fe special precautions are necessary as to concns. S. J. G.

**Spectral analysis as accessory in material testing and production.** W. GERLACH (Z. tech. Physik, 1934, 15, 451—453; Chem. Zentr., 1935, i, 1273—1274).—Spectral analysis using the interrupted arc is recommended for the detection and determination of impurities, and their distribution, in metals, and for the rapid approx. determination of minor constituents in rocks. The distribution of Fe in Au-Ag alloys is irregular, points of high [Fe] being also low in Ag. J. S. A.



**Cerimetric titration of small amounts of iron by means of 2 : 2'-dipyridyl as indicator.** C. J. VAN NIEUWENBURG and (Miss) H. B. BLUMENDAL (*Mikrochem.*, 1935, 18, 39—42).—The HCl solution is reduced by passing it through a Ag sponge reductor and titrated with 0.002—0.015*N*-Ce(SO<sub>4</sub>)<sub>2</sub> using as indicator a 0.25% solution of 2 : 2'-dipyridyl in 1 : 1 aq. NH<sub>3</sub>. A. R. P.

**Use of indigo-carmin in micro-volumetric analysis.** I. M. KORENMAN (*Mikrochem.*, 1935, 18, 31—38).—In Na<sub>2</sub>CO<sub>3</sub> solution 0.001*N*-indigo-carmin (I) can be used for the titration of Fe(CN)<sub>6</sub><sup>'''</sup> and in H<sub>2</sub>SO<sub>4</sub> solution for the titration of KMnO<sub>4</sub> and, indirectly, of Fe<sup>'''</sup>. (I) retains its titre for about a month if 20 c.c. of 1 : 5 H<sub>2</sub>SO<sub>4</sub> per litre are added. A. R. P.

**Detection of ferricyanides in the presence of ferrocyanides.** I. M. KORENMAN (*Z. anal. Chem.*, 1935, 101, 417—419).—The method depends on the power of Fe(CN)<sub>6</sub><sup>'''</sup> to bleach the blue colour of indigo-carmin solution in the presence of Na<sub>2</sub>CO<sub>3</sub>; sensitivity 1 in 6 × 10<sup>5</sup>. MnO<sub>4</sub><sup>'</sup>, OCl<sup>'</sup>, OBr<sup>'</sup>, and H<sub>2</sub>O<sub>2</sub> interfere by giving similar reactions. A. R. P.

**Detection of cobalt in presence of other cations.** R. V. VORONTZOV (*J. Appl. Chem. Russ.*, 1935, 8, 555—556).—The solution is made acid with HCl, excess of NH<sub>4</sub>CNS is added, the solution is decolorised with SnCl<sub>2</sub>, C<sub>5</sub>H<sub>11</sub>OH in COMe<sub>2</sub> is added, and the mixture is shaken. A blue coloration of the alcohol layer indicates Co. R. T.

**Determination of chromium.** I. Volumetric and colorimetric micro-determination of hexavalent chromium. D. BRARD (*Ann. Chim. Analyt.*, 1935, [iii], 17, 201—207).—Quantities of Cr > 0.2 mg. can be determined by addition of slight excess of titred FeSO<sub>4</sub> solution, and titrating the excess with 0.005*N*-KMnO<sub>4</sub>. For colorimetric determination of > 0.001 mg. Cr, the solution is treated with H<sub>3</sub>PO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> and then with a 2% EtOH solution of diphenylcarbazine, the rose-violet colour being compared with standards. J. W. S.

**Potentiometric determination of molybdenum in ores and rocks.**—See B., 1935, 677.

**Potentiometric determination of molybdenum and titanium in steel, ferro-alloys, slags, and ores in presence of iron and other metals.**—See B., 1935, 677.

**Rapid determination of polonium in a natural radio-lead by direct measurement of α-rays and Ra.** (Mlle.) M. LEBLANC (*J. Chim. phys.*, 1935, 32, 332—341).—Po was incorporated with PbCl<sub>2</sub> and PbCO<sub>3</sub> and subsequently extracted and determined by the Ag-plate and ionisation chamber method. PbCl<sub>2</sub> afforded results deviating widely from the mean which, however, agreed with the calc. val., but PbCO<sub>3</sub> afforded concordant results disagreeing with the calc. val. In presence of Ra, the Po was determined as above, and the Ra content was deduced from the emanation accumulated in a definite time after separating the Ra with Ba from the Pb. The activity due to Po in the chlorides and carbonates of natural Ra-leads is approx. equal to the total activity, compared with that of UO<sub>3</sub>, of the material collected

in a thick layer from suspension, diminished by the activity due to the Ra, providing no emanation is lost. The nitrates give anomalous results.

J. G. A. G.

**Centigram (semi-micro-)analysis of inorganic substances.** I. General considerations. T. MIŁOBĘDZKI. II. Brass. III. Dolomite. W. JANCAK (*Rocz. Chem.*, 1935, 15, 294—297, 298—303, 304—310).—I. Introductory.

II. Sn, Pb, Cu, and Zn are determined in brass by the centigram and decigram methods; the results are of the same order of accuracy, but the former procedure involves an economy of > 50% in time, and of 90% in reagents.

III. Centigram analysis of dolomite for Fe, Ca, Mg, CO<sub>2</sub>, and insol. residue requires 9—10 hr., as compared with 15 hr. for the decigram procedure. R. T.

**Precipitation of titanium as phosphate.** CHENG DA-TCHANG and L. HOANG (*Compt. rend.*, 1935, 200, 2173—2175, and *J. Chinese Chem. Soc.*, 1935, 3, 115—117).—Pptn. of Ti as phosphate is complete in presence of > 10% of HCl, and with excess of (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>. The factor for determining TiO<sub>2</sub> from the wt. of phosphate is 0.5234. Previous conclusions as to the formula are criticised (cf. A., 1922, ii, 91).

H. J. E.

**Detection of small quantities of germanium with a drop reaction.** A. S. KOMAROVSKY and N. S. POLUEKTOV (*Mikrochem.*, 1935, 18, 66—73).—The alkaline solution of GeO<sub>2</sub> is evaporated to dryness with H<sub>2</sub>O<sub>2</sub> and the residue distilled with KMnO<sub>4</sub> and 3.5—4*N*-HCl. The distillate is mixed with NH<sub>4</sub>OAc and a few drops are placed on a piece of filter-paper, which is then heated with a drop of a 7.5% solution of (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub> in 1 : 1 HNO<sub>3</sub> and a drop of 0.1% aq. benzidine acetate. A blue colour is perceptible with > 0.25 × 10<sup>-6</sup> g. of GeO<sub>2</sub> in 0.025 c.c. Procedures are given for the detection of Ge in ores and Zn electrolytes. A. R. P.

**Reactions for germanic and boric acids.** N. S. POLUEKTOV (*Mikrochem.*, 1935, 18, 48—52).—H<sub>4</sub>GeO<sub>4</sub> gives similar reactions to H<sub>3</sub>BO<sub>3</sub> with mannitol, quinalizarin in conc. H<sub>2</sub>SO<sub>4</sub>, and *p*-nitrobenzenazo-chromotropic acid in conc. H<sub>2</sub>SO<sub>4</sub>, but the reactions are not so sensitive. A. R. P.

**Spectrographic determination of traces of germanium.** Application to copper and metallic iron. R. BRECKPOT (*Ann. Soc. Sci. Bruxelles*, 1935, 55, B, 160—173).—The extraction and determination of Ge by the spectrographic method of Geilmann and Brünger (*A.*, 1931, 455) are discussed. The extraction of Ge by co-pptn. with Fe(OH)<sub>3</sub>, and as GeCl<sub>4</sub> by distillation, is reviewed and its application to the determination of Ge in Cu and Fe is discussed.

W. R. A.

**Gravimetric determination of vanadium by means of ammonium benzoate.** F. M. SCHEMJAKIN and V. F. TSCHAPIGIN (*J. Appl. Chem. Russ.*, 1935, 8, 536—542).—10 ml. of 2*N*-HCl are added to 25 ml. of solution containing > 0.1—0.15 g. of V<sub>2</sub>O<sub>5</sub>, aq. (NH<sub>4</sub>)<sub>2</sub>SO<sub>3</sub> is added to the boiling solution to complete reduction of V<sup>v</sup> to V<sup>iv</sup>, which is pptd. by adding excess (< 1 g.) of NH<sub>4</sub>OBz, boiling for 1 min., and filtering after 3 hr. The ppt. is washed



with aq. 0.37% BzOH, ignited, and weighed as  $V_2O_5$ . Fe and Cr should be absent; Mg, Al, Cu, Mo, W, and Ti do not interfere. R. T.

**Spectrographic determination of traces of bismuth, arsenic, antimony, tin, and lead in electrolytic copper.** R. BRECKPOT (Ann. Soc. Sci. Bruxelles, 1935, 55, B, 173—194).—Bi, As, Sb, Sn, or Pb present to  $10^{-5}$  or  $10^{-6}\%$  can be determined. The occlusion of Cu by  $Fe(OH)_3$  is influenced by the  $[NH_3]$  and  $[NH_4Cl]$ . The impurities are also occluded and methods of determining them in absence of Cu and in presence of Cu are outlined. W. R. A.

**Bismuth-characterising groups.** J. V. DUBSKÝ, A. OKÁČ, and J. TRTÍLEK (Mikrochem., 1935, 17, 332—343; cf. A., 1934, 377).—Bi salts give a yellow colour with thiocarbamides (I) and an orange-yellow or red cryst. ppt. with compounds containing the groups  $\cdot NH \cdot CS \cdot S \cdot C(SH) \cdot N \cdot$  or  $\cdot NH \cdot CS \cdot NR \cdot C(SH) \cdot N \cdot$  (II), attributed to the formation of a six-membered ring in which Bi is linked to two S. 24 reagents have been examined and their behaviour is accounted for on this basis. Microchemical tests with (I) and (II) are described and the influence of other ions is discussed. R. S.

**Tantalum and niobium. I. Analysis of mixtures of the pentoxides.** K. R. KRISHNASWAMI and D. S. MURTHI (J. Indian Inst. Sci., 1935, 18A, 69—73).— $Nb_2O_5$  is reduced to  $Nb_2O_4$  on heating at  $800$ — $1000^\circ$  in  $H_2$  for 1 hr.; the product is oxidised back to  $Nb_2O_5$  at  $600^\circ$  in air. Since  $Ta_2O_5$  remains unchanged the method can be used for determining  $Nb_2O_5$  in mechanical mixtures of the two oxides. No tests were made on co-pptd. mixtures. A. R. P.

**Microchemical determination of gold in presence of palladium and tin.** J. DONAU (Mikrochem., 1935, 18, 11—17).—The alloy is inquarted with Zn—Cd eutectic in a small glass tube in a current of  $H_2$  and the bead is parted first in 0.5 c.c. of 1:1  $HNO_3$  and then in 0.5 c.c. of conc.  $HNO_3$ . In presence of much Pd a second inquartation and parting are necessary and in presence of Sn the  $Au + SnO_2$  are collected by centrifuging and the  $SnO_2$  is volatilised by heating with  $NH_4Cl$ . A. R. P.

**Micro-determination of gold and silver in alloys.**—See B., 1935, 678.

**Highly sensitive reaction of indole and pyrrole [with gold].**—See this vol., 998.

**Detection and determination of gold in solutions.**—See B., 1935, 729.

**Microscopical identification of the elements of the platinum group and gold.** W. F. WHITMORE and H. SCHNEIDER (Mikrochem., 1935, 17, 279—319).—The microscopical behaviour of Ru, Rh, Pd, Os, Ir, Pt, and Au with various reagents has been investigated. The most characteristic test reagents are: for Ru,  $NEt_4Br$  and  $NH_2Me \cdot HCl$ ; for Pd, dimethylglyoxime and caffeine; for Ir,  $NH_2Me \cdot HCl$ ; for Pt,  $m\text{-}C_6H_4Me \cdot NH_2 \cdot HCl$ ,  $m\text{-}C_6H_4(NH_2)_2$ , and  $NH_4Et_3 \cdot HCl$ ; for Au, caffeine. Qual. analysis is effected by extraction of Au with  $EtOAc$  and distillation of Os, the remainder being detected by the sp. tests. R. S.

**Assay and analysis of metals of the platinum group.** W. SAVELSBERG and A. FISCHER (Metall u. Erz., 1934, 31, 451—456; Chem. Zentr., 1935, i, 935).—Sources of error in the assay of Pt metals are discussed. Fusion is effected in a fireclay or graphite crucible, Fe filings being added. The Pb regulus is re-fused with  $Na_2CO_3 +$  borax to remove Ni, which prevents complete removal of Pb during cupellation. The addition of 10—15-fold amount of Ag is advantageous. J. S. A.

**Spectro-analytically detected elements adsorbed on ferromagnetic colloidal  $\gamma$ -ferric oxide as biological indicators.**—See this vol., 1182.

**Liquefaction of hydrogen by the expansion method.** F. SIMON, A. H. COOKE, and H. PEARSON (Proc. Physical Soc., 1935, 47, 678—683).—Conditions for the satisfactory application of the expansion method to  $H_2$  are examined. N. M. B.

**Oxygen liquefier.** C. R. MARSH and C. T. KNIPP (Rev. Sci. Instr., 1935, [ii], 6, 203—204).—Gaseous  $O_2$  circulates around a tube containing liquid air boiling at atm. pressure. C. W. G.

**Apparatus for the thermal decomposition of small quantities of materials in an inert atmosphere.** R. A. SMITH (Mikrochem., 1935, 18, 98—99).—A one-piece glass apparatus for the pyrolysis of small amounts of org. compounds in an inert atm. is illustrated. A. R. P.

**Electric micro-muffle.** C. J. RODDEN (Mikrochem., 1935, 18, 97).—The wire gauze on the horizontal tube of a Pregl micro-muffle is replaced by an electric heater made by winding 18-gauge nichrome wire around a porcelain form 9 cm. long and covering the wire with asbestos paper for insulation. The heater is connected in series with a 660-watt heater of the sun-bowl type to act as a resistance and operated with 110 volts a.c. A. R. P.

**Modified boiling vessel for micro-ebullioscopic mol. wt. determinations by Pregl's method.** A. REŽEK (Mikrochem., 1935, 18, 109—111).—The vessel is broadened slightly at one side, from just below the meniscus of the solvent, to permit easier introduction of the pastille of solute. A. R. P.

**Production of temperatures below  $1^\circ$  abs. by adiabatic demagnetisation of gadolinium sulphate.** W. F. GIAUQUE and D. P. MACDOUGALL (J. Amer. Chem. Soc., 1935, 57, 1175—1185).—Apparatus and procedure are described. Starting at  $1.29^\circ$  abs., using a field of about 8000 gauss, the lowest temp. reached was  $0.242 \pm 0.0003^\circ$  abs. Tables showing the change of temp., differential susceptibility, energy and heat content accompanying adiabatic magnetisation from temp. below  $1^\circ$  abs. are given. E. S. H.

**Simplified mixture calorimeter.** H. S. VAN KLOOSTER (J. Chem. Educ., 1935, 12, 285—286).—In the apparatus described only 25 c.c. of acid and base are used. Heats of mixing  $H_2O$  and alcohols, and heats of gelation for rapidly forming gels can also be determined. L. S. T.

**Micro-burner.** V. T. JACKSON (J. Chem. Educ., 1935, 12, 216).—A method of converting a Bunsen



burner into a micro-burner giving a hot non-luminous flame which can be varied in height from a few mm. to approx. 3 cm. is described. L. S. T.

**Determination of ultra-violet absorption.** R. FABRE and L. AMY (*J. Pharm. Chim.*, 1935, [viii], 22, 1—15).—The method involves the use of a variable no. of quartz laminations to cut out the spectrum of the solvent for both qual. and quant. work. H. G. R.

**Adjustment of Lovibond red glasses.** R. S. ESTEY (*Oil and Soap*, 1935, 12, 135—138).—The methods used in the Electrical Testing Laboratories are described. Lovibond red glasses can be lightened by re-polishing the coloured surface so as to adjust them (for use with 35 yellow) to exact integral vals. on the Priest-Gibson *N''* grading scale. E. L.

**Apparatus for microscopical work at low temperatures.** S. ERK (*Physikal. Z.*, 1935, 36, 451—452).—The formation of dew etc. on a microscope objective is prevented by placing the lower part of the microscope surrounded by a cooling jacket in a Dewar vessel containing evaporating liquefied gases. Observations can be made down to  $-120^{\circ}$ . A. J. M.

**Simple filters for isolating lines in the mercury spectrum.** A. J. MADDOCK (*J. Sci. Instr.*, 1935, 12, 218—219).—Compositions of solutions, mainly inorg., are given. C. W. G.

**Standard conditions for precise prism refractometry.** L. W. TILTON (*J. Res. Nat. Bur. Stand.*, 1935, 14, 393—418).—The precision necessary in the control and measurement of the temp., pressure, humidity, and  $\text{CO}_2$  content of air used as a standard reference medium for accurate measurements of  $n$  is discussed, and expressions and tables for the reduction of observed vals. of  $n$  to standard conditions of reference are given. The range of temp. effects on the abs. val. of  $n$  and the range of pressure effects on liquids are indicated, an empirical relation between  $n$  and  $d$  for elastically deformed glass is derived, and the character of annealing and permissible degree of striation of glasses are considered. By suitable corrections it is possible to determine the  $n$  of a liquid to  $\pm 3 \times 10^{-6}$  by the classical method of min. deviation. A. R. P.

**Precision actinometer for the ultra-violet region (including an exact test of the Einstein equivalence law).** L. HARRIS and J. KAMINSKY (*J. Amer. Chem. Soc.*, 1935, 57, 1154—1159).—The Einstein equivalence law holds for the photolysis of malachite-green leucocyanide with an accuracy of 2.5% in abs. val. An actinometer using this solution is suitable for measuring very small light energies. E. S. H.

**Photo-electric colorimeter.** J. H. YOE and T. B. CRUMPLER (*Ind. Eng. Chem. [Anal.]*, 1935, 7, 281—284).—Apparatus and technique are described. Results are given for the determination of Cu in  $\text{Cu}(\text{NH}_3)_4\text{SO}_4$ . E. S. H.

**Photo-electric colorimetry in micro-analysis. Photo-electric methods in macro- and micro-analysis.** R. H. MÜLLER (*Ind. Eng. Chem. [Anal.]*, 1935, 7, 223—226).—Apparatus, technique, and applications are described. E. S. H.

**Photo-electric photometers for use in colorimetry.** C. ZINZADZE (*Ind. Eng. Chem. [Anal.]*, 1935, 7, 280—281).—Two instruments of the two-cell form are described. E. S. H.

**Colorimeter.** J. WOUDE (*Proc. K. Akad. Wetensch. Amsterdam*, 1935, 38, 585—589).—The colour of a reflecting surface, transparent medium, or coloured light is determined directly in trichromatic units by means of a visual spectrophotometer fitted with an automatic calculating device. D. R. D.

**Determination of the indices of refraction of liquids.** J. L. SHELDON (*J. Chem. Educ.*, 1935, 12, 183—186).—The method involves the use of a thin, plano-focus, meniscus lens, and a cover slip. Results showing the accuracy attained are given. L. S. T.

**Current lead-in for vacuum vessels.** H. HANDEK (*Z. tech. Physik*, 1934, 15, 494—496; *Chem. Zentr.*, 1935, i, 1282).—Ceramic materials are described with linear expansion coeffs.  $2.5\text{--}9 \times 10^6$  which give gas- and water-tight seals with glazes. Using glass as an intermediate, massive metal seals may be made into ceramic vessels. Examples are given. H. J. E.

**Sensitive a.c. vacuum-tube relay.** E. L. ELLIS (*Science*, 1935, 81, 568—569).—A relay suitable for temp. control is described. L. S. T.

**Simple cell for glass electrode work.** J. H. HIGHBERGER and F. D. THAYER (*J. Amer. Leather Chem. Assoc.*, 1935, 30, 339—341).—The glass electrode bulb is mounted in a rubber stopper fitting into a glass tube of slightly larger diameter, provided with a side arm for filling and at its lower end with a three-way tap so arranged that the cell may be emptied or connected through a short KCl-agar tube with a  $\text{Hg}_2\text{Cl}_2$  half cell. D. W.

**Syringe hydrogen electrode.** W. HERMANOWICZ (*Rocz. Chem.*, 1935, 15, 290—293).—A H electrode requiring  $> 0.2$  c.c. of solution is described; the potential becomes const. after 5 min. in buffered, and after 35—45 min. in unbuffered, solutions. The electrode is suitable for  $p_{\text{H}}$  measurements of biological fluids containing  $\text{CO}_2$ . R. T.

**Increasing the accuracy of electrolytic conductance measurements made with student-type equipment.** L. NUTTING (*J. Chem. Educ.*, 1935, 12, 286—288).—A vac.-tube oscillator and amplifier, replacing the usual microphone hammer and headphones, are described. L. S. T.

**Micropolarographic tests. I. Apparatus and technique.** V. MAJER (*Mikrochem.*, 1935, 18, 74—88).—Apparatus for carrying out polarographic tests in air or  $\text{H}_2$ , using  $> 0.005$  c.c. of solution, is described and illustrated. A. R. P.

**Sensitive method of measuring the e.m.f. of high-resistance [galvanic] elements.** F. MÜLLER and W. DÜRICHEN (*Z. physikal. Chem.*, 1935, 173, 349—352; cf. A., 1932, 814, 999).—The anode current of an electrometer tube is controlled by the unknown e.m.f., and is split into pulsating d.c. by means of a leaf contact-breaker, and suitably amplified. T. G. P.

**Cæsium photo-electric cells.**—See B., 1935, 681.



**Arrangement for demonstrating and studying the Zeeman effect.** P. KIRKPATRICK (Rev. Sci. Instr., 1935, [ii], 6, 205).—Transverse and longitudinal beams are obtained from a capillary discharge tube mounted between the poles of a magnet.

C. W. G.

**Improvements in microchemical laboratory technique.** H. K. ALBER (Mikrochem., 1935, 18, 92–96).—A modified frame, forceps, and wash-bottle for working with the Emich filter-stick, a sharpening block for glass knives, and an improved method of determining the ash of org. substances in the micro-muffle are described.

A. R. P.

**Micro-shaking apparatus and stirrer for micro-titrations.** K. SCHWARZ (Mikrochem., 1935, 18, 106–108).—Use is made of the magnetic system of a wireless loud speaker, a non-rusting steel wire replacing the membrane and terminating in a ring to hold the vessel to be shaken or in a stirring device.

A. R. P.

**Modification of the Bunsen burette.** E. W. BLANK (J. Chem. Educ., 1935, 12, 291).—The glass bead is replaced by a small hole in the side and near the sealed mouth of the burette.

L. S. T.

**Modified bulb pipette.** J. C. LOTZE (Science, 1935, 81, 596).

L. S. T.

**Apparatus for the quantitative recovery of dialysates.** P. LOCH (Z. anal. Chem., 1935, 101, 385–388).—To avoid the accumulation of large vols. of solution in quantitatively separating crystalloids from colloids by dialysis, the solution outside the membrane is siphoned continuously into a flask from which the solvent is distilled back through a condenser into the dialysing vessel and in which a conc. solution of the crystalloid accumulates.

A. R. P.

**Mechanically operated valve designed to withstand atmospheric pressure, for use in high-vacuum work.** J. A. CHILES (Rev. Sci. Instr., 1935, [ii], 6, 202–203).—A ground-glass float is raised by means of Hg.

C. W. G.

**Mercury-vapour pumps with low primary vacuum.** L. HENRY (Bull. Soc. chim. Belg., 1935, 44, 307–310).—A simple pump to be backed by a filter-pump is described.

C. W. G.

**Vacuum pump check valve.** R. L. MOBLEY (Ind. Eng. Chem. [Anal.], 1935, 7, 222).

E. S. H.

**Volume, shape, and roundness of quartz particles.** H. WADELL (J. Geol., 1935, 43, 250–280).—Methods for measuring these properties of sedimentary quartz particles are described.

L. S. T.

**Determination of moment of passage of vapour through a layer of sorbent by the method of gravimetric indication.** E. V. ALEXEEVSKI and Z. I. AZARCH (J. Appl. Chem. Russ., 1935, 8, 577–579).—The air, after passing through the layer of sorbent, passes through dry C in a cylinder suspended from one arm of a balance. The moment when H<sub>2</sub>O vapour ceases to be totally adsorbed is indicated by an increase in wt. of the cylinder.

R. T.

**Apparatus for measuring the drying power of the atmosphere.** J. R. BAKER (J. Sci. Instr., 1935,

12, 214–216).—Direct readings are obtained from a modified hair hygrometer.

C. W. G.

**Soldering aluminium-brass joints.** T. H. SIMS (J. Sci. Instr., 1935, 12, 233).—The Al is first tinned with special solder and the brass with ordinary solder.

C. W. G.

**Double liquid-air trap.** R. W. CONWAY (J. Sci. Instr., 1935, 12, 234).—One trap is made to serve for two circuits.

C. W. G.

**Microchemical balances.** M. FURTER (Mikrochem., 1935, 18, 1–10).—Temp. changes and other disturbing factors in making microchemical weighings are eliminated by using an all-metal balance with a glass front; the back, sides, and base are made of hard Al sheet and the remainder of brass, and the swing is damped by means of two light metal cylinders below the pans. Means for keeping the temp. const. are described.

A. R. P.

**Portable chemical balance.** H. LLOYD (J. Sci. Instr., 1935, 12, 222–224).—250 mg. can be weighed to 2% on the spring balance described.

C. W. G.

**Apparatus for micro-distillation.** L. V. REAKES, jun. (Mikrochem., 1935, 18, 100–102).—The flask is made by blowing a 1-c.c. bulb at the end of a piece of 10-mm. (outside diameter) tubing and the side-tube is connected to the condenser with a ground-glass joint; the apparatus gives good results with 0.5 c.c. of liquid.

A. R. P.

**Vacuum distillation device.** G. LODE (Chem.-Ztg., 1935, 59, 624).—Definite wts. of distillate may be collected during a vac. distillation by having the tubes in a Brühl receiver fixed and counterpoised on small balance arms.

E. H. S.

**Pressure regulator for vacuum distillation.** O. J. SCHIERHOLTZ (Ind. Eng. Chem. [Anal.], 1935, 7, 284–285).—The regulator operates on the flutter-valve principle and is actuated directly by the vac.

E. S. H.

**Fractional distillation. Analysis of organic liquids.** H. S. KING (Proc. Nova Scotian Inst. Sci., 1933–1934, 18, 272–275; cf. A., 1934, 398).—The apparatus and its use are described.

J. L. D.

**Höppler viscosimeter in connexion with the standardisation of viscosity measurements.** D. CANNEGIER (Chem. Weekblad, 1935, 32, 403–405).—The Höppler viscosimeter is described. Its accuracy is 0.1% between 10 and 600 and 0.27% between 0.01 and 10<sup>5</sup> centipoises. Its rapidity, simplicity, and universal applicability make it the ideal standard instrument for measuring  $\eta$ .

S. C.

**Micro-viscosimeter.** F. M. LIDSTONE (J.S.C.I., 1935, 54, 189–190t).—Viscosity is evaluated by timing the movement of a meniscus in a straight capillary tube. On account of the small quantity of liquid necessary the test is applicable to micro-analysis. The derivation of the equation in abs. units is given.  $\tau^2$  (instead of  $\tau^4$ ) occurs in the dimensional const., thus allowing a greater tolerance in calibration. The cause and prevention of the clogging of fine capillaries are discussed.

**Permanent aqueous microscopic mounts.** H. R. SMITH (Ind. Eng. Chem. [Anal.], 1935, 7, 286).—



The sealing composition recommended is made by heating anhyd. wool fat with  $\geq 20\%$  of rosin.

E. S. H.

**Hydrogenator.** J. O. RALLS and W. H. HAMMERSLEY (J. Chem. Educ., 1935, 12, 290—291).

L. S. T.

**Sodium press.** M. W. PARKER and C. E. WHITE (J. Chem. Educ., 1935, 12, 232).

L. S. T.

**Apparatus and method used in measuring the compressibility of gases at 0—325°.** J. A. BEATTIE (Proc. Acad. Arts Sci., 1934, 69, 389—405).

CH. ABS. (e)

**Fractional ultrafiltration. I. Preparation of collodion membranes of varying permeability.**

**II. Glass apparatus for ultrafiltration under pressure.** P. GRABAR (Bull. Soc. Chim. biol., 1935, 17, 965—990).

A. L.

**Measurement of low pressures with the elastic manometer.** L. HENRY (Bull. Soc. chim. Belg., 1935, 44, 311—314).—The sensitivity of a glass Bourdon gauge is increased by means of a valve circuit so that  $2 \mu$  can be detected.

C. W. G.

**Training in microchemistry and chemical microscopy.** A. A. BENEDETTI-PICHLER (Mikrochem., 1935, 17, 320—331).

R. S.

**Scientific contributions of Don Andrés Manuel Del Río.** M. E. WEEKS (J. Chem. Educ., 1935, 12, 161—166).—Historical.

L. S. T.

## Geochemistry.

**Mineralisation of water in the R. Sakma basin (Pugatshev province, Lower Volga region).** V. S. VASILIEV (Trans. Saratov Univ., 1934, 10, No. 3, 79—112).—Analytical data are recorded.

R. T.

**Variability of concentration of natural waters of European Russia.** F. F. SELIVANOV (J. Appl. Chem. Russ., 1935, 8, 445—470).—Variations in the content and concn. of salts in river- and spring-waters, over a no. of years, are recorded.

R. T.

**Isotopic composition of water from petroleum sources.** K. OKABE and T. TITANI (Bull. Chem. Soc. Japan, 1935, 10, 259).—Ten samples of water from petroleum sources, 30—1500 m. deep, have been analysed and  $d$  compared with standard Osaka conductivity water at 21°. The difference in  $d$  is not more than  $\pm 2 \gamma$ .

W. R. A.

**Effect of organic colloids on the behaviour of substances in natural waters.** W. OHLE (Naturwiss., 1935, 23, 480—484).—The salts present in waters containing colloidal org. matter (humus) are in part combined with the colloid, the cations being more available in acid and the anions, more particularly  $\text{PO}_4'''$ , in alkaline solution. The bearing of the existence of such associations of inorg. ions with colloids on the problems of soil and water chemistry is discussed.

W. O. K.

**Problems of radio-geology.** V. I. VERNADSKI (Bull. Acad. Sci. U.S.S.R., 1935, 1—18).—A discussion.

R. T.

**Age of the earth from the changes in its temperature and elastic properties.** B. GUTENBERG (Science, 1935, 82, 52).

L. S. T.

**Age of the earth from radioactive disintegration and related problems.** R. D. EVANS (Science, 1935, 82, 52).—A summary. The age is estimated to lie between 1850 and  $3500 \times 10^6$  years. The ages of 23 Fe meteorites, many of which are probably of extra-solar origin, are uniformly distributed between  $2800 \times 10^6$  years and nearly zero and show no tendency to group about any particular age.

L. S. T.

**Age of the earth from sedimentation.** G. D. LOUDERBACK (Science, 1935, 82, 51—52).—For the time from the Cambrian to the present, a first approximation of sp. sedimentation rates for separate di-

visions of geological history gives results of the same order of magnitude as the radioactive method.

L. S. T.

**Composition and contraction of the earth.** I. I. SASLAVSKY (Tsch. Min. Petr. Mitt., 1935, 46, 331—341).—Further discussion and repetition (A., 1931, 1389; 1932, 1107).

L. J. S.

**Quantitative spectral determination of germanium in the Brazilian meteorites from Bendego and Santa Luzia de Goyaz.** A. BETIM (Ann. Acad. Brasil. Sci. 1935, 7, 177—179).—Ge (determined by the author's method of spectral analysis; cf. A., 1934, 380) is present to the extent of 0.00272 and 0.00419% in the S. Luzia and Bendego meteorites, respectively.

E. L.

**Stages in the metamorphism of Samos emeries.** J. DE LAPPARENT (Compt. rend., 1935, 201, 154—157; cf. A., 1934, 386).—The rocks are described and their metamorphism is discussed.

H. J. E.

**Definition of sepiolites.** H. LONGCHAMON and G. MIGEON (Compt. rend., 1934, 200, 1946—1949; cf. this vol., 842).—Ampandrandava sepiolite is monoclinic pseudo-orthorhombic ( $c\ 5.32 \text{ \AA}$ ). All sepiolites are attacked completely by cold 10% HCl. Data are recorded for the changes on heating to 1000°. The general formula is  $\text{Si}_4\text{O}_{11}(\text{Mg}, \text{H}_2)_3, \text{H}_2\text{O}, (\text{H}_2\text{O})_x$ .  $(\text{H}_2\text{O})_x$  is driven off at  $< 350^\circ$ .  $\text{Si}_4\text{O}_{11}(\text{MgH}_2)_3, \text{H}_2\text{O}$  decomposes progressively at  $> 350^\circ$ .  $\text{Si}_4\text{O}_{11}(\text{MgH}_2)_3$  decomposes at  $750^\circ$ . Recrystallisation of enstatite and cristobalite occurs at  $800^\circ$  and 1100—1200°, respectively.

H. J. E.

**Origin of potash-rich rocks.** R. D. TERZAGHI (Amer. J. Sci., 1935, [v], 30, 141—142).—Further note and correction (this vol., 601).

L. J. S.

**Synthesis of magnesioferrite: observations on "mineralisation."** R. B. DRAPER (Amer. J. Sci., 1935, [v], 30, 106—115).—HCl gas was passed over  $\text{Fe}_2\text{O}_3$  and MgO in a long porcelain tube along which the temp. was graded. At 800—950°  $\text{FeCl}_3$  vapour reacts with MgO giving sharp octahedra of magnesioferrite ( $\text{MgO}, \text{Fe}_2\text{O}_3$ ). Further along the tube hæmatite is deposited as equidimensional crystals at 700° grading to scaly crystals at 500°. Excess of MgO yields a minutely cryst. aggregate of



periclase.  $\text{FeCl}_3$  vapour in the absence of  $\text{H}_2\text{O}$  and air reacts with  $\text{MgO}$ , with production of magnesioferrite and  $\text{MgCl}_2$ , at a lower temp. ( $500^\circ$ ). In these experiments  $\text{HCl}$  is acting as a "mineraliser."

L. J. S.

**Ilmenite sands on the Azov Sea.** P. G. PANTÉLEV (Min. Suir., 1934, 9, No. 10, 12—16).—The radioactive sands in some sections contain  $\text{TiO}_2$  35.02, Fe 37.32, and  $\text{V}_2\text{O}_5$  0.13%. Garnet, zircon, etc. were present in some specimens. CH. ABS. (e)

**Methods of petrographic investigation.** V. V. ARSCHINOV (Trans. Inst. Econ. Min. U.S.S.R., 1933, 287—298).—A review. CH. ABS. (e)

**Heavy minerals in Finnish rocks. III. Kakola granite.** A. LAITAKARI (Teknil. Aikakaus., 1934, 24, 399—402).—The minerals found were garnet, ilmenite, sillimanite, anatase, monazite, zircon, spinel, and smaller amounts of apatite, dumortierite, tourmaline, and andalusite.

CH. ABS. (e)

**Eastern end of the Newry igneous complex.** D. L. REYNOLDS (Quart. J. Geol. Soc., 1934, 90, 585—636).—Peridotite and biotite-pyroxenite were the earliest intrusives in the area. Analyses are given for the unaltered greywacke and shale, fused sedimentary rocks, peridotite, biotite-pyroxenite, augite-biotite-diorite, shonkinitic monzonite, hypersthene-monzonite, and granodiorite.

CH. ABS. (e)

**Thomsonised inclusion from Blackness sill.** (Sir) J. FLETT (Prog. Repts. Geol. Survey Gt. Britain, 1934, (1933), Pt. II, 85—90).—Analytical data are given for a xenolith consisting of a matrix of thomsonite containing smaller amounts of other minerals.

CH. ABS. (e)

**Isotopic composition of the leads of Great Bear Lake.** C. S. PIGGOT (J. Geol., 1934, 42, 641—645).—Pb from three pitchblende specimens and one of galena within the pitchblende vein contained the isotopes 206, 207, and 208 (in order of abundance), indicating pure U-Pb. A second galena from outside the vein had isotopes Pb 208, 207, and 206, indicating contamination of ordinary Pb by U-Pb.

CH. ABS. (e)

**Native iron from West Greenland.** (Sir) H. C. H. CARPENTER (Nature, 1935, 136, 152—153).—Native Fe from Oviqak, Disco Island, West Greenland has Fe 93.9, Ni 2.50, C 1.63, Co 0.98, Cu 0.21,  $\text{SiO}_2$  0.24%;  $\text{CO}_2$  is absent. The C is much > that found in meteoric Fe and the Ni is considerably lower. Photomicrographs of structures obtained by etching with 1%  $\text{HNO}_3$  in EtOH and with alkaline Na picrate are reproduced. The structure consists mainly of a white massive constituent, cementite (I), in a finely-divided duplex matrix, which is probably a eutectoid of ferrite and (I). The origin of the metal is discussed.

L. S. T.

**Topaz.** J. W. HOWARD (J. Chem. Educ., 1935, 12, 153—156).

L. S. T.

**Sulphated minerals of Chili.** H. UNGEMACH (Bull. Soc. Franç. Min., 1935, 58, 97—221).—The geometrical crystallography, chemical analyses, optical properties, and densities of the following minerals from Tierra Amarilla and Sierra Gorda are described:

botryogene, hohmannite, amarantite, copiapite, pseudo-copiapite, melanterite, roemerite, coquimbite, paracoquimbite, quenstedtite, amarillite, leucoglaucite, lapparentite, and chalcantite. Origin and paragenesis of the sulphates are discussed. L. S. T.

**Killarnean and earlier granite.** A. C. LANE (Science, 1934, 82, 60—61).—A discussion concerning age. L. S. T.

**Composition of lavrovite.** E. A. RATZBAUM and A. N. FILIPPOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 409—410).—The diopside lavrovite (Sludianka, L. Baikal) has been analysed spectroscopically, and contains, apart from Si, Ca, and Mg, Cr 1.5, Al 0.7, V 0.5, Fe 0.15, Mn 0.001%, and traces of Na, K, and Ti.

T. G. P.

**Minerals of Poeloe Berhala (Malacca Strait, Sumatra).** J. H. DRUIF (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 639—650).—The minerals found on this island are described. D. R. D.

**Chemical analyses of minerals from Poeloe Berhala.** W. VAN TONGEREN (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 634—639; cf. preceding abstract).

D. R. D.

**Colorado pegmatites.** K. K. LANDES (Amer. Min., 1935, 20, 319—333).—Microcline (I), white bull quartz (II), and riebeckite are the dominant minerals in the pegmatite at St. Peter's Dome, Pike's Peak region. The fluorides in order of deposition are cryolite; pachnolite, the most abundant mineral in the pegmatite after the feldspar and quartz; prosopite; and fluorite. A small amount of silicification and kaolinisation has occurred. At Florissant, white or pink (I), milky (II), some albite (III) and phenacite occur in the pegmatites. In the Arkansas River Valley pegmatites at Eight-Mile Park, feldspar [(I)+(III)] is the dominant constituent, (II) is next in abundance, and muscovite is present in amount sufficient to yield commercial mica. Beryl (IV) and subordinate tourmaline (V) also occur. Albitisation is the main feature in the paragenesis of these pegmatites. Pegmatites at other localities in this district are described. In Ohio City, Gunnison County, the main pegmatites are complex. The principal minerals are (I), (III), lepidolite, topaz (VI), and (IV). (I) and (V) are subordinate and columbite and samarskite are minor accessory minerals. (VI) and (IV) are unusually abundant.

L. S. T.

**Absorption and refraction of light by aquamarine and some yellow and green beryls.** H. KLANG (Neues Jahrb. Min., 1934, A, 69, 93—116; Chem. Zentr., 1935, i, 872).—Measurements are recorded. The absorption was always continuous, four types being observed. The coloration is attributed to  $\text{Fe}^{II}$  and  $\text{Fe}^{III}$ .

H. J. E.

**Realgar from Komana (Albania).** C. LAURO (Rend. Sem. Fac. Sci. Cagliari, 1933, 3, 147—148; Chem. Zentr., 1935, i, 872).—Five new cryst. forms are described.

H. J. E.

**New mineral from Långban (sahlinite).** G. AMINOFF (Geol. Fören. Stockholm, 1934, 56, 493—494; Chem. Zentr., 1935, i, 872).—A sulphur-yellow mineral of the formula  $12\text{PbO} \cdot \text{As}_2\text{O}_5 \cdot 2\text{PbCl}_2$  is



described. It has a very high  $\mu$ , hardness 2—3, and  $d$  7.95. H. J. E.

**Determination of direct and inverse forms in pyrites.** E. ONORATO (Rend. Sem. Fac. Sci. Cagliari, 1933, 3, 145—146; Chem. Zentr., 1935, i, 848).—X-Ray analysis of the two forms of pyrites of different thermoelectric behaviour shows both to be direct forms. H. J. E.

**Quantities of radioactive materials from radium and thorium emanations in air of Santa Fe.** F. E. URONDO (An. Soc. cient. Santa Fe, 1933, 5, 48—53; Chem. Zentr., 1935, i, 1032).—Results are given over a period of four months. J. S. A.

**Stochastic relations in argillaceous sediments.** F. E. KLINGNER (Neues Jahrb. Min., 1934, 69, A, 5—41; Chem. Zentr., 1935, i, 1031).—Stochastic=derived from theory of probability. A correlation between  $\text{CaCO}_3$  content and  $p_H$  of the suspension is derived. Rise of  $p_H$  with fall in  $\text{CaCO}_3$  indicates maritime deposits from saline waters. The method is applied to the deduction of the  $p_H$  etc. of seas of geological age. J. S. A.

**Microscopical investigation of Friedensville, Pennsylvania, zinc ore.** D. M. FRASER (Amer. Min., 1935, 20, 451—461).—The microscopical features of the primary minerals, sphalerite (I) and pyrite and some greenockite (II), the secondary minerals calamine [ $\text{Zn}_2\text{SiO}_4 \cdot \text{H}_2\text{O}$ ], and some smithsonite and (I) are described. Associated minerals in the oxidised ore are limonite, (II), quartz, calcite, dolomite, melanterite, and probably goslarite. Conditions of primary replacement are discussed. L. S. T.

**Copper ores of Orange County, Vermont.** N. W. BUERGER (Econ. Geol., 1935, 30, 434—443).—The ores from this Cu district represent a deposit of high-temp. type. The silicate minerals of the ore and wall rock are similar to those in the country rock. The most abundant are quartz, microcline, oligoclase-andesine, calcite, phlogopite, muscovite, and garnet. Pyrrhotite (I) is the principal ore mineral occurring intimately associated with chalcocopyrite (II). The Cu content  $\sim 0.3$ —20%. Pyrite was the first mineral to be deposited, followed by (I), (II), and sphalerite. Cubanite, valleriite, galena, and haematite are also present. The deposit is similar in many respects to those of Ducktown, Tennessee. L. S. T.

**Variations in optical properties with chemical composition in the monoclinic pyroxenes.** T. TOMITA (J. Shanghai Sci. Inst., II, 1934, 1, 41—58).—Data from the lit. are tabulated and plotted on triangular diagrams  $\text{CaSiO}_3$ — $\text{MgSiO}_3$ — $\text{FeSiO}_3$ . The diagrams do not apply to pyroxenes containing  $>2.5$  mol.-%  $\text{R}_2\text{O}_3$  and  $>1$  mol.-%  $\text{TiO}_2$ . L. J. S.

**Artificial transformation of feldspars into pyrophyllite.** R. SCHWARZ and G. TRAGESER (Naturwiss., 1935, 23, 512; cf. A., 1934, 42).—Pyrophyllite has been synthesised by treatment of orthoclase or anorthite with 0.5N-HCl under pressure in a steel bomb, at temp.  $>400^\circ$ . A. J. M.

**Milowite. An unusual form of silica.** J. N. WILSON (Chem. Trade J., 1935, 97, No. 2512, 28).—The composition and physical properties of milowite,

an unusually soft form of  $\text{SiO}_2$  occurring naturally in Milos, are given. It is suitable for use as an abrasive, as a filler for paints and rubber, a base for lake pigments, and a constituent of ceramic glazes.

D. R. D.

**Composition of some African granitoid rocks.** F. F. GROUT (J. Geol., 1935, 43, 281—296).—Analyses and brief petrographic notes are given for 21 large intrusives from the African Shield. They indicate that Central Africa is largely granite and is not abnormal in composition as indicated by analyses of alkalic and basic rocks near the coasts. Analyses of granites from Northern and Southern Rhodesia, the Transvaal, and the southern part of the Union of South Africa are tabulated and classified. L. S. T.

**Silver mine of Colquijirca, Peru.** W. LINDGREN (Econ. Geol., 1935, 30, 331—346).—The mineralisation is of the epithermal type and was probably effected at temp. gradually falling from  $250^\circ$  to approx.  $100^\circ$ . High-temp. minerals are absent. The shale has been replaced by chalcedonic  $\text{SiO}_2$  giving a brown chert. Other early gangue minerals are kaolin, dolomite, and ankerite. Barite is a later and abundant gangue especially in the Cu-Ag ores. Pyrite, poor in Ag, is the earliest metallic mineral and is followed by sphalerite, enargite, tennantite (I), galena, and chalcocopyrite. Bi minerals follow (I). Hypogene stromeyerite follows and with supergene native Ag is the principal mineral in the rich argentiferous ores. Argentite and chalcocite are not abundant. Analyses of wittichenite, stromeyerite, and tennantite are recorded. L. S. T.

**Structural features of gold deposits in certain intrusives of Western Quebec.** L. V. BELL and A. M. BELL (Econ. Geol., 1935, 30, 347—369).—The well-defined structural features which characterise the Au deposits in the plutonic rocks of the eastern part of the Abitibi Belt of Western Quebec are described. L. S. T.

**Influence of tertiary intrusive structural features on mineral deposits at Jamestown, Colorado.** E. N. GODDARD (Econ. Geol., 1935, 30, 370—386).—The general geology, the structure, and the mineral deposits of fluor spar, Pb-Ag, pyritic Au and Au-Te veins are described. The structural relations of the mineral deposits to tertiary intrusives are discussed. L. S. T.

**Petrography of the Roy, Harding County, New Mexico, meteorite.** R. E. S. HEINEMAN (Amer. Min., 1935, 20, 438—442).—The Roy aërolite is a cryst. chondrite; the chondrules are the chrysolite, bronzite, and porphyritic types. The ground-mass silicate is mainly chrysolite. Irregular grains of a Ni-Fe alloy of const. composition showing alteration to and replacement by oxidation products are present together with considerable troilite. The trias could not be distinguished. Analysis of the stone gives  $\text{SiO}_2$  36.95,  $\text{Al}_2\text{O}_3$  2.92,  $\text{Fe}_2\text{O}_3$  13.29,  $\text{FeO}$  12.57,  $\text{MgO}$  23.10,  $\text{CaO}$  2.50,  $\text{Na}_2\text{O}$  0.26,  $\text{K}_2\text{O}$  0.06,  $\text{TiO}_2$  0.12,  $\text{P}_2\text{O}_5$  0.31,  $\text{SO}_2$  0.69,  $\text{MnO}$  0.16,  $\text{NiO}$  1.27,  $\text{CoO}$  0.14,  $\text{CuO}$  0.10,  $\text{Cr}_2\text{O}_3$  0.43,  $\text{FeS}$  3.58, loss on ignition 1.88, total 100.33%. L. S. T.



**New Hampshire garnet deposits.** L. C. CONANT (Econ. Geol., 1935, 30, 387—399).—The associated rocks, the petrology, paragenesis, physical and chemical properties of the garnets, the deposits and their origin are described. Garnet from Wilmot, New Hampshire, has  $\text{SiO}_2$  37.35,  $\text{Al}_2\text{O}_3$  20.36,  $\text{Fe}_2\text{O}_3$  2.27,  $\text{FeO}$  31.36,  $\text{MgO}$  2.22,  $\text{CaO}$  2.55,  $\text{Na}_2\text{O} + \text{K}_2\text{O}$  1.69,  $\text{H}_2\text{O} + 0.16$ ,  $\text{H}_2\text{O} - 0.04$ ,  $\text{P}_2\text{O}_5$  0.59,  $\text{TiO}_2$  0.79,  $\text{MnO}$  1.18,  $\text{S}$  0.36,  $\text{NiO}$  0.01, and  $\text{CuO}$  0.05, total 100.98%. The garnet rock is probably the result of contact metamorphic alteration of certain Fe- and Al-rich portions of sedimentary rocks which had been previously dynamically metamorphosed. The schists have been impregnated by igneous material and the garnet has developed subsequent to the formation of the biotite and sillimanite with which, together with quartz, magnetite, and minor amounts of feldspar, zircon, and rutile, it is associated.

L. S. T.

**Tektites without figured shapes from Indo-China.** A. LACROIX (Compt. rend., 1935, 200, 2129—2132).—Specimens are described. H. J. E.

**Origin of tektites.** F. WATSON, jun. (Nature, 1935, 136, 105—106; cf. A., 1933, 1268).—Theories dealing with the origin of tektites are critically discussed. No satisfactory meteoritic theory of their origin has yet been advanced. L. S. T.

**Mourne Dyke Swarm.** S. I. TOMKEIEFF and C. E. MARSHALL (Quart. J. Geol. Soc., 1935, 91, 251—292).—The petrology of the intrusions, petrogenesis, and igneous sequence are described. The mineral compositions of basic and intermediate rocks of this region are tabulated. Chemical analyses are recorded. L. S. T.

**Charnockite series of Uganda.** A. W. GROVES (Quart. J. Geol. Soc., 1935, 91, 150—207).—Distribution, mode of occurrence, distinguishing features, and the constituent minerals, quartz, potash feldspar, plagioclase, pyroxenes, amphiboles, biotite, and garnet, are described. Chemical and micrometric analyses of the principal types are recorded. Geochemical characters are summarised and compared with the geochemistry of similar rocks from India and Ceylon. The variation diagram is discussed. Modifications due to dynamic metamorphism are described, the mineralogical changes being classified into (i) amphibolisation of pyroxenes, (ii) conversion

of hypersthene into garnet, and (iii) formation of reaction rims and kelyphitic borders. Petrogenesis and age are discussed, and a comparison with similar rocks in other parts of Africa is made.

L. S. T.

**Dispersion of the double refraction of a muscovite.** J. P. MATHIEU (Bull. Soc. Franç. Min., 1934, 57, 233—240; Chem. Zentr., 1935, i, 1194).—Vals. are recorded. H. J. E.

**Generative metamorphism of folds.** R. PERLIN (Compt. rend., 1935, 200, 1951—1952).—A discussion. H. J. E.

**Constitution of senonian phosphates from Egypt.** L. CAYEUX (Compt. rend., 1935, 200, 2134—2137).—A general description. H. J. E.

**Constitution of senonian phosphates from Palestine and Transjordan.** L. CAYEUX (Compt. rend., 1935, 200, 1893—1896).—A review and discussion of the chief characteristics of the deposits, compared with those of similar deposits in Syria. H. J. E.

**Geochemical frequency of strontium.** C. J. VAN NIEUWENBERG and R. H. DEWALD (Rec. trav. chim., 1935, 54, 633—638).—According to existing data the geochemical frequency of Ba is approx. the same as that of Sr, whereas in most other groups it falls markedly with increasing at. no. To test whether this is due to analytical underestimation of Sr, two independent methods of determining small amounts of Sr in presence of excess of Ca were worked out: (a) 1 c.c. of the solution was evaporated to dryness in a Pyrex tube with capillary end, taken up in 1 c.c. of  $\text{HNO}_3$ ,  $d$  1.40, and centrifuged until the height in the capillary tube was const. The apparatus was previously calibrated with known amounts of Ca and Sr. (b) A fulgurator was devised enabling the spark spectra of solutions of 15%  $\text{Ca}(\text{NO}_3)_2$  containing known amounts of Sr to be taken on the same plate as the unknown solution, the Sr content being evaluated by direct comparison. Samples of five different rocks were tested and the vals. for each rock by the two methods agreed well, but varied from one rock to another between 1 and 6 atoms Sr per 1000 atoms Ca. Since these are close to the accepted average val. for all rocks (3—4) it would appear that the above-mentioned anomaly is not due to analytical underestimation of the Sr content of the earth.

S. J. G.

## Organic Chemistry.

**Chlorination of propane.** I. Homogeneous reaction.—See this vol., 1082.

**Isomerisation of hydrocarbons.** I. Chlorination of isomerides of hexane and octane by means of antimony pentachloride, as a method for their determination. B. L. MOLDAVSKI and S. E. LIVSCHITZ (J. Gen. Chem. Russ., 1935, 5, 422—431).—0.25 ml. of a 5—10% solution of isoparaffin in  $n\text{-C}_6\text{H}_{14}$  or  $n\text{-C}_8\text{H}_{18}$  are diluted to 15—25 ml. with 0.5N-SbCl<sub>5</sub> in  $\text{CHCl}_3$ , and SbCl<sub>5</sub> formed is titrated after 2 hr. (in 3 ml. of solution) with 0.1N-KBrO<sub>3</sub>.

0.5 ml. of the mixture under analysis is treated similarly, when the content of isohydrocarbons is given by  $acef/bdg$ , where  $a$  and  $b$  are the vols. of 0.1N-KBrO<sub>3</sub> used for titration of the unknown and known solutions, respectively,  $c$  and  $d$  are the vols. of 0.5N-SbCl<sub>5</sub> added to the corresponding solutions,  $e$  and  $f$  are the % content (by wt.) and the no. of ml. of isohydrocarbon in the known mixture, and  $g$  is the vol. of unknown solution taken. The solutions should be completely  $\text{H}_2\text{O}$ -free. Induction of chlorination of  $n$ -paraffins is not observed under the above conditions. R. T.



**Ozone as an oxidising catalyst. VIII. Ozonation of propane and butane.** E. BRINER and J. CARCELLER (Holv. Chim. Acta, 1935, 18, 973—981).—Appreciable oxidation of a mixture of *n*- and *iso*-C<sub>4</sub>H<sub>10</sub> occurs with ozonised O<sub>2</sub> at 20°, yielding CH<sub>2</sub>O and HCO<sub>2</sub>H. At temp. up to 330° the oxidation of the mixture and of C<sub>3</sub>H<sub>8</sub> proceeds more rapidly in presence of O<sub>3</sub>. The excess of oxidation due to the O<sub>3</sub> is > the amount of O<sub>3</sub> consumed (cf. A., 1933, 680). F. R. G.

**Oxidation of unsaturated hydrocarbons by peracetic acid.** J. BÖESEKEN [with VAN ASPEREN, C. AUCHY, C. MATERS, and P. OTTENHOFF] (Rec. trav. chim., 1935, 44, 657—665).—Δ<sup>8</sup>-Heptene is much more slowly oxidised by AcO<sub>2</sub>H than are Δ<sup>7</sup>-heptene or β-methyl-Δ<sup>8</sup>-hexene, thus confirming the view that oxidation occurs most rapidly when alkyl groups are adjacent to the double linking. Diallyl is relatively slowly oxidised. The first O atom is very rapidly absorbed by isoprene in comparison with the second atom. The product of the action of O is mainly a monoacetate, reduced and hydrolysed to β-methylbutane-αβ-diol, which gives a CMe<sub>2</sub> ether, b.p. 135°, and a Hg compound with HgSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub>. β-Methyl-Δ<sup>8</sup>-butadiene yields mainly a diol monoacetate, which, after hydrolysis, is converted into γ-keto-β-hydroxy-β-methylbutane, decomposed into CHBr<sub>3</sub> and OH·CMe<sub>2</sub>·CO<sub>2</sub>H. H. W.

**Mechanism of the nitration process.** A. MICHAEL and G. H. CARLSON (J. Amer. Chem. Soc., 1935, 57, 1268—1276).—Additive compounds are not formed when C<sub>2</sub>H<sub>4</sub>, CPh<sub>2</sub>:CH<sub>2</sub> (I), Δ<sup>8</sup>-butene, and cyclohexene are treated with 98.6% HNO<sub>3</sub> (II) at -30° to 0° usually in presence of CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, or CCl<sub>4</sub>. CMe<sub>2</sub>:CHMe and (II) or abs. HNO<sub>3</sub> at -20° give *tert*-amyl nitrate [also formed from *tert*-amyl alcohol and (II)]; similarly, (II) and CMe<sub>2</sub>:CH<sub>2</sub> afford Bu<sup>o</sup>O·NO<sub>2</sub> [also obtained from Bu<sup>o</sup>OH and (II)]. (I) is polymerised by (II) at 0°; the same polymeride is also obtained from CPh<sub>2</sub>Me·OH and (II) (2 equivs.). Phenanthrene and (II) at -20° give NO<sub>2</sub>-derivatives and about 25% of an additive product (constitution not proved). The formation of nitroalkenes and nitroalkyl nitrates from alkenes (III) and HNO<sub>3</sub> (cf. Wieland *et al.*, A., 1920, i, 280; 1921, i, 782) is due to the reaction of (III) with nitrous gases formed during side reactions. Wieland's views (*loc. cit.*) on the addition of HNO<sub>3</sub> (as OH+NO<sub>2</sub>) and H<sub>2</sub>SO<sub>4</sub> (as OH+SO<sub>3</sub>H) to (III) and the mechanism of the nitration of C<sub>6</sub>H<sub>6</sub> are criticised and held to be untenable. The view (cf. A., 1896, i, 593; 1902, i, 69; 1904, ii, 164) that aromatic nitration proceeds primarily by aldolisation is revived; various data supporting this process are given. H. B.

**Influence of substituents on the additive reactivity of ethylene derivatives. II. Effects of catalysis on the relative rates of addition of bromine.** S. V. ANANTAKRISHNAN and C. K. INGOLD (J.C.S., 1935, 984—987; cf. A., 1931, 1267).—The previous results and new data are considered in relation to the catalytic effect of HBr on the addition of Br in competition experiments to CR<sub>2</sub>:CHR' (R=H, Me, Ph) and shown to be consistent with theory. F. R. G.

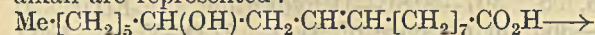
**Polymerisation of ethylene induced by methyl radicals.**—See this vol., 1084.

**Pyrogenetic reactions of condensation of hydrocarbons. II—IV.**—See this vol., 1081.

**Catalytic decomposition of alkyl bromides.** J. B. SENDERENS (Compt. rend., 1935, 200, 2137—2139).—HBr is removed from Bu<sup>o</sup>Br by ThO<sub>2</sub> at 260°, from Bu<sup>o</sup>Br by ThO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> at 280—300°, from Pr<sup>o</sup>Br by Al<sub>2</sub>O<sub>3</sub> at 250—270°, by ThO<sub>2</sub> at 235—255°, and by kaolin at 260—280°, from Pr<sup>o</sup>Br by Al<sub>2</sub>O<sub>3</sub> at 220—240° or ThO<sub>2</sub> at 180—210°, and from EtBr by ThO<sub>2</sub> at 215—230°. C<sub>4</sub>H<sub>8</sub> is obtainable only with difficulty from Bu<sup>o</sup>Br and not at all from Bu<sup>o</sup>Br owing to recombination with the HBr liberated. EtI and ThO<sub>2</sub> react at about 240° to give complex products. Bromides react only at higher temp. than do the corresponding chlorides. The catalysts do not react with the liberated acids. R. S. C.

**Analysis of mixtures of monochlorides of *n*- and *iso*-pentane.** H. B. HASS and P. WEBER (Ind. Eng. Chem. [Anal.], 1935, 7, 231—233).—The mixture of α- (I), β- (II), γ- (III), and δ-chloro-β-methylbutane (IV) obtained by the chlorination of CHMe<sub>2</sub>Et (V), is separated from polychlorides and unchanged (V) by fractional distillation. (II) is determined by aq. hydrolysis below 35°, and (III) by treatment with 0.1N-AgNO<sub>3</sub> during 60 hr. (methods: Whitmore and Johnstone, A., 1934, 168). The remaining mixture of (I) and (IV) is characterised (after redistilling) by an adaptation of Conant and Kirner's method (A., 1924, i, 273) for determination of velocity coeffs. with COMe<sub>2</sub>-KI at 60°. By fractional distillation of the chlorination products of *n*-C<sub>5</sub>H<sub>12</sub>, α-, b.p. 108.2°/760 mm., is separated quantitatively from the mixture of β- and γ-chloropentanes, analysis of which is effected by thermal examination of the resultant mixed anilides (cf. A., 1934, 753). The prep. of (I), b.p. 99.8—100°/760 mm., and (IV), b.p. 98.7—98.9°/760 mm., is described. F. N. W.

**Existence of β-epoxy-tautomerism in degradative reactions of organic compounds.** A. BARBOR (Bull. Soc. chim., 1935, [v], 2, 1438—1452).—The degradation of numerous org. compounds can be regarded from a homogeneous viewpoint if the formation of intermediate αγ-oxides is assumed. Thus the scissions of ricinoleic acid by heat and alkali are represented:



$\text{Me} \cdot [\text{CH}_2]_5 \cdot \text{CH} \begin{array}{c} \diagup \text{CH}_2 \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{CH} \cdot [\text{CH}_2]_8 \cdot \text{CO}_2\text{H}$ , with fission represented by the dotted lines. At 450°/atm.

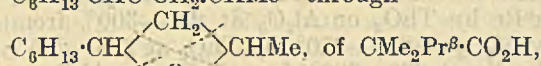
pressure,  $\text{CH}_2 \begin{array}{c} \diagup \text{CH}_2 \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{CH}_2$  gives C<sub>2</sub>H<sub>4</sub> and CH<sub>2</sub>O

and  $\text{CET}_2 \begin{array}{c} \diagup \text{CH}_2 \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{CH}_2$  affords CET<sub>2</sub>:CH<sub>2</sub> and CH<sub>2</sub>O.

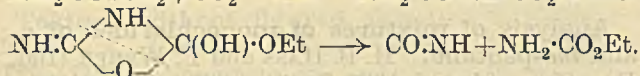
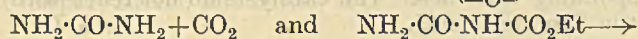
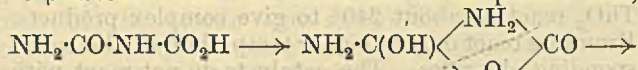
The degradation of αγ-glycols by dil. H<sub>2</sub>SO<sub>4</sub> at 130—180° is represented  $\text{OH} \cdot \text{CHR} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH} \longrightarrow$   
 $\text{CHR} \begin{array}{c} \diagup \text{CH}_2 \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{CH}_2$  [and  $\text{CH}_2 \begin{array}{c} \diagup \text{CH}_2 \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{CHR} \cdot \text{O} \cdot \text{CH}_2 \begin{array}{c} \diagup \text{CH}_2 \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{CH}_2$ ],  
whence CH<sub>2</sub>R·CH<sub>2</sub>·CHO and R·COEt; thus



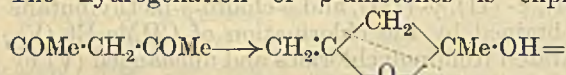
$\text{OH} \cdot [\text{CH}_2]_3 \cdot \text{OH}$  affords  $\text{EtCHO}$  when passed over pumice at  $500^\circ$  and  $\text{OH} \cdot [\text{CMe}_2]_3 \cdot \text{OH}$  gives  $\text{COMe}_2$  and  $\text{CMe}_2 \cdot \text{CMe}_2$ . The degradation of  $\beta$ -ethylenic alcohols is similarly explained. Scission in two directions as indicated by the author's hypothesis is illustrated by the decomp. of  $\text{C}_6\text{H}_{13} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2$  at  $500^\circ$  into  $\text{C}_6\text{H}_{13} \cdot \text{CH} \cdot \text{CH}_2 + \text{MeCHO}$  and  $\text{C}_6\text{H}_{13} \cdot \text{CHO} \cdot \text{CH}_2 \cdot \text{CHMe}$  through



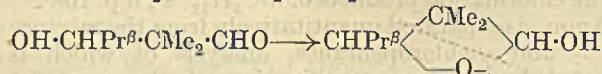
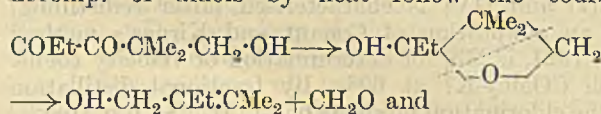
$\text{OH} \cdot \text{CHEt} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$ ,  $\text{OH} \cdot \text{CHMe} \cdot \text{CMePr} \cdot \text{CO}_2\text{H}$ ,  $\text{OH} \cdot \text{CHMe} \cdot \text{CET}_2 \cdot \text{CO}_2\text{H}$ , hexahydrosalicylic acid, and  $\text{OH} \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$ . The same considerations apply to  $\beta$ -ketonic acids and esters and to aliphatic acid,



The hydrogenation of  $\beta$ -diketones is explained,



$\text{CH}_2 \cdot \text{CO} (\longrightarrow \text{MeCHO}) + \text{CH}_2 \cdot \text{CMe} \cdot \text{OH} (\longrightarrow \text{CHMe}_2 \cdot \text{OH})$ , and a similar mechanism is involved in their fission by alkali. Scission of  $\beta$ -OH-ketones by alkali and decomp. of aldols by heat follow the courses,



$\longrightarrow \text{Pr}^\beta\text{CHO}$ . If the mol. contains several functions which can react among themselves with the formation of a  $\beta$ -epoxy-ring under conditions under which it is unstable it is shown by a series of examples that the expected products of scission are obtained.

H. W.

**Heterogeneous catalysis. IV. Dehydrogenation and hydrogenation of ethyl alcohol. V. Decomposition of formic acid.**—See this vol., 1086.

**Dehydration of ethyl alcohol by mixed catalysts.** Z. E. KOSOLAPOV (J. Gen. Chem. Russ., 1935, 5, 307—318).—Dehydration of  $\text{EtOH}$  at  $286$ — $368^\circ$  in presence of  $\text{Al}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3 \cdot \text{V}_2\text{O}_5$ ,  $-\text{CaO}$ , and  $-\text{Fe}_2\text{O}_3$  leads to production of  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{CH}_4$ ,  $\text{CH}_2\text{O}$ , and  $\text{MeCHO}$  thus:  $2\text{C}_2\text{H}_4 \leftarrow \text{CHMe} \cdot \text{CHMe} \leftarrow 2\text{EtOH} \rightarrow \text{CHMeEt} \cdot \text{OH} \rightarrow \text{MeCHO} + \text{C}_2\text{H}_6$ ;  $\text{EtOH} \rightarrow \text{CH}_4 + \text{CH}_2\text{O}$ .

R. T.

**Synthesis and constitution of a dimethylhexitol.** J. WIEMANN (Compt. rend., 1935, 200, 2021—2023; cf. this vol., 605).—Oxidation of  $\Delta^8$ -octadiene- $\delta$ -diol (cf. A., 1934, 277) gives a dimethylhexitol (I), m.p.  $161$ — $162^\circ$  (dibenzacetal, m.p.  $237$ — $238^\circ$ ;  $\text{Ac}_6$  derivative, m.p.  $108^\circ$ ). A stereochemical formula is suggested. J. L. D.

**Oils from marine animals. New group of lipins. Ether-esters of glycerol.**—See this vol., 1145.

**Preparation of mixed formals by direct acetalisation.** H. WUYTS and P. DOCQUIER (Bull. Soc. chim. Belg., 1935, 44, 297—306).— $\text{ROH}$  heated with  $\text{R}'\text{OH}$  (1 mol.) ( $\text{R}, \text{R}' = \text{alkyl}$ ),  $\text{CH}_2\text{O}$  (1 mol.), and 0.5% of  $\text{H}_2\text{SO}_4$  gives  $\text{OR} \cdot \text{CH}_2 \cdot \text{OR}'$ ,  $\text{CH}_2(\text{OR})_2$ ,  $\text{CH}_2(\text{OR}')_2$ , and  $\text{H}_2\text{O}$ . The mixed formal is separated from the other products by fractional distillation with  $\text{CS}_2$ .  $\text{OMe} \cdot \text{CH}_2 \cdot \text{OEt}$  and  $\text{OEt} \cdot \text{CH}_2 \cdot \text{OPr}^a$  were obtained in this way. The b.p. and  $d$  of these compounds, and the  $d$  and b.p. of their azeotropic mixtures with other products of the reaction, are recorded.

F. R. G.

**Constitution of benzylidene- $d$ -sorbitol. II.  $p$ -Toluenesulphonyl and anhydro-derivatives of  $d$ -sorbitol.** L. VON VARGHA (Ber., 1935, 68, [B], 1377—1384; cf. this vol., 325).—Treatment of benzylidene- $d$ -sorbitol (I) with 1 mol. of acyl chloride gives mixtures of at least 3 compounds, whereas by use of 2 mols. of  $\text{BzCl}$  a compound (II), m.p.  $172^\circ$ ,  $[\alpha]_D^{20} -10.8^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ , is smoothly obtained. This is hydrolysed by 50%  $\text{AcOH}$  to  $d$ -sorbitol  $\alpha$ -dibenzoate (III), m.p.  $141^\circ$ ,  $[\alpha]_D^{20} +1.54^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ . The possibility of acyl migration during hydrolysis is excluded, since (II) and (III) give the same dibenzylidene- $d$ -sorbitol  $\alpha$ -dibenzoate, m.p.  $208^\circ$ ,  $[\alpha]_D^{20} -1.9^\circ$  in  $\text{CHCl}_3$ , when treated with  $\text{ZnCl}_2$  and  $\text{PhCHO}$ . Further the presence of 2 primary OH in (I) is established by the ready formation of  $\alpha$ -triphenylmethylbenzylidene- $d$ -sorbitol diacetate, m.p. (indef.)  $112^\circ$ ,  $[\alpha]_D^{20} +21.3^\circ$  in  $\text{CHCl}_3$ . Since (II) and benzylidene- $d$ -sorbitol  $\alpha$ -di- $p$ -toluenesulphonate (IV), m.p.  $148^\circ$ ,  $[\alpha]_D^{20} +17.8^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ , are indifferent towards  $\text{Pb}(\text{OAc})_4$  vicinal OH are not present. (I) is therefore  $\beta\delta$ -benzylidene- $d$ -sorbitol instead of the  $\alpha\gamma$ -compound as described previously; the nomenclature of the derivatives (*loc. cit.*) requires corresponding alteration. The  $p$ - $\text{C}_6\text{H}_4\text{Me} \cdot \text{SO}_2$  groups of (IV) are readily removed by  $\text{NaOH} \cdot \text{EtOH}$ , but several anhydro-compounds appear to be produced, one of which is readily isolated as its *Et ether*, m.p.  $75^\circ$ . (IV) in  $\text{CHCl}_3$  with  $\text{NaOMe} \cdot \text{MeOH}$  affords  $\beta\delta$ -benzylidene- $\epsilon$ -anhydro- $d$ -sorbitol  $\alpha$ - $p$ -toluenesulphonate, m.p.  $137^\circ$ ,  $[\alpha]_D^{20} +4.0^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ , converted by  $\text{NaOMe} \cdot \text{MeOH}$  at  $15$ — $20^\circ$  into  $\beta\delta$ -benzylidene- $\zeta$ -methyl- $d$ -sorbitol  $\alpha$ - $p$ -toluenesulphonate, m.p.  $128^\circ$ ,  $[\alpha]_D^{20} -1.2^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ , and by 50%  $\text{AcOH}$  at  $100^\circ$  into  $\beta\epsilon$ -anhydrohexitol  $\alpha$ - $p$ -toluenesulphonate, m.p.  $146^\circ$ ,  $[\alpha]_D^{20} +3.8^\circ$  in  $\text{C}_5\text{H}_5\text{N}$  (non-cryst.  $\text{CPh}_3$  derivative,  $[\alpha]_D^{20} +16.3^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ ).

H. W.

**Polymerisation and ring-formation. XXVII. Polydecamethylene oxide.** J. W. HILL (J. Amer. Chem. Soc., 1935, 57, 1131—1132; cf. this vol., 844).—Depolymerisation of decamethylene carbonate sometimes (? when the pressure rises too high) gives much rubbery non-volatile material (I) and some  $\Delta^1$ -decen- $\alpha$ -ol (II). Hydrolysis of (I) gives a little  $\text{OH} \cdot [\text{CH}_2]_{10} \cdot \text{OH}$  and much linear polydecamethylene oxide, m.p.  $58$ — $60^\circ$ , the structure of which is proved by conversion by HI into  $\text{I} \cdot [\text{CH}_2]_{10} \cdot \text{I}$ ; the oxide is probably formed by way of (II).

R. S. C.

**$\beta$ -Chloro-derivatives of esters of oxy-acids of sulphur.** A. SPORZYŃSKI (Arch. Chem. Farm., 1935, 2, 243—247).— $\text{SOCl}_2$  and  $\text{CCl}_3 \cdot \text{CH}_2 \cdot \text{OH}$  (I) afford  $(\text{CCl}_3 \cdot \text{CH}_2 \cdot \text{O})_2\text{SO}$ , m.p.  $6$ — $7^\circ$ , b.p.  $133$ — $139^\circ/5 \text{ mm.}$



oxidised by  $\text{KMnO}_4$  in  $\text{COMe}_2$  to the sulphate,  $(\text{CCl}_3\cdot\text{CH}_2\cdot\text{O})_2\text{SO}_2$ , m.p. 118.5–119.5°, also prepared from (I) and  $\text{SO}_2\text{Cl}_2$  in  $\text{C}_5\text{H}_5\text{N}$  at 100°.  $(\text{CBr}_3\cdot\text{CH}_2\cdot\text{O})_2\text{SO}$ , m.p. 81–81.5°, is prepared analogously. R. T.

**Alkyl- and aryl-sulphinic esters.** P. CARRÉ and D. LIBERMANN (Compt. rend., 1935, 200, 2086–2089).— $\text{ClSO}_2\text{Et}$  (I) (1 mol.) (cf. A., 1934, 48, 696) in dry  $\text{Et}_2\text{O}$  (3 mols.) at 0° with  $\text{MgEtCl}$  (1.2 mols.) gives *Et ethylsulphinic acid*, b.p. 60°/18 mm. The following are prepared similarly and are stable in air (cf. A., 1931, 64): *Bu<sup>a</sup> ethylsulphinic acid*, b.p. 90–92°/13 mm.; *Et propylsulphinic acid*, b.p. 69–71°/13 mm.; *Et*, b.p. 89–91°/18 mm., and *Bu<sup>a</sup>*, b.p. 112°/13 mm., *n-butylsulphinic acid*; *Bu<sup>a</sup> n-octylsulphinic acid*, b.p. 167–172° (partial decomp.). (I) in dry  $\text{Et}_2\text{O}$  with  $\text{MgPhBr}$  affords *Et phenylsulphinic acid* which decomposes when heated, and with excess of  $\text{MgPhBr}$  gives mainly  $\text{SOPh}_2$ , but also  $\text{Ph}_2\text{S}$  and  $\text{PhCl}$ . The reaction mechanisms are discussed. J. L. D.

**Isomerides of the butadienesulphones.** H. J. BACKER and J. STRATING (Rec. trav. chim., 1935, 44, 618–621).—The isomerisation of the sulphones of  $\beta$ -alkylbutadienes in alkaline solution under the influence of ultra-violet light consists in a displacement of the double linking in the ring towards the alkyl. The isomeric sulphone of isoprene is ozonised to  $\gamma$ -keto-*n*-butylsulphonic acid (*Ba* salt). *tert*-Butylbutadiene-sulphone is isomerised to the compound,

$\text{SO}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}\cdot\text{CBu}^t$ , m.p. 96–97°, ozonised to  $\gamma$ -keto- $\delta\delta$ -dimethyl-*n*-amylsulphonic acid [*Ba* (+2H<sub>2</sub>O) salt]. H. W.

**Volumetric determination of sodium glycerophosphate: calcium glycerophosphate.** S. BABITSCH (Z. anal. Chem., 1935, 101, 398–401).—Na glycerophosphate may be determined by boiling the solution with an excess of 0.5*N*- $\text{Pb}(\text{NO}_3)_2$ , removing the pptd. Pb salt, and titrating the excess of  $\text{Pb}(\text{NO}_3)_2$  with 0.1*N*- $\text{Na}_2\text{CO}_3$  (phenolphthalein). Na cacodylate does not interfere, since it gives no ppt. with Pb salts. Ca glycerophosphate gives low results by the Pb method and low results for Ca by the oxalate- $\text{KMnO}_4$  method, indicating that part of the Ca exists as an internal complex; good results are, however, obtained acidimetrically. A. R. P.

**Dehalogenation of  $\alpha\beta$ -dibromo-acids. II. Influence of acid structure on yields of bromo-olefines.** J. K. FARRELL and G. B. BACHMAN (J. Amer. Chem. Soc., 1935, 57, 1281–1283).—The yields of  $\text{CR}'\text{R}''\text{:CBrR}'''$  from  $\text{CBrR}'\text{R}''\text{:CBrR}'''$ ,  $\text{CO}_2\text{H}$  and aq.  $\text{C}_5\text{H}_5\text{N}$  or  $\text{Na}_2\text{CO}_3$  (cf. A., 1933, 1275) vary from 0 (when  $\text{R}'=\text{R}''=\text{R}'''=\text{H}$ ) to 70–90% (when  $\text{R}'=\text{R}''$  or  $\text{R}'''=\text{Alk}$ ); when  $\text{R}'$  or  $\text{R}'''=\text{Alk}$  (variation of which has little effect), the yield is usually about 30%.  $\text{CR}'\text{R}''\text{:CBr}_2$  are similarly obtained in yields of 70–90% ( $\text{R}'=\text{R}''=\text{Alk}$  or  $\text{R}'=\text{Alk}$  and  $\text{R}''=\text{H}$ ); when  $\text{R}'=\text{R}''=\text{H}$ , the yield is 30%. The following are new:  $\alpha$ -bromo- $\gamma$ -methyl- $\Delta^a$ -butene, b.p. 99–101°;  $\beta$ -, b.p. 108–110°, and  $\gamma$ -, b.p. 110–111°, -bromo- $\Delta^a$ -pentene;  $\alpha\alpha$ -dibromo- $\beta$ -methyl- $\Delta^a$ -propene, b.p. 156–157°;  $\alpha\alpha$ -dibromo- $\gamma$ -methyl- $\Delta^a$ -butene, b.p. 159–160°;  $\alpha$ -bromo- $\Delta^a$ -isohexenoic acid, b.p. 152°/23 mm., m.p. 80.5°, converted with difficulty into  $\alpha\alpha\beta$ -tribromoiso-

hexoic acid;  $\alpha\alpha\beta$ -tribromo- $\beta$ -methylbutyric acid, decomp. 230°.  $\alpha\beta$ -Dibromo- $\alpha\beta$ -dimethylbutyric acid has m.p. 222° (corr.; decomp.) (lit. 190–191°). H. B.

**Relative mobilities of *n*-alkyl radicals from  $\text{C}_1$  to  $\text{C}_{16}$  in their chloroformates.** P. CARRÉ and H. PASSEDOUET (Compt. rend., 1935, 200, 1767–1769; cf. this vol., 606).—The decomp. temp. of  $\text{ClCO}_2\text{R}$  into  $\text{RCl}$  and  $\text{CO}_2$  in presence of quinoline ( $\text{R}=\text{n-alkyl}$ ,  $\text{C}_1\text{--C}_{16}$ ) shows an alternation effect with the no. of C in the radical for  $\text{C}>7$ . The results are compared with those for  $\text{ClSO}_2\text{R}=\text{RCl}+\text{SO}_2$ , and are discussed in terms of the mobility of the radicals. H. J. E.

**Electrolysis of nitrate-acetate mixtures.** F. FICHTER and F. METZ (Helv. Chim. Acta, 1935, 18, 1005–1007; cf. this vol., 472).—By electrolysis a solution containing  $\text{NaOAc}$  (3.7*N*),  $\text{NaNO}_3$  (1.4*N*), and  $\text{AcOH}$  (3.2*N*) with c.d. 0.130 amp. per sq. cm. at the Pt anode, 1.8 c.c. of an oil, mainly  $\text{MeNO}_3$  and  $\text{MeNO}_2$ , was obtained during the passage of 14 amp.-hr.

F. R. G.

**Action of sodium ethoxide on  $\gamma$ -halogenocrotonic esters.** R. RAMBAUD (Compt. rend., 1935, 200, 2089–2091).— $\text{CH}_2\text{Cl}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{Et}$  with  $\text{NaOEt}$  in  $\text{EtOH-Et}_2\text{O}$  or in  $\text{C}_6\text{H}_6$  gives *Et  $\gamma$ -chloro- $\beta$ -ethoxybutyrate*, b.p. 108–108.5°/20 mm., hydrolysed to  $\beta$ -ethoxy- $\gamma$ -butyrolactone, b.p. 131.5°/20 mm. Et and Me  $\gamma$ -bromocrotonate when similarly treated give *Et*, b.p. 82°/18 mm. (cf. A., 1905, i, 406), and *Me 2-ethoxycyclopropanecarboxylate*, b.p. 61–62°/16 mm., respectively, which react with Br and  $\text{KMnO}_4$ , but not with  $\text{H}_2$  or  $\text{O}_3$ . J. L. D.

**Highly unsaturated acids of the kernels of *Parinarium laurinum*.**—See this vol., 1141.

**Highly unsaturated acids in sardine oil. III. Isolation and constitution of moroctic acid,  $\text{C}_{18}\text{H}_{28}\text{O}_2$ . IV. Separation of highly unsaturated  $\text{C}_{20}$ -acids.** Y. TOYAMA and T. TSUCHIYA (Bull. Chem. Soc. Japan, 1935, 10, 232–241, 241–248; cf. this vol., 960).—III. The  $\text{C}_{18}\text{H}_{28}\text{O}_2$  acid of sardine oil called moroctic acid (I) is separated from hiragonic acid by the insolubility of the bromide of its Me ester in  $\text{C}_6\text{H}_6$ ; this was debrominated ( $\text{Zn}$ ,  $\text{EtOH}$ ,  $\text{HCl}$ ), saponified to remove unsaponifiable substance, hydrolysed ( $\text{HCl}$ ), and esterified to give *Me moroctate*,  $\text{C}_{18}\text{H}_{28}\text{O}_2$ , b.p. 208–213°/15 mm. (octabromide, m.p. 215°), ozonolysed to  $\text{EtCO}_2\text{H}$ ,  $\text{EtCHO}$ , succinic acid and semialdehyde and their Me esters,  $\text{CO}_2$ ,  $\text{AcOH}$ ,  $\text{MeCHO}$ , and  $\text{CH}_2(\text{CO}_2\text{H})_2$ . (II) with  $(\text{CNS})_2$  in  $\text{AcOH}$  gives *Me tetrathiocyanomoroctate*, obtained as its solution in  $\text{CHCl}_3$ , ozonolysis of which yields  $\text{EtCO}_2\text{H}$ ,  $\text{EtCHO}$ ,  $\text{CO}_2$ ,  $\text{AcOH}$ ,  $\text{MeCHO}$ , and an oily CNS-compound which with  $\text{Zn-EtOH-HCl}$  and subsequent hydrolysis yields  $\Delta^7$ -decadiene- $\alpha\kappa$ -dicarboxylic acid, hydrogenated to decane- $\alpha\kappa$ -dicarboxylic acid; hence (I) is  $\Delta^{7/12}$ -octadecatetraenoic acid.

IV. The Et ester fraction, b.p. > 215°/10 mm., from sardine oil was converted into Na soap and the  $\text{COMe}_2$ -sol. portion successively hydrolysed and esterified; the Me esters were fractionally distilled and the corresponding Na soaps fractionally pptd. from  $\text{COMe}_2$ . An eicosatetraenoic acid,  $\text{C}_{20}\text{H}_{32}\text{O}_2$  (octabromide, blackens 240°; Me ester, b.p. 217–220°/10 mm.), and an impure eicosapentenoic acid,  $\text{C}_{20}\text{H}_{30}\text{O}_2$  (decabromide,



blackens 240°), were obtained and the acid  $C_{20}H_{34}O_2$  may be present. F. R. G.

**Oxidation of fatty acids *in vitro*, with especial reference to that of  $\beta$ -hydroxybutyric and acetoacetic acids.** R. O. JONES and I. S. MACLEAN (Biochem. J., 1935, 29, 1690—1701).—The fatty acid is heated with  $H_2O_2$  and acid with or without  $CuSO_4$  as catalyst, and the amounts of  $H_2O_2$  and acid to be added at intervals to maintain the initial  $[H_2O_2]$  and  $[H^+]$  are determined. From the curves of  $H_2O_2$  and  $H^+$  added against time it is deduced that  $CuSO_4$  increases oxidation;  $\beta$ -hydroxybutyric acid (I) is more readily oxidised than  $CH_3Ac \cdot CO_2H$ ; lactic acid and (I) may be first oxidised to  $MeCHO$  and fatty acid. The oxidation of glucose is inhibited by Na salts of fatty acids; glucose does not favour the decomp. of fatty acids. H. D.

**Intermediate product of long life between iodine and oxalate ion.**—See this vol., 1090.

**Reaction between ethyl oxalate and ethylenediamine.** W. GAARDE (Chem. Weekblad, 1935, 32, 347—348).—When  $Et_2C_2O_4$  and  $(CH_2 \cdot NH_2)_2$  react the tendency is to form long-chain compounds and not ring systems. 2 mols. of  $Et_2C_2O_4$  and 1 mol. of  $(CH_2 \cdot NH_2)_2$  give  $Et_2$  ethylene- $\alpha\beta$ -dioxamate, m.p. 129°, and Hofmann's "ethylenoxamide," which is  $(\cdot CO \cdot NH \cdot CH_2 \cdot CH_2 \cdot NH \cdot CO \cdot CO_2Et)_2$ . By interaction of  $Et_2C_2O_4$  and  $(CH_2 \cdot NH_2)_2$  under different conditions esters or amines are formed by the successive condensation of  $\cdot CO \cdot CO \cdot$  groups (A) and  $\cdot NH \cdot CH_2 \cdot CH_2 \cdot NH \cdot$  groups (B) in long chains; the following are described: *di-esters* A : B = 4 : 3, m.p. 345°; A : B = 3 : 2, m.p. about 400°; *diamines* A : B = 1 : 2 (carbonate, m.p. 375°); A : B = 2 : 3 [carbonate, m.p. 300° (decomp.)]. S. C.

**Dehydrogenation of succinic acid by charcoal.** Model of the mode of reaction of succinodehydration. —See this vol., 940.

**Ethyl acetone-*d*-tartrate and its optical activity.** V. TSUZUKI (Bull. Chem. Soc. Japan, 1935, 10, 255—256).—Et tartrate in  $COMe_2$  heated with anhyd.  $CuSO_4$  gives  $Et_2$  d-isopropylidenedioxysuccinate, b.p. 150° (corr.)/19 mm.,  $[\alpha]_D^{25} -51.19^\circ$ . F. R. G.

**Decarboxylation of mesoxalic acid by glycer-aldehyde and methylglyoxal.** K. BALLOWITZ and R. MEIER (Z. physiol. Chem., 1935, 233, 204—208).—In presence of glyceraldehyde (I) and  $Cu^{++}$ , mesoxalic acid (II) is decarboxylated, but malonic (III) and tartronic acid (IV) are unaffected. The  $O_2$  uptake by (I) is increased by small and decreased by larger amounts of (II). (III) and (IV) produce no change in  $O_2$  uptake.  $AcCHO$  behaves similarly to (I). J. H. B.

**Condensation of  $\alpha$ -formylsuccinic esters with esters of  $\alpha$ -halogenated acids.** I. L. KNUNIANZ and M. P. GERTSCHUK (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 133—139).—Et formylsuccinate with  $CHBrEt \cdot CO_2Et$  in  $C_6H_6$ - $Et_2O$  containing  $NaOEt$  affords (cf. A., 1905, i, 563)  $Et \gamma\delta$ -oxido-*n*-hexane- $\alpha\beta\delta$ -tricarboxylate, b.p. 196°/10 mm., hydrolysed (10% HCl) to  $\delta$ -keto-*n*-hexane- $\alpha\beta$ -dicarboxylic acid, b.p. 194—197°/16 mm., which with conc.  $HNO_3$  affords  $(\cdot CH_2 \cdot CO_2H)_2$ . J. L. D.

**Absorption spectra of the metabolic acids of *Penicillium charlesii* and their relationship to the absorption of ascorbic acid.** R. W. HERBERT and E. L. HIRST (Biochem. J., 1935, 29, 1881—1886).— $\alpha$ -Ethyltetronic acid (I) has bands at 258, 233, and 258  $m\mu$  in neutral, acid, and alkaline solutions, respectively, similarly to ascorbic acid.  $\alpha$ -Acetyltetronic acid (II) has two bands at 265 and 230  $m\mu$  independent of  $p_H$ . Carlic (III), carolic (IV), carolinic, and carlosic acids have spectra similar to that of (II) which change to single-banded spectra like that of (I) on reduction. (III) and (IV) have single-banded spectra in  $EtOH$  corresponding with their dehydrated forms. The spectra of *l*- $\gamma$ -methyl- and  $\gamma$ -carboxymethyl-tetronic, ramigenic, and verticellic acids are also examined. The spectral evidence is considered to support the structures suggested by Clutterbuck (A., 1935, 327, 662, 898) for the tetronic acids. H. D.

**Ascorbic acid (vitamin-C) and hydroxytetronic acid.** F. MICHEEL and W. SCHULTE (Annalen, 1935, 519, 70—80).—Hydroxytetronic acid  $Me_2$  ether (I) heated with 0.2N-NaOH under  $H_2$  yields the corresponding 2-*Me* ether,  $O < \begin{array}{c} CO-C-OMe \\ | \\ CH_2-C-OH \end{array}$  m.p. 141°, which when ozonised and treated with  $NH_3$  gives  $(\cdot CO \cdot NH_2)_2$  and  $OH \cdot CH_2 \cdot CO_2NH_4$ . Hydroxytetronic acid with  $CH_2N_2$  gives the 3-*Me* ether,  $O < \begin{array}{c} CO-C-OH \\ | \\ CH_2-C-OMe \end{array}$  m.p. 139°, which similarly yields  $NH_2 \cdot CO \cdot CO_2NH_4$  and  $OH \cdot CH_2 \cdot CO \cdot NH_2$ . Acidic properties are therefore more pronounced in 3-OH than in 2-OH. Dimethyl-ascorbic acid, unlike (I), is readily isomerised by cold 0.1N-alkali to a product of which the mononitrobenzoate has m.p. 181°,  $[\alpha]_D +18.9^\circ$ , and, probably, the annexed structure.

F. R. G.

***l*- $\beta$ -Methylxylonic acid.** W. BOSSHARD (Helv. Chim. Acta, 1935, 18, 956—959).—3-Methyl-1 : 2-isopropylidene-*d*-glucose oxidised with  $KMnO_4$  gives *d*- $\beta$ -methyl- $\gamma\delta$ -isopropylidenexyluronic acid ( $+H_2O$ ), m.p. 63—67°,  $[\alpha]_D^{25} -67.5^\circ$  in  $H_2O$ , hydrolysed with dil.  $H_2SO_4$  and subsequently reduced ( $Na-Hg$ ) to *l*- $\beta$ -methylxylonic acid, isolated as a salt  $[Cd(C_6H_{11}O_6)_2 + CdBr_2 + 2H_2O]$ ,  $[\alpha]_D^{25} -8.43^\circ$  in  $H_2O$ . *Me d*- $\gamma\delta$ -isopropylidenexyluronate, obtained by Reichstein *et al.* (this vol., 731), when methylated with dry  $Ag_2O$  and  $MeI$  gives *Me d*- $\beta$ -methyl- $\gamma\delta$ -isopropylidenexyluronate, b.p. 151°/12 mm. F. R. G.

**Hydrolytic fission of the disulphide linking.** A. SCHÖBERL and H. ECK (Naturwiss., 1935, 23, 391).—The fission of disulphides by hydrolysis ( $RS \cdot SR + H_2O = RSH + RS \cdot OH$ ) takes place not only in alkaline but also in neutral solution. Solutions of dithiodiacetic acid and of disulphidodisuccinic acid (I) in acetate buffers and neutral solutions of their Na salts are hydrolysed when boiled. Hydrolysis of (I) also occurs even in acid solution. The decomp. of proteins containing  $\cdot S \cdot S \cdot$  by irradiation with ultra-violet light is a similar type of fission. A. J. M.

**$\beta\beta$ -Disulphopropionic acid.** H. J. BACKER and A. E. BEUTE (Rec. trav. chim., 1935, 44, 601—606).—



The prep. of  $\beta\beta$ -disulphopropionic acid ( $+2\text{H}_2\text{O}$ ), m.p.  $91-93^\circ$ , from  $\text{KHSO}_3$  and *cis*- or *trans*- $\text{SO}_3\text{H}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ ,  $\text{CH}_3\text{C}\cdot\text{CO}_2\text{H}$ , or  $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$  is described, action in the last-named case being represented  $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CO}_2\text{K} + \text{K}_2\text{SO}_3 \rightarrow \text{SO}_3\text{K}\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CO}_2\text{K} \rightarrow \text{SO}_3\text{K}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{K} \rightarrow (\text{SO}_3\text{K})_2\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{K}$ . The  $\text{K}_3$  ( $+2\text{H}_2\text{O}$ ) (crystallographic data),  $\text{Ti}_3$ , and  $\text{Ba}_3$  ( $+3\text{H}_2\text{O}$  and  $+7\text{H}_2\text{O}$ ) salts are described. During unsuccessful attempts to resolve the acid, the normal *quinine* ( $+5\text{H}_2\text{O}$ ) salt, decomp. about  $160^\circ$ , *quinine H* ( $+5\text{H}_2\text{O}$ ) salt, m.p.  $120-121^\circ$  (decomp.), *brucine H*, and *strychnine H* salts have been obtained. H. W.

$\beta\beta$ -Disulphobutyric acid. H. J. BACKER and A. E. BEUTE (Rec. trav. chim., 1935, 44, 621-626).— $\beta\beta$ -Disulphobutyric acid ( $+2\text{H}_2\text{O}$ ), m.p.  $83-84^\circ$ , obtained by the action of  $\text{NH}_4\text{HSO}_3$  on *cis*- or *trans*- $\text{CMeCl}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ ,  $\text{CMe}\cdot\text{C}\cdot\text{CO}_2\text{H}$ , or  $\text{SO}_3\text{H}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , is characterised as the  $\text{K}_3$  ( $+6\text{H}_2\text{O}$  and  $+2\text{H}_2\text{O}$ ),  $\text{Ti}_3$  ( $+2\text{H}_2\text{O}$ ),  $\text{Ba}$ , and *strychnine H* salts. Its structure is proved by its inability to afford optical antipodes and its difference from  $\alpha\beta$ -disulphobutyric acid. The  $\alpha\beta$ -dibromobutyric acids and  $(\text{NH}_4)_2\text{SO}_3$  afford  $\beta$ -sulphobutyric acid ( $\text{Ba}$  and  $\text{NH}_3\text{Ph}$ , m.p.  $162^\circ$ , salts). H. W.

Intermediate stages of aldehyde oxidation. I, II.—See this vol., 1084.

Polarographic examination of aqueous solutions of formaldehyde. F. G. JAHODA (Časopis čechoslov. Lék., 1934, 14, 225-234; Chem. Zentr., 1935, i, 1091-1092).—The mol. reduction potential of  $\text{CH}_2\text{O}$  is 1.50 volts. Reduction is an irreversible process and is facilitated by an alkaline medium.  $0.07 \times 10^{-6}$  g. of  $\text{CH}_2\text{O}$  may be determined with 10% accuracy. The method is suitable for the examination of pharmaceutical preps. which contain  $\text{EtOH}$ ,  $\text{MeOH}$ ,  $\text{MeCHO}$ ,  $\text{COMe}_2$ , or  $\text{PhCHO}$  in addition to  $\text{CH}_2\text{O}$ .

A. G. P.

Gravimetric determination and identification, by elementary analysis, of small quantities of formaldehyde at great dilutions. R. FOSSE, P. E. THOMAS, and P. DE GRAEVE (Compt. rend., 1935, 201, 105-109).— $\text{CH}_2\text{O}$  (2 mg. at a dilution of 40-200 mg. per litre) may be determined gravimetrically and identified as methylenedi- $\beta$ -naphthol (cf. this vol., 877). This is converted by boiling conc.  $\text{HCO}_2\text{H}$  into dinaphthoxanthone, the tribromide (A., 1904, i, 816) and aurichloride (A., 1905, i, 541) of which are also suitable for the identification of  $\text{CH}_2\text{O}$ . H. G. M.

Thermal reaction between chlorine and formaldehyde. R. SPENCE and W. WILD (J. Amer. Chem. Soc., 1935, 57, 1145-1146).—The production of  $\text{HCOCl}$  is considered to be small (cf. this vol., 586).

E. S. H.

Reaction between chlorine and formaldehyde. K. B. KRAUSKOPF and G. K. ROLLEFSON (J. Amer. Chem. Soc., 1935, 57, 1146).—Polemical (cf. preceding abstract).

E. S. H.

Metacetaldehyde: its preparation and influence on the rotation of ethyl tartrate. T. S. PATTERSON and G. M. HOLMES (J.C.S., 1935, 904-906).—Metacetaldehyde (improved prep.) enhances the rotation of *Et* tartrate.

F. R. G.

Constitution of the rhodinol from rose oil. J. DŒUVRE (Parfums de France, 1934, 12, 197-202; Chem. Zentr., 1935, i, 1310-1311).—The  $\text{O}_3$  method for examination of unsaturated compounds (A., 1928, 542) is modified to avoid the further oxidation of the  $\text{CH}_2\text{O}$  produced. The reaction is carried out in  $\text{AcOH}\cdot\text{EtOAc}$  at  $-15^\circ$ , excess of the Grosse-Bohle reagent is added immediately, and  $\text{CH}_2\text{O}$  is determined colorimetrically. The semicarbazone of *l*-citronellal from geranium oil contains  $> 2\%$  of the  $\alpha$ -[methylene]-form. The alcohol  $\text{C}_{10}\text{H}_{20}\text{O}$  from geranium oil is almost exclusively in the  $\beta$ -[isopropylidene]-form. The composition of rhodinol from rose oil and that from geranium oil are practically the same.

A. G. P.

Dicyclic derivatives of simple aliphatic ketones. F. E. KING (J.C.S., 1935, 982-984).—The following ketones were prepared by dry distillation of the appropriate  $\text{Pb}$  salts: *s*-di- $\Delta^1$ -cyclohexenylacetone, b.p.  $165^\circ/12$  mm. (semicarbazone, m.p.  $112^\circ$ ), *s*-di-cyclopentenylacetone, b.p.  $139^\circ/12$  mm. (semicarbazone, m.p.  $155-156^\circ$ ), *s*-di- $\beta$ -cyclopentyl *Et* ketone, b.p.  $182^\circ/15$  mm., m.p.  $25^\circ$ . cyclopentanone-2- $\beta$ -propionic acid (A., 1934, 1002) is reduced ( $\text{Zn}\cdot\text{Hg}$ , conc.  $\text{HCl}$ ) to  $\beta$ -cyclopentylpropionic acid, b.p.  $135^\circ/15$  mm., (phenylhydrazide, m.p.  $162^\circ$ ;  $\text{Pb}$  salt, cryst.).

F. R. G.

Aliphatic thioketones. I. Action of phosphorus pentasulphide on aliphatic ketones. A. E. KRETOV and J. F. KOMISSAROV (J. Gen. Chem. Russ., 1935, 5, 388-391).— $\text{P}_2\text{S}_5$  and ketones in  $\text{PhMe}$  at  $100^\circ$  yield disulphides of the general formula  $\text{CRR}'\langle\text{S}\rangle\text{CRR}'$ : with  $\text{COMe}_2$ ,  $\text{R}=\text{R}'=\text{Me}$ ; with  $\text{COMeEt}$ ,  $\text{R}=\text{Me}$ ,  $\text{R}'=\text{Et}$ , b.p.  $120-130^\circ/15$  mm. (salt with  $\text{HgCl}_2$ ), and with  $\text{COEt}_2$ ,  $\text{R}=\text{R}'=\text{Et}$ , b.p.  $135-150^\circ/9$  mm., whilst  $\text{COPr}_2$  affords  $\text{Pr}_2\text{S}_2$ , b.p.  $135-150^\circ/40$  mm., and  $\text{COBu}^2$  gives  $\text{Bu}^2\text{S}_2$  thioketone, b.p.  $105-110^\circ/10$  mm.

R. T.

Demethylation of methylsugars. K. HESS and F. NEUMANN (Ber., 1935, 68, [B], 1371-1373).— $\text{HCl}$  in any solvent with exception of the alcohols causes fission of only glucosidic  $\text{OMe}$  from methylated sugars.  $\text{HBr}$  removes all  $\text{OMe}$  groups without damaging the sugar component.  $\text{HI}$  not only demethylates but also reduces and resinifies and is therefore unsuitable for this purpose. 2:3:6-Trimethylglucose and  $\text{HBr}\cdot\text{Ac}_2\text{O}$  at  $0^\circ$  give 1- $\alpha$ -bromoglucose tetra-acetate, m.p.  $87^\circ$ ,  $[\alpha]_D^{25} + 199.3^\circ$  in  $\text{CHCl}_3$ , in good yield. Similarly, 2:3:6-trimethylglucoside 4-*p*-toluenesulphonate affords 1-bromoglucose 2:3:6-triacetate 4-*p*-toluenesulphonate, m.p.  $168^\circ$  (decomp.),  $[\alpha]_D^{25} + 137.4^\circ$  in  $\text{CHCl}_3$ ,  $+147.3^\circ$  in  $\text{C}_6\text{H}_6$ ,  $+135.6^\circ$  in  $\text{COMe}_2$ . Profound demethylation takes place with 2:3:6-trimethyl-*l*-idose, but the product contains  $\text{Br}$  resistant towards  $\text{AgOAc}\cdot\text{AcOH}$ .

H. W.

Oxidation of *d*-glucose with bromine and alkali. T. REICHSTEIN and O. NERACHER (Helv. Chim. Acta, 1935, 18, 892-896).—Contrary to Hönig and Tempas (A., 1924, i, 712) oxidation of *d*-glucose with  $\text{Ba}(\text{OBr})_2$  yields *l*-sorburonic acid (identified by its  $\text{Ca}$  salt and  $[\alpha]_D^{25} - 10.1^\circ$ ) with only a trace of *d*-ketogluconic acid.

F. R. G.



**Alkalimetric determination of glucose.** E. N. TARAN (J. Appl. Chem. Russ., 1935, 8, 562—576).—10 ml. of neutral solution, containing  $>0.1$  g. of glucose, are added to 25 ml. of 0.1N-I in KI, 30 ml. of 0.1N-NaOH are gradually added, with const. mixing, 25 ml. of 0.12N-HCl are added after 10 min., the liberated I is removed by adding sufficient 10% aq.  $\text{Na}_2\text{S}_2\text{O}_3$ , and excess of HCl is titrated with 0.1N-NaOH (thymolphthalein indicator), when % glucose =  $0.6(a-b)/v$ , where  $a$  is the total vol. of 0.1N-NaOH taken,  $b$  that of 0.12N-HCl, and  $v$  is the vol. of solution. The method requires 15—18 min., and is more accurate than those ordinarily employed (0.05% error for 0.1% solutions). R. T.

**Monomethylhexoses. I. Constitution of the supposed 4-methylglucose.** J. MUNRO and E. G. V. PERCIVAL (J.C.S., 1935, 873—875).—4-Methyl- $\beta$ -methylglucoside 2 : 3 : 6-triacetate (cf. A., 1933, 54) in  $\text{COMe}_2$  with  $\text{Me}_2\text{SO}_4$  in 30% NaOH and subsequent methylation with MeI and  $\text{Ag}_2\text{O}$  and hydrolysis yields 2 : 3 : 4 : 6-tetramethylglucopyranose, also obtained by direct methylation of 4-methylglucose (I), which is oxidised (Br,  $\text{H}_2\text{O}$ ) to 4-methyl- $\delta$ -gluconolactone,  $[\alpha]_D^{20} +54.6^\circ \rightarrow +33.9^\circ$  (const.) after 280 min., shown to be a  $\delta$ -lactone by rate of hydrolysis; this is methylated (MeI,  $\text{Ag}_2\text{O}$ ) to a lactone which with  $\text{NHPh}\cdot\text{NH}_2$  gives the phenylhydrazide of 2 : 3 : 4 : 6-tetramethylgluconic acid. Hence the structure of (I) is confirmed. F. R. G.

**Acetone derivatives of methylglycosides.** R. G. AULT, W. N. HAWORTH, and E. L. HIRST (J.C.S., 1935, 1012—1020).—2 : 3-*iso*Propylidene- $\alpha$ -methylmannopyranoside (I) with MeI and  $\text{Ag}_2\text{O}$  yields 4 : 6-dimethyl-2 : 3-*isopropylidene*- $\alpha$ -methylmannopyranoside, b.p.  $130^\circ/0.01$  mm. (bath temp.),  $[\alpha]_{D}^{20} +80.5^\circ$  in  $\text{H}_2\text{O}$ ,  $+99^\circ$  in MeOH, hydrolysed (4% HCl) to 4 : 6-dimethylmannose, a glass,  $[\alpha]_{D}^{20} +25^\circ$  in  $\text{H}_2\text{O}$  [2 : 3-*isopropylidene* derivative, b.p.  $128^\circ/0.01$  mm., m.p.  $76-77^\circ$ ,  $[\alpha]_{D}^{20} +11^\circ$  in dry MeOH,  $[\alpha]_{D}^{20} 0^\circ \rightarrow -9.5^\circ$  (equilibrium val.) in  $\text{H}_2\text{O}$ ]; this with Br- $\text{H}_2\text{O}$  gives a syrup, which when heated at  $100^\circ/0.01$  mm. yields 4 : 6-dimethyl- $\delta$ -mannolactone, m.p.  $55^\circ$ ,  $[\alpha]_{D}^{18} +145^\circ$  in EtOH,  $[\alpha]_{D}^{20} +165^\circ$  ( $\rightarrow +70^\circ$  in 150 hr.) in  $\text{H}_2\text{O}$  [amide, m.p.  $119^\circ$ ,  $[\alpha]_{D}^{18} -3^\circ$  in MeOH,  $[\alpha]_{D}^{18} +15^\circ$  in  $\text{H}_2\text{O}$ ], phenylhydrazide, m.p.  $151^\circ$ ,  $[\alpha]_{D}^{19} -3.5^\circ$  in EtOH,  $[\alpha]_{D}^{19} +14^\circ$  in  $\text{H}_2\text{O}$ ; 2 : 3-*isopropylidene* derivative, b.p.  $130^\circ/0.01$  mm. (bath temp.), m.p.  $112-113^\circ$ ,  $[\alpha]_{D}^{19} +128^\circ$  in EtOH,  $[\alpha]_{D}^{22} +121^\circ$  ( $\rightarrow +52^\circ$ ) in 50% aq. MeOH (the mutarotation in MeOH was studied in detail), methylated to 2 : 3 : 4 : 6-tetramethyl- $\delta$ -mannolactone, identified as the corresponding phenylhydrazide.

$\alpha$ -Methylmannopyranoside (II) shaken with anhyd.  $\text{CuSO}_4$  and dry  $\text{COMe}_2$  gives (I) and  $\alpha$ -methyl-2 : 3 : 4 : 6-diisopropylidenemannopyranoside (III), b.p.  $125-130^\circ/0.03$  mm. (bath temp.), m.p.  $76-77^\circ$ ,  $[\alpha]_{D}^{22} +3^\circ$  in MeOH, hydrolysed (HCl,  $\text{H}_2\text{O}$ , MeOH) to (II).  $\beta$ -Methylmannopyranoside (IV) with 1% HCl in  $\text{COMe}_2$  gives 2 : 3 : 5 : 6-diisopropylidenemannose, but with anhyd.  $\text{CuSO}_4$  and  $\text{COMe}_2$  yields  $\beta$ -methyl-2 : 3-*isopropylidene*mannopyranoside, b.p.  $145^\circ/0.03$  mm.,  $[\alpha]_{D}^{20} -80^\circ$  in MeOH,  $[\alpha]_{D}^{20} -72^\circ$  in  $\text{H}_2\text{O}$ , and  $\beta$ -methyl-2 : 3 : 4 : 6-diisopropylidenemannopyranoside,

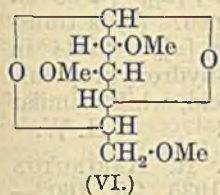
b.p.  $105^\circ/0.03$  mm., m.p.  $76-77^\circ$ ,  $[\alpha]_{D}^{20} -124^\circ$  in MeOH, both of which with HCl in aq. MeOH yield (IV).  $\alpha$ -Methylmannofuranoside (V) with anhyd.  $\text{CuSO}_4$  and  $\text{COMe}_2$  gives  $\alpha$ -methyl-2 : 3 : 5 : 6-diisopropylidenemannofuranoside (VI), b.p.  $125^\circ/0.04$  mm. (bath temp.), m.p.  $24^\circ$ ,  $[\alpha]_{D}^{21} +68^\circ$  in MeOH, hydrolysed (HCl, aq. MeOH) at room temp. to (V). (II) with  $\text{COMe}_2$  containing 5% MeOH and 1% HCl yields a mixture of (I), (III), and (VI).  $\alpha$ -Methylgalactopyranoside (VII) (improved prep.) with 1% HCl in  $\text{COMe}_2$  gives  $\alpha$ -methyl-3 : 4-*isopropylidene*galactopyranoside, b.p.  $145-150^\circ/0.02$  mm. (bath temp.), m.p.  $101-102^\circ$ ,  $[\alpha]_{D}^{20} +162^\circ$  in  $\text{H}_2\text{O}$ , hydrolysed by 0.01N-HCl to (VII) and oxidised ( $\text{KMnO}_4$ , KOH) to K  $\alpha$ -methyl-3 : 4-*isopropylidene*galacturonate.  $\beta$ -Methylfructopyranoside with 1% of HCl in  $\text{COMe}_2$  gives *isopropylidene*- $\beta$ -fructose, and with anhyd.  $\text{CuSO}_4$  and  $\text{COMe}_2$  yields *isopropylidene*- $\alpha$ -fructose, also obtained in quant. yield from ethylfructofuranoside. The structures and spatial configurations of the above *isopropylidene* derivatives are discussed. Vals. of  $n_D$  are recorded in some cases. F. R. G.

**Acetylated sugars with a free  $\alpha$ -position, and synthetic experiments with 2 : 3 : 4 : 6-tetraacetylglucose and similar compounds.** M. WEIZMANN and L. HASKELBERG (J.C.S., 1935, 1022—1024).—2 : 3 : 4 : 6-Tetraacetylglucosidyl bromide in  $\text{COMe}_2$  shaken with an aq. solution of  $\text{NaNO}_2$  yields after 24 hr. the nitrite, m.p.  $108^\circ$ ,  $[\alpha]_{D}^{20} -4.2^\circ$  in  $\text{CHCl}_3$ , but after 5 days gives glucose 2 : 3 : 4 : 6-tetraacetate (I) in 70% yield. Galactose and lactose tetraacetates were obtained by a similar reaction. (I) with  $\text{CH}_2\text{Br}\cdot\text{COBr}$  (II) in  $\text{CHCl}_3$ - $\text{C}_6\text{H}_5\text{N}$  yields glucose 2 : 3 : 4 : 6-tetraacetate 1-bromoacetate, m.p.  $127^\circ$ ,  $[\alpha]_{D}^{19} -1.17^\circ$  in  $\text{CHCl}_3$  (cf. Brauns, A., 1925, ii, 633), converted by NaI and  $\text{COMe}_2$  into the 1-iodoacetate, m.p.  $125-126^\circ$ ,  $[\alpha]_{D}^{19} -16.3^\circ$  in  $\text{CHCl}_3$ ; this with  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  in  $\text{C}_6\text{H}_6$  gives an isomeride, m.p.  $146^\circ$ ,  $[\alpha]_{D}^{19} -10.14^\circ$  in  $\text{CHCl}_3$ . Similarly diisopropylideneglucose gives diisopropylideneglucose 1-bromoacetate, m.p.  $136^\circ$ , and isopropylideneglucose 1-iodoacetate, m.p.  $74^\circ$ . *iso*Propylideneglucose yields isopropylideneglucose tribromoacetate, m.p.  $115^\circ$ ,  $[\alpha]_{D}^{19} -0.4^\circ$  in  $\text{CHCl}_3$ , and the  $\text{I}_3$ -compound, m.p.  $116^\circ$ ,  $[\alpha]_{D}^{19} -1.44^\circ$  in  $\text{CHCl}_3$ ; (I) with  $\alpha$ -bromoisohexoyl bromide similarly yields 1- $\alpha$ -glucose 2 : 3 : 4 : 6-tetraacetate 1- $\alpha$ -iodoisohexooate, m.p.  $112-113^\circ$ ,  $[\alpha]_{D}^{19} -2.2^\circ$ . F. R. G.

**Glucosyl-ketimines, ternary compounds of sugars with ammonia and  $\beta$ -diketones.** E. VOTOCEK and F. VALENTIN (Coll. Czech. Chem. Comm., 1935, 7, 299—308).—The following are obtained by the interaction of  $\text{NH}_3$  and the appropriate sugar and  $\beta$ -diketone in MeOH or EtOH : *Me* (+ $\text{H}_2\text{O}$ ), m.p.  $190-192^\circ$ ,  $[\alpha]_D -125.5^\circ$  in MeOH, and *Et*, m.p.  $185^\circ$ ,  $[\alpha]_D -121.0^\circ$  in MeOH,  $\beta$ -rhamnosyliminocrotonate; *Et*  $\beta$ -mannosyliminocrotonate, m.p.  $179^\circ$ ,  $[\alpha]_D +159^\circ$  in EtOH; *Me*, m.p.  $192.5-193^\circ$ ,  $[\alpha]_D -111^\circ$  in MeOH, and *Et*, m.p.  $191.5-192.5^\circ$ ,  $[\alpha]_D -107.5^\circ$  in EtOH,  $\beta$ -rhamnosylimino- $\alpha$ -ethylcrotonate; *Et* rhamnosylimino- $\alpha$ -methylcrotonate, m.p.  $182^\circ$ ,  $[\alpha]_D -112.5^\circ$  in EtOH;  $\delta$ -rhamnosylimino- $\Delta^7$ -penten- $\beta$ -one, m.p.  $209^\circ$  (decomp.),  $[\alpha]_D -172.50^\circ$  in MeOH. F. N. W.



**Synthetic sugar anhydrides. VIII. 2:3:6-Trimethyl-*l*-idose anhydride from 2:3:6-trimethylglucose.** K. HESS and F. NEUMANN (Ber., 1935, 68, [B], 1360—1370).—Contrary to Haworth *et al.* the complete methylation of cellulose acetate cannot be effected by a single treatment with  $\text{Me}_2\text{SO}_4$  and NaOH. After repeated treatment the product is hydrolysed at  $0^\circ$  with HCl saturated at  $-20^\circ$  and the crude material is methylated, distilled, and then hydrolysed, thus giving 2:3:6-trimethylglucose (I), m.p.  $114^\circ$ ,  $[\alpha]_D^{20} +70.5^\circ$  (equilibrium) in  $\text{H}_2\text{O}$  in 60% yield. (I) is converted by  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$  in  $\text{C}_5\text{H}_5\text{N}$  at  $15\text{--}20^\circ$  into 4-*p*-toluenesulphonyl-2:3:6-trimethylglucosido-1-pyridinium *p*-toluenesulphonate, m.p.  $140^\circ$ ,  $[\alpha]_D^{20} +14.5^\circ$  in  $\text{H}_2\text{O}$ ,  $+27.1^\circ$  in  $\text{COMe}_2$ ,  $+21.3^\circ$  in  $\text{CHCl}_3$ . Under similar conditions, 2:3:6-trimethylmethylglucoside affords 2:3:6-trimethylmethylglucoside 4-*p*-toluenesulphonate (II),  $[\alpha]_D^{20} +20.1^\circ$  in  $\text{CHCl}_3$ , which is only incompletely hydrolysed by HCl. It is therefore transformed by HCl in  $\text{Ac}_2\text{O}$  into 1- $\alpha$ -chloro-2:3:6-trimethylglucose 4-*p*-toluenesulphonate (III),  $[\alpha]_D^{20} +85.6^\circ$  in  $\text{CHCl}_3$ , which is converted by pptd.  $\text{Ag}_2\text{CO}_3$  in  $\text{COMe}_2\text{--H}_2\text{O}$  into non-cryst. 2:3:6-trimethylglucose 4-*p*-toluenesulphonate (IV),  $[\alpha]_D^{20} +51.3^\circ$  in  $\text{CHCl}_3$ . (II) and  $\text{AcOH}\text{--}\text{Ac}_2\text{O}\text{--H}_2\text{SO}_4$  at  $15\text{--}20^\circ$  afford 2:3:6-trimethylglucose 1-acetate 4-*p*-toluenesulphonate,  $[\alpha]_D^{19} +52.5^\circ$  in  $\text{CHCl}_3$ . (III) is converted by  $\text{AgOAc}$  in  $\text{AcOH}$  at  $100^\circ$  into 2:3:6-trimethylglucose 1- $\beta$ -acetate 4-*p*-toluenesulphonate,  $[\alpha]_D^{18} +4.8^\circ$  in  $\text{CHCl}_3$ , isomerised by  $\text{Ac}_2\text{O}\text{--}\text{AcOH}\text{--H}_2\text{SO}_4$  to 2:3:6-trimethylglucose 1- $\alpha$ -acetate 4-*p*-toluenesulphonate (V),  $[\alpha]_D^{18} +49.4^\circ$  in  $\text{CHCl}_3$ . Hydrolysis of (IV) or (V) with NaOMe yields 2:3:6-trimethyl-*l*-idose anhydride (VI), b.p.  $76^\circ/0.015$  mm.,  $[\alpha]_D^{19} +111.3^\circ$ ,  $[\alpha]_D^{18} +114.2^\circ$  in  $\text{H}_2\text{O}$ ,  $+103.6^\circ$  in  $\text{MeOH}$ ,  $+90.8^\circ$  in  $\text{CHCl}_3$ , hydrolysed by 1% HCl at  $100^\circ$  to 2:3:6-trimethyl-*l*-idose,  $[\alpha]_D^{19} +98.5^\circ$  in  $\text{H}_2\text{O}$ , and by saturated HBr at  $0^\circ$  to *l*-idose, identified as the phenylosazone, m.p.  $168^\circ$ , and by oxidation to *l*-idonic acid. Unexpectedly therefore Walden inversion takes place at C5 instead of C4, change taking place as a consequence of anhydride formation and not of elimination of  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2$ . H. W.



**Decomposition of fructose in glass vessels by ultra-violet light of wave-length  $366\text{ m}\mu$  from the quartz-mercury vapour lamp.** R. CANTIENI (Helv. Chim. Acta, 1935, 18, 933—935).—The presence of CO could be detected spectroscopically as its haemoglobin compound, 8 times as rapidly in a 10% solution of fructose in quartz as in glass.

F. R. G.

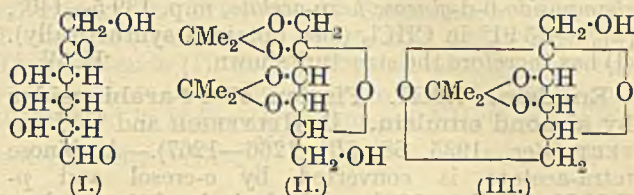
**Formation of hydrogen cyanide and carbamide by the oxidation of fructose in ammoniacal solution at room temperature.** J. PARROD (Compt. rend., 1935, 200, 1884—1886).—Fructose (not glucose) and  $\text{Cu}(\text{OH})_2$  in aq.  $\text{NH}_3\text{--}(\text{NH}_4)_2\text{SO}_3$  at  $18^\circ$  give slowly a little CuCN and a trace of  $\text{CO}(\text{NH}_2)_2$ .

R. S. C.

***l*-Psicose (2-keto-*l*-ribohexose,  $\psi$ -fructose), diacetone-*l*-psicose, and diacetone-*l*-psicuronic acid.** M. STEIGER and T. REICHSTEIN (Helv. Chim.

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Acta, 1935, 18, 790—799).—*alloDulcitol* (improved prep.), m.p.  $148\text{--}150^\circ$ , with a sorbose bacteria culture gives *l*-psicose (I) [phenylosazone, m.p.  $173\text{--}174^\circ$  (decomp.), probably identical with *l*-allosazone (A., 1934, 759)].



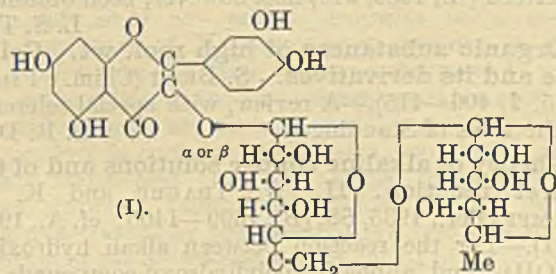
(I) with  $\text{COMe}_2$  and anhyd.  $\text{CuSO}_4$  in conc.  $\text{H}_2\text{SO}_4$  gives diisopropylidene-*l*-psicose (II), m.p.  $56.5\text{--}57^\circ$ ,  $[\alpha]_D^{20} +99^\circ$ , together with a compound,  $\text{C}_9\text{H}_{11}\text{O}_5$ , m.p.  $137\text{--}137.5^\circ$ ,  $[\alpha]_D^{20} +97.2^\circ$ , regarded as (III). (II) in an aq. solution of  $\text{Ca}(\text{OH})_2$  oxidised with  $\text{KMnO}_4$  yields diisopropylidene-*l*-psicuronic acid, m.p.  $80\text{--}81^\circ$ ,  $[\alpha]_D^{20} +80.5^\circ$ . F. R. G.

**4-Methyl-*l*-sorbose.** W. BOSSHARD and T. REICHSTEIN (Helv. Chim. Acta, 1935, 18, 959—961).—3-Methyl-*d*-glucose hydrogenated in aq. solution in presence of Ni gives  $\gamma$ -methyl-*l*-sorbitol, a syrup (*di*formal, m.p.  $133.5\text{--}134^\circ$ ), oxidised with sorbose bacterium to 4-methyl-*l*-sorbose, m.p.  $133^\circ$  (corr.),  $[\alpha]_D^{12} -30.9^\circ$  in  $\text{H}_2\text{O}$ . F. R. G.

**New reactions of lactobiose and cellobiose.** M. BERGMANN and K. GRAFE (J. Biol. Chem., 1935, 110, 173—180).—Hydrolysis of hydroxycellobial hepta-acetate (I) with NaOMe and treatment of the product with  $\text{NHPh}\cdot\text{NH}_2$  gives the phenylosazone,  $\text{C}_{18}\text{H}_{22}\text{O}_2\text{N}_4$  (II), of Bergmann *et al.* (A., 1931, 939), glucosazone, and an osazone, probably (III), in which  $\text{C}_6\text{H}_{11}\text{O}_5$  is a glucosido-residue, m.p.  $217\text{--}218^\circ$ ,  $[\alpha]_D^{21} +195.5^\circ \rightarrow 0^\circ$  in 3 hr. in  $\text{C}_5\text{H}_5\text{N}$ . In the same way hydroxylactobial

hepta-acetate gives (II), galactosazone, and an osazone, m.p.  $239\text{--}240^\circ$ , which differs from (III) only in having a galactosido- in place of the glucosido-residue. A penta-acetate (IV), m.p.  $175^\circ$ ,  $[\alpha]_D^{21} +226^\circ \rightarrow +311^\circ$  in 3 hr. in  $\text{C}_5\text{H}_5\text{N}$ , of (III) was formed by the direct action of  $\text{NHPh}\cdot\text{NH}_2$  on (I). Hydrolysis of (IV) gives (III). E. A. H. R.

**Constitution and synthesis of rutinose, the biose of rutin.** G. ZEMPLEN and A. GERECs (Ber., 1935, 68, [B], 1318—1321).—Enzymic fission of rutin (I) affords an amorphous biose, transformed by  $\text{Ac}_2\text{O}$



and NaOAc at  $100^\circ$  into  $\beta$ -1-*l*-rhamnosido-6-*d*-glucose  $\beta$ -hepta-acetate (II), m.p.  $168.5\text{--}169^\circ$ ,  $[\alpha]_D^{20} -28.54^\circ$



in  $\text{CHCl}_3$ . Rutinose acetate and  $\text{TiCl}_4$  in  $\text{CHCl}_3$  afford  $\alpha$ -chloroaceto- $\beta$ -1-l-rhamnosido-6-d-glucose, m.p. 150.5—151° after softening at 149°,  $[\alpha]_D^{20} +66.50^\circ$  in  $\text{CHCl}_3$  [also obtained from synthetic (II)], converted by  $\text{Ag}_2\text{CO}_3$  in boiling MeOH into 1-methyl- $\beta$ -1-l-rhamnosido-6-d-glucose hexa-acetate, m.p. 139.5—140°,  $[\alpha]_D^{20} -45.91^\circ$  in  $\text{CHCl}_3$  (also obtained synthetically). (I) has therefore the structure shown. H. W.

**Emulsin. XXII. Fission of  $\alpha$ -l-arabinosides by almond emulsin.** B. HELFERICH and U. LAMPERT (Ber., 1935, 68, [B], 1266—1267).—Arabinose tetra-acetate is converted by *o*-cresol and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$  at 100° and hydrolysis of the product with NaOMe in MeOH into *o*-tolyl- $\alpha$ -l-arabinoside (I), m.p. 114—116°,  $[\alpha]_D^{21} +2.1^\circ$  in  $\text{H}_2\text{O}$ . The increase in the rate of fission by almond emulsin between phenyl- $\alpha$ -l-arabinoside and (I) is comparable with that between phenyl- and *o*-tolyl- $\beta$ -d-galactosides. H. W.

**Composition of Bourdaine bark.**—See this vol., 1141.

**Glucoside from *Betula alba*, L. Betuloside and its aglucone, betuligenol.** A. Sosa (Arch. Mus. Hist. Nat. Paris, 1935, 12, 341—345).—Betuloside (A., 1933, 811) is hydrolysed to glucose and betuligenol, *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{C}_4\text{H}_8\cdot\text{OH}$ , m.p. 81° [ $Bz_2$ , m.p. 135° (Maquenne block),  $Bz$ , m.p. 59° (block), and *Me* derivatives]. F. O. H.

**Thevetin, crystalline glucoside of *Thevetia nerifolia*.** N. GHATAK (Proc. Acad. Sci. Agra and Oudh, 1934—1935, 4, 173—174).—Thevetin, the correctness of the formula  $\text{C}_{20}\text{H}_{30}\text{O}_6$  for which is upheld, is hydrolysed to glucose and thevetigenin,  $\text{C}_{14}\text{H}_{20}\text{O}$  (cf. A., 1933, 877; 1934, 820). F. O. H.

***Butea frondosa* flowers. Crystalline glucoside of butin.**—See this vol., 1181.

**Constituents of the bark of *Nerium odorum*, Soland.**—See this vol., 1180.

**Sophoricoside, a heteroside of the fruits of *Sophora japonica*, L.**—See this vol., 1141.

**Isomerisation of cyanogenic heterosides.**—See this vol., 1083.

**Products of hydrolysis of glycogen.** C. H. GRAY (Nature, 1935, 135, 1002).—Attempts to isolate a trisaccharide from the products of hydrolysis of glycogen (I) by glycerol extracts of muscle have failed (cf. this vol., 533). A hydrolytic product with a reducing power equiv. to 30—33% of (I) disappearing and yielding a phenylosazone similar to that previously described (A., 1930, 249) has, however, been obtained. L. S. T.

**Organic substances of high mol. wt. Cellulose and its derivatives.** S. BEZZI (Chim. e l'Ind., 1935, 1, 406—415).—A review, with special reference to the work of Staudinger. D. R. D.

**Theory of alkaline copper solutions and of the biuret reaction. II.** W. TRAUBE and K. E. STUMPF (Ber., 1935, 68, [B], 1399—1405; cf. A., 1930, 1421).—For the reaction between alkali hydroxide,  $\text{Cu}(\text{OH})_2$ , and aliphatic polyhydroxy-compounds or substances of the type of biuret it is essential that the latter should have a (generally weak) acidic reaction.

It then reacts in part with the alkali to form a salt the anion of which can unite with  $\text{Cu}(\text{OH})_2$ . According to the law of mass action, the reaction is continued and may eventually involve all the cupriphilic compound. It is further important that the reaction proceeds with pronounced evolution of heat and that the complex Cu compound is more strongly acidic than the initial material. Measurements of conductivity show that the complex Cu compounds of diguanide, guanil-carbamides, and substances such as trimethyldihydroxypropylammonium hydroxide are to be formulated as inner salts or zwitterions. H. W.

**Kinetics of the thermal decomposition of methylamine.**—See this vol., 1081.

**Removal of hydrogen chloride from aldchloro-imines by sodium hydroxide.**—See this vol., 939.

**Mechanism of action of glycine on potassium platinichloride.** A. A. GRÜNBERG and L. M. VOLSTEIN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 488—491).—Glycine reacts with  $\text{K}_2\text{PtCl}_4$  at room temp. if sufficient alkali is added to neutralise the  $\cdot\text{CO}_2\text{H}$ , giving mainly the *cis*-diglycine complex, with only a small amount of the usual *trans*-form. The following mechanism is proposed ( $\text{Gl}=\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\cdot$ ):  $\text{K}_2\text{PtCl}_4 + 4\text{GIH} \rightarrow [\text{Pt}(\text{GIH})_4]\text{Cl}_2 \rightarrow [\text{Pt}(\text{GIH})_2\text{Cl}_2] \rightarrow [\text{Pt}(\text{GIH})_2(\text{OH})_2] \rightarrow [\text{PtGI}_2]$ . The compounds  $\text{H}_2\text{PtGI}_4$ ,  $\text{BaPtGI}_4$ , and  $[\text{Pt}(\text{GIH})_4]\text{Cl}_2$  are described. E. W. W.

**Synthesis of optically active isoserine.** S. TSUNOO (Ber., 1935, 68, [B], 1341—1343).— $\beta$ -Chloro- $\alpha$ -hydroxypropionic acid is resolved into its optical antipodes by brucine in  $\text{H}_2\text{O}$ , whereby *d*- $\beta$ -chloro- $\alpha$ -hydroxypropionic acid (I), m.p. 91.5°,  $[\alpha]_D^{18} +2.60^\circ$  in  $\text{H}_2\text{O}$ ,  $[\alpha]_D^{10} +3.45^\circ$  in  $\text{H}_2\text{O}$ , is obtained. (I) is transformed by 30%  $\text{NH}_3$  into *l*-isoserine,  $[\alpha]_D^{10} -29.44^\circ$  in  $\text{H}_2\text{O}$ . Treatment of *dl*- $\beta$ -chloro- $\alpha$ -hydroxypropionic acid with Na-Hg yields *dl*-lactic acid, whilst similar treatment of (I) affords *d*-lactic acid. H. W.

**Synthesis of glutathione.** C. R. HARRINGTON and T. H. MEAD (Biochem. J., 1935, 29, 1602—1611).—A method is described for deacylation by means of  $\text{PH}_4\text{I}$  of *N*-carbobenzyloxy-compounds, carbobenzyloxyglycylglycine and the  $\text{CH}_2\text{Ph}$  ester of carbobenzyloxyglutamine giving yields of glycylglycine and glutamine of 80 and 35%, respectively. The method is then applied in the synthesis of glutathione and  $\gamma$ -glutamylcysteine. The acid chloride of *N*-carbobenzyloxycystine on coupling with glycine ester gave *N*-carbobenzyloxycystylglycine Et ester, which with  $\text{PH}_4\text{I}$  yielded *cysteylglutamine Et ester hydriodide* (I), m.p. 115°. *N*-Carbobenzyloxyglutamic anhydride with MeOH and Na in MeOH gave  $\alpha$ -Me *N*-carbobenzyloxyglutamate (II), an oil, the acid chloride of which on condensation with (I) in  $\text{NHET}_2$  gave  $\alpha$ -Me *N*-carbobenzyloxyglutamato-cysteylglutamine Et ester, m.p. 173°, hydrolysed with *N*-NaOH in aq. dioxan to *N*-carbobenzyloxy- $\gamma$ -glutamylcysteylglutamine, m.p. 166°, which in AcOH with  $\text{PH}_4\text{I}$  and subsequent treatment with NaOH gave glutathione, m.p. 190°,  $[\alpha]_{5461} -21.0^\circ$  in  $\text{H}_2\text{O}$  [natural product  $-18.5^\circ$  (Hopkins)]. The compound titrates with I, and with  $\text{H}_2\text{O}_2$  is converted into the oxidised form,  $[\alpha]_{5461} -107^\circ$  (natural product under same conditions  $-108^\circ$ ). Like the natural product,



it gave with extreme ease on boiling in aq. solution glutamic acid (largely as pyrrolidone-2-carboxylic acid) and cystylglycyl anhydride, m.p. 261—262° (decomp.). The structure of naturally occurring glutathione as  $\gamma$ -glutamylcysteylglycine,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}(\text{CH}_2\cdot\text{SH})\cdot\text{NH}\cdot\text{CO}\cdot[\text{CH}_2]_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ , is thus confirmed. Further, the acid chloride of (II) on condensation with cystine Et ester hydrochloride in  $\text{CHCl}_3\text{-NH}_4\text{Et}$  and purification by reduction to the thiol with pptn. as the  $\text{Cu}^+$  mercaptide gave  $\alpha$ -methyl-N-carbobenzoyloxyglutamocysteine Et ester, m.p. 97°, hydrolysed in aq. dioxan with NaOH to N-carbobenzoyloxy- $\gamma$ -glutamylcysteine, which with  $\text{PH}_4\text{I}$  in AcOH yielded  $\gamma$ -glutamylcysteine (III), m.p. 167°,  $[\alpha]_{5461} +13.6^\circ$ . The compound has marked acidic properties, an aq. solution having  $p_{\text{H}}$  2.5. The oxidised form has m.p. 187° (decomp.),  $[\alpha]_{5461} -120^\circ$ . The results suggest that Stewart and Tunnicliffe (A., 1925, i, 795) probably isolated an impure prep. of (III). P. W. C.

**Preparation of aminohydroxypropanesulphonic acid and its derivatives.** S. TSUNOO (Ber., 1935, 68, [B], 1334—1341).—Treatment of epichlorohydrin with  $\text{NaHSO}_3$  at 100° and of the product with  $\text{H}_2\text{C}_2\text{O}_4$  and then with  $\text{Pb}(\text{OAc})_2$  leads to Pb  $\gamma$ -chloro- $\beta$ -hydroxypropanesulphonate. The corresponding free acid is transformed by the requisite base at 100° into  $\gamma$ -amino- (I), m.p. 280° (decomp.),  $\gamma$ -methylamino-, m.p. 180°  $\gamma$ -dimethylamino-, m.p. 223°,  $\gamma$ -anilino-, m.p. 240°, and  $\gamma$ -methylanilino-, m.p. 235—238° (decomp.),  $\beta$ -hydroxypropanesulphonic acid. With the requisite *tert.*-base the following compounds are obtained:  $\gamma$ -trimethylamino-, m.p. 286—287° (decomp.),  $\gamma$ -pyridyl-, m.p. 242° (decomp.),  $\gamma$ -quinolyl-, m.p. >280°, and  $\gamma$ -isoquinolyl-, m.p. 270° (decomp.),  $\beta$ -hydroxypropanesulphonbetaine. Benzoylation of the dissolved acid in presence of  $\text{Ba}(\text{OH})_2$  affords  $\gamma$ -benzamido- $\beta$ -hydroxypropanesulphonic acid, m.p. 255° (decomp.) (Ba salt), hydrolysed by 48% HBr to (I), which gives the biuret and ninhydrin reactions.  $\gamma$ -Phenylureido- (Ba salt) and  $\gamma$ -2-naphthalenesulphonamido- [Na, m.p. 265° (decomp.), and Ba salts]  $\beta$ -hydroxypropanesulphonic acid are described. (I) and cholic acid afford the compound  $\text{C}_{27}\text{H}_{47}\text{O}_8\text{NS}$ , m.p. 185° after softening at 145°, decomp. 210°,  $[\alpha]_{\text{D}}^{25} +27.29^\circ$  in dil. EtOH. H. W.

**Determination of thiol and disulphide compounds, with special reference to cysteine and cystine.** II. Reaction between phospho-18-tungstic acid reagent and other substances than thiol compounds. K. SHINOHARA (J. Biol. Chem., 1935, 110, 263—277).—The influence of a no. of compounds likely to occur together with cystine (I) and cysteine (II) on the development of colour with phospho-18-tungstic acid under conditions described earlier (this vol., 877) is studied.  $\text{CH}_2\text{O}$  and  $\text{COMe}_2$  inhibit colour production due to (I) and (II) without influencing that due to  $\text{AcCO}_2\text{H}$ , furfuraldehyde, quinol, resorcinol, pyrocatechol,  $\text{Fe}^{3+}$ , and  $\text{Sn}^{4+}$ , thus providing a means of determining these substances in the presence of (I) and (II). Creatinine increases the rate of colour production in the presence

of (I) and (II) and  $\text{CH}_2\text{O}$ . Sn is a better reducing agent for (I) than is Zn. H. D.

**Absence of dissociation of thiocarbamide and substituted thiocarbamides in dilute aqueous solution.** P. CRISTOL, R. SEIGNEURIN, and J. FOUROADE (Compt. rend., 1935, 200, 2223—2225).—Thiocarbamide (I), its Me, Et, and allyl derivatives, and biuret are shown by cryoscopy,  $\kappa$ , and  $p_{\text{H}}$  to be undissociated in  $\text{H}_2\text{O}$ . (I) is thus not  $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{SH}$ , but probably  $\text{NH}\cdot\text{C}\begin{smallmatrix} \text{NH}_2 \\ \diagup \\ \text{S} \end{smallmatrix}$ . R. S. C.

**Preparation of guanidine nitrate from ammonium thiocyanate.** H. GÖCKEL (Angew. Chem., 1935, 48, 430).—Guanidine nitrate is obtained in almost quant. yield by treating  $\text{NH}_4\text{CNS}$  (100 g.) with dry  $\text{NH}_3$  (50 g.) at room temp. until liquefied, adding  $\text{Pb}(\text{NO}_3)_2$  (400 g.), and heating the mixture in an autoclave to 120°. S. C.

**Radial esters of tetrathio-orthosilicic and tetrathio-orthogermanic acids.** H. J. BACKER and F. STIENSTRA (Rec. trav. chim., 1935, 44, 607—617).—Cryst. esters of tetrathio-ortho-silicic and -germanic acid are isomorphous with one another and with esters of tetrathio-orthostannic acid. Those with compact alkyl groups crystallise readily and simply and have a high m.p. In general the m.p. of the esters falls in the order  $\text{C} > \text{Si} > \text{Ge} > \text{Sn}$ , but the Me and  $\text{Bu}^n$  compounds are exceptional. The m.p. of the latter increases with increasing wt. of the central atom, whereas those of the former apparently present a combination of the two opposed actions. The following tetrathio-orthosilicates are described with crystallographic data:  $\text{Pr}_4$ , m.p. 33.5°; tetra-n-amyl, b.p. 230—232°/3—4 mm.; tetracetyl, m.p. 50—51°; tetracyclohexyl, m.p. 101.5—102.5°;  $\text{Ph}_4$ , m.p. 114.5—115°; tetra-p-tolyl, m.p. 128.5—129°; tetra-p-tert-butylphenyl, m.p. 185—186°. The following tetrathio-orthogermanates have been obtained: tetra-n-amyl, b.p. 240—241°/3—4 mm.; tetracetyl, m.p. 50—51°; tetracyclohexyl, tetragonal, m.p. 84°, monoclinic, m.p. 88°;  $\text{Ph}_4$ , m.p. 101.5°; tetra-p-tolyl, m.p. 110—111°; tetra-p-tert-butylphenyl, m.p. 155—156°; compound  $\text{Ge}\left\{\begin{smallmatrix} \text{S}\cdot\text{CH}_2\cdot\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{S}\cdot\text{CH}_2\cdot\text{CH}_2 \end{smallmatrix} \right\}_2\text{O}$ , m.p. 159—159.5°. The physical consts. of the compounds are tabulated. H. W.

**Simplified preparation of activated magnesium for Grignard reagents.** H. GILMAN and R. H. KIRBY (Rec. trav. chim., 1935, 44, 577—583).—5 c.c. of  $\text{Et}_2\text{O}$  are added dropwise to a well-stirred mixture of Mg turnings or powder (5 g.),  $\text{C}_6\text{H}_6$  dried over Na (100 c.c.), and 2.5 g. of I. As soon as the colour of the I has disappeared the solvent is distilled from an oil-bath finally at 150—160°. The product is cooled in a dry atm., powdered, and quickly transferred to a dry bottle fitted with a rubber stopper. Immediately before use the catalyst is re-activated by being heated in a test-tube until evolution of gas ceases and a faint colour of I appears. Usually about 0.2 g. of it is used in initiating Grignard reactions. The mechanism of the catalysis is discussed. H. W.



**Yields of organomagnesium and organolithium compounds.** H. GILMAN, E. A. ZOELLNER, W. M. SELBY, and C. BOATNER (Rec. trav. chim., 1935, 44, 584—594).—Yields of Grignard compounds are recorded (i) when the compound  $RX$  in  $Et_2O$  is gradually added to Mg turnings under  $Et_2O$  when reaction has been initiated by I and halide, (ii) when the compound  $RX$  is added all at once after reaction has started, and (iii) under special conditions for each reagent. Although good yields are frequently recorded by (i) and (iii), the optimal conditions have not been secured. The quality of the available Mg is very significant in the prep. of the less common Grignard reagents. Fine Mg is not generally essential, but is preferable to Mg turnings where an increase in yield is desired or for initiating actions when an activated Mg catalyst is not available. The yields of Grignard reagents  $MgRHal$  decrease in the order  $MgRCl$ ,  $MgRBr$ ,  $MgRI$ . As reactant  $MgRCl$  is preferred, since it is formed in better yield, its prep. involves little extra attention to details as there is no appreciable decline in yield with rapid addition of  $RCl$  to Mg in  $Et_2O$ , and it is more reactive and generally gives higher yields of product. The reaction is initiated by using an activated catalyst; its use with polyfunctional reactants may involve difficulties due to its greater reactivity. *n*-Alkyl bromides with an even no. of C atoms give higher yields than the preceding bromides with an odd. no. of C atoms. The reverse is the case with the iodides, but the medium here appears to exert a marked influence. Alternation appears to take place with the chlorides, but the evidence is at present insufficient. Generalisations with regard to the prep. of organolithium compounds cannot be made at present. H. W.

**Relative rates of formation of some organomagnesium and -lithium compounds.**—See this vol., 939.

**Aldolising action of mixed secondary and tertiary organomagnesium compounds on certain ketones.** D. IVANOV and A. SPASSOV (Bull. Soc. chim., 1935, [v], 2, 1435—1438).—Mixed *sec.* and *tert.* aliphatic organomagnesium derivatives give, in addition to the usual three types of reaction, an aldolisation of certain ketones of definite structure. The examples cited are the action of  $MgPr^sCl$ ,  $MgBu^sBr$ , and  $MgBu^tCl$  on  $COMePr^s$ , of  $MgPr^sCl$ ,  $MgBu^sBr$ , and  $MgBu^tCl$  on pinacolone, of  $MgPr^sCl$  and  $MgBu^sBr$  on cyclopentanone, and of  $MgPr^sCl$  on cyclohexanone. H. W.

**Complex iron compounds. I. Formation and solvation of ferrous chloride in non-aqueous liquids.** D. R. CHESTERMAN (J.C.S., 1935, 906—910).—Purified Fe reacts rapidly with solutions of HCl in MeOH, EtOH,  $Pr^sOH$ , and  $COMe_2$  forming sol. co-ordination compounds with  $FeCl_2$ ; it reacts with HCl in  $MeOAc$ ,  $EtOAc$ ,  $Et_2O$ , and  $CHCl_3$  forming insol. co-ordination compounds, but does not react with HCl in  $CCl_4$ ,  $CS_2$ ,  $C_6H_6$ , or light petroleum. Solubility of HCl at 25° in the solvents and conductivities of the saturated solutions are recorded. The following cryst. co-ordination compounds are described: *FeCl\_2* dimethyl-, tetramethyl-, ethyl-, isopropyl-alcoholate, and monomethylacetate. F. R. G.

**Triethylenediaminecobaltic salts with mixed anions.**—See this vol., 946.

**Organic compounds of gold. V. Cyano-compounds. Production of alkyl radicals.** A. BURAWOY, C. S. GIBSON, and (in part) S. HOLT (J.C.S., 1935, 1024—1030; cf. this vol., 479).—Diethylmonobromogold in  $Et_2O$  with  $AgCN$  gives diethylnonocyanogold ( $C_5H_{10}NAu$ )<sub>4</sub> (I), m.p. 103—105°, decomp. to  $AuCN$  and  $C_4H_{10}$ , converted by boiling in  $CHCl_3$  into diethyldicyanodigold (II), decomp. 110—120°. (I) in  $C_6H_6$  with aq.  $(CH_2NH_2)_2$  gives monoethylenediaminetetraethyldicyanodigold,  $C_{12}H_{28}N_4Au_2$ , m.p. 96—98° with evolution of  $C_4H_{10}$  to give monoethylenediaminodithyldigold aurocyanide,  $C_8H_{18}N_4Au_2$ , m.p. 161—162° (decomp.), which with aq. HCl yields (II). Monoethylenediaminotetra-*n*-propyldibromodigold with aq. HBr yields di-*n*-propylmonocyanogold ( $C_7H_{14}NAu$ )<sub>4</sub> (III), m.p. 94—95° decomp. to  $AuCN$ , converted by warming in  $CHCl_3$  to di-*n*-propyldicyanodigold, decomp. 100° giving  $AuCN$  and  $C_6H_{12}$ . (III) in  $C_6H_6$  with  $(CH_2NH_2)_2$  yields monoethylenediaminotetra-*n*-propyldicyanodigold, m.p. 84—85° with formation of  $C_6H_{12}$  and monoethylenediaminodi-*n*-propylgold aurocyanide, m.p. 151—152° (decomp.). Structures are given for the above compounds. F. R. G.

**Mechanism of additions to double linkings. I. Thermochemistry and kinetics of a diene synthesis.**—See this vol., 938.

**2-Methyldicyclo-[2 : 2 : 2]-octane and its behaviour during dehydrogenating catalysis.** B. A. KASANSKY and A. F. PLATE (Ber., 1935, 68, [B], 1259—1264).—The absence of strain in the mol. and consequent structural stability which do not facilitate elimination of H at a Pt contact do not hinder the catalytic decomp. of 2-methyldicyclo-[2 : 2 : 2]-octane (I) characteristic of all hydrocarbons with a hexamethylene ring. *cndo*Ethylenetetrahydrobenzaldehyde, b.p. 90—92°/20 mm., is obtained in 40% yield when acraldehyde (II) and  $\Delta^{1:3}$ -cyclohexadiene are heated for 3½ hr. at 100° and then treated with  $K_2CO_3$ , whereby excess of (II) is polymerised. It is converted by successive treatment with  $N_2H_4 \cdot H_2O$  and KOH into 2-methyldicyclo-[2 : 2 : 2]-octene, b.p. 147.5—149°/756.7 mm., hydrogenated (Pt-black in EtOH) to (I), m.p. 33—34°. Treatment of (I) in  $CO_2$  with Pt-C at 305—315° gives a mixture of hydrocarbons containing  $C_6H_6$  and affording mainly BzOH when oxidised, thus probably indicating the formation of PhMe. H. W.

**Steric hindrance, a means of analysis of intermolecular forces.** O. ZWECKER (Ber., 1935, 68, [B], 1289—1306).—The spatial conception of the effect of *o*-substituents on the reactivity of chemical compounds is inadequate, since it fails to explain the many instances of enhanced activity. A uniform view is obtained of the displacement of the chemical properties of simply substituted  $C_6H_6$  derivatives caused by the entry of 1 or 2 *ortho*-substituents as compared with the differences in chemical properties of the corresponding "substitution pairs." The latter are the compounds obtained when the reacting substituent is regarded as united to one of the neigh-



bouring substituents. Replacement of an *ortho*-H in a simply substituted  $C_6H_6$  derivative by a second substituent (*B*) causes an alteration in the properties of the reacting substituent (*A*). The displacement of reactivity is comparable in magnitude and direction with the difference in chemical behaviour of *AH* and *AB*. If a reaction occurs more rapidly with *AH* than with *AB*, the same difference in modified form is observed when in the mono-substituted  $C_6H_6$  derivative an *ortho*-H is replaced by *B*. If the reaction of *AB* is slower than that of *AH*, retardation of the rate of reaction is caused by the *ortho*-substituent in the  $C_6H_6$  derivative. Complete repression of a reaction by the *ortho*-substituent occurs only when the difference in the rates of reaction of the corresponding "substitution pairs" is unusually great. The phenomena of hindrance are particularly obvious with  $C_6H_6$  derivatives because the reactions under consideration in the case of compounds without *ortho*-substitution usually occur more slowly than with the corresponding simple mols. At present the relationships are not quant.

H. W.

**Action of magnesium phenyl bromide on dichloriodoaryl compounds.** N. N. MELNIKOV (J. Gen. Chem. Russ., 1935, 5, 28—29).— $PhCl$ ,  $PhBr$ ,  $PhI$ , and  $Ph_2$  are formed when  $MgPhBr$  in  $Et_2O$  is added to  $C_6H_3Cl_2I$ ; the corresponding products with  $C_6H_2MeCl_2I$  are phenyltolylidonium chloride,  $PhCl$ ,  $PhBr$ ,  $p$ - $C_6H_4MeI$ ,  $Ph_2$ , and  $p$ - $C_6H_4PhMe$ .

R. T.

**Reduction of nitro-compounds with cast-iron filings.** V. O. LUKASCHEVITSCH and M. A. VOROSHILOVA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 394—399).—Reduction by Fe filings involves the conversion of Fe into  $Fe(OH)_2$  and of  $Fe(OH)_2$  into  $Fe(OH)_3$ . The rate of reaction depends on the micro-structure of the filings and their chemical composition. Soft, grey cast iron gives highly active filings in contrast with the harder varieties or with those containing little graphite. Rate of reduction in presence of electrolytes increases with the concn. of the latter up to a certain point, after which it commences to decline. With about 0.78*N* solutions of the following electrolytes the yields of  $NH_2Ph$  from  $PhNO_2$  after 32 min. boiling are as follows:  $NH_4Cl$ , 95.5%;  $HCl$  ( $FeCl_2$ ), 91.3%;  $(NH_4)_2SO_4$ , 89.2%;  $BaCl_2$ , 87.3%;  $CaCl_2$ , 81.5%;  $MgCl_2$ , 68.5%;  $NaCl$ , 50.4%;  $Na_2SO_4$ , 42.2%;  $KBr$ , 41%;  $NaOAc$ , about 10%;  $NaOH$ , 0.7%. During reduction in the presence of alkali and of certain alkaline-earth salts the solution is distinctly alkaline to phenol- and cresol-phthalein. In these cases the  $p_H$  of the medium depends on the temp. of reaction, usually decreasing with rise of temp. The amount of dissolved Fe decreases during reduction with  $FeCl_2$  probably owing to adsorption of  $Cl^-$  by the residue. After a certain point increase of  $p_H$  almost entirely inhibits reduction; diminution of  $p_H$  has much less influence. The rate of reduction by  $Fe(OH)_2$  depends on the  $p_H$  of the medium; reaction is greatly delayed by certain ions such as  $SO_4^{--}$ . The slowness of the oxidation-reduction process in presence of  $SO_4^{--}$  permits the oxidation of Fe to  $Fe(OH)_3$  to be regarded as a stepwise process;

when fine Fe powder is shaken with  $PhNO_2$  and  $FeSO_4$ , a loose, dark green residue is formed which is oxidised slowly when cold, rapidly when heated. The Fe residue consists of  $FeO$  and  $Fe_2O_3$  in very varying ratio;  $Fe_3O_4$  is not present. The ratio  $FeO : Fe_2O_3$  depends mainly on the rate of oxidation of Fe and  $Fe(OH)_2$  by org. products, but the degree of subdivision of the metallic Fe is also important.

H. W.

**Reduction of aromatic nitro-compounds. I.** V. O. LUKASCHEVITSCH (J. Gen. Chem. Russ., 1935, 5, 103—116).— $\beta$ -Arylhydroxylamines are formed as intermediate products in the reduction of  $R \cdot NO_2$  ( $R=Ph$ , *o*-, *m*-, and *p*-tolyl, *o*- $C_6H_4Cl$ , *o*- $OEt \cdot C_6H_4$ , and *o*- $OMe \cdot C_6H_4$ ); the velocity of their reduction to amines is greater in alkaline than in neutral media. Formation of azo-compounds commences after most of the  $NO_2$ -groups have been reduced, and is due to interaction of azoxy- and hydrazo-compounds. An analytical procedure for the determination of the various products of reduction of  $NO_2$ -compounds, present together, is described.

R. T.

**Reactivity of halogen in halogenated nitrobenzenes. I. Reaction with piperidine.** R. B. SANDIN and M. LISKEAR (J. Amer. Chem. Soc., 1935, 57, 1304—1306).—The % of *p*-halogen (I) replaced during treatment of the following mono-, di-, and tri-(II)-halogenonitrobenzenes (0.003685 mol.) with piperidine (0.1088 mol.) in boiling  $C_6H_6$  (20 c.c.) for 8 hr. are: *p*-chloro- 18.5, *p*-bromo- 37.7, *p*-iodo- 11.8, 3:4-di-iodo- 55.4, 4-chloro- 50.6, and 4-bromo- 90.8, -3-iodo-, 3-chloro- 73.8, and 3-bromo- 77.2, -4-iodo-, 3:4:5-tri-iodo- 38.6, 4-chloro- 14.3, and 4-bromo- 66.1, -3:5-di-iodo-, 3:5-dichloro- 76.7, and 3:5-di-bromo- 77.9, -4-iodo-; little or no *m*-halogen (III) is replaced. The mobility of (I) is increased by (III). The decreased activity of (II) is ascribed to steric factors.

H. B.

**Dichloronitroiodobenzenes.** H. C. TUAN and N. WU (J. Chinese Chem. Soc., 1935, 3, 150—152).—2:5-Dichloro-4-nitroaniline is converted into the corresponding -iodobenzene, m.p. 81—82°, identical with that obtained by Herschmann (A., 1894, i, 330). 2:4-, m.p. 62—63°, and 3:6-Dichloro-2-iodonitrobenzene, m.p. 32°, b.p. 292°, are prepared from the corresponding amines.

F. R. S.

**Hydrolysis of the aluminium benzenesulphonates.**—See this vol., 934.

**Constitution and reactivity. XII. Nitration and sulphonation of aromatic compounds.** K. LAUER. XIII. Sulphonation of toluene and the directive action of the methyl group. K. LAUER and R. ODA (J. pr. Chem., 1935, [ii], 143, 127—138, 139—142; cf. this vol., 970).—XII. Cationoid substituents in  $C_6H_6$  are considered as retarding normal further substitution, and favouring anionoid substitution; thus nitration of cationoid-substituted  $C_6H_6$  tends to be abnormal. The "self-directive" property of  $NO_2$  is assumed to be due to its capacity to react as cationoid or as anionoid.  $SO_3H$  is presumed to have a similar, though smaller, capacity, since sulphonation by  $H_2SO_4$  does not give exclusively normal products.  $SO_3$ , on the other hand, must as a dipole have a



cationoid reaction at the S atom, and anionoid (oxidising) reaction at the O atoms; sulphonation by  $\text{SO}_3$  should therefore be exclusively at anionoid C atoms. This is confirmed experimentally.  $\text{PhNO}_2$  and  $\text{SO}_3$  at  $140^\circ$  yield pure  $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ ;  $\text{PhSO}_3\text{H}$  gives pure  $m\text{-C}_6\text{H}_4(\text{SO}_3\text{H})_2$ .  $\text{BzOH}$  yields  $m\text{-SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , with no trace of *o*- or *p*-isomeride.

XIII. In contrast with the above, the 8% of  $m\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$  which is formed in the sulphonation of  $\text{PhMe}$  (A., 1911, i, 849), is obtained even when  $\text{SO}_3$  is used. That this is due to  $\text{H}_2\text{SO}_4$  formed as a result of the reaction  $2\text{PhMe} + \text{SO}_3 \rightarrow (\text{C}_6\text{H}_4\text{Me})_2\text{SO}_2 + \text{H}_2\text{O}$  is, however, proved by treating  $\text{PhMe}$  with  $\text{SO}_3$  in presence of  $\text{P}_2\text{O}_5$  or of  $\text{Ac}_2\text{O}$ , when the products are *o*- and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$  and the *p*-sulphone, without  $m\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$ . E. W. W.

**Exchange of sulphonyl groups in thiolsulphonic esters.** J. D. LOUDON and A. LIVINGSTON (J.C.S., 1935, 896—898).—The exchange  $\text{R}'\text{S}\cdot\text{SO}_2\text{R}'' + \text{R}'''\cdot\text{SO}_2\text{Na} \rightarrow \text{R}'\text{S}\cdot\text{SO}_2\text{R}''' + \text{R}''\cdot\text{SO}_2\text{Na}$  ( $\text{R}'$  or  $\text{R}'' = \text{Ph}$ ,  $p\text{-C}_6\text{H}_4\text{Me}$ ,  $\text{CH}_2\text{Ph}$ ,  $p\text{-C}_6\text{H}_4\text{Cl}$ ,  $p\text{-C}_6\text{H}_4\text{Br}$ , 2:5- $\text{C}_6\text{H}_3\text{Cl}_2$ , *o*- and *m*- $\text{C}_6\text{H}_4\cdot\text{NO}_2$ ) operates when the potential anion is more stable than the free sulphinate ion. The following thiolsulphonates were prepared: *Ph*, m.p.  $74^\circ$ ,  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2$ , m.p.  $120^\circ$ ,  $p\text{-C}_6\text{H}_4\text{Cl}$ , m.p.  $65^\circ$ ,  $p\text{-C}_6\text{H}_4\text{Br}$ , m.p.  $107^\circ$ , 2:5- $\text{C}_6\text{H}_3\text{Cl}_2$  in two forms, m.p.  $86\text{--}87^\circ$  and  $103^\circ$ , *p*-toluenethiolsulphonates, *o*-nitrophenyl benzenethiolsulphonate, m.p.  $87^\circ$ , and *p*-bromobenzenethiolsulphonate, m.p.  $137^\circ$ , 2:5-dichlorophenyl *m*-nitrobenzenesulphinate, m.p.  $116^\circ$ .

F. R. G.

**Electrochemical oxidation of toluene in aqueous-ethereal phosphoric acid solution.** V. A. PLOTNIKOV, I. L. KATZNELSON, and S. G. FRIDMAN (J. Gen. Chem. Russ., 1935, 5, 378—381).—The most suitable solvent for  $\text{PhMe}$  is 2:5  $\text{H}_3\text{PO}_4\text{--Et}_2\text{O}$ . Small (1%) yields of  $\text{PhCHO}$  are obtained by anodic oxidation (Pt anode);  $\text{PhCHO}$  is not obtained unless the anolyte is separated by a diaphragm. Relatively considerable amounts of  $\text{CO}_2$  and  $\text{CO}$  are evolved, pointing to oxidation of the  $\text{C}_6\text{H}_5$  ring. R. T.

**Preparation of *m*-xylyl chloride.** H. S. KING and M. K. MERRIAM (Proc. Nova Scotian Inst. Sci., 1933—1934, 18, 276—281).— $m\text{-C}_6\text{H}_4\text{Me}_2$  with  $\text{Cl}_2$  (conditions described) gives *m*-xylyl chloride (64%) and 1:3:4- $\text{C}_6\text{H}_3\text{Me}_3\text{Cl}$  (7%). No  $\text{Cl}_2$ -compounds are formed.  $\text{O}_2$  greatly retards chlorination. J. L. D.

**Halogenation. X. Preparation of mixed halogen derivatives of xylenes.** P. S. VARMA and K. S. V. RAMAN (J. Indian Chem. Soc., 1935, 12, 245—248).—2-Chloro-5-iodo-*p*-xylene, m.p.  $46^\circ$ , is readily obtained when 2-chloro-*p*-xylene is heated with I in  $\text{AcOH--CCl}_4$  and a mixture of nitrosulphonic (I) and fuming nitric acids (II). Similarly 4-chloro-*m*-xylene yields 4-chloro-6-iodo-*m*-xylene, m.p.  $44^\circ$ ; 4-bromo-*o*-xylene yields 4-bromo-5-iodo-*o*-xylene, m.p.  $68\text{--}5^\circ$  (also obtained by bromination of 4-iodo-*o*-xylene); 4-bromo-*m*-xylene yields 4-bromo-6-iodo-*m*-xylene, m.p.  $47^\circ$  (also obtained by bromination of 4-iodo-*m*-xylene); and 2-bromo-*p*-xylene yields 2-bromo-5-iodo-*p*-xylene, m.p.  $73^\circ$  (also obtained by bromination of 2-iodo-*p*-xylene). In the foregoing brominations a little I was used as halogen-carrier. Good yields of 4-chloro-6-bromo-*m*-xylene (Noyes, Amer.

Chem. J., 1898, 20, 798) and of 2-chloro-5-bromo-*p*-xylene (A., 1889, 965) are obtained by brominating 4-chloro-*m*-xylene and 2-chloro-*p*-xylene, respectively, in presence of a mixture of (I) and (II). H. G. M.

**Polymethylbenzenes. XI. Nitration of penta-methyl-, hexamethyl-, and hexaethyl-benzene.** L. I. SMITH and S. A. HARRIS. XII. Nitration of bromodurene and structure of the "dinitro-duroyl bromide" of Willstätter and Kubli. L. I. SMITH and D. TENENBAUM (J. Amer. Chem. Soc., 1935, 57, 1289—1292, 1293—1296).—XI.  $\text{C}_6\text{HMe}_5$  added to  $\text{HNO}_3$  (*d* 1.52) + conc.  $\text{H}_2\text{SO}_4$  (large excess) and  $\text{CHCl}_3$  at  $<10^\circ$  gives 65—74% of dinitrophenitene (I), m.p.  $176\text{--}177^\circ$ , converted by  $\text{SnCl}_2$  + conc.  $\text{HCl}$  in boiling  $\text{AcOH}$  into 2:4:5:6:7-pentamethylbenziminazole, m.p.  $264^\circ$  [hydrochloride (+2 $\text{H}_2\text{O}$ ); hydriodide, m.p.  $>350^\circ$  (formed during the action of  $\text{MeI}$  in xylene); methiodide, m.p.  $>350^\circ$  (darkens at  $310^\circ$ ); *MeH* sulphate, m.p.  $258\text{--}261^\circ$  (decomp.) (darkens at  $255^\circ$ ) (formed using  $\text{Me}_2\text{SO}_4$  in  $\text{MeOH}$ )], methylated ( $\text{Me}_2\text{SO}_4$ ,  $\text{NaOH}$ ,  $\text{MeOH}$ ) to the 1:2:4:5:6:7- $\text{Me}_6$  derivative, m.p.  $165^\circ$ , and converted (method: Bogert and Bender, A., 1914, i, 579) into 2-styryl-4:5:6:7-tetramethylbenziminazole, m.p.  $279\text{--}280^\circ$ . Similar nitration of  $\text{C}_6\text{Me}_6$  and 2:3:4:5- $\text{C}_6\text{HMe}_4\cdot\text{CO}_2\text{H}$  affords 22% and quant. yields, respectively, of (I), whilst  $\text{C}_6\text{Et}_6$  gives a poor yield of 1:4-dinitrotetraethylbenzene (II), m.p.  $143\text{--}145^\circ$ . Reduction ( $\text{SnCl}_2$ ,  $\text{HCl}$ ,  $\text{AcOH}$ ) of (II) and subsequent oxidation (aq.  $\text{FeCl}_3$ ) of the amine stannichloride gives tetraethyl-*p*-benzoquinone, m.p.  $56\text{--}58^\circ$ . Possible mechanisms for the formation of (I) are discussed.

XII. Bromodurene (I) and  $\text{HNO}_3$  (*d* 1.52) at  $0^\circ$  give the "dinitroduroyl bromide" (II), m.p.  $122\text{--}123^\circ$ , of Willstätter and Kubli (A., 1909, i, 899), which is probably  $\text{C}_{10}\text{H}_{11}\text{O}_5\text{N}_2\text{Br}$ , is reduced to aminodurene, does not react with  $\text{EtOH--AgNO}_3$ , and is converted by alkali into coloured products but no dinitroduroylic acid (III) [*Me*, m.p.  $103\text{--}106^\circ$ , and *Et*, m.p.  $99\text{--}101^\circ$ , esters; chloride (IV), m.p.  $90\text{--}91^\circ$ ]. The bromide of (III) could not be prepared ( $\text{PBr}_3$  or  $\text{SOBr}_2$ ). (I) and  $\text{HNO}_3$  (*d* 1.52) at  $25^\circ$  or  $\text{HNO}_3$  (*d* 1.6) at  $0^\circ$  give 3-bromo-5:6-dinitro- $\psi$ -cumene (V), m.p.  $181\text{--}182^\circ$ , also prepared from (a) bromonitrodurene and  $\text{HNO}_3$  (*d* 1.52) at  $0^\circ$ , (b) (II) and  $\text{HNO}_3$  (*d* 1.52) at  $25^\circ$ , (c) (II) and conc.  $\text{H}_2\text{SO}_4$ , and (d) 3-bromo- $\psi$ -cumene,  $\text{HNO}_3$  (*d* 1.52), and conc.  $\text{H}_2\text{SO}_4$ . (II) may be 3-bromo-6-nitro-2:4:5-trimethylbenzyl nitrate or (less probably) 3-bromo- $\alpha$ :6-dinitro-2:4:5-trimethylbenzyl alcohol. Reduction ( $\text{SnCl}_2$ , conc.  $\text{HCl}$ ,  $\text{EtOH}$ ) of (V) gives 5:6-diamino- $\psi$ -cumene, converted by boiling  $\text{AcOH}$  into 2:4:6:7-tetramethylbenziminazole. Chlorodurene and  $\text{HNO}_3$  (*d* 1.52) at  $0^\circ$  similarly afford a compound,  $\text{C}_{10}\text{H}_{11}\text{O}_5\text{N}_2\text{Cl}$ , m.p.  $93\text{--}94^\circ$  [which differs from (IV)], converted by conc.  $\text{H}_2\text{SO}_4$  into 3-chloro-5:6-dinitro- $\psi$ -cumene. H. B.

**Decomposition of triphenylmethyl hyponitrite.** M. A. SPIELMAN (J. Amer. Chem. Soc., 1935, 57, 1117—1119).— $\text{CPh}_3\text{Cl}$  and  $\text{Ag}_2\text{O}_2\text{N}_2$  at  $18^\circ$  give  $\text{N}_2$  (0.9 mol.), resinous products,  $(\text{CPh}_2\cdot\text{OPh})_2$ ,  $\text{COPh}_2$ ,  $(\text{CPh}_2\cdot\text{O})_2$ ,  $\text{PhOH}$ ,  $\text{CPh}_3\text{Me}$ ,  $\text{CPh}_3\cdot\text{OH}$ , and  $p\text{-CPh}_3\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , in amounts decreasing in the order



given. A reaction mechanism is postulated, based on the transitory formation of  $\text{CPh}_3\text{O}$ , which is held to be proved. R. S. C.

**Hexa-*p*-alkylphenylethanes.** Effect of *p*-alkyl group on dissociation of the ethane. J. W. COPENHAUER, M. F. ROY, and C. S. MARVEL (J. Amer. Chem. Soc., 1935, 57, 1311—1314).— $p\text{-C}_6\text{H}_4\text{Alk}\cdot\text{MgBr}$  (0.5 mol.) and  $\text{Et}_2\text{CO}_3$  (0.125 mol.) in  $\text{Et}_2\text{O}$  give  $(p\text{-C}_6\text{H}_4\text{Alk})_3\text{C}\cdot\text{OH}$ , converted by  $\text{HCl}$  in  $\text{Et}_2\text{O} + \text{CaCl}_2$  into  $(p\text{-C}_6\text{H}_4\text{Alk})_3\text{CCl}$  (I). The colours of the solutions of the ethanes obtained from (I) and mol. Ag in PhMe deepen with increase in wt. of Alk, thus indicating a progressive increase in the dissociation (cf. A., 1931, 1392). The following are described: *tri-p-ethyl*-, m.p. 157—158°, -*n*-, m.p. 88—89°, and -*iso*-, m.p. 167—168°, -*propyl*-, and -*n*-, m.p. 63°, -*iso*-, m.p. 135—136°, and -*sec*-, m.p. 132—133°, -*butyl-phenylmethyl chlorides*; *tri-p-ethyl*-, m.p. 159—160°, -*n*-, m.p. 140—141°, and -*iso*-, m.p. 162—163°, -*propyl*-, and -*n*-, m.p. 127—128°, -*iso*-, m.p. 135—136°, and -*sec*-, m.p. 147—148°, -*butyl-phenylmethyl peroxides*. The  $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{Alk}$  (numerous physical data given) are prepared (i) from  $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{MgBr}$  (II) and  $\text{Alk}_2\text{SO}_4$  or  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Alk}$  and (ii) by reduction ( $\text{H}_2$ ,  $\text{PtO}_2$ ,  $\text{EtOH}$ ) of *p*-bromoalkenylbenzenes.  $\text{CH}_2\text{:CMe}\cdot\text{CH}_2\text{Cl}$  and (II) give  $\gamma$ -*p*-bromophenyl- $\beta$ -methyl- $\Delta^a$ -propene, b.p. 98°/5 mm. *p*-Bromoisopropenylbenzene is prepared by Ziegler and Tiemann's method (A., 1923, i, 30); dehydration of the intermediate carbinol occurs during isolation.  $\text{COMeEt}$  and (II) similarly afford  $\beta$ -*p*-bromophenyl- $\Delta^a$ -butene, b.p. 111°/6 mm. H. B.

**Behaviour of unsaturated hydrocarbons towards the Grignard reagent at elevated temperatures.** C. R. KINNEY and R. G. LARSEN (J. Amer. Chem. Soc., 1935, 57, 1054—1056).— $\text{MgPhBr}$  does not react with  $\text{CPh}_2\text{:CH}_2$  (I),  $\text{CHPh:CH}_2$ ,  $\text{CPh:CHMe}$ , or  $\text{CPhMe:C:CHMe}_2$  in xylene,  $\text{Ph}_2$ ,  $\text{Ph}_2\text{O}$ , or kerosene at 130—190°. In some experiments (I) yielded  $\text{OH}\cdot\text{CPh}_2\cdot\text{CH}_2\text{Ph}$ , probably formed, however, from  $\text{CPh}_2\text{:CH}_2 > \text{O}$ , present as impurity in (I). R. S. C.

**Dipole moment and molecular structure.** XIV. 2:2'-Difluorobisdiphenylene-ethylene. E. BERGMANN. XV. Spatial configuration of the allene system. E. BERGMANN and G. C. HAMPSON (J.C.S., 1935, 987—989, 989—993).—XIV. 9:9-Dichloro-2-fluorofluorene with Ag powder in xylene gives 2:2'-difluorobisdiphenylene-ethylene, m.p. 226—227°, which is shown to have a *cis* configuration by measurement of its dipole moment by extrapolation to infinite dilution in  $\text{C}_6\text{H}_6$  solution at 16°, as 2.51D. The dielectric const. and  $d$  of bisdiphenylene-ethylene in  $\text{C}_6\text{H}_6$  at 16° were also determined.

XV.  $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CO}\cdot\text{CH:CHPh}$  with  $\text{MgPhBr}$  gives *p*-chlorophenyl  $\beta\beta$ -diphenylethyl ketone, m.p. 131°, which with  $\text{MgPhBr}$  yields  $\alpha\gamma$ -triphenyl- $\alpha$ -*p*-chlorophenyl-propyl alcohol, m.p. 127—128°; this with aq.  $\text{HCl}$  loses  $\text{H}_2\text{O}$  to give  $\alpha\gamma$ -triphenyl- $\alpha$ -*p*-chlorophenyl- $\Delta^a$ -propene, m.p. 120—121°, which with  $\text{Br}$  in  $\text{CHCl}_3$  and subsequent treatment with boiling  $\text{KOH}\text{--EtOH}$  yields  $\alpha\gamma$ -triphenyl- $\alpha$ -*p*-chlorophenylallene (I).  $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{CH:CHPh}$  with  $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{MgBr}$  gives

*p*-bromophenyl  $\beta$ -phenyl- $\beta$ -*p*-bromophenylethyl ketone, m.p. 126.5°, which with  $\text{MgPhBr}$  in  $\text{Et}_2\text{O}\text{--PhMe}$  yields  $\alpha\gamma$ -diphenyl- $\alpha\gamma$ -di-(*p*-bromophenyl)propyl alcohol, m.p. 130—131°; this boiled with aq.  $\text{HCl}$  gives  $\alpha\gamma$ -diphenyl- $\alpha\gamma$ -di-(*p*-bromophenyl)- $\Delta^a$ -propene, m.p. 126°, brominated and treated with  $\text{KOH}$  as above to give  $\alpha\gamma$ -diphenyl- $\alpha\gamma$ -di-(*p*-bromophenyl)allene (II), m.p. 139—139.5°. Dipole moments were measured as above for  $\text{C}(\text{CPh}_2)_2$ ;  $\text{C}(\text{C}_6\text{H}_4\text{Cl})_2\text{:C:CPh}_2$ , 1.57D; (I) 1.55D; (II) 1.92D. These results show that allene has the structure required by the van't Hoff theory and that  $\text{C}(\text{CRR}')_2$  should be resolvable as found by Maitland and Mills (this vol., 968).

F. R. G.

**Formation of the indene nucleus.** Phenylbenzylidenes. (MRS.) O. BLUM-BERGMANN (J.C.S., 1935, 1020—1022; cf. A., 1932, 273).—2-Benzylhydrindone with  $\text{MgPhBr}$  in  $\text{Et}_2\text{O}$  gives 3-phenyl-2-benzylindene (I), m.p. 96—98°. The compound obtained by Orskov (A., 1923, i, 454) by heating  $\text{CHPhBr}\cdot\text{CBr}(\text{CH}_2\text{Ph})_2$  is 1-phenyl-2-benzylindene (II), m.p. 97—99°, also prepared by Roger *et al.* (A., 1929, 317). (II) when boiled with  $\text{KOH}$  in  $\text{EtOH}$  isomerises to (I). Both (I) and (II) with  $\text{PhCHO}$  give 3-phenyl-2-benzyl-1-benzylideneindene, m.p. 177.5—179°.

F. R. G.

**Properties of unsaturated sulphur compounds.**

I.  $\alpha\beta$ -Unsaturated sulphones. E. P. KOHLER and H. POTTER (J. Amer. Chem. Soc., 1935, 57, 1316—1321).— $\alpha\beta$ -Unsaturated sulphones add Grignard reagents (I) in the same manner as  $\alpha\beta$ -unsaturated ketones; the sulfoxides undergo fission. Contrary to Hepworth and Clapham (J.C.S., 1921, 119, 1188), saturated sulphones react with (I) to form  $\text{MgHal}$  derivatives; they behave as saturated ketones in which the hindrance to addition is prohibitive.

*p*-Tolyl styryl sulphide, two forms, m.p. 44° and 65°, prepared from  $\text{CPh:CH}$  and  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SH}$  (II) at  $\approx 100^\circ$ , is oxidised (30%  $\text{H}_2\text{O}_2$ ,  $\text{AcOH}$ ) to the sulphoxide (III), m.p. 64° and 60°, respectively, and thence (either form) to sulphones, m.p. 77° (IV) and 121° (V). Exposure of (IV) in  $\text{CHCl}_3 + \text{I}$  to sunlight gives (V), which is also prepared (15% yield) from  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Me}$  (VI),  $\text{PhCHO}$ , and  $\text{KOH}$ . (V) is incompletely reduced ( $\text{H}_2$ ,  $\text{Pt}$ ,  $\text{AcOH}$ ) to *p*-tolyl  $\beta$ -phenylethyl sulphone (VII), m.p. 75°. (IV) and (V) add  $\text{Br}$  in sunlight to give the same dibromide, m.p. 132°, and with  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SNa}$  in  $\text{C}_6\text{H}_6\text{--Et}_2\text{O}$  afford *p*-tolyl  $\beta$ -*p*-tolylthiol- $\beta$ -phenylethyl sulphone, m.p. 175—176°, oxidised (30%  $\text{H}_2\text{O}_2$ ,  $\text{AcOH}$ ) to  $\alpha\beta$ -di-*p*-toluenesulphonyl- $\alpha$ -phenylethane, m.p.  $> 225^\circ$  (decomp.).  $\alpha\alpha$ -Di-*p*-toluenesulphonyl- $\beta$ -phenylethane, m.p. 103°, is prepared by benzylation (method: Shriner *et al.*, A., 1930, 900) of  $(p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2)_2\text{CH}_2$ .  $\text{CHNa}(\text{CO}_2\text{Et})_2$  and (IV) or (V) in  $\text{C}_6\text{H}_6$  give *Et*  $\gamma$ -*p*-toluenesulphonyl- $\beta$ -phenylpropane- $\alpha\alpha$ -dicarboxylate, m.p. 78°; with  $\text{MgPhBr}$  in  $\text{C}_6\text{H}_6$ , the  $\text{Mg}$  derivative,  $[\text{CHPh}_2\cdot\text{CH}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4]\cdot\text{MgBr}$  (VIII), results. (VIII) is hydrolysed to *p*-tolyl  $\beta\beta$ -diphenylethyl sulphone (IX), m.p. 149° [also prepared from (II) and  $\text{CPh}_2\text{:CH}_2$  with subsequent oxidation], and with  $\text{Br}$ ,  $\text{BzCl}$ ,  $\text{AcCl}$ , and  $\text{CO}_2$  gives *p*-tolyl  $\alpha$ -bromo-, m.p. 155°,  $\alpha$ -benzoyl-, (X), m.p. 253°, and  $\alpha$ -acetyl-, m.p. 205°,  $\beta\beta$ -diphenylethyl sulphones and  $\alpha$ -*p*-toluenesulphonyl- $\beta\beta$ -diphenylpropionic acid, m.p. 195—197° (decomp.).



respectively. (X) is also prepared from *Ph*  $\alpha$ -bromo- $\alpha$ -*p*-toluenesulphonylmethyl ketone, m.p. 164° [which, contrary to Arndt and Martius (A., 1933, 146), is obtained from  $\text{CH}_2\text{Bz}\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7$  and Br in  $\text{CHCl}_3$ ], by the procedure previously used (this vol., 493). *p*-Tolyl  $\alpha$ -iodo- $\beta\beta$ -diphenylethyl sulphone, m.p. 186°, was obtained by the action of Br on the compound from (IX) and  $\text{MgMeI}$ . (VII) and (IX) do not react with  $\text{MgMeI}$  (modified Zerevitinov) at room temp.; at 50–75°, however, at least 1 mol. of  $\text{CH}_4$  is evolved. (VI) reacts slowly at room temp. (VIII) is also obtained from (IX) and  $\text{MgEtBr}$ . Treatment of the product from (VI) and  $\text{MgEtBr}$  with  $\text{BzCl}$  gives *dibenzoyl-p*-toluenesulphonylmethane, m.p. 164°;  $2[\text{CH}_2\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7]\text{MgBr} + 2\text{BzCl} \rightarrow \text{CHBz}_2\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7 + \text{C}_7\text{H}_7\cdot\text{SO}_2\text{Me}$ .

(III) and  $\text{MgEtBr}$  afford *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SEt}$  and  $\alpha\delta$ -diphenylbutadiene:  $2\text{MgEtBr} + 2\text{CHPh}\cdot\text{CH}\cdot\text{SO}\cdot\text{C}_7\text{H}_7 \rightarrow (\text{CHPh}\cdot\text{CH})_2 + \text{C}_4\text{H}_{10} + \text{C}_7\text{H}_7\cdot\text{SO}\cdot\text{MgBr}$ ;  $\text{MgEtBr} + \text{C}_7\text{H}_7\cdot\text{SO}\cdot\text{MgBr} \rightarrow \text{C}_7\text{H}_7\cdot\text{SEt}$ . A similar reaction occurs with  $\text{MgPhBr}$ ; oxidation (excess of  $\text{H}_2\text{O}_2$ ) of the resulting oil gives *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Ph}$  and a little *p*-tolyl  $\beta\beta\beta$ -triphenylethyl sulphone, m.p. 229–230° [ $(\text{NO}_2)_3$ -derivative, m.p. about 265° (decomp.)], which with  $\text{PCl}_5$  at 200° affords  $\text{CPh}_3\cdot\text{CH}_2\text{Cl}$  and *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{H}$  (formed from the intermediate *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$  by way of *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CCl}_3$ ). *p*-Tolyl desyl sulphide, m.p. 63–64°, from desyl chloride and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SNa}$  in  $\text{EtOH}$ , and  $\text{MgPhBr}$  give  $\beta$ -*p*-toluenesulphonyl- $\alpha\alpha\beta$ -triphenylethyl alcohol, m.p. 275° (sinters about 180°), reduced (P, I) to *p*-tolyl  $\alpha\beta\beta$ -triphenylethyl sulphone, m.p. 187°. (IX) and  $\text{PCl}_5$  at 200° afford *p*-tolyl  $\alpha\alpha$ -dichloro- $\beta\beta$ -diphenylethyl sulphone, m.p. 157°,  $\text{CPh}_2\cdot\text{CCl}_2$ , and *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{H}$ . H. B.

**Magnetochemical investigations of organic substances. II. Existence of diradicals.** E. MÜLLER and I. MÜLLER-RODLOFF (Ber., 1935, 68, [B], 1276–1282).—Magnetochemical examination shows that triphenyl- $\alpha$ -naphthylquinodimethane,  $\text{CPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{CPh}\cdot\text{C}_{10}\text{H}_7$ , as solid or in 5% solution in  $\text{C}_6\text{H}_6$  at 18° and 74° exists very preponderantly in the quinonoid form. Diradicals, if existent in the thermal equilibrium, are present in concn.  $\approx 2\%$ . *pp'*-Tetramethyldiaminothiobenzophenone in  $\text{CHCl}_3$  at 18° has certainly  $\approx 2\%$ , probably  $\approx 1\%$ , of the diradical form. H. W.

**Colour reactions and the spectrophotometric determination of nitronaphthalenes.** B. P. FEDOROV and A. A. SPRISKOV (J. Gen. Chem. Russ., 1935, 5, 450–453).—Three 0.025-g. portions of  $\text{C}_{10}\text{H}_7\cdot\text{NO}_2$  (1-, 2-, and mixed) are dissolved in 25 c.c. of 93.8%  $\text{H}_2\text{SO}_4$ , the solutions are kept in the dark for 4 hr. at room temp., and relative absorption of light ( $\lambda=580\text{ m}\mu$ ) is determined spectrophotometrically, when the % 1- $\text{C}_{10}\text{H}_7\cdot\text{NO}_2$  content is given by  $(A_{\text{Be}}-A)/(B-A)$ , where *A* and *B* represent relative absorption by solutions of 1- and 2- $\text{C}_{10}\text{H}_7\cdot\text{NO}_2$ , respectively. 1:8- and 1:5- $\text{C}_{10}\text{H}_6(\text{NO}_2)_2$  in  $\text{C}_5\text{H}_5\text{N}$  or quinoline give, respectively, intense red-brown and yellow-brown colorations with limited quantities of  $\text{KOH}$  in abs.  $\text{EtOH}$ ; 1- and 2- $\text{C}_{10}\text{H}_7\cdot\text{NO}_2$  do not develop colorations in these conditions. The intensity of the colorations given by  $\text{C}_{10}\text{H}_6(\text{NO}_2)_2$  is

not  $\propto$  concn. Colour reactions of nitronaphthalenes with  $\text{KOH}$  in  $\text{COMe}_2$  are described. R. T.

**Mechanism of monosulphonation of naphthalene.** R. LANTZ (Compt. rend., 1935, 201, 149–152).—With 55–68%  $\text{H}_2\text{SO}_4$  at 140°  $\text{C}_{10}\text{H}_8$  is in equilibrium with its sulphonation products. The velocities of sulphonation and of desulphonation increase rapidly with increasing  $[\text{H}_2\text{SO}_4]$ , the former increasing the more rapidly. The velocity of desulphonation of 1- $\text{C}_{10}\text{H}_7\cdot\text{SO}_3\text{H}$  (I) is roughly an exponential function of the concn. (cf. A., 1907, ii, 855). The transformation of (I) into the 2-acid (II) is considered to occur in two stages—desulphonation of (I) followed by 2-sulphonation of the  $\text{C}_{10}\text{H}_8$  formed—as it occurs only when the  $[\text{H}_2\text{SO}_4]$  is such that both processes can take place. Thus, only  $\text{C}_{10}\text{H}_8$  but no (II) is formed from (I) with 45.9%  $\text{H}_2\text{SO}_4$ , which does not sulphonate  $\text{C}_{10}\text{H}_8$ . The proportion (89:11) of (I) to (II) formed by sulphonation of  $\text{C}_{10}\text{H}_8$  is independent of the  $[\text{H}_2\text{SO}_4]$  between the limits of 81.7 and 94.4%  $\text{H}_2\text{SO}_4$ . H. G. M.

**1-Methylnaphthalene derivatives.** K. DZIEWONSKI and M. OTTO (Bull. Acad. Polonaise, 1935, A, 201–208).—The methylnaphthalenesulphonic acid previously (A., 1930, 336; cf. A., 1933, 708) assigned the 1:7-configuration is the 1:6-isomere. Replacement of  $\text{SO}_3\text{H}$  by, in turn,  $\text{OH}$ ,  $\text{NH}_2$ , and  $\text{CO}\cdot\text{NHMe}$ , and oxidation, gave 6-amino- $\alpha$ -naphthoic acid identical with that prepared from 3-nitronaphthalic acid. Improved preps. of 1:6- $\text{C}_{10}\text{H}_6\text{Me}\cdot\text{SO}_3\text{H}$ , 6-hydroxy- (I) and 6-amino-1-methylnaphthalene are given. 6-Hydroxy-1-methyl-5-naphthoic acid, m.p. 169–170° (decomp.), from (I) and  $\text{CO}_2$  under pressure at 160° and 6-hydroxy-1-methyl-7-naphthoic acid, m.p. 229–230°, from (I) and  $\text{CO}_2$  under pressure at 230–240°, are described. P. G. C.

**Colour reactions for differentiating tetra- from deca-hydronaphthalene.** A. CASTIGLIONI (Z. anal. Chem., 1935, 101, 414–417).—The liquid (1 c.c.) is diluted to 50 c.c. with 95%  $\text{EtOH}$  and 1 c.c. of the solution is boiled with 1 c.c. of 30% aq.  $\text{CH}_2\text{O}$  and 10 c.c. of conc.  $\text{HCl}$ ; decahydronaphthalene (I) produces a yellow colour on cooling, tetrahydronaphthalene (II) no colour. If the  $\text{HCl}$  is replaced by 2 c.c. of conc.  $\text{H}_2\text{SO}_4$  (II) gives a brownish-red and (I) a very pale yellow colour. Under the same conditions with  $\text{HCl}$  and furfuraldehyde (II) gives a blue, (I) a pure yellow, and mixtures of both a green colour. A. R. P.

**Hydrogenation of anthracene.** A. MAILLARD (Compt. rend., 1935, 200, 1856–1880). Hydrogenation (Ni-pumice) of anthracene (I) vapour by the const.-vol. technique is similar to that of  $\text{C}_{10}\text{H}_8$  (A., 1934, 178). It is slow at 20°. At 160° 4 O are rapidly absorbed and another 4 O more slowly. The  $\text{H}_4$ -derivative is smoothly dehydrogenated to (I) at 160°, but the more hydrogenated compounds also partly decompose, yielding  $\text{CH}_4$  and other products. R. S. C.

**Synthetic uses of as-octahydrophenanthrene.** I. J. W. COOK and G. A. D. HASLEWOOD (J.C.S., 1935, 767–770).—1:2:3:4:9:10:11:12-Octahydrophenanthrene [as-octahydrophenanthrene (A.,

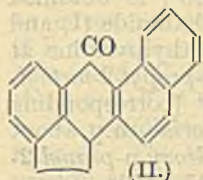


1933, 1042)] with  $\text{AlCl}_3$  and succinic anhydride in  $\text{PhNO}_2$  at  $0^\circ$  affords  $\beta$ -6-as-octahydrophenanthrolylpropionic acid (I), m.p.  $140-141^\circ$  (semicarbazone, m.p.  $185-187^\circ$ ) [and other products, the semicarbazone, m.p.  $144-146^\circ$  (decomp.), of one of which was isolated], oxidised by alkaline  $\text{KMnO}_4$  to 6-as-octahydrophenanthroic acid, m.p.  $226-228^\circ$ , dehydrogenated (Se at  $300^\circ$ ) to 3-phenanthroic acid. Clemmensen reduction of (I) yields  $\gamma$ -6-as-octahydrophenanthrylbutyric acid, m.p.  $81-83^\circ$ , b.p.  $198^\circ/0.15$  mm., cyclised by  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  at  $100^\circ$  to 5-keto-1:2:3:4:5:6:7:8:1':2':3':4'-dodecahydro-1:2-benzanthracene (II), m.p.  $120-121^\circ$ , reduced (Clemmensen) to the corresponding dodecahydro-1:2-benzanthracene, m.p.  $87-88^\circ$ , b.p.  $180^\circ/0.2$  mm. [isomeric with that already described (A., 1934, 519)]. (II) with  $\text{Mg}$ ,  $\text{C}_6\text{H}_6$ ,  $\text{Et}_2\text{O}$ , and  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$  affords a mixture of two unsaturated acids (the corresponding  $\Delta^a$ - and  $\Delta^b$ -substituted acetic acids) (*Me* esters, b.p.  $195-212^\circ/0.2$  mm.), one of which was isolated by extraction with cyclohexane and had m.p.  $226-232^\circ$  (efferv.). Both the mixture and this acid are hydrogenated (Pd-black) to the corresponding dodecahydro-1:2-benzanthryl-5-acetic acid (III), m.p.  $163-165^\circ$ . This acid and the foregoing mixture of acids are dehydrogenated and decarboxylated when heated at  $300^\circ$  with Pt-black and afford 5-methyl-1:2-benzanthracene (A., 1934, 180). Dehydrogenation (Se at  $290-300^\circ$ ) of the *Me* ester of (III) gives a little 1:2-benzanthryl-5-acetic acid, m.p.  $160-162^\circ$  (picrate, m.p.  $170-173^\circ$ ). (III) is cyclised by  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  at  $100^\circ$  to the corresponding ketododecahydrocholanthrene, m.p.  $114-116^\circ$ , reduced (Clemmensen) to dodecahydrocholanthrene, m.p.  $62-63^\circ$ , dehydrogenated by Pt-black at  $300^\circ$  to cholanthrene (cf. this vol., 968, and below).  $\text{C}_5\text{H}_5\text{MgBr}$ ,  $\text{Et}_2\text{O}$ , and (II) give a crude carbinol, dehydrated by heating at  $155-160^\circ$  to 5-allyl-1:2:3:4:7:8:1':2':3':4'-decahydro-1:2-benzanthracene, b.p.  $174^\circ/0.1$  mm. This could not be used for the prep. of (III) as it was unaffected by Na in boiling  $\text{C}_5\text{H}_{11}\cdot\text{OH}$ , but on treatment with Pt-black at  $300^\circ$  it affords 5-n-propyl-1:2-benzanthracene, m.p.  $91-91.5^\circ$  (picrate, m.p.  $131.5-132.5^\circ$ ), oxidised by  $\text{Na}_2\text{Cr}_2\text{O}_7$  in  $\text{AcOH}$  to 5-n-propyl-1:2-benzanthraquinone, m.p.  $104-105.5^\circ$ . The use of (II) for the prep. of other 5-substituted 1:2-benzanthracenes is suggested. H. G. M.

**Synthesis of 1:2-cyclopentenophenanthrene and related compounds.** W. E. BACHMANN (J. Amer. Chem. Soc., 1935, 57, 1381-1382).— $\beta$ -2-Phenanthrylpropionyl chloride (free acid, m.p.  $177-177.5^\circ$ ) and  $\text{SnCl}_4$  give 1'-keto-1:2-cyclopentenophenanthrene, m.p.  $183-184^\circ$ , reduced (Clemmensen) to 1:2-cyclopentenophenanthrene (Cook and Hewett, A., 1933, 1042). 1'-Keto-2:3-cyclopentenophenanthrene (?), m.p.  $140-140.5^\circ$ , is similarly prepared from  $\beta$ -3-phenanthrylpropionic acid, m.p.  $156-157^\circ$ . Beckmann rearrangement of the oxime, m.p.  $186^\circ$ , of 1-benzoylphenanthrene gives phenanthrene-1-carboxylanilide, m.p.  $245^\circ$ , converted by treatment with  $\text{PCl}_5$  and subsequent reduction ( $\text{SnCl}_2$ ,  $\text{HCl}$ , abs.  $\text{Et}_2\text{O}$ ) into 1-aldehydophenanthrene, m.p.  $110-111^\circ$ . This is reduced to 1-phenanthrylcarbinol, m.p.  $165^\circ$ , the bromide, m.p.  $97^\circ$ , of which is converted (malonate

method) into  $\beta$ -1-phenanthrylpropionic acid, m.p.  $189-189.5^\circ$ . 1-Hydroxy-1-methyl-, m.p.  $86-86.5^\circ$ , -1-ethyl-, m.p.  $57-57.5^\circ$ , and -1-n-propyl-, m.p.  $86-87^\circ$ , -1:2:3:4-tetrahydrophenanthrenes have been prepared. H. B.

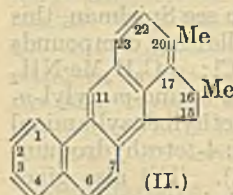
**Convenient synthesis of cholanthrene.** J. W. COOK and G. A. D. HASLEWOOD (J.C.S., 1935, 770-771).—1- $\beta$ -Naphthylhydrindene, m.p.  $52-53^\circ$  [obtained by hydrogenation of the indene, m.p.  $87^\circ$ , prepared from  $\alpha$ -hydrindone and  $2\text{-C}_{10}\text{H}_7\cdot\text{MgBr}$  (cf. A., 1929, 562, where the two first-mentioned compounds are wrongly described as the  $\alpha$ -compounds)] with Br in  $\text{CS}_2$  and a little  $\text{AlCl}_3$  affords 2-1'-hydrindyl-1-bromonaphthalene (I), b.p.  $180-192^\circ/0.2$  mm., separated from compounds brominated in the five-membered ring by treatment with boiling  $\text{C}_5\text{H}_5\text{N}$  and then with cold 80%  $\text{H}_2\text{SO}_4$ . The Grignard reagent of (I) and  $\text{CO}_2$  afford 2-1'-hydrindyl- $\alpha$ -naphthoic acid, m.p.  $155-156^\circ$ , dehydrated by  $\text{H}_2\text{SO}_4$  at  $0^\circ$  to the crude anthrone (II), reduced by Zn in boiling 3*N*- $\text{NaOH}$  to cholanthrene (cf. this vol., 968, and above). This is oxidised by  $\text{Na}_2\text{Cr}_2\text{O}_7$  in boiling  $\text{AcOH}$  to 1:2-benzanthraquinonyl-5-acetic acid, decomp.  $245-265^\circ$ , decarboxylated to 5-methyl-1:2-benzanthraquinone (*loc. cit.*). 1-Bromo-2-naphthylmagnesium iodide (prepared from 1:2- $\text{C}_{10}\text{H}_6\text{BrI}$ ,  $\text{Mg}$ ,  $\text{EtBr}$ , and  $\text{Et}_2\text{O}$ ) and  $\alpha$ -hydrindone afford a compound,  $\text{C}_{19}\text{H}_{14}\text{O}$ , m.p.  $142-143^\circ$ , b.p.  $210^\circ/0.1$  mm., which is probably a cyclic oxide. H. G. M.



**Methylcholanthrene.** J. W. COOK and G. A. D. HASLEWOOD (J. Amer. Chem. Soc., 1935, 57, 1380-1381).—A recapitulation of the work on the structure of methylcholanthrene (I). Fieser and Neuman's estimate (this vol., 859) of the over-all yield of (I) from deoxycholic acid is criticised. H. B.

**Methylcholanthrene.** L. F. FIESER (J. Amer. Chem. Soc., 1935, 57, 1381).—A reply to Cook and Haslewood (preceding abstract). H. B.

**16:20-Dimethylcholanthrene.** L. F. FIESER and A. M. SELIGMAN (J. Amer. Chem. Soc., 1935, 57, 1377-1378).—The carbinol from 4-bromo-7-methylindanone and  $\text{MgMeI}$  heated to  $190^\circ$  gives 7-bromo-3:4-dimethylindene, b.p.  $110-111^\circ/1.8$  mm., reduced ( $\text{H}_2$ ,  $\text{PtO}_2$ ,  $\text{EtOH}$ ) to 4-bromo-1:7-dimethylindane (I), b.p.  $98.5^\circ/1.5$  mm. The Grignard reagent from (I) with  $\alpha\text{-C}_{10}\text{H}_7\cdot\text{COCl}$  in  $\text{Et}_2\text{O}$  at  $-10^\circ$  affords 4- $\alpha$ -naphthoyl-1:7-dimethylindane, m.p.  $112-114^\circ$ , which when heated at  $400-405^\circ$  in  $\text{N}_2$  for 30 min. passes into 16:20-dimethylcholanthrene (II), m.p.  $169-170^\circ$  (corr.) [picrate, m.p.  $179-180^\circ$  (corr.)]. The absorption spectrum of (II) is practically identical with that of methylcholanthrene. H. B.



**Azides. III. p-Chlorobenzazide as a reagent for the identification of primary and secondary amines.** C. KAO, H. FAN, and P. P. T. SAH (J. Chinese Chem. Soc., 1935, 3, 137-140; cf. this vol., 998).—By addition of *p*-chlorobenzazide to the appropriate amine, the following -4'-chlorophenylcarbamides



have been prepared: *phenyl*-, m.p. 237°, *4-bromo*-, m.p. 289—290°, *4-chloro*-, m.p. 285° (decomp.), *4-nitro*-, m.p. 261—263°, *2-nitro*-, m.p. 206°, *2-chloro-4-nitro*-, m.p. 227°, *3-nitro*-, m.p. 212—213°, *N-acetyl*-, m.p. 240° (decomp.), *4-bromo-N-acetyl*-, m.p. 163—164°, and *3-nitro-N-acetyl-phenyl*-, m.p. 293° (decomp.), and *4-tolyl*-, m.p. 267° (decomp.), *2-tolyl*-, m.p. 209°, *3-bromo-4-tolyl*-, m.p. 220°, *3-nitro-4-tolyl*-, m.p. 233—234°, *4-*-, m.p. 285—286°, and *2-tolyl-N-acetyl*-, m.p. 293—295°,  $\alpha$ -, m.p. 235°, and  $\beta$ -*naphthyl*-, m.p. 264°, and *diphenyl*-, m.p. 162°. F. R. S.

**Action of epichlorohydrin and chlorohydroxypropylphthalimide on  $\alpha$ -picoline and aniline.** T. FUKAGAWA (Ber., 1935, 68, [B], 1344—1346).—Epichlorohydrin and  $\text{NH}_2\text{Ph}$  react vigorously when gently warmed, giving  $\alpha$ -*anilino- $\gamma$ -diphenylamino- $\beta$ -hydroxypropane*, m.p. 350° (decomp.).  $\gamma$ -*Anilino- $\beta$ -hydroxy-*n*-propylphthalimide*, m.p. 145°, is obtained from  $\gamma$ -chloro- $\beta$ -hydroxy-*n*-propylphthalimide (I) and  $\text{NH}_2\text{Ph}$  at room temp. (I) and 2-methylpyridine at 100° afford  $\gamma$ -*phthalimido- $\beta$ -hydroxy-*n*-propyl-2-methylpyridinium chloride*, m.p. 123—124° [corresponding *picrate*, m.p. 205—207°, and *platinichloride*, m.p. about 225° (decomp.)].  $\gamma$ -*Amino- $\beta$ -hydroxy-*n*-propyl-2-methylpyridinium chloride* has m.p. 165—166°. H. W.

**Action of sulphur on aniline and similar amines.** M. L. MOORE and T. B. JOHNSON (J. Amer. Chem. Soc., 1935, 57, 1287—1289).—Improvements in the prep. of 4:4'-diaminodiphenyl sulphide (I) from  $\text{NH}_2\text{Ph}$ , S, and PbO (cf. Shukla, A., 1927, 1196; Hodgson and France, A., 1933, 497; 1934, 1096) are recorded; (I) is converted into the 4:4'-(OH)<sub>2</sub>-derivative using a modification of the method previously described (A., 1930, 769).  $\text{NPhMe}_2$  and  $\text{CHPh:NPh}$  do not react with S in presence of PbO;  $\text{NHPhMe}$  affords 4:4'-dimethyldiaminodiphenyl sulphide. These results together with those (lit.) for  $\text{NHAcPh}$  and  $o\text{-C}_6\text{H}_4\text{Me.NH}_2$  indicate the following mechanism:  $2\text{NHPhR} + \text{S} \longrightarrow \text{S}(\text{NPhR})_2 \longrightarrow (\text{NHR.C}_6\text{H}_4)_2\text{S}$ ;  $\text{R} = \text{H, Me, Ac}$ . H. B.

**Condensations of aromatic amines with formaldehyde in media containing acid.** III. Formation of Tröger's base. E. C. WAGNER (J. Amer. Chem. Soc., 1935, 57, 1296—1298; cf. A., 1934, 1211).—Tröger's base (I) (for constitution see Spielman, this vol., 630) is prepared from the following compounds and 37%  $\text{CH}_2\text{O}$  in EtOH-conc. HCl: *p*- $\text{C}_6\text{H}_4\text{Me.NH}_2$  (II); (*p*- $\text{C}_6\text{H}_4\text{Me.NH})_2\text{CH}_2$  (III); *o*-amino-*m*-xylyl-*p*-toluidine [*p*-tolyl-(2-amino-5-methylbenzyl)amine] (IV); 3-*p*-tolyl-6-methyl-1:2:3:4-tetrahydroquinazoline (V) (cf. Spielman, loc. cit.). (IV) also gives some (V); in one case, an unidentified compound, m.p. 108—111° [also convertible (as above) into (I)], was also produced. (II), (III), *p*- $\text{C}_6\text{H}_4\text{Me.NH}_2\text{HCl}$ , and  $\text{PhNO}_2$  at 60° afford (IV). The production of (I) from (II) involves the changes: (II)  $\longrightarrow$  (III) or *p*- $\text{C}_6\text{H}_4\text{Me.N:CH}_2$  (or its trimeride)  $\longrightarrow$  (IV)  $\longrightarrow$  (V)  $\longrightarrow$  (I). H. B.

**Preparation of ethyl-*o*-toluidine.** H. E. FIERZ-DAVID (Helv. Chim. Acta, 1935, 18, 781).—The method of prep. of rhodamine esters previously used (cf. this vol., 206) is acknowledged as due to W. Ryser.

F. R. G.

**Anomalous mutarotation of amine salts of *d*-camphor-10-sulphonic acid.** Attempted resolution of trisubstituted nitrogen compounds. R. S. SCHREIBER and R. L. SHRINER (J. Amer. Chem. Soc., 1935, 57, 1306—1311).—*N*-Acetylbenzenesulphon-*p*-nitroanilide, m.p. 198—199° [from *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{NH.SO}_2\text{Ph}$  (I) and  $\text{Ac}_2\text{O}$  in  $\text{C}_5\text{H}_5\text{N}$ ], is reduced ( $\text{H}_2$ ,  $\text{PtO}_2$ , EtOH) to the *p*-aminoanilide, m.p. 162—163° [*d*-camphor-10-sulphonate, m.p. 174—177°, 207—208° (b)]. The Na derivative (II), m.p. 409—410° (b), of (I) and  $\text{MeSO}_2\text{Cl}$  give *N*-methanesulphonylbenzenesulphon-*p*-nitroanilide, m.p. 170—171.5°, similarly reduced to the *p*-aminoanilide, m.p. 163—164° [*d*-camphor-10-sulphonate, m.p. 153—156°, 195—196° (b)], whilst (II) and *p*- $\text{C}_6\text{H}_4\text{Me.SO}_2\text{Cl}$  in  $\text{COMe}_2$  afford *N*-*p*-toluenesulphonylbenzenesulphon-*p*-nitroanilide, m.p. 188—189°, reduced to the *p*-aminoanilide, m.p. 168—169° (slow), 154—156° (rapid heating) re-solidifying with m.p. 168—169° [*d*-camphor-10-sulphonate, m.p. 212—218°, 230° (b)]. The above salts are dextro-rotatory and exhibit mutarotation (towards —) in MeOH, EtOH, or  $\text{CHCl}_3$ ; the final vals. are dependent on the solvent and concn. Mutarotation is not due to asymmetric  $\text{N}^{\text{III}}$  atom since *NH*<sub>2</sub>*Ph* (III), m.p. 184—186°, *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{NH}_2$  (+3 $\text{H}_2\text{O}$ ), m.p. 155—157°, *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ , m.p. 176—180°, 210° (b), and *p*-aminoacetanilide (IV), m.p. 188—194°, 208—211° (b), *d*-camphor-10-sulphonates all exhibit the same phenomenon. When (IV) is heated to 220° or when a MeOH solution is kept for 4 days, the levorotatory *d*-camphor-10-sulphonic acid *p*-acetamidooanil, m.p. 375—380° (b), is obtained; (III) heated to 200° gives the (—)-*anil* (V), m.p. 294—295° (b). Solutions of (III) or (V) in  $\text{CHCl}_3 + \text{H}_2\text{O}$  (small amount) give the same final val., indicating the equilibrium (III)  $\rightleftharpoons$  (V). Decomp. of the salts and anils gives the inactive amine in each case. Deductions regarding resolution of a *r*-compound from mutarotation data alone must be made with caution.

*NN*-Dibenzenesulphonyl-*p*-nitroaniline, m.p. 213°, prepared from (II) and  $\text{PhSO}_2\text{Cl}$  (VI) in  $\text{COMe}_2$  or, in small yield, from *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{NH}_2$  and an excess of (VI), is reduced to the corresponding amine, m.p. 166—167° [*d*-camphor-10-sulphonate, m.p. 210—218°, 244—245° (b)]. Benzenesulphon-*p*-aminoanilide [*d*-camphor 10-sulphonate, m.p. 196—198°, 230° (b)] has m.p. 171—172°. All m.p. (b) are on Maquenne bloc. H. B.

**Acetylene derivatives.** IX. Catalytic hydrogenation of *oo'*-dinitrotolane. P. RUGGLI and H. ZAESLIN (Helv. Chim. Acta, 1935, 18, 853—857).—*oo'*-Dinitrotolane hydrogenated in presence of Ni yields *cis-oo'*-diaminostilbene, m.p. 107° (lit., m.p. 123°) (*picrate*, m.p. 155—156°;  $\text{Ac}_2$  derivative, m.p. 214—215°), which with a trace of acid gives the *trans*-isomeride ( $\text{Ac}_2$  derivative, m.p. 304°). F. R. G.

**Alkylated ethylenediamine derivatives.** III.  $\alpha$ -Amino- $\beta$ -benzylaminoethane. J. VAN ALPHEN (Rec. trav. chim., 1935, 44, 595—598).—Treatment of  $\text{PhCHO}$  with a large excess of hydrated  $(\text{CH}_2\text{NH}_2)_2$  in abs. EtOH at 0° gives mainly  $\alpha\beta$ -dibenzylideneaminoethane (I); the presence of  $\alpha$ -amino- $\beta$ -benzylideneaminoethane in the residues from the isolation of (I) is established by addition of  $\text{PhNCO}$ , whereby  $\beta$ -benzylideneamino- $\alpha$ -phenylcarbamidoethane, m.p.



141°, is obtained, partly disproportionated to (I) and  $\alpha\beta$ -diphenylcarbamidoethane, m.p. 298° (lit. m.p. 263°). Some  $\alpha$ -amino- $\beta$ -benzylaminoethane (II) is obtained when PhCHO and  $(\text{CH}_2\text{NH}_2)_2$  are rapidly mixed in EtOH and Na is quickly added, but the main product is  $\alpha\beta$ -dibenzylaminoethane (III), b.p. 222°/18 mm.;  $\alpha$ - $\alpha'$ -benzyl- $\gamma$ -phenylcarbamido- $\beta$ - $\gamma$ -phenylcarbamidoethane and  $\beta$ -benzamido- $\alpha$ -benzylbenzamidoethane have m.p. 180° and m.p. 187°, respectively. Treatment of (II) with PhCHO and of the product with Na in EtOH leads to (III). (II) and  $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  when similarly treated give  $\alpha$ -benzylamino- $\beta$ - $p$ -methoxybenzylaminoethane (hydrochloride), characterised by conversion into  $\alpha$ - $\alpha'$ -benzyl- $\gamma$ -phenylcarbamido- $\beta$ - $\alpha''$ - $p$ -methoxybenzyl- $\gamma''$ -phenylcarbamidoethane, m.p. 141° (block), and  $\alpha$ -benzylbenzamido- $\beta$ - $p$ -methoxybenzylbenzamidoethane, m.p. 156°. H. W.

**Character of the combination of colours in an individual molecule of a dye.** S. A. BARKOFF (Bull. Soc. chim., 1935, [v], 2, 1288—1295).—Comparison of the absorption spectra of  $p$ -fuchsin, diamine-blue 2B ( $p\text{-R}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4$ )<sub>2</sub>, and ( $p\text{-R}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4$ )<sub>2</sub>C(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NH<sub>2</sub>Cl [R=1:8:3:6. C<sub>10</sub>H<sub>3</sub>(NH<sub>2</sub>)(OH)(SO<sub>3</sub>H)<sub>2</sub> attached at 7] shows that although there is an appearance of additivity in the composition of the colours the mutual influence of the chromophores is apparent, this causing an individuality characteristic of the absorption of the compound dye. H. W.

**Thiohydrazines.** H. WUYTS and (MLLE.) A. LACOURT (Bull. Acad. roy. Belg., 1935, [v], 21, 618—627).—The following were prepared by methylating (MeI or Me<sub>2</sub>SO<sub>4</sub>) the appropriate thiohydrazines:  $\beta$ -thioacetyl-, m.p. 59°,  $\beta$ -hexahydrothiobenzoyl-, m.p. 108°,  $\beta$ -phenylthioacetyl-, m.p. 82°, and  $\beta$ - $m$ -tolylthioacetyl-, m.p. 91°,  $\alpha$ -phenyl- $\alpha$ -methylhydrazine;  $\beta$ - $o$ -thiotoluoyl- $\alpha$ - $o$ -tolyl-, m.p. 107°,  $\beta$ - $p$ -thiotoluoyl- $\alpha$ - $p$ -tolyl-, m.p. 63° (Bz derivative, m.p. 143.5°), and  $\beta$ - $p$ -thiotoluoyl- $\alpha$ - $o$ -tolyl-, m.p. 62°,  $S$ -methylhydrazine;  $\beta$ -thioacetyl- $\alpha$ -phenyl- $\alpha$ - $S$ -dimethylhydrazine, b.p. 115—120°/2 mm.;  $\beta$ -thioacetyl- $\alpha$ -phenyl- $\alpha$ -benzyl- $S$ -methylhydrazine, m.p. 78°;  $\beta$ -hexahydrothiobenzoyl-, b.p. 150°/1 mm.,  $\beta$ -phenylthioacetyl-, m.p. 76°, and  $\beta$ - $m$ -tolylthioacetyl-, m.p. 58°,  $\alpha$ -phenyl- $\alpha$ - $S$ -dimethylhydrazine. The  $N$ -Bz derivatives of thiobenz- (I), m.p. 160°, and thionaphth- (II), m.p. 181°, -phenylhydrazides,  $o$ -thiotolu- $o$ -tolylhydrazide, m.p. 182°, and phenylthioacetphenylhydrazide (III), m.p. 171°, and the  $N$ - $p$ -nitrobenzoyl derivatives of (III), m.p. 182°, and of the  $S$ -Me derivatives of (I), m.p. 188°, and (II), m.p. 151°, are described. Benzoylation occurs in all cases on the NH<sub>2</sub>aryl. The reactions of R·C(SMe)·N·NHR' and R·CS·NMe·NHR' with the Grignard reagent are discussed. NHMe·NHPh with CH<sub>2</sub>Ph·CS<sub>2</sub>H gives  $\beta$ -phenylthioacetyl- $\alpha$ -phenyl- $\beta$ -methylhydrazine, m.p. 99° (Bz derivative, m.p. 122°), which with MgEtI gives (probably)  $\alpha$ -phenyl- $\beta$ -( $\beta$ -phenylethyl)- $\beta$ -methylhydrazine, m.p. 182° (hydrochloride, m.p. 240°). CH<sub>2</sub>Ph·C(SMe)·N·NPhMe similarly yields (probably)  $\alpha$ -phenyl- $\beta$ -benzyl- $\alpha$ -methyl- $\beta$ -ethylhydrazine, m.p. 138° (hydrochloride, m.p. 235°). Demethylation (HI in Ac<sub>2</sub>O at 325°) does not occur with R·C(SH)·N·NMePh, occurs to the extent of

48% with R·CS·NMe·NHPh, and is complete with R·C(SMe)·N·NHPh and R·C(SMe)·N·NPh·CO·R', whilst R·C(SMe)·N·NMePh loses 1 Me. F. R. G.

**Resistance to heat of certain diazonium compounds and theory of the formation of azo-complexes.** E. JUSTIN-MUELLER (Bull. Soc. chim., 1935, [v], 2, 1370—1376).—Diazobenzene and its  $p\text{-NO}_2$ - and  $p\text{-SO}_3\text{H}$  derivatives were studied. The unsubstituted amine gives the least stable diazo-compound. In AcOH the latter compound is decomposed completely by heat; in dil. HCl it slowly darkens, and after sufficient heating decomp. into phenol is complete, whilst in H<sub>2</sub>SO<sub>4</sub> it darkens less when boiled and gives a purer phenol. The presence of SO<sub>3</sub>H augments considerably the stability of the diazo-compound. The chloride can be heated to boiling without much change and is more resistant in presence of HCl. Prolonged boiling is necessary to effect complete replacement of N<sub>2</sub>. In AcOH, it is transformed without other decomp. into azoxybenzene-4:4'-disulphonic acid (I). The  $p\text{-NO}_2$  has the same effect as  $p\text{-SO}_3\text{H}$  in HCl, but in AcOH there is no stabilising effect and azoxy-compound is not formed. The low resistance of diazo-compounds in weakly acid or somewhat alkaline solution is due to the transformation of the diazonium salt into the diazo-hydrate which, unstable in itself, is an intermediate in the formation of azo-compounds. The production of (I) from diazotised sulphanilic acid is explained as follows:  $2\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{OH} \rightarrow 2\text{C}_6\text{H}_4\cdot\text{N}(\text{SO}_3\text{H})_2 + 2\text{H}_2\text{O} + [\text{N}_2] \rightarrow \text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{SO}_3\text{H})_2\cdot\text{OH} + \text{H}_2\text{O}$ . H. W.

**Replacement of the amino-group of aromatic amines by hydrogen.** L. C. RAIFORD and F. W. OBERST (Amer. J. Pharm., 1935, 107, 242—244).—The yields of hydrocarbon or halogenated derivative obtained by treatment of diazotised aromatic amines with 10% excess of 10% H<sub>3</sub>PO<sub>2</sub> below 5° during 4 days (cf. A., 1902, i, 245) are > those obtained by means of EtOH in those cases where both methods give the required product. H. G. M.

**Iodo- $m$ -nitrophenols.** P. BRENANS and P. LARIVAILLE (Compt. rend., 1935, 201, 81—83).—The NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>I·OH of Schlieper (A., 1894, i, 18) is a mixture of 6-iodo-3-nitrophenol (cf. Proc.C.S., 1901, 17, 131) (*Et* ether, m.p. 84°;  $\alpha\beta$ -dihydroxypropyl ether, m.p. 113—114°; *Ac* derivative, m.p. 122°; *Na* salt, cryst.; *Ba* salt, cryst.) and a tri-iodo- $m$ -nitrophenol, m.p. 135° (*Me* ether, m.p. 126°; *Et* ether, m.p. 92°; *Ac* derivative, m.p. 185°). F. R. G.

**Manufacture of *tert*-alkylphenols.**—See B., 1935, 716.

**Manufacture of 3- and 5-chloro-2-hydroxydiphenyl.**—See B., 1935, 716.

**New method of fission of certain ethers.** M. MOTTIER (Helv. Chim. Acta, 1935, 18, 840—845).—*o*-, *m*-, and *p*-OH·C<sub>6</sub>H<sub>4</sub>·OMe heated (6 hr.) under pressure with NaNH<sub>2</sub> (2 mols.) in tetrahydronaphthalene or PhMe give 75—100% yields of the corresponding C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>. *o*-, *m*-, and *p*-C<sub>6</sub>H<sub>4</sub>Me·OMe, *o*-, *m*-, and *p*-C<sub>6</sub>H<sub>4</sub>(OMe)<sub>2</sub>, PhOMe, and Ph<sub>2</sub>O under similar conditions do not give phenols. F. R. G.



**Physical constants and configuration of the stereoisomeric isoeugenols.** K. VON AUWERS (Ber., 1935, 68, [B], 1346—1350).—Examination of the physical consts. of the stereoisomeric isoeugenols and their derivatives shows that according to m.p., b.p., and  $E\Sigma$  vals. the solid variety has the *trans* configuration (I). As judged by the val. of  $n$  the reverse Me·C·H (I.) is the case, but in this instance H·C·C<sub>6</sub>H<sub>3</sub>(OH)·OMe the rules are based on the behaviour of hydroaromatic compounds. With aromatic substances of known configuration  $n$  of the *trans* forms is > that of the *cis* varieties.

H. W.

**Catalytic reduction reactions. II.** K. PACKEN-DORFF (Ber., 1935, 68, [B], 1251—1254).—Catalytic hydrogenation (PtO<sub>2</sub>) of *m*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub> in EtOAc at room temp. causes fairly rapid absorption of 4.5 H<sub>2</sub> with production of cyclohexane (I) and cyclohexanol, also obtained from *o*- and *p*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub> and from pyrogallol. The yield of (I) increases with the activity of the catalyst. Similarly *o*-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>Et yields Et hexahydrosalicylate and Et hexahydrobenzoate. OH is not protected by conversion into OAlk, since *m*- and *p*-C<sub>6</sub>H<sub>4</sub>(OMe)<sub>2</sub> yield (I) and hexahydroanisole. The product of these changes is invariably a mixture of completely and incompletely hydrogenated material. Completion of the reaction is not effected by use of fresh catalyst, addition of HCl, etc. The production of alcohols and hydrocarbons is therefore due to independent, parallel reactions. The view that catalytic reduction of OH is possible only when at. groupings which can be adsorbed at the surface of the catalyst are present in the mol. is supported by the observation that saturated aliphatic alcohols (glycerol, hexoses, *n*-hexyl alcohol) are not reduced under the experimental conditions, whereas elimination of OH is observed from olefinic alcohols (geraniol, citronellol, linalool).

H. W.

**Molecular rearrangements of anilinothiols.** T. B. JOHNSON and M. L. MOORE (Science, 1935, 81, 643—644).—Two types of reaction product can be formed by mol. rearrangement of a given anilinothiol. *o*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·S·Cl gives with NH<sub>2</sub>Ph a good yield of *o*-nitro-*S*-anilinothiophenol, which when heated at a definite temp. or digested with NH<sub>2</sub>Ph at the b.p. is transformed into 2-nitro-4'-aminodiphenyl sulphide. When warmed with NaOH·EtOH it is transformed into *o*-nitro-*o*'-thioldiphenylamine.

L. S. T.

**Synthesis of *p*-methoxybenzyl acetate.** A. OFNER (Helv. Chim. Acta, 1935, 18, 951—956).—*p*-CH<sub>2</sub>Cl·C<sub>6</sub>H<sub>4</sub>·OMe is prepared in bulk from anisole, CH<sub>2</sub>O, and HCl gas (cf. Quelet, A., 1934, 290) and converted by NaOAc·AcOH into *p*-OAc·CH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·OMe accompanied by *o*-OAc·CH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·OMe and *pp*-CH<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>·OMe)<sub>2</sub>.

F. R. G.

**Action of iodides on sterol dibromides and the preparation of cholestenone.** R. SCHOENHEIMER (J. Biol. Chem., 1935, 110, 461—462).—When sterol dibromides are heated in EtOH solution with NaI or KI, I is liberated with regeneration of the double linking. The reaction is quant. A method is given

for the prep. of cholestenone in 89% yield from cholesterol dibromide, by oxidation with CrO<sub>3</sub> in C<sub>6</sub>H<sub>6</sub> and treatment with NaI.

J. N. A.

**Action of mercuric iodide on cholesterol.** E. MONTIGNIE (Bull. Soc. chim., 1935, [v], 2, 1367).—HgI<sub>2</sub> and cholesterol at 145—150° afford  $\alpha$ -cholesterylene and cholesteryl oxide. Under the same conditions HgCl<sub>2</sub> gives a non-cryst. mixture of saturated Cl-compounds retaining much unattacked HgCl<sub>2</sub>.

H. W.

**Degradation of sitostanol acetate by chromic acid.** E. FERNHOLZ (Helv. Chim. Acta, 1935, 18, 1003—1004; cf. this vol., 542, 617).—A reply to Ruzicka *et al.* regarding priority.

F. R. G.

**Degradation of sterol derivatives with chromic acid.** L. RUZICKA (Helv. Chim. Acta, 1935, 18, 1004).—A reply (cf. preceding abstract).

F. R. G.

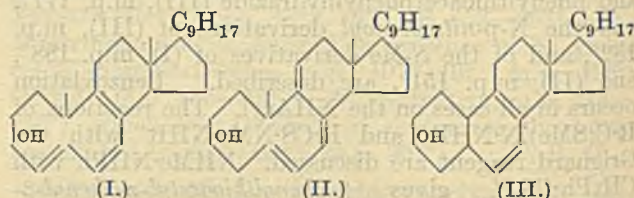
[Chemistry of] algæ.—See this vol., 1040.

**Condensation of biosterol with maleic and citraconic anhydrides.**—See this vol., 1176.

**Ring structure of calciferol.**—See this vol., 1036.

**Vitamin-D and its reaction products.**—See this vol., 1037.

**Constitution of calciferol (vitamin-D).** O. ROSENHEIM and H. KING (Chem. and Ind., 1935, 699—701).—Review of the lit. shows that the appended constitution expresses the distinctive properties of tachysterol (I), *i.e.*, (1) the intense absorption in the ultra-violet region at 280 m $\mu$  enhanced by the proximity of the 3 conjugated double linkings to OH at C3, (2) liability to autoxidation, and (3) lack of crystallising power. The ease with which calciferol (II) crystallises and its increased resistance to autoxidation appear incompatible with the presence of 3 conjugated double linkings in a 10-membered ring. In the reaction (I)  $\rightarrow$  (II) a migration of double linkings is postulated and (II) appears the most probable structure. In the conversion of (II) into pyrocalciferol (III)—isopyrocalciferol it appears that ring closure between C5 and C10 occurs, since the compound is oxidised by HNO<sub>3</sub> to C<sub>6</sub>HMe(CO<sub>2</sub>H)<sub>4</sub> and gives Diels' hydrocarbon C<sub>18</sub>H<sub>16</sub> when dehydrogenated with Se. The ring system of the sterols is therefore present in (III) for which the appended structure is suggested.



H. W.

**Molecular shape of calciferol and related substances.** J. D. BERNAL and D. CROWFOOT (Chem. and Ind., 1935, 701—702).—Details are recorded of the cell size and approx. mol. shape of a no. of sterols and allied compounds. The crystallographic evidence for or against the formulæ of Rosenheim *et al.* (preceding abstract) is difficult to assess, since no compound with a



10-membered ring has been examined by X-ray methods. Since higher cyclic hydrocarbons do not differ essentially from the corresponding fused-ring compounds, it may be considered that these new suggestions do not conflict with the X-ray evidence, whereas those of Windaus *et al.* clearly do so. Suprasterol I cannot have the spiran form, but there is no direct evidence that it has the structure (I), which demands a definite lengthening of the axis not observed in this compound. Suprasterol II is crystallographically peculiar and resembles rather closely anhyd. cholesterol with a definitely crossed ring system.

**Parachor and chemical constitution. Structure of triphenylmethane dyes.**—See this vol., 1059.

**Absorption spectrum of malachite-green leucocyanide and the mechanism of the dark reaction after photolysis.**—See this vol., 1052.

**Exchange of a halogen atom in the aromatic ring for a nitrile group under the influence of nickel cyanide.** T. ŚLEBODZIŃSKI (J. pr. Chem., 1935, [ii], 143, 115—122; cf. A., 1920, i, 44).—PhCl with KCN and NiCl<sub>2</sub> in H<sub>2</sub>O at 260—270° gives 1.8% of BzOH; from PhBr and PhI the yields are 81% and 72%, respectively. The following furnish the corresponding toluic acids in the yields noted: *o*-, *m*-, and *p*-C<sub>6</sub>H<sub>4</sub>MeCl (7.4%, 4.6%, 4.6%); *o*- and *m*-C<sub>6</sub>H<sub>4</sub>MeBr (15%, 6%); *o*-, *m*-, and *p*-C<sub>6</sub>H<sub>4</sub>MeI (35%, 32%, 32%). *p*-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> yields terephthalic acid (12%), and *m*-C<sub>6</sub>H<sub>4</sub>I·CO<sub>2</sub>H, isophthalic acid (99%). 4:4'-Dibromodiphenyl gives 4:4'-diphenic acid (5%); 1-C<sub>10</sub>H<sub>7</sub>Br yields  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·CO<sub>2</sub>H (20%). *p*-C<sub>6</sub>H<sub>4</sub>Br·NO<sub>2</sub> and *p*-C<sub>6</sub>H<sub>4</sub>Br·NH<sub>2</sub> do not give *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H or *p*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H.

**Local anæsthetics. Phenylprocaine.**—See this vol., 1155.

**Oxidation of phenyl derivatives of fatty acids with hydrogen peroxide in presence of copper.** R. O. JONES and I. S. MACLEAN (Biochem. J., 1935, 29, 1877—1880).—Phenylation of straight-chain aliphatic acids increases their rate of oxidation by H<sub>2</sub>O<sub>2</sub> in the presence of Cu; CH<sub>2</sub>Ph·CO<sub>2</sub>H is readily attacked, whilst in the absence of Cu more acid is oxidised with increasing length of chain.

**Configurative relationship of benzylmethylacetic [ $\alpha$ -benzylpropionic] to benzylmethylpropionic [ $\beta$ -benzyl-*n*-butyric] acid.** P. A. LEVENE and R. E. MARKER (J. Biol. Chem., 1935, 110, 299—309).—As part of a study of the effect of the distance of the CO<sub>2</sub>H and Ph groups from the asymmetric centre of the series of Ph acids, the change in rotation on converting *d*- $\alpha$ -benzylpropionic acid (I), b.p. 155°/2 mm., [*M*]<sub>D</sub><sup>25</sup> -48.3°, into *d*- $\beta$ -benzylbutane (II), b.p. 80°/20 mm., [*M*]<sub>D</sub><sup>25</sup> +2.67°, is determined; the effect of exhaustive hydrogenation of the Ph group is also determined. It emerges that in substances of the type CHMeR·[CH<sub>2</sub>]<sub>*n*</sub>·CO<sub>2</sub>H (R=alkyl, Ph, benzyl, or phenethyl and their H<sub>6</sub>-derivatives) the change from *n*=0 to *n*=1 causes a change in the direction of

rotation. (I) is converted into (II) through 1-*Et*  $\alpha$ -benzylpropionate, b.p. 95°/1 mm., [*M*]<sub>D</sub><sup>25</sup> -25.7°, *d*- $\beta$ -benzyl-*n*-propyl alcohol, b.p. 105°/1 mm., [*M*]<sub>D</sub><sup>25</sup> +4.3°, 1- $\alpha$ -bromo- $\beta$ -benzylpropane, b.p. 85°/1 mm., [*M*]<sub>D</sub><sup>25</sup> -17.3°, *d*- $\beta$ -benzylbutyric acid, b.p. 160°/1 mm., [*M*]<sub>D</sub><sup>25</sup> +0.94°, 1-*Et*  $\beta$ -benzylbutyrate, b.p. 110°/1 mm., [*M*]<sub>D</sub><sup>25</sup> -1.61°, *d*- $\gamma$ -benzyl-*n*-butyl alcohol, b.p. 115°/1 mm., [*M*]<sub>D</sub><sup>25</sup> 0.59°, and 1- $\gamma$ -benzyl-*n*-butyl bromide, b.p. 110°/1 mm., [*M*]<sub>D</sub><sup>25</sup> -9.51°. *d*- $\alpha$ -cyclohexylmethylpropionic acid, b.p. 136°/1 mm., [*M*]<sub>D</sub><sup>25</sup> +10.8°, is converted into *d*- $\beta$ -cyclohexylmethyl-*n*-butane, b.p. 191°/760 mm., [*M*]<sub>D</sub><sup>25</sup> -2.82°, through its *Et* ester, b.p. 105°/15 mm., [*M*]<sub>D</sub><sup>25</sup> +13.2°, 1- $\beta$ -cyclohexylmethylpropyl alcohol, b.p. 114°/15 mm., [*M*]<sub>D</sub><sup>25</sup> -5.36°, and bromide, b.p. 108°/10 mm., [*M*]<sub>D</sub><sup>25</sup> -2.06°, 1- $\beta$ -cyclohexylmethyl-*n*-butyric acid, b.p. 148°/1 mm., [*M*]<sub>D</sub><sup>25</sup> -3.96°, and its *Et* ester, b.p. 122°/12 mm., [*M*]<sub>D</sub><sup>25</sup> -3.29°,  $\gamma$ -cyclohexylmethyl-*n*-butyl alcohol, b.p. 120°/1 mm., [*M*]<sub>D</sub><sup>25</sup> -4.03°, and bromide, b.p. 112°/1 mm., [*M*]<sub>D</sub><sup>25</sup> +0.61°.

**Configurative relationship of acids of phenethyl series to those of normal series.** P. A. LEVENE and R. E. MARKER (J. Biol. Chem., 1935, 110, 311—321).—To study the effect of the distances of the CO<sub>2</sub>H and Ph from the asymmetric centre of the series of "phenyl" acids, the change in rotation on converting  $\gamma$ -phenyl- $\alpha$ -methylbutyric acid (I), b.p. 155°/2 mm., [*M*]<sub>D</sub><sup>25</sup> -48.3°, into  $\epsilon$ -phenyl- $\gamma$ -methylpentane (II), b.p. 112°/15 mm., [*M*]<sub>D</sub><sup>25</sup> -4.76°, has been determined; the effect of exhaustive hydrogenation of the Ph has also been determined. It is deduced that configuratively related  $\alpha$ -methyldecoic and  $\gamma$ -phenyl- $\alpha$ -methylbutyric acids rotate light in the same direction; it is also shown that  $\delta$ -phenyl- $\beta$ -methylvaleric and  $\gamma$ -phenyl- $\alpha$ -methylbutyric acids have opposite directions of rotation, and that exhaustive hydrogenation of the Ph has no effect on the direction of rotation except in the case of  $\alpha$ -bromo- $\epsilon$ -phenyl- $\gamma$ -methylpentane. (I) is converted into (II) through *Et*  $\gamma$ -phenyl- $\alpha$ -methylbutyrate, b.p. 120°/2 mm., [*M*]<sub>D</sub><sup>25</sup> +7.6°,  $\delta$ -phenyl- $\beta$ -methylbutyl alcohol, b.p. 157°/17 mm., [*M*]<sub>D</sub><sup>25</sup> -2.7°, and bromide, b.p. 151°/17 mm., [*M*]<sub>D</sub><sup>25</sup> -5.8°,  $\delta$ -phenyl- $\beta$ -methylvaleric acid, b.p. 162°/2 mm., [*M*]<sub>D</sub><sup>25</sup> -6.04°, its *Et* ester, b.p. 131°/2 mm., [*M*]<sub>D</sub><sup>25</sup> -4.9°,  $\epsilon$ -phenyl- $\gamma$ -methyl-*n*-amyl alcohol, b.p. 157°/17 mm., [*M*]<sub>D</sub><sup>25</sup> -3.99°, and bromide, b.p. 160°/17 mm., [*M*]<sub>D</sub><sup>25</sup> -2.29°.  $\gamma$ -cyclohexyl- $\alpha$ -methylbutyric acid, b.p. 156°/2 mm., [*M*]<sub>D</sub><sup>25</sup> +3.4°, is converted into  $\epsilon$ -cyclohexyl- $\gamma$ -methyl-*n*-pentane, b.p. 110°/15 mm., [*M*]<sub>D</sub><sup>25</sup> -2.82°, through *Et*  $\gamma$ -cyclohexyl- $\alpha$ -methylbutyrate, b.p. 101°/1 mm., [*M*]<sub>D</sub><sup>25</sup> +4.92°,  $\delta$ -cyclohexyl- $\beta$ -methylbutyl alcohol, b.p. 141°/17 mm., [*M*]<sub>D</sub><sup>25</sup> -2.09°, and bromide, b.p. 142°/15 mm., [*M*]<sub>D</sub><sup>25</sup> 0°,  $\delta$ -cyclohexyl- $\beta$ -methyl-*n*-valeric acid, b.p. 158°/2 mm., [*M*]<sub>D</sub><sup>25</sup> -2.36°, its *Et* ester, b.p. 162°/17 mm., [*M*]<sub>D</sub><sup>25</sup> -1.85°,  $\epsilon$ -cyclohexyl- $\gamma$ -methylamyl alcohol, b.p. 157°/17 mm., [*M*]<sub>D</sub><sup>25</sup> -1.84°, and bromide, b.p. 151°/15 mm., [*M*]<sub>D</sub><sup>25</sup> -1.12°.

**Configurative relationships of derivatives of benzylmethyl- and phenylethylmethyl-, methylheptyl-, and methyloctyl-acetic acids.** P. A. LEVENE (J. Biol. Chem., 1935, 110, 323—328).—*d*- $\alpha$ -Methylbutyric acid (I) is converted into *d*- $\alpha$ -phenyl- $\beta$ -methylpentane, and *d*- $\alpha$ -benzylpropionic acid (II) leads to *l*- $\alpha$ -phenyl- $\beta$ -methylpentane; hence (I) and



(II) are configuratively related. Since (I) is related to *d*- $\alpha$ -methylnonoic acid (III), (III) is related to (II). Since also *d*- $\alpha$ -methyldecoic acid (IV) is related to *d*- $\gamma$ -phenyl- $\alpha$ -methylbutyric acid (V) and (III) and (IV) are related, it follows that (II) and (V) are related. The correlation of the configuration of (I) and *d*- $\alpha$ -phenyl- $\beta$ -methylbutane (VI), b.p. 80°/12 mm.,  $[M]_D^{25} + 1.85^\circ$ , involved the conversion of *d*-valeraldehyde by MgPhBr into  $\alpha$ -phenyl- $\beta$ -methyl-*n*-butyl alcohol, b.p. 68–70°/0.3 mm., and this was converted into (VI) with HI. On the basis of the max. rotation of (VI) those of the derivatives of  $\beta$ -phenyl- $\alpha$ -methylpropionic acid are calc. H. D.

Maximum rotations of configuratively related carboxylic acids containing a phenyl or a cyclohexyl group. P. A. LEVENE and R. E. MARKER (J. Biol. Chem., 1935, 110, 329–342; cf. A., 1933, 821).—The max. rotations for substances of the type  $\text{CHPhR} \cdot [\text{CH}_2]_n \cdot \text{CO}_2\text{H}$  (I) and of similar substances with Ph replaced by cyclohexyl (II) (R=Me or Et) are determined. With (I) there is a periodicity in the changes in direction of rotation on increasing *n* for the acids and their derived esters, carbinols, and halides. The acids and their esters do not follow Freudenberg's rule. With (II) and its derivatives for *n*=0 and *n*=1 the direction of rotation for R=Me is opposite to that for R=Et. *r*- $\beta$ -Phenyl-*n*-valeric acid is resolved with quinine and converted through *l*-Et  $\beta$ -phenylvalerate, b.p. 105°/1 mm.,  $[M]_D^{25} - 8.88^\circ$ ,  $\gamma$ -phenyl-*n*-amylalcohol, b.p. 118°/1 mm.,  $[M]_D^{25} - 4.41^\circ$ , and bromide, b.p. 102°/1 mm.,  $[M]_D^{25} - 29.5^\circ$ , *l*- $\gamma$ -phenyl-*n*-hexoic acid, b.p. 156°/4 mm.,  $[M]_D^{25} - 1.17^\circ$ , its *Et* ester, b.p. 121°/1 mm.,  $[M]_D^{25} - 4.09^\circ$ , *d*- $\delta$ -phenyl-*n*-hexyl alcohol, b.p. 125°/5 mm.,  $[M]_D^{25} + 0.37^\circ$ , and *l*-bromide, b.p. 125°/3 mm.,  $[M]_D^{25} - 3.25^\circ$ , *l*- $\delta$ -phenylheptoic acid, b.p. 161°/1 mm.,  $[M]_D^{25} - 6.04^\circ$ , its *Et* ester, b.p. 135°/1 mm.,  $[M]_D^{25} - 4.00^\circ$ , and *l*- $\epsilon$ -phenyl-*n*-heptyl alcohol, b.p. 123°/1 mm.,  $[M]_D^{25} - 4.96^\circ$ , into *l*- $\alpha$ -bromo- $\epsilon$ -phenyl-*n*-heptane, b.p. 125°/1 mm.,  $[M]_D^{25} - 11.6^\circ$ .  $\beta$ -Phenylbutyric acid is resolved with quinine and converted through *l*-Et  $\beta$ -phenylbutyrate, b.p. 111°/4 mm.,  $[M]_D^{25} - 2.92^\circ$ , *l*- $\gamma$ -phenyl-*n*-butyl alcohol, b.p. 117°/8 mm.,  $[M]_D^{25} - 2.60^\circ$ , and bromide, b.p. 120°/11 mm.,  $[M]_D^{25} - 7.58^\circ$ , *l*- $\gamma$ -phenyl-*n*-valeric acid, b.p. 137°/1 mm.,  $[M]_D^{25} - 1.89^\circ$ , its *Et* ester, b.p. 112°/1 mm.,  $[M]_D^{25} - 2.54^\circ$ , and *l*- $\delta$ -phenyl-*n*-amyl alcohol, b.p. 109°/1 mm.,  $[M]_D^{25} - 1.48^\circ$ , into *l*- $\alpha$ -bromo- $\delta$ -phenyl-*n*-pentane, b.p. 125°/15 mm.,  $[M]_D^{25} - 1.84^\circ$ . *d*- $\alpha$ -cyclohexylpropionic acid, b.p. 105°/1 mm.,  $[M]_D^{25} + 8.1^\circ$ , is converted through its *Et* ester, b.p. 100°/15 mm.,  $[M]_D^{25} + 11.6^\circ$ , *l*- $\alpha$ -cyclohexyl-*n*-propyl alcohol, b.p. 110°/15 mm.,  $[M]_D^{25} - 0.55^\circ$ , and bromide, b.p. 110°/15 mm.,  $[M]_D^{25} + 3.8^\circ$ , into *d*- $\beta$ -cyclohexylbutyric acid, b.p. 145°/4 mm.,  $[M]_D^{25} + 2.5^\circ$ . H. D.

Synthesis of 4-iodo- $\alpha$ -naphthoic acid. H. GOLDSTEIN, R. MOHR, and T. BLEZINGER (Helv. Chim. Acta, 1935, 18, 813–816).—A diazotised solution of 4:1- $\text{NH}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{CN}$  in dioxan with KI in dil.  $\text{H}_2\text{SO}_4$  gives 4-iodo-1-naphthonitrile, b.p. 200°/12 mm., m.p. 128° (corr.), hydrolysed ( $\text{H}_2\text{SO}_4$ ) to 4-iodo- $\alpha$ -naphthoic acid, m.p. 213° (corr.).  $\alpha$ -Naphthyloxamic acid with ICl yields 4-iodo- $\alpha$ -naphthyloxamic acid, decomp. 198° (corr.), not convertible into 4-iodo- $\alpha$ -naphthyl-

amine, and with Br yields 4-bromo- $\alpha$ -naphthylloxamic acid, decomp. 193° (corr.), hydrolysed to 4-bromo- $\alpha$ -naphthylamine. F. R. G.

Substituted phenylacetone nitriles and derivatives. I. Phenyl-1-cyanocyclopropane,  $\alpha$ -phenyl- $\gamma$ -hydroxybutyronitrile,  $\alpha$ -phenyl- $\gamma$ -chlorobutyronitrile, and  $\alpha$ -phenylcrotononitrile. E. C. KNOWLES and J. B. CLOKE (Rensselaer Polytech. Inst. Bull., Eng. Sci. Ser., No. 49, 24 pp.).—The substance, m.p. 177–178°, previously reported (A., 1932, 739) to be  $\alpha$ -phenylacetacetamide is actually  $\alpha$ -phenyl- $\beta$ -methylglycidamide.

CH. ABS. (r)

*iso*Amyloxyvanadyl salicylates. P. BRAUMAN (Compt. rend., 1935, 200, 1854–1855).—Distillation of 50% aq.  $\text{VOCl}_2$  with *iso*amyl alcohol until the temp. of the vapour reaches 129–130° gives an anhyd. solution of  $\text{VOCl}_2$ , which with  $\text{Li}_2\text{CO}_3$  affords probably  $(\text{C}_5\text{H}_{11}\text{O})_2\text{VO}$ ; addition of *o*- $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{R}$  affords the following *iso*amyloxyvanadyl salicylates,  $\text{C}_5\text{H}_{11}\text{O} \cdot \text{VO} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{R}$ , blue when solid, black or brown when molten (unchanged in absence of  $\text{O}_2$  and  $\text{H}_2\text{O}$ ): *Me*, m.p. 175.5–176.5°; *Et*, m.p. 179–180°; *iso*amyl, m.p. 149.5–151.5°; *Ph*, m.p. 252–253°;  $\beta$ - $\text{C}_{10}\text{H}_7$ , m.p. 179.5–180.5°. R. S. C.

Acetylation of phenolic hydroxyl groups. M. A. VJAZKOVA (J. Appl. Chem. Russ., 1935, 8, 471–475).—*o*- $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ ,  $\text{Ac}_2\text{O}$ , and  $\text{H}_3\text{PO}_4$  in  $\text{C}_6\text{H}_6$  at room temp. afford *o*- $\text{OAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , in 80% yield, and of high purity. The method is of general applicability. R. T.

Substitutions in tyrosine and histidine. H. BAUER and E. STRAUSS [with, in part, E. MASCHMANN] (Ber., 1935, 68, [B], 1108–1115; cf. A., 1932, 402).—Model experiments with  $\text{NH}_2$ -acids in relationship to substitutions in proteins are recorded. Treatment of tyrosine (I) in  $\text{H}_2\text{O}$ - $\text{NaHCO}_3$  with I slowly affords di-iodotyrosine (II), m.p. 204° (decomp.). The corresponding *Me*, decomp. 190°, and *Et*, decomp. 171°, esters are similarly obtained. (I) cannot be iodinated in acid solution, but the influence of the “basic situation” is pronounced in the amide, which in  $\text{AcOH}$  gives *di*-iodotyrosineamide, decomp. 180°. Treatment of the Na salt of (I) with  $\text{Hg}(\text{OAc})_2$  does not immediately yield a mercurated product, but if the mixture is warmed tyrosine-3-mercurihydroxide separates; it is transformed by I-KI in  $\text{H}_2\text{O}$  into (II). A monoiodotyrosine could not be obtained. Iodination of nitrotyrosine, its *Me* ester [m.p. 173° (slight decomp.)] (hydrochloride, decomp. 197°), or 3-nitrotyrosineamide, m.p. 196° (decomp.), could not be effected in presence of  $\text{NaOH}$ ,  $\text{NaHCO}_3$ ,  $\text{NH}_3$ , or  $\text{C}_5\text{H}_5\text{N}$  or by  $\text{HgO}$  and I; similarly, the introduction of Hg appears impossible. Addition of I-KI to a solution of *isobenzoyl*histidine *Me* ester in  $\text{H}_2\text{O}$ - $\text{EtOH}$  containing  $\text{NaIO}_3$  gives the *I*<sub>1</sub>-derivative  $\begin{array}{c} \text{NH} \cdot \text{Cl} \\ | \\ \text{CH} = \text{N} \end{array} > \text{C} \cdot \text{CH}_2 \cdot \text{CH}(\text{NHBz}) \cdot \text{CO}_2\text{Me}$ , decomp.

183°. The view that substitution of I in the glyoxaline ring occurs initially at N from which the halogen becomes transferred to C is supported by the non-occurrence of the reaction when the group is substituted and the inability of such compounds to couple with diazo-derivatives. *N*-Bromoacetyl-3-nitro-



tyrosine, m.p. 175° (decomp.), its *Me* ester, m.p. 127°, *N*-glycyl-3-nitrotyrosine, m.p. 247° (decomp.), and 3'-nitro-4'-hydroxybenzylketopiperazine, decomp. 254°, are incidentally described. H. W.

**Anacardic acid.** I. Anacardic acid and tetrahydroanacardic acid. II. Constitution of tetrahydroanacardic acid. P. P. PILLAY (J. Indian Chem. Soc., 1935, 12, 226—231, 231—236).—I. Anacardic acid (I),  $C_{22}H_{32}O_3$ , m.p. 23—25° (improved method of purification described) (cf. J.C.S., 1887, 51, 663) has 2 active H (Zerevitnov) and 2 aliphatic double linkings. The *Et* ester [prepared from the Ag salt of (I) and *EtI*] decomposes on distillation. Oxidation of (I) with  $HNO_3$  affords  $H_2C_2O_4$ , but with  $KMnO_4$  cœnanthic acid and other dicarboxylic acids are also formed. (I) gives an intense violet coloration with  $FeCl_3$ -*EtOH*, and has a phenolic OH, but is not acetylated by boiling  $Ac_2O$  nor methylated by  $Me_2SO_4$  and alkali. (I) is hydrogenated (Pd-C) to tetrahydroanacardic acid (II),  $C_{22}H_{36}O_3$ , m.p. 92.5—93° [*Me*, m.p. 49°, and *Et* ester, m.p. 38°; *Ac* derivative (III), m.p. 78°; *Br*<sub>1</sub>-derivative, m.p. 77°], oxidised by  $KMnO_4$  in  $COMe_2$  and  $H_2O$  to palmitic and oxalic acids.

II. When heated at about 200° in an atm. of  $N_2$  (I) loses  $CO_2$  and yields a resin and anacardol (IV),  $C_{21}H_{32}O$ , b.p. 215—220°/14 mm., hydrogenated (Pd-C) to tetrahydroanacardol (V), m.p. 53—54° [*Ac* derivative, m.p. 42°, also obtained when (III) is heated; *Bz* derivative, m.p. 54°; *phenylcarbamate*, m.p. 79—80°; *Na* derivative], also obtained together with some tetrahydroanacardyl tetrahydroanacardate, m.p. 49°, hydrolysed to (II) and (V). (V) is readily oxidised by  $KMnO_4$  in  $COMe_2$  to oxalic and palmitic acids. (IV) is decomposed by distillation under atm. pressure, and the resulting phenols on fusion with  $KOH$  give salicylic acid. From the foregoing reactions, together with the fact that (II) gives a violet coloration with  $FeCl_3$ , it is concluded that (II) is 2-hydroxy-3-n-pentadecylbenzoic acid.

H. G. M.

**$\psi$ -Chlorides and  $\psi$ -esters of *o*-dicarboxylic acids.** A. KIRPAL, A. GALUSCHKA, and E. LASSAK (Ber., 1935, 68, [B], 1330—1334).—The action of  $PCl_5$  on phthalic and 4-chlorophthalic anhydride leads exclusively to the normal chlorides, whereas under similar conditions the more highly substituted anhydrides yield  $\psi$ -chlorides which can only be partly isomerised to the true chlorides by prolonged heating at the b.p.  $C_6H_4\langle\begin{smallmatrix} OCl_2 \\ CO \end{smallmatrix}\rangle O$  is converted by  $MeOH$  containing pptd.  $CaCO_3$  at 15—20° into *Me*<sub>2</sub>  $\psi$ -phthalate, m.p. 53°, which passes below its b.p. into  $C_6H_4(CO_2Me)_2$ . as-3:6-Dichlorophthalyl chloride (I), m.p. 122°, is partly isomerised at its b.p. to 3:6-dichlorophthalyl chloride, m.p. 31°, which slowly when solid, more rapidly in solution, and instantaneously in the presence of animal C reverts to (I). Even in absence of a neutralising medium (I) is converted into *Me*<sub>2</sub> 3:6-dichloro- $\psi$ -phthalate, m.p. 134°; *Me* 3:6-dichlorophthalate, from  $C_6H_4(CO_2Ag)_2$  and  $MeI$ , has m.p. 82°. 3:4-Dichlorophthalic anhydride and  $PCl_5$  give 3:4-dichloro- $\psi$ -phthalyl chloride, m.p. 133°, whence *Et*<sub>2</sub> 3:4-

dichloro- $\psi$ -phthalate (II), m.p. 79° (*Et*<sub>2</sub> 3:4-dichlorophthalate has m.p. 80°). (II) is hydrolysed by a small amount of  $H_2O$  to 1-*Et* H 3:4-dichlorophthalate (II), m.p. 184°, also obtained by esterification of 3:4- $C_6H_2Cl_2(CO_2H)_2$  with *EtOH* and  $H_2SO_4$ . 2-*Et* H 3:4-dichlorophthalate, m.p. 164°, is obtained by partial hydrolysis of the *Et*<sub>2</sub> ester or by the action of abs. *EtOH* on 3:4- $C_6H_2Cl_2(CO_2H)_2$ . (II) and  $SOCl_2$  in  $CCl_4$  yield chloroethoxy-3:4-phthalide, m.p. 87°. H. W.

**Preparation of  $\beta$ -amino-acids.** J. V. SOUDI (J. Amer. Chem. Soc., 1935, 57, 1279).—Slow evaporation of a mixture of  $CHPh:C(CO_2Et)_2$  and 10% *EtOH-NH*<sub>3</sub> and passage of  $HCl$  into the *Et*<sub>2</sub>O extract of the product, gives 47% of the hydrochloride of *Et*  $\beta$ -amino- $\beta$ -phenylethane- $\alpha\alpha$ -dicarboxylate, which is hydrolysed (dil.  $HCl$ ) to  $\beta$ -amino- $\beta$ -phenylpropionic acid [also obtained by evaporation of a mixture of  $CHPh:C(CO_2H)_2$  and 10% aq.  $NH_3$ ]. H. B.

**Condensation of homophthalaldehyde to 2-phenylnaphthalene-5:2'-dialdehyde.** P. BAUMGARTEN (Ber., 1935, 68, [B], 1316—1317).—2-Phenylnaphthalene-5:2'-dialdehyde (I), m.p. 126.5°, is formed by the action of boiling 1%  $NaOH$  on homophthalaldehyde (II), thus strengthening the hypothesis that (II) is an intermediate compound in the formation of (I) from *o*-aldehyde- $\omega$ -aminostyrene-*N*-sulphonic acid. H. W.

**Synthesis of dimethoxycinnamaldehydes.** K. FEUERSTEIN (J. pr. Chem., 1935, [ii], 143, 174—178).—Veratraldehyde and *o*-veratraldehyde condensed with  $MeCHO$  ( $MeOH-KOH$ ) yield, respectively, 3:4-dimethoxycinnamaldehyde, m.p. 83.5°, b.p. 164°/3 mm. (semicarbazone, m.p. 185°; oxime, m.p. 82°; thiosemicarbazone, m.p. 182°; aldazine, m.p. 200°; phenylhydrazone, m.p. 133°), and 2:3-dimethoxycinnamaldehyde, m.p. 77.5°, b.p. 160—161°/5 mm. (semicarbazone, m.p. 198°; oxime, m.p. 115°; thiosemicarbazone, m.p. 200°; aldazine, m.p. 182.5°; phenylhydrazone, m.p. 134°). E. W. W.

**Complete synthesis of dicyclo-[2:2:2]-octanone and dicyclo-[2:2:2]-octane.** G. KOMPPA (Ber., 1935, 68, [B], 1266—1272).—Oxidation of *p*-isopropylphenylacetonitrile, b.p. 140—142°/16 mm., with boiling  $HNO_3$  (*d* 1.21) gives homoterephthalic acid (I) accompanied by considerable amounts of terephthalic acid (II). Since oxidation of *p*-isopropylbenzyl chloride yields (II) exclusively, the best method of preparing (I) consists in treating  $CN\cdot C_6H_4\cdot CH_2\cdot CN$  with  $H_2SO_4-H_2O$  at 100°. Hydrogenation of *Me*<sub>2</sub> homoterephthalate, b.p. 161—165°/8 mm., in *AcOH* containing colloidal Pt at 45°/4 atm. and hydrolysis of the product with boiling  $HCl$  affords hexahydrohomoterephthalic acid, m.p. 146—147° (which is not dehydrated by  $AcCl$ ), and small amounts of the (?) corresponding *cis*-acid, m.p. 121—125°. Dry distillation of *Mg* hexahydrohomoterephthalate (the *Ca*, *Ba*, *Zn*, and *Pb* salts are less satisfactory) gives dicyclo-[2:2:2]-octanone (III), m.p. 176°, in 50—60% yield. Reduction of dicyclo-[2:2:2]-octanone oxime, m.p. 117—118°, with *Na* and *EtOH* yields dicyclo-[2:2:2]-octylamine, m.p. 138—140° in sealed tube (hydrochloride, m.p. > 300°; picrate, m.p. 222—223°;



corresponding *carbamide*, m.p. 182.5—183°. (III) is reduced by Na and EtOH to dicyclo-[2 : 2 : 2]-*octanol*, m.p. 216—217° in sealed tube (*phenylurethane*, m.p. 138—139°; *acetate*, b.p. 121—123°/15 mm.), converted by PCl<sub>5</sub> into dicyclo-[2 : 2 : 2]-*octyl chloride*, which is transformed by Na and abs. EtOH into dicyclo-[2 : 2 : 2]-*octane*, m.p. 168° (corr.). H. W.

**Isomerism of halochromic compounds. III.** P. PFEIFFER, K. SCHWENZER, and K. KUMETAT (J. pr. Chem., 1935, [ii], 143, 143—156).—Colourless NH<sub>4</sub> salts and coloured oxonium salts of unsaturated basic ketones, obtained with HClO<sub>4</sub> (A., 1933, 1052; 1934, 76), are similarly obtained with HBF<sub>4</sub> or H<sub>2</sub>SiF<sub>6</sub>. Thus *p*-dimethylaminostyryl Me ketone forms a blue *borofluoride*, m.p. 152° (decomp.), fairly stable to H<sub>2</sub>O, which when dissolved in HCO<sub>2</sub>H and treated with HBF<sub>4</sub> and Et<sub>2</sub>O isomerises to the colourless *borofluoride*, m.p. about 150° (decomp.), immediately hydrolysed by H<sub>2</sub>O. Ph *p*-dimethylaminostyryl ketone treated in EtOH with HBF<sub>4</sub> yields a colourless *borofluoride*, m.p. about 172° (decomp.), converted by CH<sub>2</sub>Cl·CO<sub>2</sub>H into the reddish-violet *borofluoride*. *p*-Chlorophenyl *p*'-dimethylaminostyryl ketone similarly gives a colourless and a bluish-violet *borofluoride*, the latter obtained by treating the former with AcOH and HBF<sub>4</sub>. By treatment in AcOH with H<sub>2</sub>SiF<sub>6</sub>, *p*-dimethylaminostyryl Me ketone forms colourless and reddish-violet *silicofluorides*, and *p*-chlorophenyl *p*'-dimethylaminostyryl ketone a colourless *silicofluoride*.

From saturated ketones, only colourless NH<sub>4</sub> perchlorates are obtained. *p*-Dimethylaminobenzophenone gives a *perchlorate*, m.p. 162°, and *p*-dimethylamino-*p*'-methoxybenzophenone a *perchlorate*, m.p. 161°; in each case the solution of the perchlorate in AcOH or EtOH is bright yellow, suggesting the existence of a coloured form. Michler's ketone gives a colourless *diperchlorate*, m.p. 210°, and a yellow *perchlorate*, m.p. 147°. Ph *p*-dimethylaminophenylethyl ketone, m.p. 49.5—50.5° (*oxime*, m.p. 89—89.5°; *H sulphate*, m.p. 70°), obtained by reduction (PtO<sub>2</sub>) of Ph *p*-dimethylaminostyryl ketone, yields a *perchlorate*, m.p. 167°. Ph *p*-nitrodiethenyl ketone, new m.p. 157° (cf. B., 1933, 662), obtained from *p*-nitrodiethenyl and BzCl (AlCl<sub>3</sub> in PhNO<sub>2</sub>), is reduced (SnCl<sub>2</sub>) to Ph *p*-aminodiphenylethyl ketone, m.p. 143°, which gives a *perchlorate*, decomp. 218°. *p*-Aminophenyl *p*-diphenylethyl ketone forms a *perchlorate*, m.p. 230°, and its Bz derivative, a yellow *perchlorate*. E. W. W.

**α-Halogenoketones. α-Chlorodibenzyl ketone.** C. PREVOST and A. SOMMIÈRE (Bull. Soc. chim., 1935, [v], 2, 1151—1165).—The reactivity of the halogen and CO of α-halogenoketones towards mildly alkaline reagents is compared. α-*Chlorodibenzyl ketone* (I) (prep. by S<sub>2</sub>Cl<sub>2</sub>), m.p. 68.5°, b.p. 195°/12 mm. (decomp.) (oxidised to > 1 mol. of BzOH), with HCN-EtOH gives the *cyanohydrin* (II), m.p. 135—136° (only the less sol. isomeride is isolated), but with NaOAc-AcOH the α-*OAc-ketone*, b.p. 197°/13 mm., hydrolysed by NaOH-EtOH (slightly > 1 mol.) to α-*γ-diphenylpropan-α-ol-β-one* (III), m.p. 116°; (III) is also obtained from (I) and hot aq. Na<sub>2</sub>CO<sub>3</sub>, is oxidised by CrO<sub>3</sub> to PhCHO and BzOH, and with alkali gives the dienolic form, OH·CPh·C(OH)·CH<sub>2</sub>Ph, since acidification of its alkaline solution yields some

CH<sub>2</sub>Ph·CH(OH)·COPh (IV); (IV) is equally isomerised by alkali to give some (III). (III) and S<sub>2</sub>Cl<sub>2</sub> in CCl<sub>4</sub> give γ-*chloro-α-γ-diphenylpropan-α-ol-β-one*, m.p. 95°. With NaOMe at 100° (I) gives α-*phenoxydibenzyl ketone*, m.p. 68°, which is decomposed by distillation/11 mm. to give some PhOH and (?) α-*γ-diphenyl-β-γ-oxido-Δ<sup>4</sup>-propylene* (V), b.p. 173°/11 mm. (I) and NaOMe under other conditions give (V), which, with 1 : 3-*diphenyl-1 : 3-dibenzylcyclobuta-2 : 4-dione*, m.p. 153° (obtained by polymerisation of CH<sub>2</sub>Ph·CPh·CO initially formed), is also obtained by use of KOH in hot dry Et<sub>2</sub>O. (I) and conc. aq. KCN (4—5 mols.) give α-*β-oxido-β-cyano-α-γ-diphenylpropane* (VI), m.p. 118.5°, hydrolysed by 5% H<sub>2</sub>SO<sub>4</sub> or aq. HCl to a mixture of (IV) and β-*cyano-α-γ-diphenylpropane-α-β-diol*, m.p. 129°, also obtained from (III) and an excess of HCN in EtOH. (II) with KOH gives (I), but with KCN-EtOH affords (IV). (VI) and HCl in C<sub>6</sub>H<sub>6</sub> give (I) and (II). R. S. C.

**Fluorene series. II. 3-Nitrofluorenone and its derivatives.** F. E. BARDOUT (Anal. Assoc. Quim. Argentina, 1934, 22, 123—132; cf. A., 1932, 153).—3-Hydroxyfluorenone [*oxime*, m.p. 188° (decomp.)] in 10% aq. NaOH with Me<sub>2</sub>SO<sub>4</sub> gives 3-*methoxyfluorenone*, m.p. 96—97°. Diazotised 3-amino-fluorenone with Cu<sub>2</sub>Br<sub>2</sub> (Sandmeyer) gives 3-*bromo-fluorenone*, m.p. 165° (corr.). Variations in the recorded m.p. of 3-nitrofluorenone and its oxime are discussed. F. R. G.

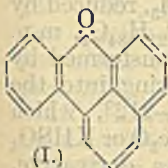
**Addition reactions of phenyl vinyl ketone. V. Anthrone.** C. F. H. ALLEN and S. C. OVERBAUGH (J. Amer. Chem. Soc., 1935, 57, 1322—1325).—Anthrone (I) and CH<sub>2</sub>Cl·CH<sub>2</sub>·COPh (II) in 70% H<sub>2</sub>SO<sub>4</sub> at 100° (bath) for 10—15 min. give 63% of 9-β-*benzoyl-ethyl-* (III), m.p. 141—144°, and 15% of 9 : 9-*di-β-benzoyl-ethyl-10-anthrone* (IV), m.p. 187—188° (*dioxime*, m.p. 244—245°). (IV) is similarly obtained from (II) and (III). A solution of (III) in MeOH-NaOH (trace) slowly deposits (IV). (III) and (IV) are both oxidised (CrO<sub>3</sub>, AcOH) to anthraquinone [also formed from (III) and Br in CHCl<sub>3</sub>]. (III) is converted by 80% H<sub>2</sub>SO<sub>4</sub> at 100° (bath) into Bz-1-*phenylbenzanthrone* (V), m.p. 182—183°, also formed from (I) and CHPh·CH·CHO in 1-C<sub>10</sub>H<sub>7</sub>Cl at 250—260°, which is oxidised (CrO<sub>3</sub>, AcOH) to 1-benzoylanthraquinone. Mechanisms suggested (lit.) for the production of benzanthrone from (I) and unsaturated aldehydes are discussed. MgBu<sup>+</sup>Cl and (V) give 10-*tert-butyl-Bz-1-phenylbenzanthron-10-ol*, m.p. 159—160°; with other Grignard reagents 1 : 4-addition occurs (cf. this vol., 751) and affords 4-*ethyl-* (VI), m.p. 120—122°, 4-*n-butyl-* (VII), m.p. 81—82°, 4-*n-hexyl-* (VIII), m.p. 88°, 4-*cyclohexyl-*, m.p. 190—191°, 4-*phenyl-* (IX), m.p. 223—224°, 4-*benzyl-* (X), m.p. 179—180°, 4-β-*phenylethyl-*, m.p. 154—155°, and 4-*styryl-* (XI), m.p. 186—187°. Bz-1-*phenylbenzanthrone* (VI), (VII), and (VIII) are oxidised (method: *loc. cit.*) to 1-benzoyl-4-*ethyl-*, m.p. 198°, 4-*n-butyl-*, m.p. 123—124°, and 4-*n-hexyl-*, m.p. 128°, -*anthraquinone*, respectively; these are all oxidised (CrO<sub>3</sub>, aq. AcOH) to 4-benzoylanthraquinone-1-carboxylic acid, also obtained directly from (IX). (X) similarly gives 1 : 4-dibenzoylanthraquinone. (IX) could not be oxidised. H. B.



**Addition of magnesium methyl iodide to benzylidenepropiophenone.** L. I. SMITH and L. I. HANSON (J. Amer. Chem. Soc., 1935, 57, 1326—1328).—Decomp. of the product (I) from benzylidenepropiophenone and  $\text{MgMeI}$  with cold dil.  $\text{HCl}$  (method: Kohler, A., 1904, i, 595) gives 1-phenyl-2:3-dimethylindene (II), m.p. 68—69°, oxidised (2%  $\text{KMnO}_4$ ) to  $\alpha\text{-C}_6\text{H}_4\text{Bz}\cdot\text{CO}_2\text{H}$ . Decomp. of (I) with aq.  $\text{NH}_4\text{Cl}$  affords  $\alpha\gamma$ -diphenyl- $\beta$ -methyl- $\Delta^4$ -buten- $\gamma$ -ol, decomp. on attempted distillation, which is oxidised ( $\text{KMnO}_4$  in  $\text{H}_2\text{O}$  or  $\text{COMe}_2$ ;  $\text{O}_3$ ) to  $\text{BzOH}$  and  $\text{COPhMe}$  and is converted by  $\text{MeOH}$ -conc.  $\text{HCl}$  into (II) [probably by way of  $\text{CPhMe}\cdot\text{CMe}\cdot\text{CHPh}\cdot\text{OH}$  (or the chloride) and subsequent loss of  $\text{H}_2\text{O}$  (or  $\text{HCl}$ )]. 3-Phenyl-2-methylindene (III) and  $\text{MgMeI}$  (2 mols.) give 1-hydroxy-3-phenyl-1:2-dimethylindene, m.p. 107—109°, which could not be converted into 3-phenyl-1:2-dimethylindene. (III) is reduced (red P,  $\text{HI}$ ,  $\text{AcOH}$ ) to the indanone, which with  $\text{MgMeI}$  affords 1-hydroxy-3-phenyl-1:2-dimethylindane, m.p. 101—102°, dehydrated ( $\text{AcOH}$ - $\text{H}_2\text{SO}_4$ ) to (II).

H. B.

**Nitration of 1:9-benzanthrone by nitrogen dioxide and formulation of 1:9-benzanthrone.** K. LAUER and K. ATARASHI (Ber., 1935, 68, [B], 1373—1376).—Benzanthrone (I), solid or in solution, is very readily attacked by  $\text{NO}_2$  giving *Bz*-1-nitrobenzanthrone and small amounts of a complex product, apparently a dihydroxydibenzanthronyl or dihydroxydibenzanthrone. The *Bz*-ring does not therefore exist in a radical form nor as part of the  $\text{C}_{10}\text{H}_8$  system, but is an unsaturated arrangement with aliphatic properties. (I) has therefore the annexed constitution.



H. W.

**Free radicals.** R. A. LABRIOLA (Anal. Asoc. Quím. Argentina, 1934, 22, 109—122).—A solution of  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$  in  $\text{C}_6\text{H}_5\text{N}$  heated with  $\text{CPh}_3\text{Cl}$  yields  $\alpha$ -( $\beta$ -phenylpropionyl)- $\beta$ -triphenylmethylhydrazine, m.p. 165—166° (decomp.), oxidised ( $\text{Br}\cdot\text{H}_2\text{O}$ ) to the corresponding azo-derivative (I), m.p. 55—56°, which when heated in xylene in an atm. of  $\text{CO}_2$  gives  $\text{N}_2$  and  $\text{CPh}_3\cdot\beta$ -phenylethyl ketone, m.p. 125°. (I) when heated in  $\text{C}_6\text{H}_6$  ( $\text{O}_2$  atm.) yields  $\text{CPh}_3$  peroxide;  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$  similarly yields  $\alpha$ -cinnamoyl- $\beta$ -triphenylmethylhydrazine, m.p. 161—162°, which with saturated aq.  $\text{CaCl}_2$  ( $\text{CO}_2$  atm.) gives a compound, m.p. 185—186°, containing  $\text{Cl}$  and  $\text{N}$ , and  $\text{CPh}_3\cdot\text{CO}\cdot\text{CH}\cdot\text{CHPh}$ .  $\text{CPh}_3\cdot\text{C}\cdot\text{COCl}$  and  $\text{CPh}_3\cdot\text{NH}\cdot\text{NH}_2$  in  $\text{Et}_2\text{O}$  give  $\alpha$ -phenylpropionyl- $\beta$ -triphenylmethylhydrazine (II), m.p. 158—159°, and in  $\text{C}_6\text{H}_5\text{N}$  give  $\alpha$ -( $\beta$ -chlorocinnamoyl)- $\beta$ -triphenylmethylhydrazine (III), m.p. 193—194°. (II) in  $\text{CHCl}_3$  oxidised by aq.  $\text{K}_3\text{Fe}(\text{CN})_6$  gives the corresponding azo-derivative, m.p. 70°. (III) in  $\text{CHCl}_3$  with 2*N*- $\text{NaOH}$  yields a  $\text{Cl}$ -free compound, m.p. 70°, which when heated in  $\text{C}_6\text{H}_6$  ( $\text{CO}_2$  atm.) gives  $\text{N}_2$  and a resin.

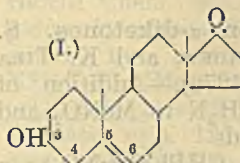
F. R. G.

**Polyterpenes and polyterpenoids. XCVIII. Steric inversion of C 3 of sterols and male sexual hormones.** L. RUZICKA, H. WIRZ, and J. MEYER (Helv. Chim. Acta, 1935, 18, 998—1003).—*epi*-Dihydrocholesterol is converted by  $\text{PCl}_5$  into  $\alpha$ -

cholestyl chloride, m.p. 114—115°, and by  $\text{PBr}_3$  to  $\alpha$ -cholestyl bromide, m.p. 115—115.5°; these with  $\text{CrO}_3$  in  $\text{AcOH}$  give, respectively, 3-chloro- $\alpha$ -tioallocholan-17-one (I), m.p. 173°, obtained by Butenandt *et al.* (this vol., 413) and the 3-*Br*-compound, m.p. 163—164°, sublimes 130—140°/0.01 mm. [semicarbazone, m.p. 262° (decomp.)]. (I) has no activity in the capon test, but its isomeride, m.p. 128° (cf. A., 1934, 1221), is active. (I) is an intermediate of unknown orientation in the conversion of dehydroandrosterone (*trans*) into androsterone (*cis*).

F. R. G.

**Sexual hormones. V. Artificial preparation of the male sexual hormone *trans*-dehydroandrosterone and of androstene-3:17-dione.** L. RUZICKA and A. WETTSTEIN. VI. Androstane-diols and their methyl derivatives. Specificity of male sexual hormone activity. L. RUZICKA, M. W. GOLDBERG, and J. MEYER (Helv. Chim. Acta, 1935, 18, 986—994, 994—998; cf. this vol., 346).—V. Cholesteryl acetate dibromide with  $\text{CrO}_3$  in  $\text{AcOH}$  gives Na 3-acetoxy- $\Delta^{5:6}$ -cholenate (3-*OAc*-acid, m.p. 186—187°; 3-*OH*-acid, m.p. 241—242°) and 3-acetoxy- $\Delta^{5:6}$ - $\alpha$ -tiocholen-17-one, m.p. 171—172°, isolated as its semicarbazone, m.p. 273—275°, hydrolysed ( $\text{H}_2\text{SO}_4$ ) to 3-hydroxy- $\Delta^{5:6}$ - $\alpha$ -tiocholen-17-one (I) in two readily interconvertible forms, m.p. 140—141° and 152—153°, of which the latter is identical chemically and physiologically with dehydroandrosterone isolated by Butenandt *et al.* (this vol., 413; cf. Schoeller *et al.*, this vol., 981) from men's urine. (I) brominated in  $\text{AcOH}$ , subsequently oxidised ( $\text{CrO}_3$ ,  $\text{AcOH}$ ), and then reduced ( $\text{Zn}$ ,  $\text{AcOH}$ ) yields  $\Delta^{4:5}$ - $\alpha$ -tiocholen-3:17-dione.



VI. Androsterone (II) with  $\text{MgMeI}$  in  $\text{Et}_2\text{O}$  gives 3-*epihydroxy*-17-hydroxy-17-methylandrosterane (methyl-androstanediol) (III), m.p. 184—185°. Androstane-3:17-dione with  $\text{MgMeI}$  in  $\text{Et}_2\text{O}$  gives 3:17-di-hydroxy-3:17-dimethylandrosterane (dimethylandrostanediol) (IV), m.p. 150°. The monosuccinyl derivative, m.p. 185—185.5°, of (II) was hydrogenated ( $\text{PtO}_2$ ,  $\text{H}_2$ ) to 3-monosuccinyl-dihydroandrosterone, m.p. 207—208°. All m.p. are corr. The activity of the above compounds in the capon test is described. (III) is more active than (II) but (IV) is inactive.

F. R. G.

**Constitution of dehydroandrosterone and its preparation from cholesterol.** E. S. WALLIS and E. FERNHOLZ (J. Amer. Chem. Soc., 1935, 57, 1379—1380).—Dehydroandrosterone (I) has been prepared (as acetate) by oxidation ( $\text{CrO}_3$ ) of cholesteryl acetate dibromide. The stereochemical arrangement of the  $\text{OH}$  in (I) is, therefore, the same as in cholesterol [but not as in androsterone (Butenandt and Dannenbaum, this vol., 413)].

H. B.

**Androsterone. IV, V.**—See this vol., 1033.

**Action of alkali on acylated ketoximes. I. Effect of structure and configuration.** R. P. BARNES and A. H. BLATT (J. Amer. Chem. Soc., 1935, 57, 1330—1332; cf. A., 1934, 773).— $\alpha$ -Benzoin-oxime propionate, benzoate, and cinnamate (I),



anisoyl-phenyl- and -*o*-chlorophenyl-carbinol oxime acetates, isobutyroinoxime acetate, and  $\alpha$ -benzoyl- $\alpha$ -phenylethyl alcohol oxime acetate undergo fission (to aldehyde and nitrile; cf. *loc. cit.*) when treated with cold aq. 5% NaOH [for (I) aq. EtOH-NaOH is used].  $\beta$ -Benzoinoxime propionate, benzoate, and cinnamate and  $\beta$ -benziloxime propionate and cinnamate similarly regenerate the oxime. From the above and other (lit.) data, it follows that the structural factor determining fission of an acylated ketoxime is the presence of OH, CO<sub>2</sub>H, or CO in the  $\alpha$ -position to the C:N linking. Furthermore, when one of these groups is *anti* to the OAcyl, fission (a second-order Beckmann rearrangement) occurs; hydrolysis takes place only if the group is *syn*. H. B.

**Mechanism of the diacetyl reaction.** H. MÜLLER (Z. physiol. Chem., 1935, 233, 276—280).—Lang's view (A., 1932, 834) of the reaction between creatine and AcBz could not be confirmed. Attempts to condense guanidine or derivatives with AcBz usually gave labile amorphous products. *as*-Phenylmethylguanidine (I) affords a compound containing (I) and AcBz in approx. the ratio 1:1 (not 3:2 as assumed by Lang). Condensation of AcBz with CO(NH<sub>2</sub>)<sub>2</sub> in acid or alkaline solution gives a cryst. *bisglyoxalone* (?), C<sub>11</sub>H<sub>12</sub>O<sub>2</sub>N<sub>4</sub>. J. H. B.

**Action of nitromethane on  $\alpha$ -diketones.** S. FUJISE, O. TAKEUCHI, T. KAMIOKA, and K. TIBA (Ber., 1935, 68, [B], 1272—1276).—Addition of benzil in powder form or in C<sub>5</sub>H<sub>5</sub>N to MeNO<sub>2</sub> and NaOEt in well-cooled EtOH yields OH·CHPh·CH:NO<sub>2</sub>Na (whence CHPh·CH·NO<sub>2</sub>), a little PhCHO, and considerable amount of EtOBz. With KOH as condensing agent, CH<sub>2</sub>Bz·NO<sub>2</sub> is formed. Fural in presence of NaOEt affords  $\alpha$ -nitro- $\beta$ -furylethylene and Et furan-2-carboxylate (I), whereas Ph 2-furyl diketone gives CHPh·CH·NO<sub>2</sub> and (I). H. W.

**Preparation of chloroacetylpyrocatechol.** H. D. HOBERMAN (J. Amer. Chem. Soc., 1935, 57, 1382).—CH<sub>2</sub>Cl·CO<sub>2</sub>H (50 g.), *o*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub> (50 g.), and freshly distilled POCl<sub>3</sub> (50 g.) heated in SO<sub>2</sub> for 1 hr. give chloroacetylpyrocatechol (53.6 g.), m.p. 173°. H. B.

**2-Mesityl-1:4-naphthaquinone and its derivatives.** H. C. TUAN (J. Chinese Chem. Soc., 1935, 3, 141—149).—Mesitylene and  $\alpha$ -naphthaquinone condense (AlCl<sub>3</sub>) to 2-mesityl-1:4-naphthaquinone (I), m.p. 172°, reduced to the -1:4-dihydroxynaphthalene, m.p. 168—169°. (I) is brominated to 3-bromo-2-mesityl-1:4-naphthaquinone, m.p. 147°, which with HNO<sub>3</sub> yields 3-bromo-2-(3:5-dinitro-2:4:6-trimethylphenyl)-1:4-naphthaquinone, m.p. 232—233°, with NaOEt forms 3-ethoxy-2-mesityl-1:4-naphthaquinone (II), m.p. 97—98°, and with CN·CH<sub>2</sub>·CO<sub>2</sub>Et affords *Et* 3-mesityl-2- $\alpha$ -naphthaquinonylecyanoacetate, m.p. 113—120°, hydrolysed to a substance, C<sub>21</sub>H<sub>11</sub>O<sub>5</sub>N, m.p. 318—320°. (II) and AcCl lead (AlCl<sub>3</sub>) to 3-hydroxy-2-(3-acetyl-2:4:6-trimethylphenyl)-1:4-naphthaquinone, m.p. 203°. F. R. S.

**Blue-fluorescing substance in the corpus luteum.**—See this vol., 1145.

**Echinenone and pentaxanthin: two new carotenoids found in the sea-urchin.**—See this vol., 1145.

**Chemistry of heparin.**—See this vol., 1144.

**Lactone of sulphite waste and tsugaresinol.** H. EMDE (Helv. Chim. Acta, 1935, 18, 807; cf. this vol., 623).—Tsugaresinol has the composition C<sub>20</sub>H<sub>20</sub>O<sub>6</sub> and not C<sub>19</sub>H<sub>20</sub>O<sub>6</sub> as stated by Slotta (this vol., 754). F. R. G.

**Neutral saponins. II. Degradation of a genin of the neutral sapogenins to a derivative of the bile acids.** R. TSCHESCHE and A. HAGEDORN (Ber., 1935, 68, [B], 1412—1420).—The relationship of the neutral saponins of *Digitalis* to the bile acids is established and the presence of 27 C atoms in the genin skeleton is placed beyond doubt. Tigogenin (isolation described) is converted by NaOAc and boiling Ac<sub>2</sub>O into its acetate, m.p. 219°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -49.5° in CHCl<sub>3</sub>, which when drastically oxidised with CrO<sub>3</sub> gives as main product an acid, C<sub>27</sub>H<sub>42</sub>O<sub>5</sub>, m.p. 221—222° (oxidised by CrO<sub>3</sub> to a substance, C<sub>27</sub>H<sub>40</sub>O<sub>5</sub>, m.p. 184.5°), one or more further acids, and (in 10% yield) an acetylated lactone, m.p. 219°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -49.5° in CHCl<sub>3</sub>, hydrolysed to a lactone, C<sub>22</sub>H<sub>34</sub>O<sub>3</sub>, m.p. 233.5°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -41.2° in CHCl<sub>3</sub>. Oxidation of the latter substance by CrO<sub>3</sub> in AcOH yields the ketolactone, C<sub>22</sub>H<sub>32</sub>O<sub>3</sub>, m.p. 254°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -22.8° in CHCl<sub>3</sub>, reduced by Zn-Hg and 15% HCl to the lactone, C<sub>22</sub>H<sub>34</sub>O<sub>2</sub>, m.p. 199°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -44.4° in CHCl<sub>3</sub>. This is transformed by MgPhBr with opening of the lactone ring into the diphenylcarbinol, C<sub>34</sub>H<sub>46</sub>O<sub>2</sub>, m.p. 211—212°, which contains 2 OH; under the influence of Ac<sub>2</sub>O or KHSO<sub>4</sub> it loses 1 H<sub>2</sub>O giving a tetrahydrofuran derivative, C<sub>34</sub>H<sub>44</sub>O, m.p. 173.5°, the formation of which shows the OH to be in the 1:4-position to one another. Oxidation of the carbinol affords a neutral substance, an acid, C<sub>34</sub>H<sub>42</sub>O<sub>4</sub>, m.p. 216—217° after softening at 132—133° (sparingly sol. Na salt; Me ester, m.p. 189.5°), and an acid, m.p. 253—254° (decomp.) (anhydride, m.p. 186°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -58.7° in CHCl<sub>3</sub>), identical with aetioallobilanic acid. H. W.

**Constitution of hederagenin and oleanolic acid. VII, VIII, and IX.** Z. KITASATO [with C. SONE] (Acta Phytochim., 1935, 8, 207—220, 254—262, 315—324).—VII. Treatment of the mother-liquor from the crystallisation of the Br-lactone (I), obtained by the action of HBr-AcOH on dehydrodiacetyl-hederagenin Me ester, with KOH-MeOH affords dehydrohederagenin, C<sub>30</sub>H<sub>46</sub>O<sub>4</sub>, m.p. >300° (decomp.) (Ac<sub>2</sub> derivative, m.p. 152°, and its Me ester, m.p. 198°). (I) is transformed by KOH-MeOH, Zn dust and AcOH, or AcOH into the lactone of dehydrodiacetylhederagenin, m.p. 245—247°. The re-formation of a double linking by treatment of a Br-derivative with Zn dust and AcOH is further exemplified since oleanylene (II), readily obtained by heating acetyloleanolic acid at about 300°, adds HBr in AcOH-CHCl<sub>3</sub> giving the Br<sub>2</sub>-compound, C<sub>29</sub>H<sub>48</sub>Br<sub>2</sub>, m.p. 186—188° (decomp.), re-converted into (II). Oleanonic acid (III) and excess of Br in MeOH afford dibromo-oleanonolactone, m.p. 275° (decomp.), converted by KOH-MeOH into the substance, C<sub>31</sub>H<sub>45</sub>O<sub>4</sub>Br or C<sub>31</sub>H<sub>47</sub>O<sub>4</sub>Br, m.p. 195—198°. (III) is transformed

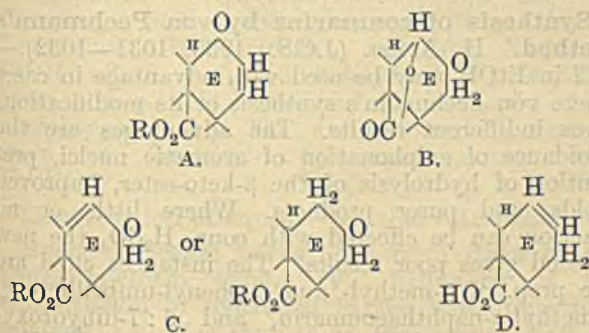


by conc. HCl in boiling AcOH into *oleanonolactone* (IV),  $C_{30}H_{46}O_3$ , m.p.  $354^\circ$  (*oxime*, m.p.  $>300^\circ$ ). Me oleanonate and conc. HCl in AcOH at  $100^\circ$  afford (IV) and *Me epioleanonate*, m.p.  $168-170^\circ$ . *Oleanonolactone* has m.p.  $335-337^\circ$  (decomp.). Treatment of (III) with P and HI in AcOH appears to lead to acetyloleanololactone, m.p.  $337-338^\circ$ , and anhydro-oleanyleno- or -oleaneno-lactone, m.p.  $248^\circ$ .  $Me_2$  hederagenonedicarboxylate and HBr-AcOH at room temp. give the *monolactone*, m.p.  $285^\circ$  (decomp.), of hederagenonedicarboxylic acid. Bromination of the lactone of  $Me_2$  oleanolate gives the *compound*,  $C_{22}H_{49}O_7Br$ , m.p.  $244^\circ$  (decomp.).  $[\alpha]_D$  is recorded for many derivatives of hederagenin and oleanolic acid.

VIII.  $\psi$ -Ketohederagenin is transformed by  $Ac_2O-NaOAc$  into the  $Ac_2$  derivative (V), m.p.  $215^\circ$ . Treatment of the lactone of ketodiacetylhedera-genin (VI) with HBr-AcOH causes opening of the lactone ring, giving *isoketodiacetylhedera-genin* (VII),  $C_{34}H_{50}O_7$ , m.p.  $275-279^\circ$ ,  $[\alpha]_D^{25} -72.7^\circ$  in  $CHCl_3$ . Similar treatment of the monobromolactone of diacetylhedera-genin affords the *compound*,  $C_{34}H_{49}O_6Br$ , transformed by  $Me_2SO_4$  and KOH-MeOH into the *substance*,  $C_{31}H_{49}O_4Br$ , m.p.  $158^\circ$ . Reduction of (V) with Na-Hg in boiling 90% EtOH yields the *compound*,  $C_{30}H_{46}O_4$ , m.p.  $347^\circ$  ( $Ac_2$  derivative, m.p.  $257-260^\circ$ ,  $[\alpha]_D^{25} +39.6^\circ$  in  $CHCl_3$ ), isomeric with the lactone of *allodehydrohederagenin*. Similar treatment of (VII) affords the *substance*,  $C_{30}H_{46}O_4$ , m.p.  $316^\circ$ ,  $[\alpha]_D^{25} +228.2^\circ$  in  $CHCl_3$ .

IX. Ketoacetyloleanololactone and HBr-AcOH yield *isoketoacetyloleanolic acid*, m.p.  $324-330^\circ$ ,  $[\alpha]_D^{25} +46.6^\circ$  in  $CHCl_3$ , converted by  $CH_2N_2$  into the *Me ester* (VIII), m.p.  $205^\circ$ . The following reductions with Na-Hg are described: (VII) to *isodehydro-oleanolic acid*,  $C_{30}H_{46}O_3$ , m.p.  $295-300^\circ$ ,  $[\alpha]_D^{25} +206.8^\circ$  in  $CHCl_3$  (*Me ester*, m.p.  $198^\circ$ , and its  $Ac$  derivative (IX), m.p.  $215-219^\circ$ ,  $[\alpha]_D^{25} +229.7^\circ$  in  $CHCl_3$ ); *Me isoketoacetyloleanolate* to (IX), transformed by HBr-AcOH in  $CHCl_3$  into the *lactone*,  $C_{32}H_{49}O_4Br$ ; *Me  $\psi$ -ketoacetyloleanolate* to *dehydro-oleanololactone*,  $C_{30}H_{46}O_3$ , m.p.  $337^\circ$  ( $Ac$  derivative, m.p.  $347^\circ$ ); ketoacetyloleanololactone to a *substance* transformed by  $CH_2N_2$  into *Me ketoacetyloleanolate*, m.p.  $193-195^\circ$ ,  $[\alpha]_D^{25} -9.5^\circ$  in  $CHCl_3$ .

The relationships of the various keto-compounds with regard to the structure of the E ring are there-fore summarised as follows:



A is common to (VI), ketohedra-gonic acid, keto-acetyloleanolic acid, keto-oleanonic acid, and the *Me esters* of these substances, whilst all keto-lactones

from diacetylhedera-genin, hedra-gonic acid, hedra-gonenedicarboxylic acid, acetyloleanolic acid, and oleanonic acid have B in common. Structure C is shared by ketohedra-genonedicarboxylic acid and *Me ketohedratricarboxylate*, all keto-acids (or *Me esters*) from Br-lactones (by action of EtOH-KOH) and those from keto-lactones (by action of Na-Hg), and by *isoketodiacetylhedera-genin Me ester* and (VIII). Structure D is common to ring E of hederagenin and oleanolic acid.

H. W.

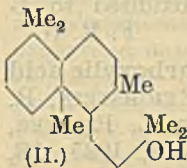
**Pyrolysis of pinene.** Pyronenes, a new type of monocyclic terpene. G. DUPONT and R. DULOU (Compt. rend., 1935, 201, 219-221).—Examination of the Raman spectra of the products of pyrolysis of pinene vapour at  $350^\circ$  shows the presence of limonene and *alloocimene* (cf. Arbusov, A., 1934, 658) together with  $\alpha$ - and  $\beta$ -pyronene, probably  $CH_2:C \begin{smallmatrix} CMe=CH \\ CMe_2 \cdot CH_2 \end{smallmatrix} > CH_2$  and  $CHMe \begin{smallmatrix} CMe=CH \\ CMe_2 \cdot CH \end{smallmatrix} > CH$ , which by catalytic hydrogenation both give 1 : 1 : 2 : 3-tetramethylcyclohexane, also obtained by catalytic hydrogenation of methyl- $\gamma$ -cyclogeraniolene (Escourrou, A., 1926, 1238).

F. R. G.

**Optical activity and chemical constitution.** I. **Optically active bases and acids.** M. SINGH (J. Indian Chem. Soc., 1935, 12, 219-225).— $[\alpha]_D$  of *p*-dimethylaminoanillocamphor (I), m.p.  $135.5^\circ$ , prepared by heating camphorquinone with *p*- $NH_2 \cdot C_6H_4 \cdot NMe_2$ , EtOH, and anhyd.  $Na_2SO_4$ , and  $[\alpha]_D$ ,  $[\alpha]_{3780}$ , and  $[\alpha]_{5461}$  of *m*-dimethylaminoanillocamphor, m.p.  $125-126^\circ$ , similarly prepared, have been determined in a no. of solvents. The effect of solvents of the type PhX (X= $NH_2$ ,  $NO_2$ , halogen, H, Me) is discussed. (I) has a very high  $[\alpha]_D$ , viz.,  $3000^\circ$  in  $NH_2Ph$  solution.

H. G. M.

**Diterpene alcohol from the wood of *Dacrydium biforme*.** I. J. R. HOSKING and C. W. BRANDT (Ber., 1935, 68, [B], 1311-1316).—Extraction of the wood with boiling EtOH gives a small amount of an acid, m.p.  $158^\circ$ , and 7% of a neutral oil which when fractionally distilled yields *manool* (I),  $C_{20}H_{34}O$ , m.p.  $53^\circ$ , b.p.  $144-145^\circ/0.2$  mm.,  $[\alpha]_D^{25} +30.4^\circ$  in abs. EtOH. (I) is unsaturated and when hydrogenated ( $PtO_2$ ) in neutral medium affords *tetrahydromanool* (II), m.p.  $55-56^\circ$ , whereas in presence of Pt-black *dihydromanool* (III), b.p.  $151-152^\circ/0.2$  mm., m.p.  $44-45^\circ$ , is produced. (I) contains 1 OH (Zerevitinov) which is *tert.* since it fails to react with *o*- $C_6H_4(CO)_2O$ . It yields an *acetate* and a *benzoate*. With HCl in dry  $Et_2O$  (I) gives a trihydrochloride, m.p.  $119^\circ$ , identical with that from manoyl oxide, whilst the dihydrochloride, m.p.  $120^\circ$ , from (III) is identical with that from dihydromanoene or dihydroscleareol. Treatment of (I) with 98%  $HCO_2H$  yields a tricyclic hydrocarbon,  $C_{20}H_{32}$ , b.p.  $121^\circ/0.3$  mm. (II) is converted by HCl in  $Et_2O$  into a non-cryst. *hydrochloride*, transformed by  $NH_2Ph$  at  $100^\circ$  into *tetrahydromanoene*, b.p.  $141-142^\circ/0.2$  mm., which is ozonised and then transformed by  $H_2O$  into a *ketone*,  $C_{18}H_{32}O$ , b.p.  $150^\circ/0.4$  mm.





(semicarbazone, m.p. 202°), and an acid,  $C_{16}H_{28}O_2$ , m.p. 129°. H. W.

**Hinokinin as the enantiomorph of cubebinolide.** L. H. BRIGGS (J. Amer. Chem. Soc., 1935, 57, 1383—1384).—The physical data for hinokinin (Yoshiki and Ishiguro, J. Pharm. Soc. Japan, 1933, 53, 73) and cubebinolide (I) (Mameli, A., 1922, i, 347) show that these are enantiomorphous. The structure  $\begin{matrix} \text{CHR}\cdot\text{CH}_2 \\ \text{CHR}\cdot\text{CO} \end{matrix} > \text{O}$  (II),  $R=3:4\text{-CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot$ , is suggested for (I). Matairesinol (Easterfield and Bee, J.C.S., 1910, 97, 1028) is probably (II),  $R=4:3\text{-(OH)(OMe)C}_6\text{H}_3\cdot\text{CH}_2\cdot$ . H. B.

**Volatile vegetable substances. III. Constitution and synthesis of carlina oxide.** A. S. PFAU, J. PICTET, P. PLATTNER, and B. SUSZ (Helv. Chim. Acta, 1935, 18, 935—951).—2-Furylacetylene (modified prep.) with  $\text{MgEtBr}$  and  $\text{CH}_3\text{PhCl}$  in  $\text{Et}_2\text{O}$  gives benzyl-2-furylacetylene, b.p. 115°/1 mm. (cf. Gilman *et al.*, A., 1933, 1055), which gives a Raman spectrum, and has  $n_D^{20}$  and  $d_4^{20}$  and oxidation products identical with those of natural carlina oxide, which was hydrogenated in presence of Ni to  $\alpha$ -phenyl- $\gamma$ -2-furylpropane (I), also obtained by hydrogenation of the crude extract of the roots of *Carlina acaules*, L. Hydrogenation of 2-furfurylideneacetophenone yields 2-furfurylacetylene, m.p. 37—37.5°, the semicarbazone, m.p. 104°, of which when distilled with KOH in EtOH gives (I) (Raman spectrum recorded), which with maleic anhydride in  $\text{Et}_2\text{O}$  gives (Diels-Alder) 3:6-endo-3- $\gamma$ -phenylpropyl- $\Delta^4$ -tetrahydrophthalic anhydride, m.p. 77.5—78° (decomp.); this in aq.  $\text{Na}_2\text{CO}_3$  is hydrogenated (Ni) to 3:6-endo-3- $\gamma$ -phenylpropylhexahydrophthalic acid, m.p. 146° (decomp.) (corr.) (anhydride, m.p. 96.5°). F. R. G.

**Preparation of saturated tertiary carboxylic acids.** T. REICHSTEIN, H. R. ROSENBERG, and R. EBERHARDT (Helv. Chim. Acta, 1935, 18, 721—724).—*tert*- $\text{C}_5\text{H}_{11}\text{Cl}$  with Me pyromucate and  $\text{AlCl}_3$  in  $\text{CS}_2$  gives the Me ester, b.p. 108—110°/11 mm., of 5-*tert*-amylfuran-2-carboxylic acid, m.p. 68.5—69°, oxidised ( $\text{KMnO}_4$ ) to  $\text{CMe}_2\text{Et}\cdot\text{CO}_2\text{H}$ . Similarly 1-chloro-1-methylcyclohexane yields the Me ester, b.p. 145—146°/11 mm., of 5-(1-methylcyclohexyl)furan-2-carboxylic acid, m.p. 110°, oxidised to 1-methylcyclohexane-1-carboxylic acid. F. R. G.

**Synthesis of coumarone-2-[1-]carboxylic acid and of hydroxycoumarones.** T. REICHSTEIN, R. OPPENAUER, A. GRÜSSNER, R. HIRT, L. RHYNER, and C. GLATTHAAR (Helv. Chim. Acta, 1935, 18, 816—830; cf. A., 1933, 281).—*o*-Vanillin with excess of  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$  and NaOEt in EtOH gives the Me ether, m.p. 219.5—220.5° (corr.), sublimes 190—200°/low pressure, of 6-hydroxycoumarone-1-carboxylic acid, m.p. 229—230° (corr.), sublimes 190°/low pressure (Me ester, m.p. 78°; Na salt, cryst.), decarboxylated (Cu-quinoline) to 6-hydroxycoumarone, b.p. 71°/0.4 mm., m.p. 42° [Me ether, b.p. 68°/0.4 mm. ( $\text{NO}_2$ -derivative, b.p. 135°/0.25 mm., m.p. 149—150°)]. 2:3:4-(OMe) $_3\text{C}_6\text{H}_2\cdot\text{CHO}$  heated with  $\text{AlCl}_3$  in PhMe gives 2-hydroxy-3:4-dimethoxybenzaldehyde, m.p. 71—72°, which with  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$  and NaOEt in EtOH yields 5:6-dimethoxycoumarone-1-carboxylic acid, m.p.

202° (corr.), sublimes 180—200°/0.2 mm., decarboxylated to 5:6-dimethoxycoumarone, m.p. 55°. Resorcyaldehyde with  $\text{CH}_2\text{PhCl}$  and NaOEt in EtOH gives 2-hydroxy-4-benzoyloxybenzaldehyde (I), b.p. 135—155°/0.1 mm., m.p. 77—80°, together with 2-hydroxy-4-benzoyloxy-3- or -5-benzylbenzaldehyde, b.p. 180—200°/0.1 mm., m.p. 94—95°, 2:4-dibenzoyloxybenzaldehyde, b.p. 220°/0.1 mm., m.p. 89—90.5°, 2:4-dibenzoyloxy-3- or -5-benzylbenzaldehyde, m.p. 230—240°/0.015 mm., m.p. 81.5—82.5° (semicarbazone, m.p. 180°), a compound,  $\text{C}_{21}\text{H}_{18}\text{O}_3$ , m.p. 154.5—155°, sublimes 185—195°/0.02 mm., and a compound,  $\text{C}_{14}\text{H}_{12}\text{O}_3$  (?), m.p. 150—152°. (I) with  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$  and NaOEt in EtOH yields 5-benzoyloxy-4-hydroxycoumarone-1-carboxylic acid, m.p. 208—209° (corr.), the Me ester, m.p. 112° (corr.), of which with HCl in AcOH give 5-hydroxycoumarone-1-carboxylic acid, m.p. 255—270° (decomp.) [Me ester, m.p. 180° (corr.)], decarboxylated to 5-hydroxycoumarone, b.p. 85°/0.3 mm., m.p. 57—58°. 2:4-Dihydroxy-6-methoxybenzaldehyde (II) with  $\text{CHPhN}_2$  gives 2-hydroxy-4-benzoyloxy-6-methoxybenzaldehyde (III), b.p. 190—195°/0.5 mm., m.p. 103° (corr.). (II) with  $\text{CH}_2\text{PhCl}$  gives 2:4-dihydroxy-6-methoxy-3- or -5-benzylbenzaldehyde, m.p. 201° (corr.), a compound,  $\text{C}_{15}\text{H}_{14}\text{O}_4$ , m.p. 91°, and a compound,  $\text{C}_{22}\text{H}_{20}\text{O}_4$ , m.p. 148°. (III) with  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$  and NaOEt in EtOH yields 5-benzoyloxy-3-methoxycoumarone-1-carboxylic acid, m.p. 207—208° (corr.) [Me ester (IV) (two forms), m.p. 89—90° and 106—107° (corr.)]. Similarly 2-hydroxy-4:6-dimethoxybenzaldehyde gives 3:5-dimethoxycoumarone-1-carboxylic acid, m.p. 235—237° (corr.) [Me ester (V), m.p. 116—117°]. (IV) heated with HCl in AcOH gives 5-hydroxy-3-methoxycoumarone-1-carboxylic acid, m.p. 210°, sublimes [Me ester, m.p. 250° (corr.)], which with excess of  $\text{CH}_2\text{N}_2$  yields (V) and is decarboxylated to 5-hydroxy-3-methoxycoumarone, b.p. 110°/0.6 mm., m.p. 55—57°. The Na salt of 5-hydroxycoumarone heated in  $\text{CO}_2$  at 180—200° yields probably 5-hydroxycoumarone-4-carboxylic acid, m.p. 210—215° (decomp.). *m*- $\text{C}_6\text{H}_4(\text{OH})_2$ ,  $\text{Pr}^s\text{COCl}$ , and  $\text{AlCl}_3$  in  $\text{PhNO}_2$  give 2:4-dihydroxyisobutyrophenone, b.p. 150°/0.3 mm., which with 1 mol.  $\text{Me}_2\text{SO}_4$  and NaOMe in MeOH yields 2-hydroxy-4-methoxyisobutyrophenone, b.p. 120—123°/0.2 mm., m.p. 27°, and this with  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$  and NaOEt in EtOH gives 5-methoxy-2-isopropylcoumarone-1-carboxylic acid, m.p. 180°, decarboxylated to 5-methoxy-2-isopropylcoumarone, b.p. 95°/0.2 mm., m.p. —8° to —7° (picrate, m.p. 65°). F. R. G.

**Synthesis of coumarins by von Pechmann's method.** H. APPEL (J.C.S., 1935, 1031—1032).—HCl in EtOH may be used with advantage in cases where von Pechmann's synthesis or its modifications gives indifferent results. The advantages are the avoidance of sulphonation of aromatic nuclei, prevention of hydrolysis of the  $\beta$ -keto-ester, improved yields, and purer products. Where little or no reaction can be effected with conc.  $\text{H}_2\text{SO}_4$  the new method gives poor results. The instances cited are the prep. of  $\beta$ -methyl- and  $\beta$ -phenyl-umbelliferone, 4-methyl- $\alpha$ -naphthacoumarin, and 6:7-dihydroxy-4-methylcoumarin. H. W.

**Synthesis of flavonol and of dihydroflavonol.** M. MURAKAMI and T. IRIE (Proc. Imp. Acad. Tokyo,



1935, 11, 229—231).—*o*-Hydroxychalkone is converted by alkali (2*N*-NaOH,  $\text{NEt}_3$ , or dil. aq.  $\text{NH}_3$ ) and  $\text{H}_2\text{O}_2$  at room temp. into a mixture of flavonol (also obtained from flavonone with the above reagents) and dihydroflavonol, the latter being the main product.

P. G. C.

**Yellow colouring matter from the wood of *Adina cordifolia*, Hook.** J. B. LAL and S. DUTT (J. Indian Chem. Soc., 1935, 12, 257—261).—Extraction of the wood with EtOH gives cryst., optically active, yellow *adinin* (I),  $\text{C}_{16}\text{H}_{14}\text{O}_7 \cdot 3\text{H}_2\text{O}$  ( $3\text{H}_2\text{O}$  lost at  $120^\circ$ ), which darkens at  $195$ — $196^\circ$ , shrinks at  $200^\circ$ , and then gradually decomposes without melting (*hydrobromide*,  $\text{C}_{16}\text{H}_{14}\text{O}_7 \cdot \text{HBr}$ , decomp. without melting;  $\text{NH}_4$  salt, m.p.  $130^\circ$ ). Solutions of (I) in EtOH, PhOH, and  $\text{H}_2\text{SO}_4$  are fluorescent. On treatment with  $\text{Mg-EtOH-HCl}$  and with  $\text{Zn-NH}_3\text{-H}_2\text{O}$ , (I) becomes colourless. (I) contains 1 OMe (Zeisel), and on demethylation with HI yields yellow *nor-adinin*, which shrinks at  $213$ — $214^\circ$  and decomposes above  $232^\circ$  without melting. The absorption spectrum of (I) in 1% EtOH solution has a band between 4250 and 4650 Å., max. at 4590 Å. (I) may be a xanthone or an isoflavone. H. G. M.

**Synthetical experiments in the chromone group. XVI. Chalkones and flavanones and their oxidation to flavones by selenium dioxide.** H. S. MAHAL, H. S. RAI, and K. VENKATARAMAN (J.C.S., 1935, 866—868).—Flavones are conveniently prepared in one stage by the oxidation of *o*-hydroxy-chalkones with  $\text{SeO}_2$ . 2-Hydroxy-4-benzoyloxyphenyl styryl ketone, m.p.  $135^\circ$ , is converted by prolonged boiling with  $\text{P}_2\text{O}_5$  in EtOH containing a little  $\text{H}_2\text{O}$  into 7-benzoyloxyflavanone, m.p.  $104^\circ$  after softening at  $102^\circ$ . 2-Hydroxy-4-benzoyloxyphenyl 4-methoxystyryl ketone, m.p.  $132$ — $133^\circ$ , similarly yields 7-benzoyloxy-4'-methoxyflavanone, m.p.  $114^\circ$ . 2-Hydroxy-4-benzoyloxyphenyl 4-benzoyloxy-styryl ketone has m.p.  $139^\circ$ . Protocatechualdehyde,  $\text{CH}_2\text{PhCl}$ , and  $\text{K}_2\text{CO}_3$  in  $\text{COMe}_2$  afford 3:4-dibenzoyloxybenzaldehyde, m.p.  $93^\circ$ , whence 2-hydroxy-4-benzoyloxyphenyl 3:4-dibenzoyloxy-styryl ketone, m.p.  $137^\circ$ . 2-Hydroxy-4-methoxyphenyl 4-benzoyloxy-styryl ketone, m.p.  $125$ — $126^\circ$ , gives 7-methoxy-4'-benzoyloxyflavanone, m.p.  $98$ — $99^\circ$ , debenzylated to 4'-hydroxy-7-methoxyflavanone, m.p.  $160^\circ$ .  $\beta$ -Naphthafavanone is oxidised by  $\text{SeO}_2$  in xylene at  $140$ — $150^\circ$  to  $\beta$ -naphthafavone, m.p.  $163^\circ$ . *o*-Hydroxyphenyl styryl ketone similarly yields flavone. 7-Benzoyloxyflavone, m.p.  $187^\circ$ , is debenzylated to 7-hydroxyflavone, m.p.  $240^\circ$ . 7-Benzoyloxy-4'-methoxyflavone has m.p.  $137^\circ$ . 1-Acetyl-2-naphthol,  $\text{CHPh} \cdot \text{CH} \cdot \text{CHO}$ , and 50% NaOH in EtOH afford 3-styryl-2:3-dihydro-1:4- $\beta$ -naphthapyrone, m.p.  $144^\circ$ , oxidised to 3-styryl-1:4- $\beta$ -naphthapyrone, m.p.  $200^\circ$ , also obtained by condensation of 3-methyl-1:4- $\beta$ -naphthapyrone with PhCHO. H. W.

**Constitution of equol.**—See this vol., 1032.

**Spectrographic investigation of dyes of the benzopyrylium type. IV. Influence of the substitution of hydroxyl in the benzopyrylium nucleus.** K. HAYASHI (Acta Phytochim., 1935, 8, 179—206).—The relationships between absorption spectra and chemical constitution of hydroxy-

flavylium chlorides are extremely complicated. Not only the first well-developed band, but also the second and the third are important in the spectrochemical characterisation of anthocyanidins (I). The complete character of the graph, which is peculiar to each individual, is of decisive importance. It is not sufficient to determine the absorption curve in the visible end for the identification of (I). The following flavylium chlorides, usually obtained by condensation of the requisite aldehyde and substituted acetophenone in EtOAc saturated with HCl, are described: 4'-hydroxy-, decomp.  $127$ — $128^\circ$ ; 7-hydroxy-, gradual decomp.  $>140^\circ$  after becoming discoloured at  $130^\circ$ ; 7:4'-dihydroxy-, m.p.  $>260^\circ$  after softening at  $180^\circ$ ; 7-hydroxy-4'-methoxy-, decomp.  $182^\circ$ ; 3:7:4'-trihydroxy-, decomp.  $>290^\circ$  after shrinking at  $260^\circ$ ; 3:7-dihydroxy-4'-methoxy-, decomp.  $211^\circ$  after softening at  $208^\circ$ ; 7-hydroxy-4'-methoxy-5-methyl-, decomp.  $242$ — $243^\circ$  after shrinking at  $125^\circ$ ; 4'-hydroxy-8-methoxy-, m.p.  $138$ — $139^\circ$  after softening at  $115^\circ$ ; 6:4'-dimethoxy-, decomp.  $138$ — $139^\circ$ ; 3:3':4'-trihydroxy-, decomp.  $222$ — $223^\circ$  after softening at  $160^\circ$ ; 3:7:3':4'-tetrahydroxy-, m.p.  $>270^\circ$ ; 3:6:7:4-tetrahydroxy-3':5'-dimethoxy-, decomp.  $257$ — $258^\circ$ ; 7:8:4'-trihydroxy-, decomp.  $267^\circ$  after becoming brown at  $100^\circ$  and softening at  $250^\circ$ ; 7:8-dihydroxy-4'-methoxy-, decomp.  $193$ — $194^\circ$  after softening at  $180^\circ$ . H. W.

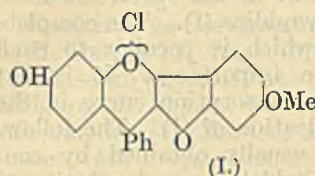
**Synthetical experiments in the chromone group. XVII. Further observations on the action of sodamide on *o*-acyloxyacetophenones.** D. C. BHALLA, H. S. MAHAL, and K. VENKATARAMAN (J.C.S., 1935, 868—870).—Further examples of the  $\text{NaNH}_2$  method of flavone synthesis are described (this vol., 90). The acid chlorides are prepared by  $\text{SOCl}_2$ . *O*-Acyl derivatives (I) of ketones are made in  $\text{C}_5\text{H}_5\text{N}$ . Reaction with  $\text{NaNH}_2$  is effected by shaking with (I) in Et<sub>2</sub>O for 1—10 days. *o*-Benzoyloxyacetophenone and  $\text{NaNH}_2$  afford *o*-hydroxydibenzoylmethane, m.p.  $121$ — $122^\circ$ , and a substance,  $\text{C}_{15}\text{H}_{12}\text{O}_3$ , m.p.  $110$ — $111^\circ$ , both of which are transformed by  $\text{H}_2\text{SO}_4$  into flavone. The following are described: *o*-acetylphenyl *o*-methoxybenzoate, m.p.  $81^\circ$ ; *o*-acetylphenyl 2:4-dimethoxybenzoate, m.p.  $77^\circ$ ; 2-hydroxy-, m.p.  $70^\circ$ ; and 2-benzoyloxy-, m.p.  $68^\circ$ ; 5-benzoyloxyacetophenone; 2-hydroxy-5-benzoyloxydibenzoylmethane, m.p.  $68^\circ$ ; 2-hydroxy-5-benzoyloxydibenzoylmethane, m.p.  $103$ — $104^\circ$ ; 6-benzoyloxyflavone, m.p.  $144$ — $145^\circ$ ; 1-acetyl-2-naphthyl benzoate, m.p.  $85$ — $86^\circ$ ;  $\beta$ -naphthafavone, m.p.  $165^\circ$ , and small amounts of a substance,  $\text{C}_{19}\text{H}_{14}\text{O}_3$ , m.p.  $171^\circ$ ; 1-acetyl-2-naphthyl *o*-methoxybenzoate, m.p.  $102$ — $103^\circ$ ; 2'-methoxy- $\beta$ -naphthafavone, m.p.  $188$ — $189^\circ$ ; 2-acetyl-1-naphthyl cinnamate, m.p.  $111^\circ$ ;  $\omega$ -cinnamoyl-2-acetyl-1-naphthol, m.p.  $158^\circ$ ; 2-styryl-1:4- $\alpha$ -naphthapyrone, m.p.  $177^\circ$ ; 2-acetyl-1-naphthyl *p*-methoxycinnamate, m.p.  $137$ — $138^\circ$ ;  $\omega$ -*p*-methoxycinnamoyl-2-acetyl-1-naphthol, m.p.  $176$ — $177^\circ$ ; 2-*p*-methoxystyryl-1:4- $\alpha$ -naphthapyrone, m.p.  $207^\circ$ ; 3-phenyl-2-methyl-1:4- $\alpha$ -naphthapyrone, m.p.  $203$ — $204^\circ$ ; 2-phenyl-acetyl-1-naphthyl cinnamate, m.p.  $146$ — $147^\circ$ ; 2-styryl-3-phenyl-1:4- $\alpha$ -naphthapyrone, m.p.  $262$ — $263^\circ$ .

H. W.

**Synthesis of chromylium salts. II.** R. ROBISON and J. WALKER (J.C.S., 1935, 941—946).—The un-



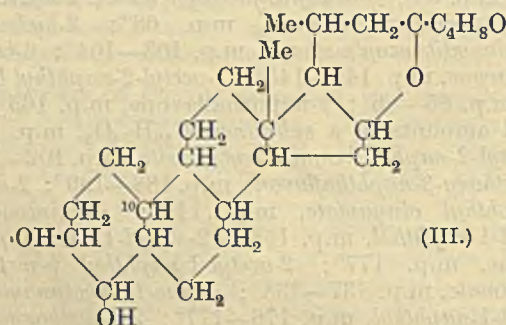
saturated ketone is condensed with  $m\text{-C}_6\text{H}_4(\text{OH})_2$  in EtOH containing HCl and chloranil. Thus 6-methoxy-2-benzylidenecoumaranone yields 7-hydroxy-6'-methoxy-4-phenyl-2:3-coumareno-(3':2')-chromylium chloride (I), demethylated to 7:6'-dihydroxy-4-phenyl-2:3-coumareno-(3':2')-



chromylium chloride. 2-Benzoylcoumarone similarly affords 7-hydroxy-3:4-coumareno-(2':3')-flavylum chloride, and 7-hydroxy-4-p-dimethylaminophenyl-2:3-indeno-(3':2')-chromylium chloride hydrochloride is obtained from 2-p-dimethylaminobenzylidene-1-hydrindone. In order to examine the lake-forming properties of the product, the salicylic acid residue has been introduced into an oxonium salt. Thus, 5-aldehydsalicylic acid, 1-hydrindone, and KOH in EtOH yield the acid,  $\text{C}_{17}\text{H}_{12}\text{O}_4$ , m.p. 285°, the Et ester, m.p. 172°, of which is transformed by  $m\text{-C}_6\text{H}_4(\text{OH})_2$  and chloranil in dioxan into 7-hydroxy-4-(4'-hydroxy-3'-carboxyphenyl)-2:3-indeno-(3':2')-chromylium chloride. 7-Hydroxy-4-p-hydroxyphenyl-flavylum chloride and 7:4'-dihydroxy-4-phenylflavylum chloride (+2H<sub>2</sub>O) are obtained by demethylation of known substances. It is shown that the reactive phenol component can be varied within the usual limits by the prep. of the following: 5:7-dihydroxyflavylum chloride from  $o\text{-C}_6\text{H}_4(\text{OH})_2$  and Ph vinyl ketone; 7:8-dihydroxy-4-phenylflavylum chloride (+3H<sub>2</sub>O) from benzylideneacetophenone; 2-phenyl-4-anisyl-5:6-naphtha-(1':2')-pyrylium picrate, m.p. 204°, from anisylideneacetophenone; 6:7-dihydroxy-4-phenylflavylum picrate, m.p. 235°; 6-hydroxy-5:7-dimethoxy-4-phenylflavylum picrate, m.p. 220° (decomp.).

H. W.

**Digitalis sapogenins.** W. A. JACOBS and J. C. E. SIMPSON (J. Biol. Chem., 1935, 110, 429—438).—Oxidation of tigogenin (I),  $\text{C}_{26}\text{H}_{42}\text{O}_3$ , and tigogenone with  $\text{CrO}_3$  in AcOH yields gitogenic acid (II) (Me ester, m.p. 210°; Me<sub>2</sub> ester, m.p. 145°; anhydride, m.p. 205—206°), identical with the acid obtained from gitogenin [provisional formula (III)]. (I) contains one of the two vicinal OH of (III). The  $\text{C}_{26}$  formul-



ation is more probable than  $\text{C}_{27}$ , but in the latter case the extra Me would probably be on  $\text{C}_{10}$ . The ketone obtained on dehydrogenation of (III) is not Me isohexyl ketone. Thermal decomp. of (II) or its anhydride yields a ketone,  $\text{C}_{25}\text{H}_{38}\text{O}_3$  (oxime, m.p. 237—238°).

J. N. A.

**Synthesis of rotenone and its derivatives. VI. Chromenochromones.** H. I. KING and A. ROBERTSON (J.C.S., 1935, 993—996).—Treatment of 5-methoxysalicylaldehyde with  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$  and anhyd.  $\text{K}_2\text{CO}_3$  in boiling  $\text{COMe}_2$  affords Et 2-aldehydo-4-methoxyphenoxyacetate, b.p. 187—188°/2 mm., m.p. 51° (semicarbazone, m.p. 171°), which condenses with hippuric acid in presence of NaOAc and  $\text{Ac}_2\text{O}$  to the azlactone (I),  $\text{C}_{21}\text{H}_{19}\text{O}_6\text{N}$ , m.p. 127°. (I) is hydrolysed by boiling 10% NaOH and, after removal of BzOH, is heated with conc. HCl, whereby 4-methoxyphenoxyacetic acid-2-pyruvic acid (II) is obtained; this is converted through the oxime, m.p. 150—151°, into 4-methoxyphenoxyacetic acid-2-acetonitrile (III), m.p. 140° (Me ester, m.p. 45°). The yield of (III) is greatly increased if crude (II) is directly oximated. (III),  $m\text{-C}_6\text{H}_4(\text{OH})_2$ , and  $\text{ZnCl}_2$  in  $\text{Et}_2\text{O}$  saturated with HCl give 4-methoxyphenoxyacetic acid-2-resacetophenone, m.p. 163°, or (?) hydrated, m.p. 121—124°, cyclised by boiling  $\text{Ac}_2\text{O}$  containing NaOAc to 7-hydroxy-6-methoxychromeno-[3':4':2:3]-chromone, decomp. 248—249° after slight darkening at 243—245° (acetate, m.p. 190°). *o*-Vanillin,  $\text{CH}_3\text{Br}\cdot\text{CO}_2\text{Et}$ , and  $\text{K}_2\text{CO}_3$  in boiling  $\text{COMe}_2$  yield Et 2-aldehydo-6-methoxyphenoxyacetate (IV), m.p. 75° (semicarbazone, m.p. 205°), converted by  $\text{NaHSO}_3$  followed by NaCN into the corresponding cyanohydrin, which is transformed by  $\text{SOCl}_2$  into Et 6-methoxyphenoxyacetate-2-chloroacetonitrile (V), m.p. 46°. Treatment of (V) with Zn dust, EtOH, AcOH, and H<sub>2</sub>O affords Et 6-methoxyphenoxyacetate-2-acetonitrile (VI), m.p. 53°. (IV), hippuric acid, NaOAc, and  $\text{Ac}_2\text{O}$  give the corresponding azlactone, m.p. 126°, hydrolysed and transformed by boiling HCl into 6-methoxyphenoxyacetic acid-2-pyruvic acid, the oxime, m.p. 164°, of which is transformed by  $\text{Ac}_2\text{O}$  into 6-methoxyphenoxyacetic acid-2-acetonitrile, m.p. 93°. 6-Methoxyphenoxyacetic acid-2-resacetophenone, m.p. 180.5°, is transformed by boiling  $\text{Ac}_2\text{O}$  containing NaOAc into 7-hydroxy-8'-methoxychromeno-[3':4':2:3]-chromone, m.p. 263—265° (decomp.) (acetate, m.p. 196°). (VI),  $o\text{-C}_6\text{H}_4(\text{OMe})_2$ , and  $\text{ZnCl}_2$  in  $\text{Et}_2\text{O}$  give 6-methoxyphenoxyacetic acid-2:2':4'-O-dimethylphloracetophenone hydrate, m.p. 143—144° (whence 5:7:8'-trimethoxychromeno-[3':4':2:3]-chromone, m.p. 210°), and 6-methoxyphenoxyacetic acid-2:2':6'-O-dimethylphloracetophenone, m.p. 174°.

H. W.

**Charcoal as a catalyst of stereoisomeric change in disulphoxides.** T. W. J. TAYLOR and W. C. J. COUGHTREY (J.C.S., 1935, 974—976).—The isomerisation of oximes by charcoal has been attributed to the exchange of O atoms between the charcoal surface and the oxime group. A similar isomerisation is observed with thianthren disulphoxides in tetrahydronaphthalene containing blood-C at 180° but not in boiling  $\text{C}_6\text{H}_6$ . A sufficiently accurate method is not available for the quant. analysis of mixtures of the two disulphoxides, but points of resemblance between the isomerisation and that of  $\alpha$ -benzilmonoxime are traced.

H. W.

**Additive compounds of arsenic trichloride.**—See this vol., 1090.

**Yellow coloration of mixtures of fructose and pyridine by ultra-violet light.** R. CANTIENI (Helv.



Chim. Acta, 1935, 18, 808—812; cf. this vol., 68).—The yellow coloration of aq. solutions of  $C_5H_5N$  by irradiation is increased by addition of fructose (I). The colour of mixtures of  $C_5H_5N$  and (I) is more stable than the yellow coloration of pure  $C_5H_5N$ . Subsequent addition of (I) to irradiated  $C_5H_5N$  stabilises the colour, but the stability is not so great as that produced by irradiation of mixtures of  $C_5H_5N$  and (I).

F. R. G.

**Synthesis of yellow tetrapyrroline ferrous thiocyanate.** G. SPACU and V. ARMEANU (Bul. Soc. Stiinte Cluj, 1934, 7, 566—567; Chem. Zentr., 1935, i, 1024).—An improved method of prep. is given.

J. S. A.

**Dehalogenation of  $\alpha\beta$ -dibromo-acids. III. Acids of pyridine and quinoline series.** A. A. ALBERTS and G. B. BACHMAN (J. Amer. Chem. Soc., 1935, 57, 1284—1287).—The product (95% yield) from 2-methylquinoline, chloral, and  $C_5H_5N$  at 100° (bath) is hydrolysed (EtOH-KOH) to  $\beta$ -2-quinolylacrylic acid (I), m.p. 194—196° (hydrobromide, m.p. 218—220°; hydrochloride, m.p. 216—218°; acetate, m.p. 203°). The dibromide, m.p. 228—230° (corr.) (lit. 180—181°) (prepared under varying conditions), of (I) when treated with aq. KOH,  $Na_2CO_3$ , or  $C_5H_5N$ , EtOH-KOH, anhyd.  $C_5H_5N$ , and boiling  $H_2O$  or EtOH, regenerates (I); contrary to Carlier and Einhorn (A., 1891, i, 83), 2-quinolylacetylene is not obtained using aq.  $Na_2CO_3$  or  $K_2CO_3$ . The product (16—18% yield) from 4-methylpyridine, chloral, and a little  $ZnCl_2$  at about 34° (24 hr.) and 100° (2 hr.) is hydrolysed (method: Rabe and Kindler, A., 1922, i, 361) to  $\beta$ -4-pyridylacrylic acid (II), m.p. 293—295°, the dibromide, m.p. 258—260°, of which also regenerates (II) when treated with alkali. Dehalogenation of  $CHBrPh\cdot CHBr\cdot CO_2H$  with anhyd.  $C_5H_5N$  gives a considerable amount of  $CHPh\cdot CH\cdot CO_2H$ ; with aq.  $C_5H_5N$  and/or  $Na_2CO_3$ , 65—75% of  $CHPh\cdot CHBr$  results.

3-Acetylpyridine and  $PCl_5$  in  $C_6H_6$  give  $\alpha$ -chloro- $\alpha$ -3-pyridylethylene, b.p. 112—114°/24 mm. (hydrochloride, m.p. 138—140°), converted by EtOH-KOH into 3-pyridylacetylene, b.p. 83—84°/30 mm., m.p. 38.5°.

H. B.

**Syntheses of pyridiniummethanols. II. Mechanism of the condensation reaction. isoQuinoliniummethanols.** F. KRÖHNKE (Ber., 1935, 68, [B], 1351—1359).—The condensation of phenacylpyridinium salts with aldehydes occurs according to the

scheme  $COR\cdot CH_2\cdot N(C_5H_5)X \xrightarrow{R\cdot CHO} COR\cdot CH(CHR\cdot OH)\cdot N(C_5H_5)X \rightarrow OH\cdot CHR\cdot CH_2\cdot N(C_5H_5)X$ . Reactivity is due to the influence of COR on  $CH_2$  and the reaction is therefore common to all pyridinium salts with activated  $CH_2$  and hence to the allyl and  $CH_2Ph$  derivatives. The following are obtained by condensing phenacylpyridinium bromide (1 mol.) with NaOH (1 mol.) and excess of the requisite aldehyde in 90% EtOH at room temp.:  $\beta$ -hydroxy- $\beta$ -p-chlorophenylethyl-, m.p. 182—183°;  $\beta$ -hydroxy- $\beta$ -2:5-dichlorophenylethyl-, m.p. 259—261°;  $\beta$ -hydroxy- $\beta$ -2-chloro-5-nitrophenylethyl- (hydrate and anhyd.), m.p. 238—239° after marked softening;  $\beta$ -hydroxy- $\beta$ -o-methoxyphenylethyl-, m.p. 208°;  $\beta$ -hydroxy- $\beta$ -3:4:5-trimethoxyphenyl-

ethyl-, m.p. 200—202°;  $\beta$ -hydroxy- $\beta$ -p-ethoxyphenylethyl-, m.p. 166°;  $\beta$ -hydroxy- $\beta$ -1-naphthylethyl-, m.p. 208—211° after softening (corresponding perchlorate, m.p. 181°);  $\gamma\delta$ -trichloro- $\beta$ -hydroxyamyl-, decomp. 219°, and  $\beta$ -hydroxy- $\beta$ -n-hexylethyl-, m.p. 223° (decomp.) [hydrate, m.p. 53—54°; corresponding perchlorate, m.p. (indef.) 54°], -pyridinium bromide.  $\beta$ -Hydroxy- $\beta$ -isobutylethylpyridinium picrate has m.p. 125—126°. Benzylpyridinium bromide and o- $C_6H_4Cl\cdot CHO$  yield  $\beta$ -hydroxy- $\alpha$ -phenyl- $\beta$ -o-chlorophenylethylpyridinium bromide, m.p. 222° after softening at 160°.  $CH_2\cdot CH\cdot CH_2Br$  and  $C_5H_5N$  at 0° give allylpyridinium bromide (I), m.p. 92—94° (corresponding perchlorate, m.p. 71.5—72.5°, and picrate, m.p. 69.5—70.5°). (I) and PhCHO in presence of NaOH afford  $\alpha$ -hydroxyphenylmethyl- $\Delta^{\beta}$ -propenylpyridinium bromide, m.p. 227° after softening and becoming discoloured, reduced (Pd-BaSO<sub>4</sub>) and converted by  $HClO_4$  into  $\alpha$ -hydroxyphenylmethyl-n-propylpyridinium perchlorate, m.p. 142—142.5°; the corresponding bromide, m.p. 199—202°, is obtained from n-propylpyridinium bromide and PhCHO. (I) and the requisite aldehyde yield the following substances:  $\alpha$ -hydroxy-o-chlorophenylmethyl- $\Delta^{\beta}$ -propenyl-, m.p. 203—204° after much softening;  $\alpha$ -hydroxy-o-nitrophenylmethyl- $\Delta^{\beta}$ -propenyl-, slow decomp. > 200°;  $\alpha$ -hydroxy-1-naphthylmethyl- $\Delta^{\beta}$ -propenyl-, m.p. 190—192° after softening (corresponding perchlorate);  $\alpha$ -hydroxy-2-furylmethyl- $\Delta^{\beta}$ -propenyl-, m.p. indef. 140°, -pyridinium bromide. Allylisoquinolinium bromide, m.p. 99—100° (corresponding perchlorate, m.p. 111°), gives the compounds:  $\alpha$ -hydroxy-o-chlorophenylmethyl- $\Delta^{\beta}$ -propenyl-, decomp. about 225°;  $\alpha$ -hydroxy-o-nitrophenylmethyl- $\Delta^{\beta}$ -propenyl-, decomp. 220° after becoming discoloured;  $\alpha$ -hydroxy-m-nitrophenylmethyl- $\Delta^{\beta}$ -propenyl-, decomp. 213—215°, -isoquinolinium bromide. Benzylisoquinolinium bromide, m.p. 110—111.5° (corresponding picrate, m.p. 177° after softening, and perchlorate, m.p. 167—168°), gives  $\beta$ -hydroxy- $\alpha$ -phenyl- $\beta$ -o-chlorophenylethyl-, m.p. 223° (decomp.), and  $\beta$ -hydroxy- $\alpha\beta$ -diphenylethyl-, m.p. 218° (decomp.), -isoquinolinium bromide.  $\beta$ -Hydroxy- $\beta$ -phenylethyl-2-methylpyridinium bromide, m.p. 218—221° after softening, and  $\beta$ -hydroxy- $\beta$ -phenylethyl-3-methylpyridinium bromide, m.p. 153—155°, are described.  $\beta$ -Hydroxy- $\beta$ -p-isopropylphenylethylpyridinium bromide (monohydrate) has m.p. 190—192°.

H. W.

**4:7-Dimethyloxindole.** V. LIVOVSKI (Compt. rend., 1935, 201, 217—219).—p-Xylidine with  $CH_2Cl\cdot COCl$  and  $AlCl_3$  gives 4:7-dimethyloxindole, b.p. 200°, m.p. 159° (3-benzylidene, m.p. 188°; 3-p-chlorobenzylidene, m.p. 212—215°; 3-o-sulphobenzylidene; 3:3'-benzylidenedi-, m.p. 172°; 3:3'-m-hydroxybenzylidenedi-, m.p. 164°, derivatives), which with isatin in  $HCl\cdot AcOH$  yields 4:7-dimethylisoindigotin (I), cryst. (Na disulphonate, cryst.), but in EtOH with a trace of  $C_5H_{11}N$  gives 4:7-dimethylisatan, dehydrated to (I).

F. R. G.

**Constitution of abrin.** T. HOSHINO (Proc. Imp. Acad. Tokyo, 1935, 11, 227—228).—Abrin (I), m.p. 295°,  $[\alpha]_D^{25} + 44.4^\circ$ , an  $NH_2$ -acid occurring in the seeds of *Abrus precatorius*, loses  $CO_2$  when heated in vac. to give 3- $\beta$ -methylaminoethylindole, m.p. 89—90°. Methylation of (I) and of L-tryptophan gives the same



Me  $\beta$ -3-indolylpropionate  $\alpha$ -trimethylammonium iodide (picrates, m.p. 163—164° and 155—156°). (I) is therefore  $\alpha$ -methylamino- $\beta$ -3-indolylpropionic acid.  
P. G. C.

**Action of nitrous acid on tryptophan.** N. J. DEMJANOV and N. I. PUTCHIN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 390—393).—The action of HNO<sub>2</sub> on tryptophan affords 1-nitrosoindole-3-acrylic acid (dibromide). Absence of ring enlargement is ascribed to the attachment of NH<sub>2</sub> in the side-chain to C not directly united to the ring.  
H. W.

**Complexes of polynitro-compounds. I. Compounds of polynitro-hydrocarbons with 1-keto-1:2:3:4-tetrahydrocarbazole.** A. KENT (J.C.S., 1935, 976—978).—1-Ketotetrahydrocarbazole (improved prep.) gives a *p*-nitrophenylhydrazone, m.p. 252—253° (also +1EtOH) (hydrochloride, decomp. 210—212°), and a picrate, m.p. 165—166°. It forms complexes with the following substances, the proportions being stated in parentheses: 1:3:5-C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>3</sub> (1:2), m.p. 180—182°; 1:2:4-C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>3</sub> (1:1), m.p. 129—131°; *m*-C<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub> (1:2), m.p. 120—139°; *p*-C<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub> (1:2), m.p. 140—142°; 2:4:6-C<sub>6</sub>H<sub>2</sub>Me(NO<sub>2</sub>)<sub>3</sub> (1:1), m.p. 129—131°; 2:4:5-C<sub>6</sub>H<sub>2</sub>Me(NO<sub>2</sub>)<sub>3</sub> (1:2), m.p. 127—140°; 2:4-C<sub>6</sub>H<sub>3</sub>Me(NO<sub>2</sub>)<sub>2</sub> (1:1), m.p. 98—126°; 2:5-C<sub>6</sub>H<sub>3</sub>Me(NO<sub>2</sub>)<sub>2</sub> (1:2), m.p. 142—143°; 3:5-C<sub>6</sub>H<sub>3</sub>Me(NO<sub>2</sub>)<sub>2</sub> (1:1), m.p. 108—118°. No evidence is obtained that any of the compounds could be obtained cryst. with its components in alternative proportion.  
H. W.

[Preparation of] bromine-substituted allyl 2-phenylquinoline-4-carboxylate.—See B., 1935, 750.

**Asymmetric platinum atom. VI.** H. REIHLER and W. HÜHN (Annalen, 1935, 519, 80—96; cf. A., 1933, 74).—*d*- and *l*-NH<sub>2</sub>·CHPh·CH<sub>2</sub>·NH<sub>2</sub> in Et<sub>2</sub>O with K<sub>2</sub>PtCl<sub>4</sub> in H<sub>2</sub>O yield dichlorophenylethylenediamineplatinum (two forms), which when boiled with 3-methyl-2-aminomethyl-4-ethylquinoline hydrochloride and dil. NaOH gives (less sol.)  $\alpha$ -phenylethylenediamine-3-methyl-4-ethyl-2-aminoethylquinolineplatinum chloride in two forms (+1½H<sub>2</sub>O), [M]<sub>D</sub> +855° in H<sub>2</sub>O, converted into the nitrate, [M]<sub>D</sub> +865° in H<sub>2</sub>O, chloroplatate, cryst., low-rotating *d*-bromocamphor- $\pi$ -sulphonate (+2½H<sub>2</sub>O), [M]<sub>D</sub> +1500° ([M]<sub>D</sub> +864° for ion), and 1-bromocamphor- $\pi$ -sulphonate (+4H<sub>2</sub>O) [M]<sub>D</sub> +220° ([M]<sub>D</sub> +856° for ion), high-rotating *d*-bromocamphor- $\pi$ -sulphonate (+2½H<sub>2</sub>O), [M]<sub>D</sub> +1720° ([M]<sub>D</sub> +1080° for ion), and 1-bromocamphor- $\pi$ -sulphonate (+4H<sub>2</sub>O), [M]<sub>D</sub> +440° ([M]<sub>D</sub> +1075° for ion), and (+2H<sub>2</sub>O) [M]<sub>D</sub> -852° in H<sub>2</sub>O, converted into the perchlorate, [M]<sub>D</sub> -860°, low-rotating 1-bromocamphor- $\pi$ -sulphonate, [M]<sub>D</sub> -1490° ([M]<sub>D</sub> -854° for ion), high-rotating *d*-bromocamphor- $\pi$ -sulphonate, [M]<sub>D</sub> -442° ([M]<sub>D</sub> -1080° for ion), and 1-bromocamphor- $\pi$ -sulphonate, [M]<sub>D</sub> -1720° ([M]<sub>D</sub> -1080° for ion), also (more sol.)  $\beta$ -phenylethylenediamine-3-methyl-2-aminoethyl-4-ethylquinolineplatinum chloride (acetate, [M]<sub>D</sub> +470°; chloroplatate; bromocamphor- $\pi$ -sulphonate). The structural relations of these isomerides are discussed.  
F. R. G.

**3:6-Dialkoxy-10-alkylacridinium derivatives with various kinds of amino-group on the 9-carbon atom. IV. Synthesis of 3:6-dialkoxy-9-arylamino-10-alkylacridinium chlorides.** K. ISHIIHARA (J. Chem. Soc. Japan, 1934, 55, 858—877; cf. this vol., 93).—The following are prepared by condensing aromatic amines with 9-chloro-3:6-dialkoxy-10-alkylacridinium chlorides: 9-anilino-, decomp. 234—235°; 9-o-, decomp. 256—257°, 9-m-, decomp. 247°, and 9-p-toluidino-, decomp. 225—236°; 9-p-phenetidino-, decomp. 235—237°, -3:6-dimethoxy-10-methyl-, 9-anilino-, decomp. 212—214°; 9-o-, decomp. 223—224°, 9-m-, decomp. 205—206°, and 9-p-toluidino-, decomp. 200—201°; 9-p-phenetidino-, decomp. 203—204°, -3:6-dimethoxy-10-ethyl-, 9-anilino-, decomp. 250—251°; 9-o-, decomp. 253—255°, 9-m-, decomp. 256—257°, and 9-p-toluidino-, decomp. 225—226°; 9-p-phenetidino-, decomp. 228—230°, -3:6-diethoxy-10-methyl-, 9-anilino-, decomp. 239—241°; 9-o-, decomp. 242—244°, 9-m-, decomp. 237°, and 9-p-toluidino-, decomp. 219—225°; 9-p-phenetidino-3:6-diethoxy-10-ethyl-acridinium chloride.  
CH. ABS. (r)

**Synthesis of 8:9-benzoylene-3:4-phthalylphenanthridine-5-carboxylic acid.** R. SCHOLL and H. K. MEYER (Ber., 1935, 68, [B], 1307—1309).—Et 1-chloroanthraquinone-2-carboxylate, m.p. 140—141°, is converted by Cu powder in boiling PhNO<sub>2</sub> into Et<sub>2</sub> 1:1'-dianthraquinonyl-2:2'-dicarboxylate, m.p. 264—266°. The corresponding acid is transformed by BzCl in boiling PhNO<sub>2</sub> into the anhydride, whence the monoamide (NH<sub>4</sub> salt) which passes under the influence of NaOCl, doubtless through the NH<sub>2</sub>-acid, into 8:9-benzoylene-3:4-phthalylphenanthridine-5-carboxylic acid. 1:1'-Dianthryl-2:2'-dicarboxylic acid under dehydrating conditions passes into *amphi*-isopyranthrene, which is also obtained from 9:10:9':10'-tetrahydro-1:1'-dianthryl-2:2'-dicarboxylic acid, m.p. 288—290°, prepared by reduction (Zn dust-NaOH) of 1:1'-dianthraquinonyl-2:2'-dicarboxylic acid.  
H. W.

**Synthesis of antipyrene and pyramidone.** A. L. KLEBANSKI and A. L. LEMKE (J. Appl. Chem. Russ., 1935, 8, 269—276).—Antipyrene (I) is obtained in 83—88% yield from 1-phenyl-3-methylpyrazole and Me<sub>2</sub>SO<sub>4</sub> in PhMe at the b.p. (6—8 hr.), or in xylene (4—5 hr.). Directions for the purification of (I) are given. Pyramidone is prepared from Na sulphaminoantipyrene and CH<sub>2</sub>O and HCO<sub>2</sub>H, in 80% yield, at 100° (14 hr.).  
R. T.

**Pseudo-atoms and isoteric compounds. V. Relation between constitution and reactions of pyrazolone derivatives.** H. ERLÉNMEYER and E. WILLI (Helv. Chim. Acta, 1935, 18, 740—743; cf. this vol., 431).—Pyramidone and isopropylantipyrene in which ·N· is replaced by ·CH· form mixed crystals and have similar pharmacological properties.  
F. R. G.

**5:5-Diphenylbarbituric acid.** S. M. McELVAIN (J. Amer. Chem. Soc., 1935, 57, 1303—1304).—Alloxan monohydrate (modified prep.; cf. Biltz and Heyn, A., 1917, i, 289), C<sub>6</sub>H<sub>6</sub>, and conc. H<sub>2</sub>SO<sub>4</sub> at 75—80° give some 5:5-diphenylbarbituric acid (I), m.p. 290—292° (corr.) [hydrolysed (10% KOH) to NH<sub>3</sub>, CO<sub>2</sub>,



and  $\text{CHPh}_2\cdot\text{CO}_2\text{H}$ ], and (mainly) an acidic substance, m.p.  $320\text{--}325^\circ$ . (I), in sub-lethal doses, is ineffective as a hypnotic.

H. B.

**Derivatives of piperazine. IV. Reactions with derivatives of chloroacetic acid.** D. E. ADELSON and C. B. POLLARD (J. Amer. Chem. Soc., 1935, 57, 1280—1281).—Piperazine (I) and  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{R}$  in  $\text{EtOH} + \text{Na}_2\text{CO}_3$  give *Me*, b.p.  $156\text{--}157^\circ/5$  mm., m.p.  $62.5^\circ$ , *Et* (II), b.p.  $158.5\text{--}159^\circ/4$  mm., m.p.  $47.5^\circ$  (*H sulphate*), *Pr*<sup>a</sup>, b.p.  $177\text{--}178^\circ/5$  mm. (*H sulphate*), *Bu*<sup>a</sup>, b.p.  $194\text{--}194.5^\circ/4$  mm. (*H sulphate*), and *n-hexyl*, b.p.  $228\text{--}230^\circ$  (slight decomp.)/5 mm., m.p.  $39.5^\circ$  (*H sulphate*), piperazine-1:4-diacetates, which with conc. aq.  $\text{NH}_3$  afford piperazine-1:4-diacetamide (III), chars  $> 250^\circ$ , also formed from (I),  $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}_2$ , and  $\text{Na}_2\text{CO}_3$  in PhMe. (III) is dehydrated to piperazine-1:4-diacetonitrile, m.p.  $165^\circ$ , and converted by  $\text{NaNO}_2$  in conc.  $\text{H}_2\text{SO}_4$  into piperazine-1:4-diacetic acid ( $+2\text{H}_2\text{O}$ ), decomp.  $> 250^\circ$  (*H sulphate*; *Na salt*). Reduction ( $\text{Na}$ ,  $\text{Bu}^\circ\text{OH}$ ) of (II) gives 1:4-di- $\beta$ -hydroxyethylpiperazine, m.p.  $135\text{--}135.5^\circ$ . *n-Hexyl chloroacetate* has b.p.  $218.5\text{--}219.5^\circ/758$  mm.

H. B.

**Relationships between constitution and magnitude of mol. heat of fusion of organic compounds. II. Synthesis of 1:4-endoazocyclohexane.** J. PIRSON and J. JÖRGL (Ber., 1935, 68, [B], 1324—1330).—Evidence is adduced in favour of the view that, in addition to dependence on m.p., the type of space fulfilment is decisive for the magnitude of the mol. latent heat of fusion and the nature of the atoms constituting the compound has little if any influence.  $\Delta^{1:3}\text{-cycloHexadiene}$  and  $\text{Et}_2\text{azodicarboxylate}$  in ligroin yield *Et*, 1:4-endohydrazocyclohexene- $\text{NN}'$ -dicarboxylate, b.p.  $155^\circ/1.5$  mm. (slight decomp.), which in presence of  $\text{Pd-C}$  absorbs  $2\text{H}$  with formation of cyclohexane and  $(\text{-NH}\cdot\text{CO}_2\text{Et})_2$ . After complete hydrogenation and treatment of the product with  $\text{KOH}$ , impure 1:4-endohydrazocyclohexane is obtained; it is transformed by  $\text{CuCl}_2$  into the azo-cuprous complex,  $\text{C}_6\text{H}_{10}\cdot\text{N}_2\text{CuCl}$ , from which 1:4-endoazocyclohexane (I), m.p.  $141.4^\circ$ , is obtained by action of alkali. The mol. m.p. depressions of (I), endomethylenedehydropiperidazine, and endomethylenepiperidazine are  $32.2$ ,  $29.4$ , and  $32.4$ , respectively.

H. W.

**Rearrangement of methoxy-pyrimidines and -purines.** E. BERGMANN and H. HEDMOLD (J.C.S., 1935, 955—957).—4-Chloro-2':6-dimethoxypyrimidine is converted by  $\text{MeI}$  at  $90^\circ$  into 4-chloro-1:3-dimethyluracil, m.p.  $113^\circ$ . 2:6-Dimethoxy-7-methylpurine, m.p.  $199^\circ$ , from 2:6-dichloro-7-methylpurine and  $\text{NaOMe-MeOH}$  at  $100^\circ$ , is transformed into caffeine when heated at  $210^\circ$  or, preferably, with  $\text{MeI}$  at  $100^\circ$ . 2-Chloro-6-methoxy-7-methylpurine, m.p.  $219^\circ$  (decomp.), from 2:6-dichloro-7-methylpurine and  $\text{NaOMe}$  in boiling  $\text{MeOH}$ , has marked thermal stability but is transformed by  $\text{MeI}$  at  $100^\circ$  into 2-chloro-1:7-dimethylhypoxanthine methiodide, m.p.  $228^\circ$  (decomp.), a periodide, m.p.  $158\text{--}160^\circ$ , being also formed. In addition to the allyl derivatives only the methylpurine compounds appear capable

of rearrangement by heat; 2:6-dipropoxy-7-methylpurine, however, is stable at  $150^\circ$ .

H. W.

**Action of aromatic aldehydes on the additive products obtained from aromatic amidines and glyoxal.** J. B. EKELEY and A. R. RONZIO (J. Amer. Chem. Soc., 1935, 57, 1353—1356).— $\text{NH}_2\cdot\text{CPh}\cdot\text{NH}$  (I) and polyglyoxal (II) in aq.  $\text{KOH}$  give a compound,  $\text{C}_9\text{H}_{10}\text{O}_2\text{N}_2$  (III), m.p.  $160^\circ$  (all m.p. are on Maquenne block unless stated otherwise) [*hydrochloride*, m.p.  $157\text{--}213^\circ$  (decomp.) (tube)], which gives  $(\text{CHO})_2$  when dissolved in  $\text{H}_2\text{O}$  and is converted by warm alkali into red compounds. (III) and  $\text{PhCHO}$  in aq.  $\text{EtOH-KOH}$  afford (probably) 5-hydroxy-2:4-diphenylpyrimidine (IV), m.p.  $284^\circ$  [*hydrochloride* (mixture of mono- and di-); *platinichloride* ( $+2\text{H}_2\text{O}$ ), m.p.  $264^\circ$  (decomp.) (tube)], also formed directly from equimol. amounts of (I), (II), and  $\text{PhCHO}$  in aq.  $\text{EtOH-KOH}$ , which is oxidised (alkaline  $\text{KMnO}_4$ ) to  $\text{NH}_2\text{Bz}$ ,  $\text{BzOH}$ , and  $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ . (IV) is considered to be stable in alkaline solution but to rearrange in acid ( $\text{HCl}$ ) to  $\text{CH}=\text{N}\cdot\text{CHBz}\cdot\text{N}\geq\text{CPh}$ . (I), (II), and the appropriate  $\text{ArCHO}$  similarly give 5-hydroxy-2-phenyl-4-p-tolyl-, m.p.  $319^\circ$ , -4-o-hydroxyphenyl-, m.p.  $338^\circ$ , -4-5'-bromo-2'-hydroxyphenyl-, m.p.  $335^\circ$ , -4-o-, m.p.  $283^\circ$ , and -p-, m.p.  $307^\circ$ , -anisyl-, -4-m-nitrophenyl-, m.p.  $262^\circ$ , -4-m-, m.p.  $241^\circ$ , and -p-, m.p.  $292^\circ$ , -aldehydophenyl-, and -4-furyl-, m.p.  $293.5^\circ$ , -pyrimidines.  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{C}(\text{NH})\cdot\text{NH}_2$  and (II) similarly afford a compound,  $\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_2$ , m.p.  $164^\circ$ ; 5-hydroxy-4-phenyl-, m.p.  $310^\circ$ , -4-p-tolyl-, m.p.  $295^\circ$ , -4-o-hydroxyphenyl-, m.p.  $323.5\text{--}337^\circ$ , -4-m-nitrophenyl-, m.p.  $295^\circ$ , -4-5'-bromo-2'-hydroxyphenyl-, m.p.  $344.5\text{--}351.5^\circ$ , and -4-furyl-, m.p.  $310^\circ$ , -2-p-tolylpyrimidines are prepared. The compound,  $\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_2$ , m.p.  $148^\circ$ , from  $m\text{-C}_6\text{H}_4\text{Me}\cdot\text{C}(\text{NH})\cdot\text{NH}_2$  and (II) with  $\text{PhCHO}$  gives 5-hydroxy-4-phenyl-2-m-tolylpyrimidine, m.p.  $258.5^\circ$ , which with  $\text{PCl}_5 + \text{POCl}_3$  affords the 5-Cl-derivative, m.p.  $285.5^\circ$ . Compounds,  $\text{C}_9\text{H}_9\text{O}_2\text{N}_2\text{Cl}$ , m.p.  $188^\circ$ , and  $\text{C}_{13}\text{H}_{12}\text{O}_2\text{N}_2$ , decomp.  $164\text{--}207^\circ$ , are prepared from (II) and  $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{C}(\text{NH})\cdot\text{NH}_2$  (V) and  $\beta\text{-C}_{10}\text{H}_7\cdot\text{C}(\text{NH})\cdot\text{NH}_2$  (VI), respectively. 5-Hydroxy-4-phenyl-2-p-chlorophenyl-, m.p.  $331.5^\circ$ , -2-p-nitrophenyl-, m.p.  $326^\circ$ , and -2- $\beta$ -naphthyl-, m.p.  $281^\circ$ , -pyrimidines are formed from (II),  $\text{PhCHO}$ , and (V),  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{NH})\cdot\text{NH}_2$ , and (VI), respectively. When the mother-liquors from the prep. of (III) are kept for some weeks and then acidified, 5-hydroxy-2-phenylpyrimidine-4-carboxylic acid(?), m.p.  $250^\circ$  (tube),  $310^\circ$ , is pptd.; this arises from the  $\text{CHO}\cdot\text{CO}_2\text{H}$  present in (II). Alkaline solutions of the hydroxypyrimidines often show fluorescence when  $\text{EtOH}$  is added.

H. B.

**Indoles and isatogens. XVIII. Preparation of a vat dye from *oo'*-dinitrotolane and its conversion into dindole.** P. RUGGLI and H. ZAESLIN (Helv. Chim. Acta, 1935, 18, 845—852).—2:2'-Dinitrobenzil (I) in  $\text{EtOAc}$ ,  $\text{EtOH}$ , and  $\text{H}_2\text{O}$  hydrogenated in presence of  $\text{Ni}$  gives 2-o-aminophenylindolone (II), m.p.  $167^\circ$  (leuco-compound; *Ac derivative*, m.p.  $192^\circ$ ; *phenylhydrazone*, m.p.  $186^\circ$ ; *semicarbazone*, decomp.  $206^\circ$ ), and a compound,  $\text{C}_{14}\text{H}_{10}\text{O}_2\text{N}_2$ , m.p.  $344^\circ$  (*Ac derivative*, m.p.  $220^\circ$ ). (I) and (II) when reduced with  $\text{SnCl}_2\text{-HCl}$  both yield dindole (cf. Heller, A., 1917, i, 708).

F. R. G.



**isoIndigotin and related compounds.** A. WAHL (Bull. Soc. chim., 1935, [v], 2, 1221—1244).—A lecture.

**Quinazolines. XL. Synthesis of a quinazoline derivative structurally related to papaverine.** E. B. MARR and M. T. BOGERT (J. Amer. Chem. Soc., 1935, 57, 1329—1330).—6-Aminoveratraldehyde, prepared in 90% yield by reduction ( $\text{FeSO}_4$ , aq.  $\text{NH}_3$ ) of the  $\text{NO}_2$ -derivative (modified prep.), and homoveratroyl chloride in 50%  $\text{AcOH} + \text{NaOAc}$  give 6-homoveratramidoveratraldehyde, m.p. 141.2—142.2° (corr.), which with  $\text{MeOH-NH}_3$  at 100—120° affords 6:7-dimethoxy-2-veratrylquinazoline, m.p. 134—135° (corr.). H. B.

**Pyrrole-blues. I. Absorption spectra in visible light. II. Absorption spectra in the ultra-violet.** P. PRATESI (Annali Chim. Appl., 1935, 25, 195—203, 203—208).—The spectra for 5-(2:3-dimethylpyrrolenyl)- $\beta$ -isatin (2:3-dimethylpyrrole-blue), 5-(2:4-dimethyl-3-ethylpyrrolenyl)- $\beta$ -isatin (cryptopyrrole-blue), and 5-(4-methyl-3-ethylpyrrolenyl)- $\beta$ -isatin (opsopyrrole-blue) confirm the analogy in constitution of these three compounds.

T. H. P.

**Flavins.** R. KUHN (Bull. Soc. Chim. biol., 1935, 17, 905—926).—A lecture.

**Improvement of the flavin synthesis. Boric acid process.** R. KUHN and F. WEYGAND (Ber., 1935, 68, [B], 1282—1288).—The yields of flavins are increased almost tenfold when the corresponding diamines are condensed with alloxan in presence of  $\text{H}_3\text{BO}_3$ . The action does not appear to depend on the formation of complexes of  $\text{H}_3\text{BO}_3$  and the OH groups of the sugar-like side-chain, since lactoflavin forms such compounds in dil. aq. solution which are characterised by marked reversal of the sign of rotation, whereas in such solution  $\text{H}_3\text{BO}_3$  has no influence on the yield of flavin provided the solution is acid. Further, the effect of  $\text{H}_3\text{BO}_3$  is most marked in anhyd. media. Also it greatly increases the yield of flavins which do not contain OH suitable for condensation. The action of  $\text{H}_3\text{BO}_3$  appears similar in the anthraquinone and flavin series. 4:5-Dinitro-*o*-xylene and *d*-arabamine in 80% EtOH at 135° yield 4-nitro-5-*d*-arabitylamino-*o*-xylene (I), m.p. 213—214° [corresponding dl-compound (II), m.p. 203—204°]. The tetra-acetates of (I), (II), and 4-nitro-5-*l*-arabitylamino-*o*-xylene have m.p. 113—114°, 143—144°, and 113—114°, respectively. Treatment of (I) with Zn dust and  $\text{H}_3\text{BO}_3$  in boiling AcOH followed by addition of alloxan in AcOH gives 6:7-dimethyl-9-*d*-araboflavin, m.p. 302—303° (decomp.),  $[\alpha]_D^{20} +78.6^\circ$ ,  $+70.9^\circ$ ,  $+63.0^\circ$  in 0.1*N*-NaOH ( $c=0.509$ ,  $0.254$ , and  $0.127$ , respectively),  $[\alpha]_D^{20} -44.1^\circ$  in 0.05*N*-NaOH +  $\text{Na}_2\text{B}_4\text{O}_7$  (tetra-acetate, m.p. 221—222°). 6:7-Dimethyl-9-*l*-araboflavin has m.p. 202—203° (decomp.),  $[\alpha]_D^{20} -77.9^\circ$ ,  $-69.7^\circ$ ,  $-57.4^\circ$  in 0.1*N*-NaOH ( $c=0.488$ ,  $0.244$ , and  $0.122$ , respectively),  $[\alpha]_D^{20} +44.8^\circ$  in 0.05*N*-NaOH +  $\text{Na}_2\text{B}_4\text{O}_7$  (tetra-acetate, m.p. 221—222°). 6:7-Dimethyl-9-*dl*-araboflavin, m.p. 295—296°, and its tetra-acetate, m.p. 283—284°, are obtained by admixture of equal wts. of the optical antipodes. *o*-Aminodiphenylamine is converted into 9-phenylflavin, m.p.  $> 370^\circ$ , and 9-phenyl-3-methylflavin, m.p.  $> 360^\circ$ . H. W.

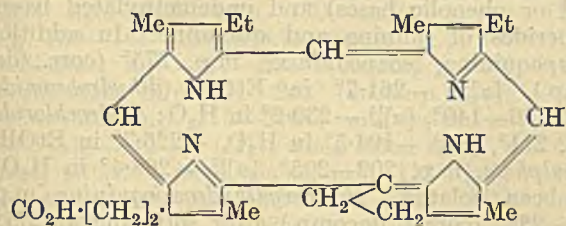
**Flavin syntheses. VI. Synthesis of three further stereoisomerides of lactoflavin.** P. KARRER, H. SALOMON, K. SCHÖPP, F. BENZ, and B. BECKER (Helv. Chim. Acta, 1935, 18, 908—910; cf. this vol., 760).—By methods analogous to those already described the following new compounds are obtained from pentoses with 3-amino-4-carbethoxy-amino-*o*-xylene and alloxan: 2-carbethoxyamino-4:5-dimethylphenyl-1-ribamine, m.p. 172°, -*d*-arabamine, m.p. 175°, -*d*-lyxamine, m.p. 169°, hydrolysed by alkali to 1-*d*-lyxityl-2-hydroxy-5:6-dimethylbenzimidazole, m.p. 216°; 6:7-dimethyl-9-*l*-1'-ribityl-, m.p. 280°, -*d*-1'-arabityl-, m.p. 305° (corr.), -*d*-1'-lyxityl-isalloxazine, m.p. 280—282° ( $\text{Ac}_4$  derivative, m.p. 225—226°). F. R. G.

**Fluorescence curves of lactoflavin and synthetic flavins.** P. KARRER and H. FRITZSCHE (Helv. Chim. Acta, 1935, 18, 911—914; cf. preceding abstract).—6:7-Dimethyl-9-*d*-1'-ribityl- (I), -9-*d*-1'-sorbityl-, -9-*d*-1'-lyxityl-, -9-*d*-1'-rhamnityl-, and -9-*l*-1'-arabityl-, 7-methyl-9-*d*-1'-arabityl-, and 9-*l*-1'-arabityl-isalloxazine in aq. solutions buffered with phosphate ( $pH$  7.0) give fluorescence spectra having a max. intensity in 0.003% solution. The curves for (I) and natural lactoflavin practically coincide. F. R. G.

**Chlorophyll. LVIII. Synthesis of  $\beta$ -unsubstituted deoxophyllerythrins and an isomeric deoxophyllerythrin.** H. FISCHER and W. ROSE. LIX. Conversion of the vinyl group of chlorophyll and its derivatives into a hydroxyethyl group; oxopyrroporphyrin. H. FISCHER and J. HASENKAMP. LX. Fine structure of chlorophyll-*a* and -*b*. Detection of two asymmetric carbon atoms. H. FISCHER and A. STERN (Annalen, 1935, 519, 1—42, 42—58, 58—69; cf. this vol., 871).—LVIII. The *Me* ester (I), m.p. 98°, of 4-carbethoxy-2-methyl-3-ethylpyrrole-5-carboxylic acid (A., 1912, i, 899) with 2 mols. of  $\text{SO}_2\text{Cl}_2$  in  $\text{Et}_2\text{O}$  gives the 2- $\alpha'$ - $\text{Cl}_2$ -derivative, cryst., hydrolysed (NaOH) to 2-aldehydo-4-carbethoxy-3-ethylpyrrole-5-carboxylic acid (II), m.p. 131° [*Me* ester, m.p. 82°; azine, m.p. 264° (decomp.); oxime, m.p. 188°]. (I) with 3 mols. of  $\text{SO}_2\text{Cl}_2$  in  $\text{Et}_2\text{O}$  gives 5-carbomethoxy-4-carbethoxy-3-ethylpyrrole-2-carboxylic acid, m.p. 158°, which with 50% KOH yields 3-ethylpyrrole; this with cryptopyrrolealdehyde in EtOH and 48% HBr gives 3':5'-dimethyl-3:4'-diethylpyrromethene hydrobromide (III), m.p. 183° (decomp.) [ $\text{Br}_2$ -derivative (IV), m.p.  $> 300^\circ$ ]. (II) hydrolysed with 6% NaOH gives 2-aldehydo-3-ethylpyrrole-4:5-dicarboxylic acid, blackens at 205°; this and (II) with cryptopyrrole (V) in 48% HBr and AcOH give, respectively, 4:5-dicarboxy-, decomp. 208°, and 5-carboxy-4-carbethoxy-3':5'-dimethyl-3:4'-diethylpyrromethene hydrobromide, m.p. 180° (decomp.). 2-Methyl-3-ethylpyrrole (VI) (improved prep.) with  $\text{MgEtBr}$  in  $\text{Et}_2\text{O}$  and  $\text{ClCO}_2\text{Et}$  gives *Et* 2-methyl-3-ethylpyrrole-5-carboxylate, m.p. 85°, the 4-*Br*-derivative, m.p. 117°, of which with  $\text{SO}_2\text{Cl}_2$  in  $\text{Et}_2\text{O}$  yields the *Et* ester, m.p. 107° (azine, m.p. 239°), of 4-bromo-2-aldehydo-3-ethylpyrrole-5-carboxylic acid, m.p. 190°, which with (V) in AcOH gives 4-bromo-5-carboxy-, decomp. 265°, brominated to 4:5-dibromo-3':5'-dimethyl-3:4'-diethylpyrromethene hydrobromide, identical in appearance with (IV), showing that (III) is



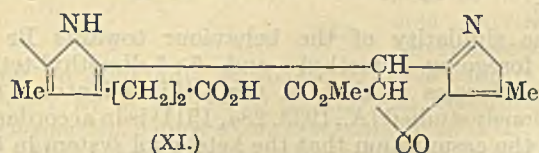
$\begin{array}{c} \text{CH}\cdot\text{C}^{\text{Me}}\text{Et} \\ \text{CH}\cdot\text{NH} \end{array} > \text{C}\cdot\text{CH}\cdot\text{C} < \begin{array}{c} \text{C}^{\text{Me}}\text{Et} \\ \text{N}=\text{C}^{\text{Me}} \end{array}$  and not  
 $\begin{array}{c} \text{C}^{\text{Me}}\text{Et} \\ \text{CH}\cdot\text{CH} \end{array} > \text{C}\cdot\text{CH}\cdot\text{C} < \begin{array}{c} \text{C}^{\text{Me}}\text{Et} \\ \text{N}=\text{C}^{\text{Me}} \end{array}$  The identity of these  
 $\text{Br}_2$ -derivatives is also shown by succinic acid fusion with 5-carboxy-4:4':5'-trimethyl-3-bromovinylpyrromethene-3'-propionic acid hydrobromide (VII), giving the same 1-demethyldeoxyphylloerythrin, the Me ester, m.p. 258°, of which, is oxidised with conc.  $\text{H}_2\text{SO}_4$  to 1-demethylphylloerythrin. 1-Bromodeoxyphylloerythrin, m.p. 278°, 1:5-bisdemethyl-, 1-bromo-5-demethyl-, and 1:5-dibromo-actioporphyrin were also isolated from the melt. Similarly from (VII) and 3:5-dibromo-4:3':5'-trimethyl-4'-ethyl-, 5:3'-dibromo-4:5'-dimethyl-3:4'-diethyl- [blackens 180°, prep. from (VI) and 5-aldehydo-3-methyl-4-ethylpyrrole-carboxylic acid], and 5:4'-dibromo-4:3':5'-trimethyl-3-ethyl-pyrromethene hydrobromides, respectively, are obtained the following porphyrins: 2-de-ethyldeoxyphylloerythrin Me ester (VIII) (2-Br-derivative; Fe salt; Cu salt), identical with the product from chlorophyll-a (cf. A., 1934, 1371), the vinyl group of which must therefore be in position 2, and (VIII) with  $\text{H}_2\text{SO}_4$  gives 2-de-ethylphylloerythrin; deuteractioporphyrin II ( $\text{Br}_1$ -derivative); 3-demethyldeoxyphylloerythrin Me ester (IX), m.p. 246° (Br-derivative), identical with the product from chlorophyll-b, the CHO of which must therefore be in position 3, and (IX) with  $\text{H}_2\text{SO}_4$  yields 3-demethylphylloerythrin; 4-de-ethyldeoxyphylloerythrin Me ester, m.p. 259° (4-Br-derivative; Fe salt; Cu salt), which with  $\text{H}_2\text{SO}_4$  yields 4-de-ethylphylloerythrin. Succinic acid fusion of 5-carboxy-4:3':5'-trimethyl-3-bromovinylpyrromethene-4'-propionic acid hydrobromide with 5-bromo-5'-bromomethyl-4:3'-dimethyl-3:4'-diethylpyrromethene hydrobromide gives a deoxyphylloerythrin,  $\text{C}_{33}\text{H}_{36}\text{O}_2\text{N}_4$  [Me ester, m.p. 263°; Fe salt; Cu salt; phylloerythrin (Me ester, m.p. 264°); rhodin], having the appended formula:



LIX. Phæophorbide-a with red P and HBr in AcOH and subsequent treatment with 20% HCl yields 2- $\alpha$ -hydroxydihydrophæophorbide-a, which with  $\text{CH}_2\text{N}_2$  in  $\text{Et}_2\text{O}$  gives 2- $\alpha$ -hydroxydihydrochlorin- $e_6$  Me<sub>3</sub> ester together with the Me ester, m.p. 261°, of 2- $\alpha$ -hydrodihydropyrophæophorbin-a (X) decomp. 220°. Similarly pyrophæophorbide-a yields (X), which with MeOH yields the Me ester of its Me ether, m.p. 240°; this with HI in AcOH gives oxophylloerythrin Me ester, whilst reduction ( $\text{H}_2$ , Pd, AcOH) and subsequent reoxidation yields phylloerythrin Me ester. Dihydrophæophorbide-a with HI in AcOH gives phæoporphyrin- $a_5$  but no oxophæoporphyrin- $a_5$ . The colourless residue of *Rhodiovibrio* after extraction with  $\text{COMe}_2$  (cf. this vol., 362) yields by further extraction ( $\text{CHCl}_3$ ) a compound,  $(\text{C}_4\text{H}_6\text{O}_2)_n$ , depolymerised by sublimation to give crotonic acid together with (probably)

isocrotonic acid.  $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$  fusion of oxorhodoporphyrin gives oxopyrroporphyrin [Me ester, m.p. 255°; oxime, m.p. 272°; hæmin, cryst.; Ac derivative, m.p. 290°, identical with the Ac<sub>2</sub> derivative of 2-de-ethylpyrroporphyrin Me ester]. Data are given for the absorption spectra of most of the above compounds.

LX. Vals. of  $[\alpha]^{20}$  in  $\text{COMe}_2$  or  $\text{C}_5\text{H}_5\text{N}$  are given for chlorophyll, chlorophyllide-a, phæophorbide-a, methylphæophorbide-b, pyrophæophorbide-a and -b (XI), pyrophæophorbide-a Me ester (XII), 10-ethoxymethylphæophorbide-a and -b, 10-ethoxyethylphæophorbide-a, chlorin- $e_4$  Me<sub>2</sub> ester, chlorin  $p_6$  Me<sub>3</sub> ester, phæoporphyrin- $a_5$ , phylloerythrin, probophorbide-a, and oxochloroporphyrin- $e_4$ . As (XII) is optically active it must contain an asymmetric C, which is considered to be  $\text{C}_\gamma$ ; hence (XI) must have asymmetric C at  $\text{C}_\gamma$  and  $\text{C}_{10}$  as shown. Derivatives of (XI) have analogous formulæ.



F. R. G.

Preparation of 4-methylthiazole-5-carboxylic acid. M. L. TOMLINSON (J.C.S., 1935, 1030—1031).— $\text{COMe}\cdot\text{CHBr}\cdot\text{CO}_2\text{Et}$  and  $\text{HCS}\cdot\text{NH}_2$  give Et 4-methylthiazole-5-carboxylate, b.p. 215—220°, m.p. 27—28°, in 50% yield, hydrolysed to 4-methylthiazole-5-carboxylic acid (I), m.p. 280° (decomp.) after softening at 270° [Me ester (II), m.p. 74—75°]. (I) and (II) are identical with the products obtained by Windaus by degradation of vitamin- $\text{B}_1$ .

H. W.

Production of thiazole compounds.—See B., 1935, 749.

Formation and stability of polybromide derivatives of heterocyclic compounds. V. Bromination of some 2-arylimino-4-keto-3-aryl-5-methyltetrahydrothiazoles and their 3:5-dimethyl homologues: theory of singlet linkages. B. AHMAD, R. D. DESAI, and R. F. HUNTER (J. Indian Chem. Soc., 1935, 12, 237—245).—Treatment of 2-anilo-4-keto-3-phenyl-5-methyltetrahydrothiazole, m.p. 105° [from  $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$  (I),  $\text{CS}(\text{NPh})_2$  (II),  $\text{NaOEt}$ , and  $\text{EtOH}$ ], with Br in  $\text{CHCl}_3$  at 0—3° affords a hydropentabromide,  $\text{C}_6\text{H}_{13}\text{ON}_2\text{SBr}_5\text{HBr}(\text{Br}_2)$ , m.p. 149°, converted by  $\text{H}_2\text{SO}_3$  into 2-anilo-4-keto-3-p-bromophenyl-5-methyltetrahydrothiazole, m.p. 121—122° [also obtained by heating  $\text{NPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Br}$  (III),  $\text{NaOEt}$ ,  $\text{EtOH}$ , and (I)]. Similarly 2-anilo-4-keto-3-phenyl-5:5-dimethyltetrahydrothiazole, m.p. 160° [from (II),  $\text{NaOEt}$ ,  $\text{EtOH}$ , and  $\text{CMe}_2\text{Br}\cdot\text{CO}_2\text{Et}$  (IV)], yields a hydropentabromide, m.p. 196° (decomp.), which loses Br on exposure to the air forming a hydro-tetrabromide. This is reduced by  $\text{H}_2\text{SO}_3$  to 2-anilo-4-keto-3-p-bromophenyl-5:5-dimethyltetrahydrothiazole, m.p. 163° [also obtained from (III) and (IV)]. By similar methods 2-p-tolylimino-4-keto-3-p-tolyl-5-methyltetrahydrothiazole, m.p. 110°, affords an indefinite bromo-additive compound, m.p. 92°, reduced by  $\text{H}_2\text{SO}_3$  to 2-p-tolylimino-4-keto-3-o-bromo-p-tolyl-5-methyltetrahydrothiazole, m.p. 157° [also obtained from



(I) and *s-p*-tolyl-*o*-bromo-*p*-tolylthiocarbamide, m.p. 168°; 2-*p*-tolylimino-4-keto-3-*p*-tolyl-5:5-dimethyl-tetrahydrothiazole, m.p. 167°, yields an indefinite hydroperbromide, m.p. 98°, reduced by  $\text{H}_2\text{SO}_3$  to 2-*p*-tolylimino-4-keto-3-*o*-bromo-*p*-tolyl-5:5-dimethyl-tetrahydrothiazole, m.p. 109° [also obtained from *s-p*-tolyl-*o*-bromo-*p*-tolylthiocarbimide and (IV)]; 2-*p*-bromoanilo-4-keto-3-*p*-bromophenyl-5-methyltetrahydrothiazole, m.p. 120°, yields a hydrotribromide, m.p. 86° (decomp.), reduced by  $\text{H}_2\text{SO}_3$  to 2-*p*-bromoanilo-4-keto-3-*op*-dibromophenyl-5-methyltetrahydrothiazole, m.p. 90° [also obtained from (I) and *s-p*-bromophenyl-*op*-dibromophenylthiocarbamide, m.p. 180°], and 2-*p*-bromoanilo-4-keto-3-*p*-bromophenyl-5:5-dimethyltetrahydrothiazole, m.p. 165–166°, yields a hydrotribromide, m.p. 84° (decomp.), reduced by  $\text{H}_2\text{SO}_3$  to 2-*p*-bromoanilo-4-keto-3-*op*-dibromophenyl-5:5-dimethyltetrahydrothiazole, m.p. 140° [also obtained from the appropriate tribromothiocarbamide and (IV)].

The similarity of the behaviour towards Br of the foregoing 5-methyl- and 5:5-dimethyl-tetrahydrothiazoles to that of the  $\psi$ -thiohydantoins (V) previously studied (A., 1933, 284, 1311) is in accordance with the assumption that the keto-enol system in (V) plays no part in their bromination.

1-Aminobenzthiazole hydrodibromide (A., 1934, 309) is not paramagnetic and hence does not contain a  $[\text{Br}_2]^0$  ion which involves a "singlet linking"; a structure is proposed. The evidence for this type of linking is not conclusive. H. G. M.

Reaction of bismuth salts with the products of condensation of bis-phenylthiocarbamide. J. V. DUBSKÝ and J. TRTILEK (Chem. Listy, 1935, 29, 33–34).— $\text{BiCl}_3$  yields an orange-yellow salt with 3-anilino-5-thiol-4-phenyl-1:2:4-triazole, an orange-red salt,  $\text{Bi}(\text{C}_6\text{H}_5\text{N}_3\text{S}_2)_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ , with 3:5-dithiol-4-phenyl-1:2:4-triazole, a white salt with 3:5-dianilino-4-thio-1:2-diazole, and a yellow salt with 3-anilino-5-thiol-4-thio-1:2-diazole. R. T.

*d*-Nornicotine, an alkaloid of *Duboisia Hopwoodii*, F. v. Muell. E. SPÄTH, C. S. HICKS, and E. ZAJIC (Ber., 1935, 68, [B], 1388–1393).—Extraction of the dried leaves with EtOH and removal of non-basic material gives a crude alkaloid from which a fraction, b.p. 117°/3.6 mm.,  $[\alpha]_D^{25} + 38.3^\circ$ , is isolated. Analyses indicating the formula  $\text{C}_8\text{H}_{12}\text{N}_2$  and absorption spectrum point to the presence of *d*-nornicotine (I); this is confirmed by its oxidation to nicotinic acid. Methylation with  $\text{CH}_2\text{O}$  and  $\text{HCO}_2\text{H}$  gives a substance the dipicrate of which does not depress the m.p. of the dipicrate of *l*- or *dl*-nicotine.  $[\alpha]$  of the volatile base from the *Duboisia* dipicrate shows the presence of 62% of *d*-nicotine and 38% of *dl*-nicotine. The presence of nicotine in the *Duboisia* base is excluded since it is quantitatively benzoylated by  $\text{Bz}_2\text{O}$  at 20°, and although (I) has a tendency towards racemisation under the influence of HCl (*d* 1.11) at 90–95° it is improbable that such change takes place under the much milder conditions of methylation. It must therefore be assumed that the *Duboisia* base contains about 62% of (I) and 38% of *dl*-nornicotine; this view is confirmed by comparison of its salts with those of *l*- and *dl*-nicotine. H. W.

[Simplification of Pictet's nicotine synthesis.] G. HAHN and O. SCHALES (Ber., 1935, 68, [B], 1310).—A reply to Späth *et al.* (this vol., 635). H. W.

Amination of alkaloids by sodamide and potassamide.  $\alpha$ - and  $\alpha'$ -aminoanabasines. IV. Nitration of  $\alpha'$ -aminoanabasine. M. M. KATZNELSON and M. I. KABATSCHEV (Ber., 1935, 68, [B], 1247–1251).—Treatment of  $\alpha'$ -aminoanabasine (I) in conc.  $\text{H}_2\text{SO}_4$  at 0° with  $\text{HNO}_3$  (*d* 1.4) affords 2-nitroamino-5-2'-piperidinopyridine [sulphate (II), m.p. 233° (decomp.)], isomerised by conc.  $\text{H}_2\text{SO}_4$  at 70–80° to 3-nitro-2-amino-5-2'-piperidinopyridine, m.p. 178.5–179°, also obtained by direct nitration of (I) at a somewhat higher temp., whereby also a compound, m.p. 70°, is produced. (II) is transformed by boiling  $\text{Ac}_2\text{O}$  into 2-hydroxy-5-2'-piperidinopyridine [*Na* derivative; picrate, m.p. 241° (decomp.)], also obtained by diazotisation of (I). H. W.

Resolution of peganine (vasicine) into its optically active forms. E. SPÄTH, F. KUFFNER, and N. PLATZER (Ber., 1935, 68, [B], 1384–1388).—Treatment of peganine with *d*-tartaric acid in MeOH leads to the isolation of *l*-peganine (I), m.p. 211–212° (vac.) after marked softening at 197–200°,  $[\alpha]_D^{25} - 159^\circ$ ,  $-189^\circ$ , and  $-203^\circ$  in  $\text{CHCl}_3$  (*c*=1.04, 2.01, and 2.66, respectively),  $[\alpha]_D^{25} + 31.4^\circ$  in HCl (1:35). The mother-liquors from (I) when treated with *l*-tartaric acid give *d*-peganine,  $[\alpha]_D^{25} + 163^\circ$  (*c*=1.16),  $[\alpha]_D^{25} + 188^\circ$  (*c*=2.33),  $[\alpha]_D^{25} + 203^\circ$  (*c*=3.45), all in  $\text{CHCl}_3$ ,  $[\alpha]_D^{25} - 30.7^\circ$  in HCl (1:35). Racemisation of the optically active forms occurs when they are repeatedly sublimed in high vac. or slowly when they are heated with 5% HCl at 100°. H. W.

Modified cinchona alkaloids. II. Action of sulphuric acid on quinine and quinidine. T. A. HENRY, W. SOLOMON, and E. M. GIBBS (J.C.S., 1935, 966–971).—The products of the action of 60%  $\text{H}_2\text{SO}_4$  on the alkaloids are *apo*-bases (demethylated or phenolic bases) and undemethylated bases, isomerides of quinine and quinidine. In addition to *apo*quinine, isoapoquinine, m.p. 275° (corr., decomp.),  $[\alpha]_D^{15} - 261.7^\circ$  in EtOH (*dihydrobromide*, m.p. 136–140°,  $[\alpha]_D^{15} - 230.2^\circ$  in  $\text{H}_2\text{O}$ ; *hydrochloride*, m.p. 271°,  $[\alpha]_D^{15} - 194.5^\circ$  in  $\text{H}_2\text{O}$ ,  $-226.7^\circ$  in EtOH; *H sulphate*, m.p. 202–205°,  $[\alpha]_D^{15} - 268.4^\circ$  in  $\text{H}_2\text{O}$ ), has been isolated. *Hydroxydihydroapoquinine*, m.p. 281–284° (corr.; decomp.) after softening at 277°,  $[\alpha]_D^{15} - 205.4^\circ$  in 0.1N- $\text{H}_2\text{SO}_4$  [*hydrochloride*, m.p. 264–268° (corr.; decomp.),  $[\alpha]_D^{15} - 177.3^\circ$  in 0.1N-HCl,  $-103.9^\circ$  in  $\text{H}_2\text{O}$ ,  $-110.4^\circ$  in EtOH; *sulphate*, m.p. 287–293° (corr.; decomp.),  $[\alpha]_D^{15} - 175.5^\circ$  in 0.1N- $\text{H}_2\text{SO}_4$ ; *H sulphate*, blackens at 230° after darkening at 215°,  $[\alpha]_D^{15} - 154^\circ$  in 0.1N- $\text{H}_2\text{SO}_4$ ; *dihydrobromide*, m.p. variable,  $[\alpha]_D^{15} - 130.6^\circ$  in  $\text{H}_2\text{O}$ ], has been obtained. From quinidine, in addition to isoapoquinidine, there is derived apoquinidine, m.p. 185–190° (corr.; decomp.),  $[\alpha]_D^{15} + 291.4^\circ$  in 0.1N- $\text{H}_2\text{SO}_4$ ,  $+208.6^\circ$  in EtOH (also  $+1\text{EtOH}$  and  $+1\text{COMe}_2$ ) [*hydrochloride*, m.p. 183–185° (corr.; decomp.),  $[\alpha]_D^{15} + 177.0^\circ$  in  $\text{H}_2\text{O}$  (also  $+1\text{EtOH}$  and  $+2\text{H}_2\text{O}$ ); *sulphate*, m.p. 260° (corr.; decomp.),  $[\alpha]_D^{15} + 248.5^\circ$  in 0.1N- $\text{H}_2\text{SO}_4$  (also  $+2\text{EtOH}$  and  $+1\text{H}_2\text{O}$ ); *dihydrobromide*, m.p. 280° (corr.; decomp.),  $[\alpha]_D^{15} + 192.5^\circ$  in  $\text{H}_2\text{O}$ ; *zincchloride*, m.p. 290° (corr.;



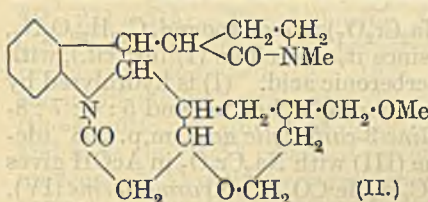
decomp.),  $[\alpha]_D^{15} + 175.3^\circ$  in  $H_2O$ . A third isomeride, provisionally named *phenolic base A*, m.p.  $250^\circ$  (corr.; decomp.),  $[\alpha]_D^{15} + 209.5^\circ$  in  $0.1N-H_2SO_4$ ,  $+139.5^\circ$  in EtOH [*hydrochloride*, m.p.  $180-190^\circ$  (corr.; decomp.),  $[\alpha]_D^{15} + 139.3^\circ$  in  $H_2O$  (also  $+1EtOH$ )], has been isolated in small amount.

The undemethylated bases recovered from quinine have so far yielded only one cryst. product, *apo-quinine Me ether*, m.p.  $183-185^\circ$ ,  $[\alpha]_D^{15} - 201.9^\circ$  in EtOH, which is the  $\beta$ -isoquinine of earlier workers. The *sulphate*, m.p.  $220^\circ$ ,  $[\alpha]_D^{15} - 171.2^\circ$  in  $H_2O$ , and *dihydrobromide*, m.p.  $219^\circ$  (corr.; decomp.),  $[\alpha]_D^{15} - 196^\circ$  in  $H_2O$  (also  $+1H_2O$ ), appear new.  $\alpha$ -iso-Quinine has not been found. From quinidine two well-defined isomerides have been isolated, one of which is  $\beta$ -isoquinidine now shown to be *isoapoquinidine Me ether*, m.p.  $180-181^\circ$ ,  $[\alpha]_D^{15} + 278.8^\circ$  in  $0.1N-H_2SO_4$  [*hydrochloride*, m.p.  $267^\circ$  (corr.; decomp.),  $[\alpha]_D^{15} + 174.7^\circ$  in  $H_2O$ ; *dihydrobromide*, m.p.  $210-215^\circ$  (corr.; decomp.),  $[\alpha]_D^{15} + 186.3^\circ$  in  $H_2O$ ]. A possible third isomeride, m.p.  $120^\circ$ ,  $[\alpha]_D^{15} + 233.5^\circ$  in  $0.1N-H_2SO_4$ ,  $+136.5^\circ$  in EtOH, is described. H. W.

**Third oxide base derived from quinidine.** T. DOMAŃSKI and J. SUSZKO (Arch. Chem. Farm., 1935, 2, 205-219).— $\alpha$ -isoQuinidine (I), as prepared by the method previously described (A., 1933, 517), contains up to 20% of a third isomeride,  $\gamma$ -isoquinidine (II), isolated as follows. The tartrates derived from the (I) fraction are converted into hydrochlorides, the aq. solution of which is allowed to crystallise during several weeks, the cryst. hydrochloride of (I) is separated, the mother-liquor is made alkaline with NaOH, excess of dil.  $HNO_3$  is added, and the cryst. nitrate of (II), which then separates, is converted by aq.  $NH_3$  into (II),  $+2H_2O$ , m.p.  $70^\circ$ ,  $[\alpha]_D^{15} + 51.1^\circ$  [*dinitrate*, m.p.  $196^\circ$ ,  $[\alpha]_D^{15} + 50^\circ$  in  $H_2O$ ; *oxalate*, m.p.  $185-188^\circ$  (decomp.),  $[\alpha]_D^{15} - 56.9^\circ$  in  $H_2O$ ; *hydriodide*, m.p.  $180-183^\circ$ ; *tartrate* (III), m.p.  $160-161^\circ$  (decomp.); *picrate*, m.p.  $183-193^\circ$ ; *methiodide*, m.p.  $227-235^\circ$  (decomp.),  $[\alpha]_D^{15} + 12^\circ$ ; *dimethiodide*, m.p.  $241-244^\circ$  (decomp.),  $[\alpha]_D^{25} - 95^\circ$ ; *perbromide*, m.p.  $213-216^\circ$ ; *aminooxide*, m.p.  $80-100^\circ$ ,  $[\alpha]_D^{15} + 42^\circ$ ]. (III), when dried at  $60^\circ$  and then fused, affords  $\gamma$ -isoquinidine, m.p.  $113^\circ$ ,  $[\alpha]_D^{15} - 40.0^\circ$  [*tartrate*, *nitrate*, and *hydriodide*, oils; *N-NO*-, m.p.  $103-105^\circ$ , and *N-Me* derivative, an oil (*dinitrate*, m.p.  $155^\circ$ ); *methiodide*, m.p.  $90-100^\circ$ ,  $[\alpha]_D^{15} - 11.0^\circ$ ]. (II) and AcOH ( $100^\circ$ ; 32 hr.) give  $\gamma$ -hydroxydihydroquinotoxine, m.p.  $110-118^\circ$ ,  $[\alpha]_D^{15} - 15.0^\circ$  (*tartrate*, m.p.  $60^\circ$ ; *N-NO*-derivative, an oil,  $[\alpha]_D^{15} - 17.0^\circ$ ; *p-nitrophenylhydrazone*, m.p.  $90^\circ$ ). (II) is converted by heating at  $70-80^\circ$  with conc.  $H_2SO_4$  into  $\beta$ -isoquinidine (IV), and by heating with conc. aq. HBr ( $100^\circ$ ; 14 hr.) into hydrobromocupreidine dihydrobromide. (II) differs from (I) and (IV) probably not structurally, but stereochemically. The optical data given above relate, unless otherwise specified, to solutions in 96% EtOH. R. T.

**Strychnine and brucine.** XXXIII. Methoxymethylchanodihydrostrychnanic acid and its resistance to facile dehydrogenation. (Miss) T. M. REYNOLDS and R. ROBINSON (J.C.S., 1935, 935-940).—Reply is made to Leuchs (this vol., 505).

The possibility that methoxymethylchanodihydrostrychnone (I) may be an aldehyde is not further entertained, since it is quantitatively recovered after being refluxed with HgO in  $H_2O$ . Oxidation of it with Br in HBr affords (?) *pentabromomethoxymethylchanodihydrostrychnonic acid hydrobromide*, decomp.  $157^\circ$  after darkening at  $152^\circ$ . Oxidation of methoxymethyl-dihydrostrychnine with  $KMnO_4$  in  $COMe_2$  at  $-10^\circ$  affords (I) in 10% yield, whereas use of  $BzO_2H$  leads to a remarkably pure product. It has been suggested that strychnine and its derivatives contain a blocked dihydroindole nucleus, but the stabilisation of the indole nucleus does not extend to methoxymethylchanodihydrostrychnane (II), and there appears no reason why it should not be readily oxidised to an indole derivative. Nevertheless it is



stable to  $Hg(OAc)_2$  in AcOH at  $100^\circ$  and is not affected by S in boiling  $C_{10}H_8$ . In confirmation, *methoxymethylchanodihydrostrychnanic acid* (III), m.p.  $205-206^\circ$  (slight decomp.) after softening at  $203^\circ$ , has been compared with *cis*-hexahydrocarbazole (IV) in its behaviour towards dehydrogenating agents. Conditions are given under which (IV) is transformed into tetrahydrocarbazole by  $Hg(OAc)_2$  in cold dil. AcOH or by S in quinoline at  $175-180^\circ$ ; in parallel experiments (III) remains unchanged. (III) is prepared by the action of hot  $Ba(OH)_2 \cdot MeOH$  in  $N_2$  on (II) and the reverse change is effected by boiling (III) with 5% HCl or by heating it in  $C_{10}H_8$  at  $180-186^\circ$ . The stability of the  $\cdot N(b) \cdot CO \cdot$  group is remarkable, but its presence is confirmed since (III) is acid to litmus and gives a *nitrosoamine*, decomp.  $190^\circ$  after softening and darkening at  $187^\circ$ , which does not form a hydrochloride. The colour reactions of the acid show that the group  $\cdot N(a) \cdot CO \cdot$  is the one that is hydrated.

H. W.

**Ergot alkaloids.** V. Hydrolysis of ergotinine. W. A. JACOBS and L. C. CRAIG (J. Biol. Chem., 1935, 110, 521-530).—Alkaline hydrolysis of ergotinine (I) yields *isobutyrylformic acid* (II), *lysergic acid* (III), and a *dipeptide*,  $C_{14}H_{18}O_3N_2$ , m.p.  $252^\circ$  (decomp.), whilst acid hydrolysis gives (II), (III), phenylalanine, and proline. (I) and ergotoxine are regarded as being composed of proline and phenylalanine combined in peptide linking with (II) and (III) and perhaps  $NH_3$ , and the structures are discussed. It is concluded that (III) is related biogenetically to tryptophan, for it may be degraded to simple indoles.

J. N. A.

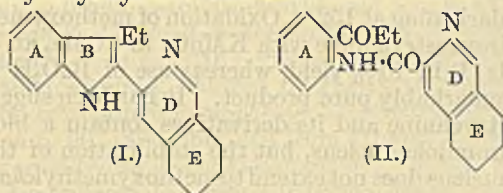
**Alkaloid from ergot.** W. A. JACOBS and L. C. CRAIG (Science, 1935, 82, 16-17).—Extraction with dil. acid of the ergot powder residue which remains after removal of  $Et_2O$ -sol. alkaloids, neutralisation with  $Na_2CO_3$ , and extraction with  $CHCl_3$  yields ergobasine (I) identical with that described by Stoll *et al.* (this vol., 995). Hydrolysis with KOH-EtOH yields lysergic acid (II), but no  $NH_3$ , *isobutyrylformic* or pyruvic acid. Hydrolysis with strong acid of the material left after removal of (II) gave an amino-propanol, isolated as the sulphate,  $(C_3H_7ON)_2 \cdot H_2SO_4$ .



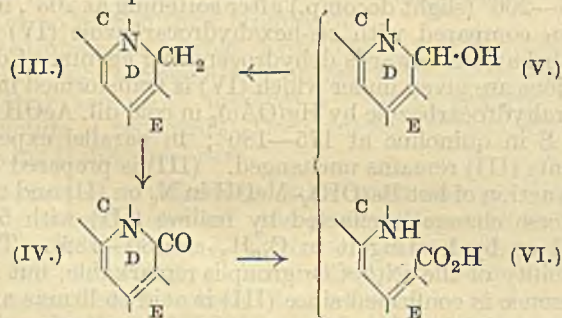
(di-*p*-bromobenzoate,  $C_{17}H_{15}O_3NBr_2$ , m.p.  $155^\circ$ ,  $[\alpha]_D^{25} + 48^\circ$ ). (I) is the hydroxyisopropylamide of (II).

L. S. T.

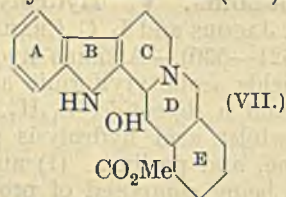
**Constitution of yohimbine.** C. SCHOLZ (Helv. Chim. Acta, 1935, 18, 923—933; cf. A., 1934, 89).—Tetrahydroxybyrine is shown to have structure (I) by



oxidation ( $O_3$  or  $Na_2Cr_2O_7$ ) to a compound,  $C_{19}H_{20}O_2N_2$ , regarded as (II), since it, as well as (I) (*loc. cit.*), with dil.  $HNO_3$  gives berberonic acid. (I) is hydrolysed by  $10N-H_2SO_4$  to *o*-aminopropiophenone and 5 : 6 : 7 : 8-tetrahydroisoquinoline-3-carboxylic acid, m.p.  $208^\circ$  (decomp.). Yohyryne (III) with  $Na_2Cr_2O_7$  in AcOH gives *o*- $C_6H_4(CO_2H)_2$ , *o*- $C_6H_4MeCO_2H$ , and oxyyohyryne (IV), m.p.  $185^\circ$ , reduced (KOH, amyl alcohol) to (III), a compound (V),  $C_{19}H_{18}ON_2$ , m.p.  $193-194^\circ$ , and an amphoteric compound (VI), m.p.  $255^\circ$ . These reactions are represented:

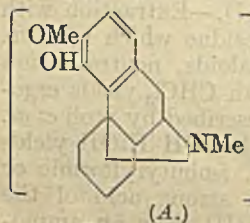


Tryptamine boiled with homophthalic anhydride in  $C_6H_6$  gives indolyethylhomophthalimide, an oil, which when heated under reduced pressure yields a compound,  $C_{19}H_{16}O_2N_2$ , m.p.  $210^\circ$ , but no (IV). Yohimbine is consequently formulated as (VII).



F. R. G.

**Sinomenine.** XLI. *d*- and *l*-bis-1 : 1'-β-Tetrahydrodeoxycodeine. K. GOTO and H. SHISHIDO (Bull. Chem. Soc. Japan, 1935, 10, 252—255; cf. A., 1934, 908).—Deoxodemethoxydihydrosinomenine (I) in EtOH with aq.  $AgNO_3$  yields bis-1 : 1'-deoxodemethoxydihydrosinomenine (A), m.p.  $230-237^\circ$ ,  $[\alpha]_D^{25} + 91.57^\circ$  in EtOH [methiodide, m.p.  $275-279^\circ$  (decomp.); hydrochloride, m.p.  $293-297^\circ$  (decomp.)]. Similarly β-tetrahydrodeoxycodeine (II) gives bis-1 : 1'-β-tetrahydrodeoxycodeine (A), m.p.  $230-238^\circ$ ,  $[\alpha]_D^{25} - 91.32^\circ$  in EtOH (methiodide, m.p.  $276-279^\circ$ ), and equal



(A.)

parts of (I) and (II) give dl-bis-1 : 1'-β-tetrahydrodeoxy-

codeine, m.p.  $255-260^\circ$ ,  $[\alpha]_D^{25} 0^\circ$  in EtOH. The following were prepared similarly to their optical isomerides (A., 1931, 1172): *de*-N-methyl-β-tetrahydrodeoxycodeine, m.p.  $145-148^\circ$ ,  $[\alpha]_D^{25} + 65.45^\circ$  in MeOH; *dl*-*de*-N-methyl-β-tetrahydrodeoxycodeine, m.p.  $133-136^\circ$ ,  $[\alpha]_D^{25} 0^\circ$  in MeOH; *dehydro-d-thebanan*, m.p.  $107-112^\circ$ ,  $[\alpha]_D^{25} + 175.54^\circ$  in MeOH; *dehydro-dl-thebanan*, m.p.  $90-92^\circ$ ,  $[\alpha]_D^{25} 0^\circ$  in MeOH; *dihydrode-N-methyl-β-tetrahydrodeoxycodeine*, m.p.  $161^\circ$ ,  $[\alpha]_D^{25} - 78.42^\circ$  in MeOH- $CHCl_3$ ; *dl-dihydrode-N-methyl-β-tetrahydrodeoxycodeine*, m.p.  $135-140^\circ$ ,  $[\alpha]_D^{25} 0^\circ$  in MeOH- $CHCl_3$ ; *d-thebanan*, m.p.  $48-54^\circ$ ,  $[\alpha]_D^{25} + 3.25^\circ$ . F. R. G.

**Tubocurarine.** H. KING (Chem. and Ind., 1935, 739—740).—The active principle of tubocurarine (cf. A., 1928, 1264) is a crystalline substance in the form of *tubocurarine chloride*,  $C_{38}H_{44}O_6N_2Cl_2$ . Hofmann degradation of *O-methylbebeerine methochloride* (I) gives three methine methiodides, two inactive and one dextrorotatory, which are also obtained, with a levorotatory form, from *O-methyltubocurarine chloride* (II); these methine methiodides, on further degradation, all give a substance,  $C_{36}H_{32}O_6$ . (II) and (I) are thus diastereoisomerides, and can be represented by the symbols *dl'* and *dd'*. This suggests that the botanical origin of tubocurarine is in a Brazilian *Chondodendron* (fam. Menispermaceae). E. W. W.

**Mechanism of the preparation of tribenzylarsine according to Michaelis and Paetov.** J. DODONOV and H. MEDOX (Ber., 1935, 68, [B], 1254—1258).—The action of Na on  $AsCl_3$  and  $CH_2PhCl$  in  $Et_2O$  in an indifferent gas gives  $As(CH_2Ph)_3$  (I) in 45.11% yield in contrast with a max. yield of 21.81% recorded by Michaelis *et al.*; the formation of  $OH \cdot AsCl(CH_2Ph)_3$  (II) is not observed and > minimal amounts of  $(CH_2Ph)_2AsO \cdot OH$  (III) are produced. Pure (I) is not rapidly oxidised by air at room temp., although catalytic impurities sometimes induce a vigorous oxidation giving (III),  $PhCHO$ , and  $As_2O_3$ . (I) and  $O_2$  in  $Et_2O$  containing HCl afford (III),  $(CH_2Ph)_3AsCl \cdot OH$  (IV), and  $PhCHO$ . The change is therefore  $3CH_2PhCl + AsCl_3 + 6Na \rightarrow (I) + 6NaCl$ .  $(I) + O + HCl \rightarrow (IV)$ .  $(I) + 3O \rightarrow (III) + PhCHO$ .  $CH_2NaPh$  and  $EtOAc$  are regarded as primary products. (II) and KBr in boiling  $H_2O$  afford the compound  $OH \cdot As(CH_2Ph)_3 \cdot O \cdot AsBr(CH_2Ph)_3$ , m.p.  $162.5^\circ$ , transformed by HBr into tribenzylarsine oxybromide, m.p.  $129.5^\circ$ . H. W.

**Hydroxy-salts of secondary and tertiary arsines.** G. J. BURROWS (J. Proc. Roy. Soc. New South Wales, 1934, 68, 72—79).—Oxidation of  $AsPhMe_2$  in moist air yields  $AsPhMeO \cdot OH$  (corresponding arsonium chloride, m.p.  $111^\circ$ , nitrate, m.p.  $151^\circ$ , and sulphate, m.p.  $70^\circ$ ), whilst oxidation ( $H_2O_2$ -EtOH) in  $HNO_3$  or HCl gives *phenyldimethylhydroxyarsonium nitrate*, m.p.  $152^\circ$ , or *chloride*, m.p.  $174^\circ$ .  $AsPh_2MeO$ , m.p.  $142^\circ$ , is obtained by oxidation ( $H_2O_2$ -EtOH) of  $AsPh_2Me$ , and *p*- $C_6H_4Me \cdot AsMeO \cdot OH$ , m.p.  $151^\circ$  (corresponding arsonium chloride, m.p.  $133^\circ$ , nitrate, m.p.  $157^\circ$ , and sulphate, m.p.  $85^\circ$ ), is obtained similarly from  $(p-C_6H_4Me \cdot AsMe)_2O$  (I), b.p.  $220/12$  mm. (prepared by methylation of Na tolyl arsenite), in AcOH solution. (I) with HCl gives  $C_6H_4Me \cdot AsMeCl$ , b.p.  $147/24$  mm.,  $138/14$  mm.,



whilst  $C_6H_4Me \cdot AsCl_2$ , m.p.  $42^\circ$  (lit.  $31^\circ$ ), with  $Na_2CO_3$  yields  $p-C_6H_4Me \cdot AsO$ . F. N. W.

**Catalytic reduction of nitroarylsarsinic acids.** M. R. STEVINSON and C. S. HAMILTON (J. Amer. Chem. Soc., 1935, 57, 1298—1299).—The  $NO_2$ -acids (as Na salts in  $H_2O$ ) (0.1 mol.) are reduced with  $H_2$  (initial pressure 30 lb.) and Raney Ni (10 g.). *m*-Amino-, 2-chloro-5-amino-, 3-amino-4-hydroxy-, -4-isoamylamino-, -4- $\beta$ -hydroxyethylamino-, -4- $\beta$ -hydroxy-*n*-propoxy-, and -2-carboxymethylamino-, and 5-amino-2- $\beta$ -hydroxyethylamino-phenylarsinic acids are thus prepared in 52—99% yield. The effect of various inorg. substances on the time of reduction (similar conditions) of  $p-NO_2 \cdot C_6H_4 \cdot OH$  is studied; retardation is pronounced with KCN,  $Na_3AsO_3$ , and  $NaNO_2$ , whilst slight acceleration is found with  $CuSO_4$  (10% wt.). H. B.

**Preparation and properties of 3 : 3'-bis(azo-*m*-phenylenediamine)- and 3 : 3'-bis(azo-2 : 6-diaminopyridine)-4 : 4'-dihydroxyarsenobenzene.** A. E. JURIST and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1935, 24, 457—459).—The compounds named were prepared by treating diazotised salvarsan with  $m-C_6H_4(NH_2)_2$  and 2 : 6-diaminopyridine, respectively. They are both rapid tissue penetrants, but are too toxic for therapeutic uses. The diaminopyridine derivative is bacteriostatic but not germicidal to *B. typhosus* and *B. staphylococcus*. E. H. S.

**Arsenamides. Compounds containing the As-N linking.** G. O. DOAK (J. Amer. Pharm. Assoc., 1935, 24, 453—457).—The compounds ("arsenamides") are obtained by treating the appropriate amines with arsenious halides, both in *n*-heptane solution. Trianilinoarsine trihydrochloride,  $As(NH_2 \cdot PhCl)_3$ , and anilindichlorarsine,  $AsCl_2 \cdot NHPh$ , m.p.  $89^\circ$ ; tripiperidinoarsine trihydrochloride, m.p.  $240-242^\circ$  (trinitrate, m.p.  $144^\circ$ ; triacetate, m.p.  $304^\circ$ ), and a yellow oil, b.p.  $98^\circ/1$  mm. (piperidinodichlorarsine?); diethylaminodichloroarsine, b.p.  $107^\circ/38$  mm.; di-( $\beta$ -aminoethylamino)chloroarsine dihydrochloride,  $AsCl(NH \cdot CH_2 \cdot CH_2 \cdot NH_3Cl)_2$  (chars  $> 225^\circ$ ), methyl-anilindichloroarsine, b.p.  $116^\circ/3$  mm. Tri(benzyl-amino)arsine trihydrochloride, m.p.  $246^\circ$  (decomp.); tri(dibenzylamino)arsine trihydrochloride, m.p.  $252-254^\circ$  (decomp.); tri(tribenzylamino)chloroarsine,  $As[N(CH_2Ph)_3Cl]_3$ , m.p.  $209-211^\circ$  (decomp.); di-piperidinoethylarsine dihydrochloride, m.p.  $196^\circ$ ; piperidinoethylchloroarsine, b.p.  $108^\circ/8$  mm.; anilino-ethylodochlorarsine, b.p.  $110^\circ/10$  mm.; piperidinodimethylarsine,  $C_5H_{10}N \cdot AsMe_2$ , b.p.  $75^\circ/8$  mm. E. H. S.

**Reactivities of groups as revealed by hydrogen bromide cleavage of substituted germanes.** J. K. SIMONS (J. Amer. Chem. Soc., 1935, 57, 1299—1302).—Ge tri-*m*-tolyl bromide (I) with  $p-C_6H_4Me \cdot MgBr + ZnCl_2$  in xylene gives Ge tri-*m*-tolyl *p*-tolyl (II), m.p.  $98.5-100.5^\circ$ ; Ge *o*-tolyl tri-*p*-tolyl, m.p.  $164-166^\circ$ , is similarly prepared from Ge tri-*p*-tolyl bromide. Ge tri-*p*-tolyl chloride, m.p.  $121^\circ$ , is formed from the oxide and EtOH-conc. HCl. Treatment of the following compounds with HBr in  $CHCl_3$  gives the products quoted in square brackets and shows that the order of decreasing reactivity of

the following groups is *p*-tolyl, *m*-tolyl, Ph, benzyl: Ge tetra-*m*-tolyl [(I) 83.9%; PhMe 43.8%]; (I) [Ge di-*m*-tolyl dibromide (III), b. p.  $189-190^\circ/4$  mm., 37.7%; PhMe 72.9%]; Ge tetra-*o*-tolyl [Ge tri-*o*-tolyl bromide 30.8%; PhMe 55.5%]; Ge tetrabenzyl [Ge tribenzyl bromide 10.3%; PhMe 18.6%]; Ge triphenyl *p*-tolyl [GePh<sub>3</sub>Br 36%; PhMe 38.3%]; Ge triphenyl *m*-tolyl [GePh<sub>3</sub>Br 15.8%; some  $C_6H_5$ ]; (II) [(I) 27.4%; PhMe 72.2%; some impure (III)]. H. B.

**Preparation of organo-mercury compounds of phenols and aromatic amines.** II. P. NEOGI and G. K. MUKHERJEE (J. Indian Chem. Soc., 1935, 12, 211—215).—The following Hg derivatives of aromatic compounds are prepared by the method previously described (A., 1928, 783). They are sol. in dil. alkalis, couple with diazotised  $\beta-C_{10}H_7 \cdot NH_2$  (the resulting products are described in parentheses), and have the  $\cdot HgCl$  attached directly to the aromatic nucleus.  $\beta$ -Naphtholmercurichloride, m.p.  $180^\circ$  (decomp.) [ $\beta$ -naphthylazochloromercuri- $\beta$ -naphthol, m.p.  $170^\circ$  (decomp.)];  $\alpha$ -naphthol-2-mercurichloride, m.p.  $205^\circ$  (decomp.) (4- $\beta$ -naphthylazo-derivative, decomp.  $180^\circ$ ); carvacrol-3-mercurichloride, m.p.  $182^\circ$  (decomp.) (5- $\beta$ -naphthylazo-derivative, decomp.  $160^\circ$ ); thymol-2-mercurichloride, m.p.  $160^\circ$  (decomp.) (6- $\beta$ -naphthylazo-derivative, decomp.  $195^\circ$ ), different from the compound prepared by Dimroth (A., 1902, i, 850), which is regarded as thymol-6-mercurichloride; 2-nitro-6(?)-chloromercuriphenol, m.p.  $185^\circ$  (decomp.); 4-nitro-2(or 6)-chloromercuriphenol, m.p.  $180^\circ$  (decomp.). 8-Hydroxyquinoline, however, affords quinoline-8-oxymmercurichloride, decomp.  $205^\circ$ . The following amines form coloured mercurichloride derivatives (decomp. temp. in parentheses) in which an  $NH_2 \cdot H$  is replaced by  $\cdot HgCl$ :  $\alpha$ - ( $125^\circ$ ) and  $\beta$ - $C_{10}H_7 \cdot NH_2$  (m.p.  $170^\circ$  [decomp.]); *o*- ( $165^\circ$ ), *m*- ( $180^\circ$ ), and *p*-toluidine ( $130^\circ$ ); xylidine ( $115^\circ$ ); *o*- ( $240^\circ$ ), *m*- ( $140^\circ$ ), and *p*-nitroaniline ( $225^\circ$ ). H. G. M.

**Passage of phenyl radicals from metallo-organic compounds.** G. A. RAZUVAYEV and M. M. KOTON (J. Gen. Chem. Russ., 1935, 5, 361—365).— $HgPh_2$  (I) and  $(NHPh)_2$  in ligroin at  $150^\circ$  give Hg,  $C_6H_6$ , and  $(\cdot NHPh)_2$ . (I) yields Hg and resinous products, but not  $C_6H_6$  or  $Ph_2$ , with isoprene, divinyl, or pyrrole.  $HgPh \cdot OH$  and  $H_2$  afford Hg,  $C_6H_6$ , and  $H_2O$ .  $SnPh_4$  or  $PbPh_4$  and S at  $150^\circ$  afford  $(SPh)_2$  and  $SnS_2$  or  $PbS$ , whilst  $Hg(CH_2Ph)_2$  and S yield dibenzyl and HgS. The above reactions indicate that Ph, but not  $CH_2Ph$ , derivatives liberate free radicals on thermal decomp. R. T.

**Organic compounds of selenium.** VI. W. E. BRADT (Proc. Indiana Acad. Sci., 1934, 43, 72—98; cf. A., 1933, 256).—An exhaustive bibliography of selenonium compounds. CH. ABS. (r)

**Organic derivatives of thallium.** I. Determination of thallium in organic compounds. II. Reaction of thallium chloride with diazo-compounds. S. S. NAMETKIN and N. N. MELNIKOV (J. Gen. Chem. Russ., 1935, 5, 371—372, 373—377).—I. Lehmann and Rupp's method (B., 1911, 508) is applicable to the determination of Tl.



II. The compounds,  $R \cdot N_2 \cdot TiCl_4$ , have been prepared by adding aq.  $TiCl_3$  to aq.  $R \cdot N_2Cl$  at  $-5^\circ$ :  $R=Ph$ , decomp.  $68-69^\circ$ ;  $R=m-C_6H_4Me$ , decomp.  $59^\circ$ ;  $R=p-C_6H_4Me$ , decomp.  $93^\circ$ ;  $R=p-OEt \cdot C_6H_4$ , decomp.  $66^\circ$ ;  $R=p-NO_2 \cdot C_6H_4$ , decomp.  $91^\circ$ ;  $R=m-NO_2 \cdot C_6H_4$ , decomp.  $111-112.5^\circ$ ;  $R=\alpha-C_{10}H_7$ , decomp.  $71-72.5^\circ$ .  $o-NO_2 \cdot C_6H_4 \cdot N_2Cl$  affords  $2(o-NO_2 \cdot C_6H_4 \cdot N_2Cl) \cdot TiCl_3$ , decomp.  $98-98.5^\circ$ . The compounds decompose thus:  $R \cdot N_2 \cdot TiCl_4$  (I)  $\rightarrow TiCl_3 + N_2 + RCl$ ;  $2(I) \rightarrow 2TiCl_3 + N_2 + R_2 + Cl_2$ ;  $TiCl_3 \rightarrow TiCl + Cl_2$ ;  $(I) + H_2O \rightarrow TiCl_3 + R \cdot OH + N_2 + HCl$ . R. T.

#### Complex salts of amino-acids and peptides.

II. Determination of *l*-proline with the aid of rhodanilic acid. Structure of gelatin. M. BERGMANN (J. Biol. Chem., 1935, 110, 471-479).—A new reagent for the determination is *tetrathiocyanatodanilidochromiato-acid*,  $[Cr(CNS)_4(NH_2Ph)_2]H$ , (termed "rhodanilic acid") [*aniline*,  $NH_4$ , *pyridinium*, and *l*-proline salts, m.p.  $133-134^\circ$  (decomp.)]. Proline rhodanilate is characterised by its slight solubility and rapid crystallisation. Hydroxyproline can be determined as Reineckate after removal of arginine and proline. It is suggested that in the gelatin mol. every third  $NH_2$ -acid may be glycine, every sixth proline, and every ninth hydroxyproline. Such an arrangement could be represented as  $\cdots G \cdot P \cdot X \cdot G \cdot X \cdot X \cdots$ , where  $G$ =glycyl,  $P$ =prolyl, and  $X$ =other  $NH_2$ -acids. J. N. A.

**Azoproteins.** W. C. BOYD and P. MOVER (J. Biol. Chem., 1935, 110, 457-459).—N and As analyses of proteins (I) coupled under different conditions with diazotised arsanilic acid agree with earlier results; i.e., the ratio As:N can be  $>$  that calc. on the assumption that diazotised amines couple with (I) only through the tyrosyl and histidyl groups. No explanation has been found. J. N. A.

**Unrecognised forms of sulphur in proteins.** D. BLUMENTHAL and H. T. CLARKE (J. Biol. Chem., 1935, 110, 343-349).—Aq. Br converts compounds containing  $\cdot CS$ , or  $\cdot SH$  with N or O on the same C, into  $SO_4^{2-}$ ;  $C_6H_4Me \cdot SH$  is an exception. These compounds also yield PbS on treatment with  $PbCO_3$ . Cystine (I) is oxidised to  $SO_4^{2-}$  by boiling fuming  $HNO_3$ , whilst methionine (II) is not. By applying these facts to the study of the hydrolysates of proteins it is concluded that besides (I) and (II) two other substances containing S are present, one yielding  $SO_4^{2-}$  with aq. Br and PbS with  $PbCO_3$ , and the other  $SO_4^{2-}$  with  $HNO_3$  and no PbS with  $PbCO_3$ . H. D.

**Preheater in the micro-analytical determination of carbon and hydrogen.** W. F. BRUCE (Mikrochem., 1935, 18, 103-105).—To overcome the difficulty of obtaining satisfactory blanks when the combustion apparatus is not used constantly, the  $O_2$  is first passed through a hard glass tube filled with CuO wire and supported on two layers of nichrome gauze which is heated by a micro-burner. Asbestos shields are provided to prevent the heat reaching other parts of the apparatus. A. R. P.

**Chromic acid modification of the Kjeldahl method for determination of nitrogen in organic compounds.** J. M. SHEWAN (J.S.C.I., 1935, 54,

172-174T).—With a wide variety of org. compounds it has been found that when  $K_2Cr_2O_7-H_2SO_4$  is used the accuracy of N determinations is affected chiefly by the nature of the compound and the concn. of the reagents. This modification of the Kjeldahl method is therefore not recommended in soil analysis.

**Micro-methods for determination of ammonia, carbamide, total nitrogen, uric acid, creatinine (and creatine), and allantoin.** H. BOROOK (J. Biol. Chem., 1935, 110, 481-493).—Improved micro-methods are described in detail for the determination of  $NH_3$ , uric acid, creatinine, and allantoin. In every case, the procedure ends in a colorimetric measurement, and the improvements give greater stability of colour, increased sensitivity and specificity. The min. amounts of substances that can be determined are  $NH_3$  ( $5 \times 10^{-4}$  mg. of N per c.c.), urea-N ( $1 \times 10^{-3}$  mg. per c.c.), creatinine ( $1 \times 10^{-3}$  mg.), and allantoin ( $5 \times 10^{-4}$  mg., in 2 c.c.). J. N. A.

**Determination of ammoniacal and urea-nitrogen.**—See this vol., 1092.

#### Detection of elements in organic compounds.

III. Detection of phosphorus, arsenic, and antimony. C. L. TSENG (J. Chinese Chem. Soc., 1935, 3, 122-136).—The solution from the Na fusion (cf. this vol., 876) is boiled (a) with  $6N-HNO_3$ ; a yellow ppt. obtained on boiling with tartaric acid and  $NH_4$  molybdate indicates P; (b) with  $6N-HCl$ ;  $As_2S_3$  or  $Sb_2S_3$  is pptd. on passing  $H_2S$  after the addition of  $N-KI$ . R. S.

(A) Determination of small quantities of water in solid organic substances. W. ŚWIĘTOSŁAWSKI and S. MIERNIK. (B) Ebulliometric measurements of the moisture content in standard benzoic acid. W. ŚWIĘTOSŁAWSKI, M. WOJCIECHOWSKI, and S. MIERNIK (Bull. Acad. Polonaise, 1935, A, 53-58, 59-64; cf. A., 1933, 586).—(A) The method, based on the changes in b.p. and temp. of condensation of an azeotropic  $C_6H_6-EtOH$  mixture produced by small amounts of  $H_2O$ , is described.

(B) Determinations of  $H_2O$  in standard BzOH are described. Adsorption of  $H_2O$  by BzOH does not give appreciable errors in calorimetric determinations of its heat of combustion. H. J. E.

**Activity of sulphuric acid in the oxidation of organic substances with chromic acid.** H. C. S. SNETHLAGE (Rec. trav. chim., 1935, 54, 651-656).—The optimum concn. of  $H_2SO_4$  is 80% for the determination of mannitol, sucrose, BzOH, or other acids by oxidation with  $K_2Cr_2O_7-H_2SO_4$  and titration with  $Na_2S_2O_3$  after approx. neutralisation and addition of KI. P. G. C.

**Crystal precipitation by salting out.** II. L. ROSENTHALER (Mikrochem., 1935, 18, 50-52).—The following org. compounds yield characteristic cryst. ppts. on adding  $(NH_4)_2SO_4$ ,  $NaNO_3$ , or alkali chlorides to their solutions:  $\alpha$ - and  $\beta$ - $C_{10}H_7 \cdot OH$ , quinol ( $>1\%$ ), veronal, luminal, chloramine, 1:2:5-tolylenediamine ( $>0.5\%$ ), *m*- and *p*- $C_6H_4(NH_2)_2$ , 1:2:5-*p*-diaminoanisole. A. R. P.

**Titration of organic acids with ferric chloride.** W. D. TREADWELL and E. WETTSTEIN (Helv. Chim. Acta, 1935, 18, 981-986).—Solutions of Na citrate,



benzoate, malate, and oxalate can be titrated potentiometrically with  $\text{FeCl}_3$ . E. S. H.

**Volumetric micro-determination of *o*-nitrophenols with methylene-blue.** A. BOLLINGER (J. Proc. Roy. Soc. New South Wales, 1934, 68, 51—57).—The method previously described for the determination of picric acid (A., 1934, 1017) is applicable to the micro-determination of 2 : 4- and 2 : 6-dinitrophenol, 2 : 4-dinitro-resorcinol and  $\alpha$ -naphthol, and 2 : 6-dinitro-*p*-cresol in aq. solution as the alkali or alkaline-earth salt. F. N. W.

**Macro-, micro-, and histo-chemical detection of cineole.** R. WASICKY and E. GMACH (Sci. Pharm., 1934, 5, 113—120; Chem. Zentr., 1935, i, 1095).—Formation of the compound of cineole (I) with tetraiodopyrrole (II) (sublimes  $120^\circ$ , decomp.  $135^\circ$  on slow heating) is the most sensitive microchemical test. An excess of (II) is added, forming the (I)–(II) compound, which is washed with light petroleum. Addition of aq. KOH regenerates (I). J. S. A.

**Microchemical identification of coniine and nicotine.** R. FISCHER and W. PAULUS (Mikrochem., 1935, 17, 356—360).—Coniine vapour is allowed to react with picrolonic acid solution on a slide in a special apparatus. The picrolonate is characterised by micro-m.p. Sublimation of coniine hydrochloride and determination of the m.p. is less sensitive. Nicotine can be similarly identified as picrate. R. S.

**Determination of pilocarpine and its salts.** J. A. SANCHEZ (Ann. Chim. Analyt., 1935, [iii], 17, 122—123).—The pilocarpine (I) salt is dissolved in aq. EtOH and neutralised with 0.1N-NaOH (phenolphthalein); 10 c.c. of 0.1N-NaOH are added and the solution is boiled, hydrolysing (I) to Na pilocarpate. Excess of NaOH is then titrated. J. S. A.

**Determination of alkaloidal salts by direct titration of their acid radicals.** F. A. ROTONDARO (Amer. J. Pharm., 1935, 107, 237—241).—Alkaloidal salts may be determined by titrating (phenolphthalein) a solution in  $\text{CH}_2\text{Ph}\cdot\text{OH}$  with KOH. H. G. M.

## Biochemistry.

**Regulation of the respiration of *Lumbricus*.** J. B. THOMAS (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 673—677).—In a closed vessel respiration of normal worms declines until the  $[\text{O}_2]$  reaches 15%, and subsequently remains const. until  $[\text{O}_2]$  becomes < 3%. In CO-poisoned worms, respiration does not exceed the level corresponding with 15% of  $\text{O}_2$  even at high  $\text{O}_2$  tensions. The rôle of hæmoglobin is discussed. A. G. P.

**Fœtal respiration.** J. BARCROFT (Proc. Roy. Soc., 1935, B, 118, 242—263).—A lecture. H. G. R.

**Relation between oxygen capacity and molecular state of hæmoglobin.** H. NAGAOKA (J. Biochem. Japan, 1935, 21, 355—365).—Denaturation and mol. aggregation (indicated by diminution in  $\text{O}_2$  capacity and colloid-osmotic pressure, respectively) of hæmoglobin were determined in isotonic  $\text{PO}_4^{3-}$  buffer at  $p_{\text{H}}$  6.7 at  $55^\circ$  or  $59^\circ$  for varying periods. Denaturation is more rapid than aggregation at  $55^\circ$ ; at  $59^\circ$  the reactions have more nearly equal velocities. F. O. H.

**Micro-determination of hæmoglobin. Modification of the benzidine reaction.** T. V. LETONOFF (J. Lab. Clin. Med., 1934, 20, 66—69).—To 1 c.c. of dil. blood (1 : 1000) in an isotonic solution containing 0.65% NaCl and 0.15%  $\text{Na}_2\text{C}_2\text{O}_4$  are added 15 c.c. of 0.02% solution of benzidine, 3 c.c. of 0.25% aq. AcOH, and 1 c.c. of 1%  $\text{H}_2\text{O}_2$ . The mixture is cooled in ice and after 30—40 min. is compared colorimetrically with a standard prepared by mixing 6.5 c.c. of 1% aq.  $\text{K}_4\text{Fe}(\text{CN})_6$  in approx. 450 c.c. of  $\text{H}_2\text{O}$  with 5 c.c. of a 1% solution of gum ghatti and 10 c.c. of 1% aq.  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$  and diluting to 500 c.c. The standard is equiv. to the colour produced by 10 g. of hæmoglobin in 100 c.c. of blood. CH. ABS. (p)

**Action of heat on proteins in solution.** W. DUCE (Boll. Soc. Ital. Biol. sperim., 1935, 10, 73—75).—Exposure of solutions of hæmoglobin to temp.

close to the coagulation temp., or to those causing changes in  $\eta$ , produces no alterations of  $n_{\text{D}}$ . In partly coagulated solutions  $n_{\text{D}}$  of the uncoagulated protein is increased, or sometimes unchanged. R. N. C.

**Treatment of methæmoglobin in the blood by glucose.** M. M. BROOKS (Calif. and Western Med., 41, No. 2).—Methæmoglobin (I) was formed in rabbits by intravenous injection of 0.15 g. of  $\text{NaNO}_2$  per kg. body-wt., and was determined spectrophotometrically. Injection of glucose converts (I) into oxyhæmoglobin. CH. ABS. (p)

**Measurement of red-cell volume. VI. Different "fragility" of the red cells of various mammals.** E. PONDER (J. Physiol., 1935, 83, 352—358).—The differences of fragility in hypotonic serum of the red cells of different mammals are due to the differences in crit. vol.  $\text{H}_2\text{O}$  content and the degree of perfection of the cell as an osmometer play only a minor part. The max. increase in cell area compatible with the integrity of the cell is a linear function of the cell vol. in sheep, ox, rabbit, and human red cells. R. N. C.

**Relation of red-cell diameter and number to the light-transmission of suspensions.** E. PONDER (Amer. J. Physiol., 1935, 111, 99—106).—Determination of the no. of red cells in a suspension by measurement of transmitted light can only be approx. The opacity of suspensions containing equal nos. of cells and the individual cell diameter are simply related, but variations in cell shape etc. make the determination of the cell diameter from opacity measurements untrustworthy. R. N. C.

**Erythrocyte sedimentation rate. Comparison of the methods commonly employed for its determination.** G. E. BEAUMONT and J. W. MAYCOCK (Lancet, 1935, 229, 19—20).—The Westergren, the modified Zeckwer-Goodell, and the micro-methods are compared. L. S. T.



**Blood of domestic fowl.** V. E. MORGAN and D. C. CHICHESTER (*J. Biol. Chem.*, 1935, 110, 285—298).—The inorg. constituents and protein in erythrocytes and serum of fowl blood, the Donnan ratio of  $\text{Cl}'$  and  $\text{HCO}_3'$ , the buffer val. of serum (A., 1931, 753) and of oxygenated whole blood (A., 1930, 1053), the  $\text{O}_2$  dissociation curves, and the effect of  $p_{\text{H}}$  on the affinity of blood for  $\text{O}_2$  are compared with the corresponding properties of dog and human blood. A nomogram embodying the vals. obtained is constructed. H. D.

**Ageing of serum.** A. ROCHE and F. MARQUET (*Compt. rend. Soc. Biol.*, 1935, 119, 1147—1149).—The ppt. appearing in serum kept for a month at  $0^\circ$  is chiefly composed of lipins, proteins, and salts; cholesterol is present only in small quantities. The P/N ratio of the phospholipins is high as compared with that of the supernatant serum, suggesting that the ppt. is formed from phosphatides by the hydrolytic fission of the N-containing constituents. R. N. C.

**Mol. wt. of human serum-albumin.** A. ROCHE, M. DORIER, and F. MARQUET (*Compt. rend. Soc. Biol.*, 1935, 119, 1150—1151).—The osmotic pressure-concn. curve for human serum-albumin (I) is identical with that for horse-albumin. The mol. wt. of (I) is therefore 69,000. R. N. C.

**Crystallisation of seralbumins.** R. WERNICKE (*Nature*, 1935, 136, 30; cf. this vol., 508).—Photomicrographs of crystals of human and guinea-pig seralbumin (I) are reproduced. Cryst. (I) has also been obtained [by M. GRINSTEIN] from horses, asses, and mules but not from rabbits, llamas, pigs, oxen, dogs, and birds. L. S. T.

**Chemical and physical methods of determining [ethyl] alcohol in blood.** A. GRONOVER (*Z. Unters. Lebensm.*, 1935, 70, 34—40).—Widmark's (A., 1922, ii, 789) and Kionka and Hirsch's (A., 1924, i, 1366) methods are equally trustworthy. Small errors are introduced by the presence of  $\text{COMe}_2$ ,  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{H}$ , or  $\text{MeCHO}$  in blood. E. C. S.

**Blood-sugar regulation in exercise.** D. B. DILL, H. T. EDWARDS, and S. MEAD (*Amer. J. Physiol.*, 1935, 111, 21—30).—Blood-sugar remains near the rest level in easy work in which lactic acid does not accumulate, but increases in work that results in exhaustion after moderate time, continuing to increase for 5—10 min. after cessation of work. It does not change during activity that brings on exhaustion in < 3 min. with anaerobic energy production, but increases during recovery. R. N. C.

**Transplantation of endocrine glands and blood-sugar.** V. PASSEK and M. RUBINSTEIN (*Compt. rend. Soc. Biol.*, 1935, 119, 1019—1021).—Blood-sugar is not affected by transplantation of endocrine glands in rabbits except in the cases of the pituitary and the adrenal cortex, when it falls. R. N. C.

**Lactose in the plasma of pregnant and lactating women.** R. S. HUBBARD and H. J. BROCK (*J. Biol. Chem.*, 1935, 110, 411—420).—Lactose (I) was either absent from, or present in very small amount in, all specimens from normal and from pregnant women.

2 mg. of (I) per 100 c.c. of plasma were present in some specimens of blood from lactating women. It is concluded that the renal threshold for (I) is very low. J. N. A.

**Physico-chemical study of the reducing action of glucose.**—See this vol., 1083.

**Modification of the Folin-Wu blood-sugar method using permanent standards.** H. BROWN (*J. Lab. Clin. Med.*, 1934, 20, 86—89).—A solution containing 50 mg. of alizarin-blue GS and 10 mg. of alizarin-blue-black BG in 100 c.c. is mixed with a second solution of 20 mg. of alizarin-cyanine-green-B extra per litre of  $\text{H}_2\text{O}$ , in proportions to give the same colour as is obtained with known amount of glucose. The customary method is followed, using acid molybdate solution and heating for 8 instead of 6 min. CH. ABS. (p)

**Phospholipins of blood.** C. P. STEWART and E. B. HENDRY (*Biochem. J.*, 1935, 20, 1683—1689).—The determination of blood-phospholipins (I) by the Fiske-Subbarow (A., 1926, 443) determination of P in the ashed  $\text{EtOH}\cdot\text{Et}_2\text{O}$  extract of blood is examined. The final  $[\text{H}_2\text{SO}_4]$  in the ashed residue must be < 1.2N; large excess of  $\text{H}_2\text{MoO}_4$  is to be avoided. That the P determined in this way represents (I) is shown by the fact that addition of a no. of non-lipin P-containing substances has little influence on the determined vals.; further, determination of P in the pptd. lipins (A., 1929, 837) gives vals. agreeing with those obtained as above. The ratio P : fatty acid in (I) is 1.5 : 1 and it is deduced that (I) contain equal proportions of sphingomyelin and a mixture of lecithin and cephalin. H. D.

**Determination of creatinine in urine and blood.** H. LIEB and M. K. ZACHERL (*Wien. klin. Woch.*, 1934, 47, 1572—1573; *Chem. Zentr.*, 1935, i, 937).—Creatinine is determined photometrically after treatment with picric acid. J. S. A.

**Volumetric determination of the nitrogen in 0.04—0.05 c.c. of blood (serum, plasma) without distillation.** F. RAPPAPORT and R. PISTINER (*Mikrochem.*, 1935, 18, 43—47).—The proteins are removed by warming with dil.  $\text{H}_2\text{SO}_4$  and phosphomolybdic acid, an aliquot portion of the filtrate is evaporated with  $\text{H}_2\text{SO}_4$  to destroy org. matter, diluted, neutralised (methyl-red) with NaOH, and treated with an excess of buffered NaOBr solution, and the excess is determined iodometrically. A. R. P.

**Determination of blood-chlorine.** C. VAILLE and P. HAUTVILLE (*J. Pharm. Chim.*, 1935, [viii], 22, 61—67).—After deproteinising with  $\text{Zn}_3\text{Fe}(\text{CN})_6$ , and pptg. as AgCl, excess of  $\text{AgNO}_3$  is determined volumetrically. For normal children, the following results were obtained : total blood-Cl 2.86, plasma-Cl 3.42, erythrocyte-Cl 1.76 g. per litre. A method for determining corpuscle- and plasma-vol. is described. H. G. R.

**Exchange of mineral matter between corpuscles and plasma in blood.** H. WAELSCH, S. KITTEL, and A. BUSZTIN (*Z. physiol. Chem.*, 1935, 234, 27—53).—In human blood > 1.5—2.0 hr. after removal from the body Ca and Na pass from plasma



to corpuscles, whilst K and Mg pass from these to plasma. These elements move, in some cases in the same, in others in opposite, ways according to the state of health or disease of the subject. Such alterations always occur when mineral matter passes into or out of colloidal solutions. W. McC.

**Calcium and inorganic phosphorus content of the blood-plasma of normal dairy cattle.** J. R. HAAG and I. R. JONES (J. Biol. Chem., 1935, **110**, 439—441).—Ca ranged from 8.05 to 11.48 mg. per 100 c.c. Inorg. P for mature cattle is approx. 5.2 mg. per 100 c.c. J. N. A.

**Graphic representation of ionic equilibria in blood-serum.** J. F. McCLENDON (Science, 1935, **81**, 569—570). L. S. T.

**Hydrogen-ion concentration in the blood of Europeans in temperate zones and in that of inhabitants of the tropics.** G. M. STREEF (Arch. néerl. Physiol., 1935, **20**, 278—283).—The average  $p_H$  of the blood of Europeans in temperate zones was  $7.57 \pm 0.0013$  at  $30^\circ$  (the subjects remained at  $18^\circ$ ); this is the same as that of natives in Batavia, but  $0.02 <$  that of Europeans in the tropics. P. G. M.

**Determination of blood- $p_H$  by the glass electrode. I. Acid change in shed blood.** H. YOSHIMURA (J. Biochem. Japan, 1935, **21**, 335—353).—The so-called "first acid change" in shed blood (A., 1929, 1189) could not be confirmed. The whole course of diminution in  $p_H$  is due to glycolysis and is inhibited by  $K_2C_2O_4$  and NaF, but not Na citrate, hirudin, or heparin. Lowering of temp. delays the acid change (cf. A., 1930, 1462). F. O. H.

**Blood-coagulation as a chain reaction.** A. FISCHER (Biochem. Z., 1935, **279**, 108—114).—Initiation of coagulation (hen's plasma) by heating or addition of HCl, active organ extracts, and lipins produces a continuous formation of coagulation-inducing substance. Coagulation in fresh plasma induced by addition of coagulating plasma occurs to an extent  $\propto$  the amount added and the duration of primary coagulation. Completion of coagulation is accompanied by a rapid decline in coagulation-promoting activity due to an "internal neutralisation" of the mol. concerned (cf. A., 1934, 795). F. O. H.

**Coagulation of the blood as a chain reaction.** H. J. FUCHS (Nature, 1935, **136**, 184; cf. this vol., 1002). L. S. T.

**Concanavalin-A and hæmagglutination.** J. B. SUMNER, S. F. HOWELL, and A. ZEISSIG (Science, 1935, **82**, 65—66).—Neutral suspensions of higher fatty acids, coconut, linseed, olive, almond, and jack-bean oils are agglutinated by the addition of a salt solution of concanavalin-A (I). Suspensions of butter, castor oil, lecithin, and cholesteryl acetate are not agglutinated by (I), and suspensions of lipins extracted from erythrocytes are only partly agglutinated. Suspensions of rice-starch, maize-starch, and baker's yeast are readily agglutinated by (I), and boiled starch is pptd. Glycogen (II) is completely pptd. at neutrality. Cow-erythrocytes are agglutinated only after a trace of (II) has been added. After laking, the erythrocytes of the horse, cat, and dog give a heavy ppt. with (I), but erythrocytes

which are not agglutinatable or only so with difficulty (e.g. cow, goat, sheep, man) give no ppt. Erythrocytes which agglutinate do so because of the formation of this ppt. The substance which forms the ppt. appears to be a protein. Agglutination appears to be due to an insol. compound formed by this substance and (I). When (II) is added to cow red cells it is adsorbed on their surfaces and forms a hydrophobic compound when (I) is added.

L. S. T.

**Influence of neutral salts and sugar on hypertonic hæmolysis and formation of acid hæmatin.** A. JODLBAUER (Arch. exp. Path. Pharm., 1935, **178**, 719—723).—Hypertonic salt solutions hæmolysed erythrocytes:  $Cl' < Br' < I' < SCN'$ . Isolated stromata are lysed and liberated hæmoglobin is changed by hypertonic  $I'$  and  $SCN'$ . In 0.9% aq. NaCl, isotonic  $I'$  and  $SCN'$  enhance the acid-sensitivity of hæmoglobin, decomp. being initiated at  $p_H$  4.9, 4.9, 5.3, and 6.2 with  $Cl'$ ,  $Br'$ ,  $I'$ , and  $SCN'$ , respectively. The increases in sensitivity and hæmolysis are inhibited by sucrose.

F. O. H.

**Hæmolysis by Australian snake venoms. IV. Copperhead hæmolysin.** H. F. HOLDEN (Austral. J. Exp. Biol., 1935, **13**, 103—112; cf. A., 1934, 1022).—Hæmolysis of rabbit's erythrocytes by copperhead venom is accelerated by lipins from rabbit's cells, by ovoidin, and by traces of  $CaCl_2$  and inhibited by lipins from sheep's cells. Velocity curves for hæmolysis with and without  $CaCl_2$  are given.

F. O. H.

**Antigenic action of starch.** S. FUJIMURA (J. Biochem. Japan, 1935, **21**, 371—380).—The antigenic action of starch is due to impurities and is not destroyed by amylolytic digestion. F. O. H.

(A) Formaldehyde and serum-proteins. Immunological characteristics. (B) Formaldehyde hypersensitiveness. F. L. HORSFALL (J. Immunol., 1934, **27**, 553—567, 569—581).—(A) Formolised serum-proteins (I), when injected into rabbits, produce precipitins for the homologous formolised serum, the homologous native serum, and heterologous formolised sera, and also anaphylactins which may be transferred passively to the guinea-pig uterus. Such uteri become sensitive to the homologous formolised serum, the homologous native serum, and heterologous formolised sera. Formolised  $NH_2$ -acids do not saturate precipitins produced by injection of (I), although free  $CH_2O$  inhibits their action. Following injection of (I), rabbits show a progressive skin-hypersensitiveness to free  $CH_2O$ .

(B) Hypersensitiveness is attributed to the formation of a foreign substance by union of  $CH_2O$  with a constituent of the skin (probably protein).

CH. ABS. (p)

**Lactogelification of blood-sera of immunised animals.** J. BOUCEK (Compt. rend. Soc. Biol., 1935, **119**, 1134—1136).—The gelification of sera by *dl*-lactic acid is modified by the formation of antitoxins in the sera, the time of gelification being inversely  $\propto$  the quantity of antitoxin present. Gelification is also affected by the age of the serum and possibly the species, and by the presence of antiseptics. R. N. C.



**Concentration of antivenenen by the ammonium sulphate method.** S. D. S. GREVAL (Indian J. Med. Res., 1934, 22, 365—371).—Immunised horse-plasma is fractionally pptd. with  $(\text{NH}_4)_2\text{SO}_4$ . The pseudoglobulin fraction, which contains antivenenen, is dialysed for 96 hr. against  $\text{H}_2\text{O}$  to remove  $(\text{NH}_4)_2\text{SO}_4$ . It is dissolved in 1% NaCl, adjusted to  $p_{\text{H}}$  7.5—7.6 with  $\text{Na}_2\text{CO}_3$ , preserved for 2 weeks under  $\text{Et}_2\text{O}$  and tricresol, and, if not toxic, filtered and bottled.

R. N. C.

**Spontaneous super-contraction of animal hair.** R. O. HALL (Nature, 1935, 136, 28—29).—Super-contraction in the guard-hairs of fur-bearing animals has been observed. Exposure to steam accentuates the deformation. Immersion in acid reduces and sometimes reverses the curvature, but washing and drying leads to an increase in the initial direction. The results are discussed in terms of the oxidation of the  $\cdot\text{S}\cdot\text{S}\cdot$  linking of the keratin.

L. S. T.

**Composition of cartilage, bone, dentin, and enamel.** M. A. LOGAN (J. Biol. Chem., 1935, 110, 375—389).—The inorg. constituents of cartilage, bone, dentin, and enamel are determined to elucidate the process of calcification. In rat bone the  $\text{CO}_3^{''}$ :Ca ratio increases from 10.7% to 15.8% with development, accompanied by increases in inorg.  $\text{PO}_4^{'''}$ . In human and dog dentin the ratio Mg:total base is 3—4 times that in enamel, and the Ca:total base is the same in both. The Mg content of dog dentin and enamel is not different from that of carious human teeth; in the latter, however, the  $\text{CO}_3^{''}$  is  $>$  normal. In bone the total base=total acids, and it is concluded that the bases exist as tertiary phosphates.  $\text{Na}+\text{K}$  in cartilage is 50%  $>$  in plasma; Ca and Mg in cartilage are 3 to 4 times  $>$  in plasma with no corresponding increase in inorg.  $\text{PO}_4^{'''}$ , hence a large proportion of the base exists as salts of the org. constituents of cartilage. H. D.

**Physicochemical factors affecting intraocular pressure.** W. S. DUKE-ELDER (Physiol. Rev., 1934, 14, 483—513).—A review. CH. ABS. (p)

**Chromosome micelle and the banded structure of chromosomes in the salivary gland.** D. M. WRINCH (Nature, 1935, 136, 68—69; cf. this vol., 882).—The genetic identity of a chromosome is located in its protein constituent, and the protein pattern of an individual is defined as a sequence of protein mols. placed end to end in salt linkings. This meets the essential requirement of genetics that genes form a linear array. So far as concerns the protein constituent, the chromosome micelle is regarded as an aggregate of identical sequences of mols., the protein patterns lying side by side, and these will lie on and constitute a quasi-cylindrical surface. The nucleic acid will polymerise in rings around the micelle. The banded structure of certain salivary chromosomes is interpreted as due to the alternation of basic and non-basic units in the protein pattern. L. S. T.

**Changes in the pancreas after ligation of the pancreatic duct.** S. TSUNOO (J. Biochem. Japan, 1935, 21, 399—407).—Ligation of the pancreatic duct in dogs produces an increase in the  $\text{EtOH}+\text{Et}_2\text{O}$ -sol. fat, whilst in the tissue-protein, lysine and  $(\text{NH}_2)_1$ -acid decrease and arginine and histidine increase. Changes

also occur in  $[\alpha]$  and N,  $\text{NH}_2\text{-N}$ , and sugar contents of the pancreatic blood. F. O. H.

**Composition of larval sacs of sacciferous larvæ (Psyche).** K. KUSUI (J. Biochem. Japan, 1935, 21, 453—455).—Hydrolysis of the sacs yields glycine (5.72%), glutamic acid (3.97%), alanine (3.62%), tyrosine (2.31%), approx. 13 other  $\text{NH}_2$ -acids, and a reducing substance. F. O. H.

**Fish and rabbit liver-glycogens.** D. J. BELL (Nature, 1935, 136, 184—185).—Methylation of liver-glycogen from *Gadidæ* by the method of Haworth and Percival gave a product (45.5% OMe) identical with the corresponding derivative from rabbit liver-glycogen. Hydrolysis with aq.  $\text{HCl}+\text{AcOH}$  gave similar amounts of tetramethylglucopyranose in each case, corresponding with 12 glucose units for the glycogen mol. Both methylated glycogens give a deep red-brown colour with I. These and other results with acylated glycogens show that fish and rabbit liver-glycogens are probably chemically identical.

L. S. T.

**Chemistry of heparin.** E. JORPES (Biochem. J., 1935, 29, 1817—1830).—Heparin prepared from ox-liver by the method of Charles and Scott contains Ac, hexuronic acid, hexosamine, and combined ethereal sulphate. By pptn. as the brucine salt, a fraction of high heparin activity was obtained having the composition of a chondroitintrisulphuric acid.

W. O. K.

**Composition of the muscle of certain sea animals. I. Proteins of the muscle tissue of *Mugil cephalus*.** A. CARTENI and A. MORELLI (Quad. Nutriz., 1934, 1, 185—191; Chem. Zentr., 1935, i, 1258).—The N distribution of the protein is examined and compared with that of other marine animals.

A. G. P.

**A normal paraffin as a minor constituent in hydrogenated sardine oil.** Y. TOYAMA (J. Soc. Chem. Ind. Japan, 1935, 38, 258—261B).—*n*-Heptadecane, m.p. 22—22.5°, has been identified in the distillate obtained during the vac. deodorisation (steam-distillation) of hydrogenated sardine oil.

E. L.

**Whale-shark-liver oil.** M. TSUJIMOTO and H. KOYANAGI (J. Soc. Chem. Ind. Japan, 1935, 38, 271—272B).—The liver of a specimen of *Rhinodon typicus*, Smith (Jap. "Jinbei" or "Ebisu-zamé"), which died in captivity after 4 months' starvation, contained 61.6% of fat. By heating 54.9% of semi-solid fat was obtained having m.p.  $> 40^\circ$ ,  $d_4^{20}$  0.8977, acid val. 25.0, sap. val. 182.5, I val. (Wijs) 108.6, Reichert-Meissl val. 0.11, unsaponifiable matter 5.04% [containing selachyl and (probably) batyl alcohol and 43.8% of cholesterol, and giving a blue coloration with  $\text{SbCl}_3$ ]. The fatty acids had m.p. 41—42°, neutralisation val. 201.4, I val. 116.7,  $\text{Et}_2\text{O}$ -insol. bromides 27.8% (70.23% Br), and yielded 40.9% of solid acids (I val. 18.0; mainly palmitic acid) by the Pb salt- $\text{Et}_2\text{O}$  method, and 19.5% of highly unsaturated acids (neutralisation val. 167.0, I val. 330.5) by the Li salt- $\text{COMe}_2$  method. The fatty acids consisted mainly of  $\text{C}_{16-22}$  acids, the unsaturation of the  $\text{C}_{20}$  and  $\text{C}_{22}$  acids being very high.

E. L.



**Shark-liver oils.** M. TSUJIMOTO (J. Soc. Chem. Ind. Japan, 1935, 38, 272—273B).—Analyses are detailed of the liver oils from "Aizamé" (*Centrophorus* sp.), "Zaraka" or "Momijizamé" (*Lepidorrhinus foliaceus*, Günther), "Togaritsunozamé" (*Squalus japonicus*, Ishikawa), cat-shark or "Nekomamé" (*Heterodontus japonicus*, Dumeril), "Gaikotsuzamé" (*Pristurus eastmani*, Jordan and Synder), "Yoshikirizamé" (*Prionace glauca*, Linné), Porbeagle or "Nezumizamé" (*Lamna cornubica*, Gmelin), and hammer-headed shark or "Shumokuzamé" (*Sphyrna zygaena*, Linne). Aizamé and Zaraka liver oils, which have a high squalene content, give a pale blue colour in the  $\text{SbCl}_3$  test; squalene is absent from the other oils. E. L.

**Oils from marine animals. New group of lipins. Ether-esters of glycerol.** E. ANDRÉ and A. BLOCH (Bull. Soc. chim., 1935, [v], 2, 789—802).—The name "diglycerides-monoglyceroxides" (I) is suggested for the mixed ether-esters  $\text{OR} \cdot \text{C}_3\text{H}_5(\text{O}_2\text{C} \cdot \text{R})_2$  of glycerol and batyl or selachyl alcohols present in elasmobranch-liver oils. Analysis of the liver oil of *Scymnorrhinus lichia*, Bonnatere, and the Ac val. of the unsaponifiable matter indicate a composition hydrocarbons 57%, triglycerides 21.7%, (I) 21.3%, together with small amounts of free fatty acids and cholesteryl esters. By the method of fractional extraction (B., 1933, 353) using  $\text{MeOH} \cdot \text{COMe}_2$  (3:1 by vol.), hydrocarbons are accumulated in the less sol. fractions, since the optical rotation of the latter fractions increases more rapidly than does their sap. val.; these fractions contain approx. hydrocarbons 1—2%, triglycerides 25%, and (I) 75—80%. Attempted separation of (I) from the less sol. fractions by fractional crystallisation at  $-4^\circ$  afforded only a triglyceride, m.p.  $40.8^\circ$ , as a solid product. (I) are highly laevorotatory and, by hydrolysis, give alcohols of high Ac val. J. W. B.

**Oil of the eggs of *Bombyx mori*.** J. OZAKI and B. KASAI (J. Agric. Chem. Soc. Japan, 1934, 10, 745—749).—The eggs contained 7.88—11.10% of crude fat, the fatty acids being palmitic, isopalmitic, stearic, myristic, oleic, linoleic, and  $\beta$ -linoleic. The eggs yielded a clear, red-brown,  $\text{EtOH}$ -insol. oil having  $n_D^{20}$  0.9351, acid val. 29.07, sap. val. 199.05, I val. 138.84, Ac val. 39.04, Reichert-Meissl val. 2.13, unsaponifiable matter 0.35%, and insol. fatty acids 88.96%. CH. ABS. (e)

**Occurrence of carotenoids in marine animals.** P. KARRER and U. SOLMSEN (Helv. Chim. Acta, 1935, 18, 915—921).—Cryst. astacene has been isolated from the sea-aster (*Echinaster sepositus*) and the red sponge (*Axinella crista-galli*) and is present in *Suberites domuncula*. No carotenoid was found in the coral (*Astroides calycularis*). That of the mussel (*Cardium tuberculatum*) is probably xanthophyll. The carotenoids of the molluscs, *Pecten jacobaeus* and *Pleurobranchus elegans*, the sea-lily (*Antedon rosacea*), and the sea-squirt (*Cynthia papillosa*) have also been examined. F. R. G.

**Echinenone and pentaxanthin: two new carotenoids found in the sea-urchin (*Echinus esculentus*).** E. LEDERER (Compt. rend., 1935, 201, 300—302).—The sexual glands of *E. esculentus* are

extracted with  $\text{COMe}_2$ ; the product re-extracted with light petroleum and fractionated by adsorption yields a pigment, echinenone,  $\text{C}_{40}\text{H}_{58}\text{O}$  ( $\pm \text{H}_2$ ), m.p. 192—193°, with ill-defined absorption max. at 520, 488, and 450  $\text{m}\mu$  in  $\text{CS}_2$ . The product from whole animals extracted with  $\text{COMe}_2$  and with  $\text{C}_6\text{H}_6$ , when fractionally adsorbed, yields pentaxanthin,  $\text{C}_{40}\text{H}_{56}\text{O}_5$  ( $\pm \text{H}_2$ ), a xanthophyll resembling lutein in its absorption. E. W. W.

**Flavin from fish-eyes.** P. KARRER, H. VON EULER, and K. SCHÖPP (Arkiv Kemi, Min., Geol., 1935, 11, B, No. 54, 2 pp.).—Cryst. flavin may be isolated from the retina of fish-eyes. It is identical with lactoflavin and possesses vitamin- $B_2$  activity. E. A. H. R.

**Blue-fluorescing substance in the corpus luteum.** H. VON EULER and K. M. BRANDT (Arkiv Kemi, Min., Geol., 1935, 11, B, No. 51, 5 pp.).—A blue-fluorescing substance is obtained from corpora lutea by extraction with  $\text{COMe}_2$  and purified chromatographically. It is not reduced by Zn dust at  $p_H$  2 nor appreciably by  $\text{Na}_2\text{S}_2\text{O}_4$  at  $p_H$  10. It is not extracted from aq. solution by  $\text{Et}_2\text{O}$  or  $\text{CHCl}_3$ . It gives max. fluorescence at  $p_H$  2—8. E. A. H. R.

**Fluorescence spectra of hepatoflavin before and after irradiation.** H. BIERRY and B. GOUZON (Compt. rend., 1935, 200, 2116—2118).—Hepatoflavin (greenish-yellow fluorescence) when irradiated in 0.5N-NaOH gives lumiflavin (green fluorescence), but in neutral solution affords lumichrome (blue fluorescence). The spectra of flavins from egg and adrenals are identical. J. L. D.

**Determining the reducing substance of the anterior pituitary.** W. T. SALTER, A. GREEN, and T. J. PUTMAN (J. Lab. Clin. Med., 1934, 20, 74—77).—The reducing substance is associated with the globulin fraction and its concn. is not paralleled by that of growth-promoting or other hormones present in this fraction. To determine the activity of the preps. the  $p_H$  is adjusted to 8.0 and the sample is placed in a Thunberg tube containing 0.1 c.c. of 1:1000 methylene-blue and 0.15 c.c. of  $M$ -phosphate buffer solution ( $p_H$  8.0) and the whole diluted to 2.5 c.c. After evacuation the tubes are placed in boiling  $\text{H}_2\text{O}$  and the time required for bleaching is observed. CH. ABS. (p)

**Role of lipins in the X-ray diffraction patterns of nerve.** F. O. SCHMITT, R. S. BEAR, and G. L. CLARK (Science, 1935, 82, 44—45).—Large well-oriented spacings, apparently due to lipins, in the diffraction patterns of nerve, are described and discussed. L. S. T.

**Solvation and desolvation of nerve.** F. O. SCHMITT and L. J. WADE (Amer. J. Physiol., 1935, 111, 169—176).—Solvating agents such as  $\text{HCO} \cdot \text{NH}_2$ ,  $\text{NaCNS}$ , acids, and alkalis produce shortening and increase in wt. of nerve at room temp., and lower the temp. of thermal shortening. On the other hand,  $\text{PhMe}$ ,  $\text{Et}_2\text{O}$ ,  $\text{COMe}_2$ , and other desolvating agents produce shortening but increase the temp. of thermal shortening, as does also unification of the micellar structure by "tanning" with  $\text{CH}_2\text{O}$  or  $\text{OsO}_4$ . R. N. C.

**Potassium content of the human and animal nervous system.** A. LEULIER, B. POMMÉ, and A.



BERNARD (Compt. rend. Soc. Biol., 1935, **119**, 1228—1229).—Normal nerve-K is < that of fresh brain or marrow, and falls still further in disease. Fresh brain- and marrow-K are of the same order as that of striated muscle, the vals. for the dry fat-free tissues agreeing still more closely.  
R. N. C.

**Chlorate-osmic-formalin method for staining degenerating myelin.** R. L. SWANK and H. A. DAVENPORT (Stain Tech., 1935, **10**, 87—90).—An aq. solution containing 60 c.c. of 1%  $\text{KClO}_3$ , 20 c.c. of 1%  $\text{OsO}_4$ , 1 c.c. of  $\text{AcOH}$ , and 12 c.c. of 37%  $\text{CH}_2\text{O}$  is recommended. After fixation in  $\text{CH}_2\text{O}$  solution for 2 days, brain and spinal cord are stained in the solution for 7—10 days.  
H. W. D.

**Modification of the cresyl-violet technique for staining nerve cells.** G. TRESS and M. TRESS (Stain Tech., 1935, **10**, 105—106).—After fixation in  $\text{CH}_2\text{O}$  the tissue is embedded in cellulose nitrate (I) and sections are stained in an aq. solution containing 0.5% of cresyl-violet and 4 drops of 10%  $\text{AcOH}$ . The sections are treated with 70%  $\text{EtOH}$  until the (I) is practically free from stain and then placed in a mixture of 60 c.c. of  $\text{CHCl}_3$ , 10 c.c. of  $\text{EtOH}$ , and 10 c.c. of  $\text{Et}_2\text{O}$  for 2—5 min. The cells are differentiated in a solution made by adding 4 drops of 1%  $\text{HCl}$  to 100 c.c. of 95%  $\text{EtOH}$ . The sections are then neutralised in 95%  $\text{EtOH}$  containing a small quantity of  $\text{NaHCO}_3$ , dehydrated in  $\text{BuOH}$ , and cleared in xylene.  
H. W. D.

**Iron in common sponge.** P. ROBIN (J. Pharm. Chim., 1935, [viii], **21**, 600—604).—The yellowish-grey surface coloration and the brown coloration of the interior parts and of the foot of Mediterranean sponges are due to  $\text{Fe}^{\text{III}}$ . The average content of Fe according to the variety is 0.092—0.38% in the interior and 0.916—4.2% in the foot. In sponges from the Bahamas and Antilles the Fe content is 0.025—0.085% in the interior and 0.06—0.53% in the foot.  
M. T.

**Cryolysis, diffusion, and particle size.**—See this vol., 932.

**Constituents of mulberry leaves: proteins.** VI. Variation in the amount of protein synthesised. VII. Indirect causes which affect the quantity, in the silkworm and the silk, of the proteins that have been accumulated from the proteins in mulberry leaves. VIII. Metabolism of the proteins in silkworms when the quantity of the soluble carbohydrates contained in the mulberry leaves is small. X. Quantity of sericin and fibroin in the silk due to difference in the constituents of the mulberry leaves and the growth of the leaves. Y. KISHI (Bull. Agric. Chem. Soc. Japan, 1935, **11**, 70—71, 71—72, 72—73, 76—77).—VI. The amounts and types of protein synthesised in mulberry leaves vary according to the amount of sunshine and the rate of growth of the leaves.

VII. The higher is the % of carbohydrate in the leaves, the greater is the amount of protein accumulated in the silkworm.

VIII. When the amount of carbohydrate is very small as in the youngest leaves soon after sprouting,

there is an increase in the metabolism of the protein, with a corresponding decrease in the % accumulated by the silkworm.

X. Young leaves produce less sericin (I) but more fibroin (II) than mature leaves. The amount of (I) increases with decrease in carbohydrate, but if sugars be given with the leaves, the amount of silk and (II) increases, whilst (I) decreases.  
J. N. A.

**Genetics of the silkworm. I. Colour of the cocoon.** C. JUCCI (Mem. R. Accad. Italia, Cl. Sci. fis. mat. nat., 1934, **5**, 347—477; Chem. Zentr., 1935, i, 1145).—The colours of the blood, cocoon, and eggs of the silkworms arise from their nutrition, the "permeability" of the intestine permitting the absorption of pigments into the blood. The characteristic green or yellow of the cocoon is due to the ability of the silk gland to absorb flavones or carotenoids, respectively. Crossing of species with different blood- and cocoon-colours show that the permeabilities for carotenoids and flavones are Mendelian factors, which belong to different allelomorphic pairs.  
R. N. C.

**Silk fibroin.** W. TRAUBE and H. HÄRTING [with V. SENFTNER and S. KELL] (Ber., 1935, **68**, [B], 1405—1408).—Silk fibroin is almost completely sol. in aq.  $\text{NaOH}$  ( $\text{KOH}$ )— $\text{Cu}(\text{OH})_2$  and from the solution  $\text{EtOH}$  ppts. a complex in which the ratio  $\text{Cu} : \text{Na}(\text{K}) : \text{N} = 1.0 : 1.8 : 3.8—4.0$ . Addition of acid to the moderately fresh solution ppts. the fibroin almost quantitatively, but if the solution is preserved the fibroin is degraded to compounds sol. in  $\text{H}_2\text{O}$  which are most readily isolated if  $\text{KOH}$  ( $\text{NaOH}$ ) is replaced by  $\text{Ba}(\text{OH})_2$ . Degradation is due to the conjoint action of  $\text{Cu}(\text{OH})_2$  and  $\text{Ba}(\text{OH})_2$  and does not occur in the presence of  $\text{Ba}(\text{OH})_2$  alone. In the degraded and original products the ratio  $\text{N} : \text{C} = 1.0 : 2.86$  and  $1.0 : 3.2$ , respectively. The degraded product gives an intense biuret reaction. Treatment with  $\text{MeOH}$  shows that it is not homogeneous. Unlike fibroin it is completely sol. in  $\text{EtOH}$  saturated with  $\text{HCl}$ .  
H. W.

**Saliva.** F. DUYVENSZ (Proc. Roy. Soc. Med., 1934, **27**, 839—848).—The Ca and  $\text{SCN}'$  contents and  $p_{\text{H}}$  of saliva are discussed. Pituitary hormones have been demonstrated in saliva.  
CH. ABS. (p)

**Alleged occurrence of acetylcholine and adrenaline in cat's saliva.** P. S. LARSON (J. Pharm. Exp. Ther., 1935, **54**, 341—345).—Ultrafiltration removes the vascular activity, which cannot be due to acetylcholine or adrenaline, from cat's saliva.  
H. G. R.

**Variations in the saccharogenic power of human saliva.** F. WALKER and L. SHEPPARD (Amer. J. Physiol., 1935, **111**, 192—195).—The activity of saliva samples from the same individual varies from day to day. It increases after ingestion of food, particularly in the morning, and declines slowly during the day but considerably at night. Saccharogenic power varies qualitatively, but not quantitatively, with rate of secretion of saliva, and possibly with total solids content.  
R. N. C.

**Secretory function of the stomach in the course of experimental hyperaminoacidemia.** J. LA BARRE and P. DESTREE (Compt. rend. Soc. Biol., 1935,



119, 1177—1179).—Intravenous injection of hypoglycaemic doses of glycine in the dog produces an increased total gastric secretion and an increased HCl content of the juice. The effect is abolished by vagotomy. R. N. C.

**Detection of free hydrochloric acid in stomach contents.** M. WAGENAAR (Pharm. Weekblad, 1935, 72, 837—841).—A drop of a saturated solution of resorcinol and vanillin is evaporated to dryness and the "spot" treated with a drop of stomach fluid. A deep violet colour shows  $>0.0015N\text{-HCl}$ . Strong inorg. acids also give the colour,  $\text{H}_2\text{BO}_3$  a pale coloration, and all org. acids except  $\text{H}_2\text{C}_2\text{O}_4$  a negative test. S. C.

**Presence of taurocholate in the bile of cats and snakes.** M. IWATO and K. WATANABE (J. Biochem. Japan, 1935, 21, 211—212).—Taurocholic acid was isolated. F. O. H.

**Liver diathermy and hepatic function. II. Excretion of dyes.** Y. MITANI (J. Biochem. Japan, 1935, 21, 381—397).—Diathermy of the liver, which increases the vol. of bile secreted, does not affect the excretion of bile-pigments but tends to increase that of injected dyes, especially during pregnancy or following salvarsan injection. F. O. H.

**Liver diathermy and hepatic function. I. Bile secretion.** Y. MITANI (J. Biochem. Japan, 1935, 21, 309—328).—Application of diathermic currents of 400—1500 milliamp. to the liver (dog) increases the excretion of bile, the excretion of bilirubin and bile acids being increased during and for some time after the application. The effect is inhibited by administration of atropine and adrenaline or by severe liver disease. F. O. H.

**Hæmoglobin and bile-pigment over-production in the splenectomised bile-fistula dog.** R. E. KNUTTI, W. B. HAWKIN, and G. H. WHIPPLE (J. Exp. Med., 1935, 61, 127—138).—Blood destruction associated with *Bartonella* or with a drug ( $\text{N}_2\text{H}_4$ ) produces a large amount of pigment in the bile. New hæmoglobin and bile-pigment are formed in large amounts on a diet which causes only small production of new hæmoglobin in anæmic dogs. CH. ABS. (p)

**Proof of a humoral control of intestinal secretion.** E. S. NASSET, H. B. PIERCE, and J. R. MURLIN (Amer. J. Physiol., 1935, 111, 147—158).—Food in the digestive tract in dogs is accompanied by increased secretion in a completely isolated jejunal loop, thus proving the presence of a humoral control. Enzyme production in the loop is augmented by feeding. R. N. C.

**Physiology of milk secretion.** V. N. NIKITIN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 434—440).—Comparison of the composition of blood samples drawn from the jugular and from abdominal veins of lactating cows indicates that lactose is formed in the udder from blood-glucose, and that milk-protein is derived, at least in part, from the residual N of the blood. Variations in the amount of milk produced by different cows depend on the total amount of blood circulating in the udder and not on differences in the amount of constituent materials withdrawn from unit vol. of blood. A. G. P.

**Influence of thyroxine on milk secretion.** E. L. JACK and S. I. BECHDEL (J. Dairy Sci., 1935, 18, 195—205).—Intravenous injection of thyroxine in cows resulted in increased milk production especially in the later stages of the lactation. The composition of the milk was not significantly altered. A. G. P.

**Seasonal variations in the lipase content of milk.** J. L. HILEMAN and E. COURTNEY (J. Dairy Sci., 1935, 18, 247—257).—The lipase content of milk reaches a min. in early summer and a max. in early winter. The amount of lipase secreted increases as lactation is prolonged. A. G. P.

**Utilisation of the mercury-cadmium reagent for micro-determination of lactose in milk.** M. BIERRY and C. DUMAZERT (Compt. rend. Soc. Biol., 1935, 119, 1029—1031).—The use of the  $\text{Hg}(\text{NO}_3)_2\text{-Cd}(\text{NO}_3)_2$  reagent permits the determination of lactose in 1 c.c. of milk to an accuracy of 2%. R. N. C.

**Nutritional anæmia, calcium, phosphorus, and nitrogen balance of rats fed raw vs. pasteurised milk.** H. A. LASBY and L. S. PALMER (J. Dairy Sci., 1935, 18, 181—192).—Milk pasteurised in glass showed no change in Cu or Fe contents and did not induce more severe anæmia than did raw milk. Commercially pasteurised milk sometimes caused less severe anæmia than did raw milk. No significant differences appeared in the Ca, P, and N retentions of rats receiving raw and pasteurised milks. A. G. P.

**Composition of human perspiration.** B. A. MCSWINEY (Proc. Roy. Soc. Med., 1934, 27, 839—848).—Analyses are recorded. The presence of large amounts of lactic acid is not confirmed. Sweat glands are not affected by adrenaline, but are excited by pilocarpine and paralysed by atropine. CH. ABS. (p)

**Comparison of human with animal urine.** M. TAKAMATSU (J. Biochem. Japan, 1935, 21, 427—433).—Comparative data for  $p_{\text{H}}$ ,  $d$ , depression of f.p.,  $\kappa$ , total ash and its solubility in  $\text{H}_2\text{O}$ , and the contents of  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{SO}_4$ ,  $\text{Cl}$ , total N, urea, uric acid, and creatinine are given for the urines of man, dog, cat, horse, ox, elephant, pig, goat, rabbit, guinea-pig, frog, toad, turtle, hen, and duck. F. O. H.

**Organic constituents of elephant's urine.** M. TAKAMATSU (J. Biochem. Japan, 1935, 21, 435—438).—The principal N constituent is urea, whilst, unlike with most herbivores, hippuric acid forms a smaller part of the N excretion; creatinine is also present. F. O. H.

**Detection of protein and glucose in urine.** E. SACHS (Deut. med. Woch., 1934, 60, 1923—1924; Chem. Zentr., 1935, i, 1280).—A no. of new tests using sulphosalicylic acid paper are described. H. N. R.

**Origin of *l*-xyloketose (urine-pentose).** M. ENKLEWITZ and M. LASKER (J. Biol. Chem., 1935, 110, 443—456).—Administration of glycuronic acid causes a greatly increased elimination of *l*-xyloketose in the urine. J. N. A.

**Value of Gerhardts and Legal tests for determining ketonic compounds.** A. ESCUDERO (Rev. méd. lat.-amer., 1931, 14, 877).—The Legal reaction



in urine is positive when the sum of  $\text{COME}_2$  and  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{H}$  (I) is  $> 0.25$  g. per 1000. The Gerhardt reaction is positive when (I) is  $> 0.20$  g. per 1000.

CH. ABS. (p)

**Effects of carbon dioxide on urine formation and glomerular blood-flow.** E. A. ADOLPH (Amer. J. Physiol., 1935, 111, 64—74).—High  $\text{CO}_2$  tensions inhibit urine formation and decrease glomerular blood-flow in frogs.

R. N. C.

**Oxygen tension and urine production in frogs.** E. A. ADOLPH (Amer. J. Physiol., 1935, 111, 75—82).—The rate of urine production diminishes sharply with the  $\text{O}_2$  tension in pithed frogs; it is independent of it in normal frogs, by virtue of their breathing, when the tension is  $>$  that of room air, but declines rapidly in lower tensions. The response of the renal arterioles that reduces the blood-flow, and probably also the glomerular capillary pressure, is apparently under the influence of  $\text{O}_2$  tension.

R. N. C.

**Effect of hypertonic solutions of sodium chloride on the elimination of pigments by the kidney.** E. MICHALOWSKI and Z. M. BIELINSKI (Compt. rend. Soc. Biol., 1935, 119, 1216—1218).—Hypertonic NaCl solutions accelerate the renal excretion of dyes in the dog through their diuretic action.

R. N. C.

**Guanine in the excreta of arachnids.** K. VAJROPALA (Nature, 1935, 136, 145).—Using the sp. deaminating enzyme guanase, 12 wt.-% of the excreta of the common garden spider is found to consist of guanine.

L. S. T.

**Copper therapy in nutritional anaemia.** J. C. HAWKSLEY (Proc. Roy. Soc. Med., 1934, 27, 1066—1068).—Among 80 cases of anaemia, 4 required addition of Cu to Fe medication to effect return to normal. Microcytosis occurred in Cu deficiency and was corr. by Cu administration.

CH. ABS. (p)

**Basedow's disease and cholelithiasis.** A. JUGENBURG and B. M. SCHLEPAKOV (Ann. Roentgenol. Radiol. U.S.S.R., 1934, 13, No. 3, 200—209).—Irradiation of the thyroid and thymus produced better regulation of the disturbed cholesterol metabolism, lowered basal metabolism, and generally improved condition. Thyrotoxicosis creates all conditions favourable to development of cholelithiasis and may contribute to the formation of calculi. CH. ABS. (p)

**Flocculating power of cancerous sera.** M. L. CHEVREL-BODIN, F. CHEVREL, and M. CORMIER (Ann. Inst. Pasteur, 1935, 55, 108—123).—EtOH extracts of normal organs or of cancerous tissue diluted with aq. NaCl or KCl do not give sp. ppts. with cancerous sera but EtOH extracts of normal organs diluted with  $\text{CaCl}_2$  or  $\text{Ca}(\text{OAc})_2$  give increased pptn. with such sera, for which considerable specificity is claimed.

W. O. K.

**Enzymes in cancer.**  $\beta$ -Glycerophosphatase of the erythrocytes. J. W. SCHOONOVER and J. O. ELY (Biochem. J., 1935, 29, 1809—1816).—The optimum substrate  $p_H$  for normal and cancer human-erythrocyte- $\beta$ -glycerophosphatase (I) activity in 0.2M-acetate buffer at  $37^\circ$  is 5.6—5.8. Over the  $p_H$  range 5.0—6.0 the (I) activity of erythrocytes from cancerous individuals is  $>$  that of erythro-

cytes of normals of the same sex. The abs. increase of activity by  $\text{Mg}^{++}$  is the same for cancerous as for normal erythrocytes so that the % increase is smaller for the cancerous erythrocytes. Cancerous erythrocytes probably contain tissue- $\beta$ -glycerophosphatase not activated by  $\text{Mg}^{++}$ .

W. O. K.

**Tissue metabolism. VII. Action of tumour extracts on hexose diphosphate.** E. BOYLAND and M. E. BOYLAND (Biochem. J., 1935, 29, 1910—1914).—Dialysed tumour (mouse, rat, rabbit) extracts contain zymohexase [converting hexose diphosphate (I) into dihydroxyacetone phosphate (II)] to an extent approx. 10% of that with muscle from the same animal. Dialysed tissue extracts aërobically oxidise (II) to a more stable P compound, a stage of glycolysis with which the Pasteur reaction is possibly concerned. Dialysed mouse tumour extracts convert (I) into lactic acid if sufficient adenylyl pyrophosphate is added to compensate for the rapid decomp. of the latter substance.

F. O. H.

**Dental decay as an indicator of dietary fault.** N. P. LARSEN, M. R. JONES, and G. P. PRITCHARD (Amer. J. Dis. Children, 1934, 48, 1228—1233).—Decay disappears when the usual diet of carbohydrates with an acid residue is replaced by one of alkaline starches with small amounts of vegetables. Resistance to other diseases is also increased.

CH. ABS. (p)

**Blood-fats in diabetic lipaemia.** F. K. HERBERT (Biochem. J., 1935, 29, 1887—1893).—In severe diabetic lipaemia increases in plasma-neutral fat, -cholesterol, and -phospholipins occurred, the greatest increase being in neutral fat, which also decreases most rapidly under treatment. Comparison of the I vals. of ingested and plasma-fatty acids indicates that a proportion of the fats is derived from the tissues.

H. D.

**Attempts to reduce the symptoms of experimental diabetes by irradiation of the pituitary.** W. A. SELLE, J. J. WESTRA, and J. B. JOHNSON (Endocrinol., 1935, 19, 97—104).—The fasting blood-sugar level of depancreatized dogs is not reduced by intensive X-irradiation of the pituitary; in some cases it is raised. The response to ingested glucose is always typical of severe diabetes. Sensitivity to insulin is not increased, and the min. quantity of insulin required to prevent glycosuria is unchanged.

R. N. C.

**Dietary hæmorrhagic disease in chicks.** H. J. ALMQUIST and E. L. R. STOKSTAD (Nature, 1935, 136, 31).—The disease can be prevented by rice meal or bran which has been kept moist and by dehydrated lucerne. The anti-hæmorrhagic factor (cf. this vol., 903) is located in the unsaponifiable,  $\text{Et}_2\text{O}$ -extractable portion of lucerne.

L. S. T.

**Depigmentation, a new dietary deficiency disease, cured by copper.** F. J. GORTER (Nature, 1935, 136, 185; cf. A., 1934, 1132).—Depigmentation in rats is cured by addition of Cu to the diet. The min. dose varies considerably owing to its availability and the anti-Cu effect of certain growth-promoting food factors which should always be present in a satisfactory diet.

L. S. T.



**Relation of the regulatory mechanism of respiration to clinical dyspnoea.** D. W. RICHARDS, jun., A. Cournand, and I. Rappaport (Proc. Nat. Acad. Sci., 1935, 21, 498—501).—Dyspnoea is not determined by any physicochemical bodily function, but by local difficulty or disturbance in the mechanical function. H. G. R.

**Blood chemistry in epilepsy.** R. T. FLETCHER and O. D. PEDEN (Lancet, 1935, 228, 1382—1383).—There is no marked difference in composition of the blood during a convulsion, except possibly a greater variation in % vol. of red cells and a slight rise in serum-Ca. Serum-protein, -P, and -phosphatase and blood-Cl' remain practically unchanged. L. S. T.

**Effect of cortin on intra-ocular tension in glaucoma.** E. M. JOSEPHSON (Science, 1935, 82, 62).—Administration of cortin relieves the heightened intra-ocular tension in glaucoma, and reduces or arrests progressive myopia. The mechanism of both diseases can be explained as a disturbance of H<sub>2</sub>O-salt metabolism. L. S. T.

**Intermediary metabolism of purines in gout.** M. LABBÉ, P. L. VIOLLE, and F. NEPVEUX (Compt. rend. Soc. Biol., 1935, 119, 1095—1098).—Gout is accompanied by an increase in free and a decrease in combined purine-N of the serum, total purine-N remaining normal. The increase of uric acid in serum is probably due to its being in a form eliminated only with difficulty by a normal kidney. R. N. C.

**Hepatectomy and nitrogenous substances in the blood.** M. FRANKE, T. TOCZYSKI, and J. LANKOSZ (Compt. rend. Soc. Biol., 1935, 119, 1209—1211).—Hepatectomy in the dog provokes a fall of protein-N, urea, and creatinine, and a rise in other non-protein N substances. R. N. C.

**Total cholesterol and its fractions in the blood after hepatectomy.** M. FRANKE and S. MALCZYNSKI (Compt. rend. Soc. Biol., 1935, 119, 1212—1216).—Hepatectomy in the dog provokes a slow steady fall of total blood-cholesterol (I). Esterified (I) shows a more marked fall; in consequence, free (I) rises, whilst the esterified:total (I) ratio is diminished. Injection of isotonic glucose solution causes a fall of total and esterified (I). R. N. C.

**Bromine level of the blood and maniacal-depressive insanity.** H. FLEISCHACKER and G. SCHEIDERER (Mschr. Psychiat. Neurol., 84, 348—370; Chem. Zentr., 1935, i, 919).—Roman's method for determining blood-Br' is untrustworthy. The Zondek-Bier hypothesis is therefore founded on untrustworthy analytical results. R. N. C.

**Tyrosine index of polypeptidæmia in mental illnesses.** T. SIMON, J. C. ROUX, and R. GOFFON (Compt. rend. Soc. Biol., 1935, 119, 926—928).—Polypeptide-tyrosine in human blood increases considerably in mental disorders. R. N. C.

**Glucose tolerance test in leprosy.** D. G. LAI (Amer. J. Trop. Med., 1934, 14, 575—584).—Apart from individual variations, leprosy without complications tends to give a normal blood-sugar curve. A low renal threshold is, however, common. CH. ABS. (p)

**Atebrin in the treatment of malaria in the Philippine Islands.** P. E. McNABB and S. C. SCHWARTZ (Amer. J. Trop. Med., 1934, 14, 309—317).—The action of atebrin on gametocytes and schizonts resembles that of quinine. CH. ABS. (p)

**Observations in Panama with reference to control with atebrin. I. Malaria control with atebrin.** W. H. W. KOMP and H. C. CLARK (Amer. J. Trop. Med., 1934, 14, 381—396).—Atebrin reduces fever as quickly as does quinine, but the parasite frequently remains and relapses are frequent. CH. ABS. (p)

**Effect of saline ions on flocculation and superflocculation of the serum of paludics.** F. TRENSZ (Compt. rend. Soc. Biol., 1935, 119, 966—968).—Saline ions interfere in melanoflocculation through their chemical nature; their actions on flocculation and superflocculation of the serum of paludics are different. R. N. C.

**Different indicators replacing melanin in the Henry reaction.** R. C. PRUDHOMME (Compt. rend. Soc. Biol., 1935, 119, 1115—1117).—Melanin (I) can be replaced by carmine in the Henry reaction. The serum of paludics has no sp. affinity for (I), which acts as an indicator of the instability of the serum in distilled H<sub>2</sub>O. R. N. C.

**Relation of hypercholesterolaemia to increased tolerance for thyroid preparations in nephrosis.** R. S. AITKEN (Clin. Sci., 1934, 1, 241—244).—In liver cirrhosis, hypercholesterolaemia did not inhibit thyroxine action or produce increased tolerance to thyroid preps. CH. ABS. (p)

**Crystallisation of sodium chloride in the serum of pregnant women.** V. BERGAUER, V. STICH, and Z. ZLABEK (Compt. rend. Soc. Biol., 1935, 119, 1131—1133).—NaCl crystallises from pregnancy serum in concentric circles, which change partly to the glaciated form from 10 days before, and completely to aggregates immediately before or after, parturition. This indicates that pregnancy is accompanied by hyperpituitarism, followed by hyperthyroidism. R. N. C.

**Rickets. Control with 50 units (Steenbock) of cod-liver oil vitamin-D concentrate in milk.** D. J. BARNES (Amer. J. Dis. Children, 1934, 48, 1258—1267).—Satisfactory control is recorded. The customary ratio 40:240 for the equiv. rat units of vitamin-D in irradiated milk to that in cod-liver oil is not confirmed. When the concentrate is given in milk the required units are approx. equal. CH. ABS. (p)

**Phosphatase. V. Serum-phosphatase as a criterion of severity and rate of healing of rickets.** A. BODANSKY and H. L. JAFFE (Amer. J. Dis. Children, 1934, 48, 1268—1278; cf. A., 1934, 560, 1129).—Serum-phosphatase increases in rickets and declines after effective therapy. It is a better criterion of the severity of the disease and of healing than are the serum-Ca and -P. CH. ABS. (p)

**Experimental scurvy. XXV. Content of fatty acid, cholesterol, unsaponifiable matter, and nitrogen in faeces of scorbutic guinea-pigs. XXVI. Acid value of petrol extract of faeces.**



**XXVII. Serum-lipase. XXVIII. Volume and constitution of bile.** Y. AIZAWA (J. Biochem. Japan, 1935, 21, 457—467, 469—475, 477—485, 487—504).—XXV. Scurvy produces an increase in the faecal fatty acids and in their ratio to the fatty acids ingested; the corresponding vals. for cholesterol and unsaponifiable material are diminished. The N balance is unchanged.

XXVI. The acid val. of the light petroleum extract of the faeces is decreased by approx. 23%.

XXVII. Scurvy diminishes the serum-lipase to an extent  $\propto$  the severity of the disease. The decrease does not depend merely on inanition.

XXVIII. The vol. of bile and its content of taurocholic acid and cholesterol in guinea-pigs are diminished in scurvy. F. O. H.

**Diazo-urine. V. Small-pox urine. VI. Antoxyproteic acid.** S. NAKAYAMA (J. Biochem. Japan, 1935, 21, 439—442, 443—448).—V. The urines of scarlet fever and small-pox patients give a positive diazo-reaction which, with the latter, appears to be due to a substance other than antoxyproteic acid (I).

VI. Urines from typhoid, scarlet fever, measles, or phthisis patients appear to contain the same (I) (13.05—13.39% N, 28.15—29.50% Ba in Ba salt, 0.46%  $\text{NH}_3\text{-N}$ , free from S, and not hydrolysed by erepsin). The relation between (I), oxyproteic acid (A., 1906, i, 122), urochromogen, chromogen, and kynurenic acid is discussed (cf. A., 1927, 170; 1934, 201). F. O. H.

**Report of chemistry section.** B. C. ASTON (New Zealand Dept. Agric. Ann. Rept. [1932—1933], 1933, 30—36).—The blood-Mg of cows suffering from "grass staggers" is markedly subnormal. In rats the blood-Mg level is directly related to the Mg of the diet and can be raised  $>$  normal by supplementary feeding of  $\text{MgCO}_3$ ,  $\text{MgSO}_4$ ,  $\text{MgCl}_2$ , or Mg phosphates.

No relationship exists between the enlarged thyroid glands of "bobby" calves and their I contents. The % of I in glands of lambs varied in the same direction as that of the soils and pastures of the district, high vals. occurring in rich limestone areas and low vals. in alluvial plains. CH. ABS. (p)

**Calcium therapy in tropical diseases.** P. BEREGOFF (Canad. Med. Assoc. J., 1935, 32, 177—178).—Prolonged residence in the tropics is associated with a deficiency in blood-Ca. Satisfactory treatment with Ca gluconate is recorded. CH. ABS. (p)

**Isolation of an unsaponifiable substance from the spleen in a case of Werloff's disease.** A. FIESCHI (Boll. Soc. Ital. Biol. sperim., 1935, 10, 46—47).—The spleen contains an unsaponifiable substance that gives a greenish-yellow colour with EtOH. It is extracted from the dried spleen by saponification with Na, extraction with light petroleum, pptn. from EtOH solution with digitonin, and re-extraction with light petroleum. R. N. C.

**Cod-liver oil salve treatment of fresh wounds, burns, and phlegmonous wounds.** W. LÖHR (Zentr. Chirurgie, 1934, 61, 1686).—Bacteria commonly occurring in infected wounds are destroyed by cod-liver oil. Salves prepared from the oil

rapidly liquefy necrotic tissue and stimulate growth. The effects are ascribed to the vitamin-A and -D in the oil. CH. ABS. (p)

**Culture of whole organs.** A. CARREL and C. A. LINDBERGH (Science, 1935, 81, 621—623).—In the method described an organ or any part of the body is transplanted to a sterile chamber in which it is fed artificially by a nutrient fluid through the arteries. L. S. T.

**Metabolism of retina.** H. LASER (Nature, 1935, 136, 184).—Respiration of rat retina and Crocker mouse sarcoma in  $\text{HCO}_3^-$  Ringer's solution is approx. twice that in  $\text{PO}_4^{3-}$  Ringer's solution. Respiration of the tumour is inhibited by approx. 90% in both media by small amounts of HCN, but respiration of retina is not inhibited by similar amounts of HCN in  $\text{HCO}_3^-$  Ringer's solution. L. S. T.

**Rate of oxygen consumption of the isolated terrapin heart when perfused with various solutions.** C. H. McDONALD and A. C. McDONALD (Amer. J. Physiol., 1935, 111, 51—54).— $\text{O}_2$  consumption is increased by perfusion with isotonic NaCl or NaCl- $\text{CaCl}_2$  solution, and decreased by isotonic NaCl-KCl or glucose solution. The effect of NaCl solution is inhibited by KCN in concn. 1 : 10,000. R. N. C.

**Lability of the basal metabolism of the dairy cow.** F. G. BENEDICT and E. G. RITZMAN (Proc. Nat. Acad. Sci., 1935, 21, 304—308).—The basal metabolism of the dairy cow is not const. even for short periods and in non-lactating animals is highest in the pasture season (June) and lowest in March. H. T.

**Chemical reactions in muscle. VII. Dephosphorylation of phosphoglyceric acid in fluoride-poisoned muscle. T. MANN. VIII. Phosphoglyceric and adenylic acids. P. OSTERN, T. BARANOWSKI, and J. REIS. IX. Rôle of phosphagen. J. K. PARNAS and P. OSTERN (Biochem. Z., 1935, 279, 82—84, 85—93, 94—98; cf. A., 1934, 1027).—VII. The marked  $\text{NH}_3$  production by frog's muscle in 0.02M-NaF is not influenced by 0.01M-K phosphoglycerate (I). With 0.005M-NaF, less  $\text{NH}_3$  is formed, liberation of  $\text{PO}_4^{3-}$  increases, and adenosine triphosphate (II) remains unchanged. Higher concns. of (I) produce  $\text{AcCO}_2\text{H}$ , adenylic acid (III) being phosphorylated at the expense of (I).**

VIII. Dephosphorylation of (I) does not occur in absence of (II) or (III). Creatine+(I) produce creatine phosphate only when formation and dephosphorylation of (II) in presence of (III) results in an accumulation of (II). Under certain conditions no liberation of  $\text{PO}_4^{3-}$  occurs in the system (I)-(II)-creatine-creatine phosphate but  $\text{PO}_4$  is transferred from mol. to mol.

IX. The rôle of creatine phosphate (phosphagen) and possibly of arginine phosphate in the reaction (II)  $\rightleftharpoons$  (III) is discussed. F. O. H.

**Phosphate metabolism in muscular work.** A. SZAKÁLL (Arbeitsphysiol., 1934, 8, 316—334).—During prolonged muscular work in the dog,  $\text{PO}_4^{3-}$ , after a small temporary increase, disappears from the urine, but reappears during recovery, the extent of these changes being dependent on the amount of work.



Work increases the  $\text{PO}_4'''$  balance. Inorg.  $\text{PO}_4'''$  in the blood, and also the leucocyte count, show no change during work, but increase considerably during recovery. Acid-sol.  $\text{PO}_4'''$  in the blood increases during work, but in cases of prolonged  $\text{PO}_4'''$ -deficiency is maintained at the normal level. R. N. C.

**Reversible reactions in biological glycolysis.** O. MEYERHOF (Naturwiss., 1935, 23, 490—493).—The chemical reactions occurring in muscle and involving org. phosphate compounds are of two types, (a) reversible, associated with small energy changes, and (b) irreversible, and yielding larger amounts of energy. The latter are especially associated with the adenylic acid-adenosinetriphosphoric acid system (cf. Lohmann, A., 1931, 1184), whilst characteristic examples of the former are the equilibria, hexose diphosphate  $\rightleftharpoons$  dihydroxyacetonephosphoric acid  $\rightleftharpoons$  glyceraldehyde-phosphoric acid and  $\beta$ -phosphoglyceric acid  $\rightleftharpoons$   $\alpha$ -phosphoglyceric acid  $\rightleftharpoons$  phosphopyruvic acid. W. O. K.

**Influence of adenylic and cholic acids and secondary phosphate on liver-glycogenesis.** K. WATANABE (J. Biochem. Japan, 1935, 21, 197—201).—The enhanced liver-glycogenesis in rabbits from glucose due to  $\text{HPO}_4''$  is further increased by injection of adenylic acid; simultaneous oral administration of cholic acid effects a still further increase. F. O. H.

**Comparative effect of adding different sugars to the perfusion liquid through frog's heart and the influence of insulin over it.** R. K. PAL and S. PRASAD (J. Physiol., 1935, 83, 285—291).—Addition of glucose, fructose, lactose, maltose, or sucrose to the perfusing fluid increases the efficiency of the heart-beat, the effect being most lasting with glucose. The action of all these sugars is enhanced by insulin. Lowering of  $p_H$  in the course of perfusion produces a temporary dilatation of the heart with diminution of the amplitude, followed by true augmentation. Insulin scarcely affects the vagus when combined with suitable doses of any of the sugars. Injection of insulin, followed in 0.5 hr. by glucose, acts as an efficient cardiac stimulant. R. N. C.

**Effect of creatine on carbohydrate metabolism.** D. JAHN (Deut. Arch. klin. Med., 1934, 177, 121—138; Chem. Zentr., 1935, i, 1084).—After dosage with creatine (I) strong ketonæmia and depression of the blood-sugar level occur in cases of glycogen-poor liver. (I) stimulates the muscle-glycogen-forming action of insulin, and assists the blood-sugar-depressing action. H. J. E.

**Metabolism of galactose. II. Synthesis of lactose by active mammary gland *in vitro*.** G. A. GRANT (Biochem. J., 1935, 29, 1905—1909).—Glucose, but not fructose, mannose, or galactose, is readily converted into lactose (determined by fermenting with *S. fragilis*) when kept in 0.9% aq. NaCl at 37° with tissue-slices of lactating mammary gland (guinea-pig). A slight synthesis of org.  $\text{PO}_4'''$  from added glucose +  $\text{PO}_4'''$  on addition of yeast-hexokinase indicates the possible presence of a hexosephosphatase. F. O. H.

**Fate of mannide and isomannide in the animal body.** J. C. KRANTZ, jun., W. E. EVANS, jun., and

C. J. CARR (Quart. J. Pharm., 1935, 8, 213—217).—Mannide (I) and isomannide (II) cannot be stored as glycogen in rat-liver, do not relieve insulin shock in mice, and do not raise the fasting blood-sugar level of rabbits. (I) increases the R.Q. of rats, whereas (II) does not. H. G. R.

**Fate of conjugated glycuronic acids in the body.** M. KOIKE and Y. TOSAWA (Japan. J. Med. Sci., IV, 1933, 7, 110).—Orally administered phenyl- or benzoyl-glycuronic acid or urochloralic acid was largely excreted unchanged in urine by rabbits. No increase in ethereal sulphates occurred.

CH. ABS. (p)

**Utilisation of variations of the respiratory quotient to determine the part played by ethyl alcohol in basal exchange. Case of carbohydrate diet.** E. LE BRETON (Compt. rend. Soc. Biol., 1935, 119, 1014—1016).—The R.Q. method does not give trustworthy results, only direct measurement of the coeff. of EtOH oxidation being exact in all cases. R. N. C.

**Transport of lipins in the animal organism.** T. CAHN and J. HOUGET (Compt. rend., 1935, 201, 166—168).—Previous work supports the view that mobilisation of lipins occurs as cholesteryl esters, which are distributed from the liver to various tissues as phosphatides. H. G. R.

**Carotenoid pigments in fishes. III. Effects of ingested carotenoids on the xanthophyll content of *Fundulus parvipinnis*.** F. B. SUMNER and D. L. FOX (Proc. Nat. Acad. Sci., 1935, 21, 330—340; cf. A., 1934, 555).—When the fishes are fed a carotene-rich diet containing no xanthophylls the total xanthophyll content is increased. H. T.

**Fat metabolism. XV. Biological degradation of fatty acids, esters, and fats to dicarboxylic acids.** B. FLASCHENTRÄGER and K. BERNHARD (Helv. Chim. Acta, 1935, 18, 962—972; cf. A., 1934, 1027).—When Na deoate, Me or Et laurate is added to a dog's diet, only 0.5—1% is recovered as sebatic acid (I) in the urine. From Me deoate the oxidation products are (I) and suberic acid. The results are attributed to  $\omega$ -oxidation followed by successive  $\beta$ -oxidations. F. R. G.

**Fat metabolism in fishes. VII. Depôt-fats of certain fish fed on known diets.** J. A. LOVERN (Biochem. J., 1935, 29, 1894—1897).—The composition of the body-fats of *Ctenopharyngodon idellus* and of its dietary grasses, and of those of *Hypophthalmichthys nobilis* and *H. molitrix* and their dietary mud, was determined. Apparently the fishes synthesise their own body-fats. H. D.

**Effect of choline on the liver-fat of rats in various stages of nutrition.** C. H. BEST and M. E. HUNTSMAN (J. Physiol., 1935, 83, 255—274).—The liver-fat of white rats on a diet of grain and beef-fat rises to a steady max. in 3 weeks. Addition of choline (I) to the diet causes a rapid fall of liver-fat. Omission of the beef-fat also causes a fall, which is accelerated by (I). Liver-fat is maintained or increased by a complete diet with low (I) content, whether or not beef-fat is given. A diet of pure sucrose increases liver-fat in both normal and fatty-



livered animals, this effect being prevented by (I), which rapidly reduces liver-fat to normal. Liver-fat is reduced by a diet low in (I). Fasting in rats with fatty livers produces a rapid decrease of liver-fat, only slightly accelerated by (I). R. N. C.

**Choline and liver-fat in phosphorus poisoning.** C. H. BEST, D. L. MACLEAN, and J. H. RIDOUT (J. Physiol., 1935, 83, 275—284).—Choline (I) accelerates the disappearance of liver-fat in rats during recovery from P poisoning, but does not inhibit fat deposition after injection of large quantities of P. Liver-fat accumulation produced by complete diets poor in (I) is less rapid than that from P poisoning. Liver-fat does not decrease in rats with fatty livers produced by P poisoning when kept on a (I)-poor diet. The histological picture does not suggest that (I) affects the duration of the degenerative changes produced by P, apart from fat accumulation. R. N. C.

**Excretion of exogenous fats through the intestinal mucosa.** G. PERETTI (Boll. Soc. Ital. Biol. sperim., 1935, 10, 79—81).—Oral administration of "iodipin" to a dog with a Thiry-Vella fistula results in secretion of considerable quantities of I-containing fat from the mucosa of the fistula, suggesting that part of the exogenous fat is normally excreted by this route. R. N. C.

**Relation of the fat content of milk to the passage of the milk curd from the stomach of the calf.** D. L. ESPE and C. Y. CANNON (J. Dairy Sci., 1935, 18, 141—147).—Curd from milk containing >6% of fat tends to leave the stomach more rapidly than skimmed milk as a result of the different texture of the curd formed. The fat in whole milk does not inhibit gastric secretion or motility. A. G. P.

**Protein, fat, and carbohydrate metabolism in the white rat. I. In the normal rat.** R. WETZEL, H. WOLLSCHITT, H. RUSKA, and T. OESTREICHER (Arch. exp. Path. Pharm., 1935, 179, 86—114).—Results of determinations of the dry wt.,  $H_2O$ , total N, protein, fat, total reducing substances, carbohydrate, glycogen, and lactic acid contents of the organs of male rats are recorded. The respiration of the tissues was measured. W. McC.

**Dog plasma-protein given by vein utilised in body metabolism of dog. Horse plasma and dog hæmoglobin not similarly utilised.** W. T. POMMERENKE, H. B. SLAVIN, D. H. KARIHER, and G. H. WHIPPLE (J. Exp. Med., 1935, 61, 283—297).—Foreign plasma-protein (horse) introduced parenterally into the protein-fasting dog is not utilised but is eliminated as excess urinary N. Dog plasma, under similar conditions, will maintain the N equilibrium, and a small portion of dog hæmoglobin thus administered is used to maintain red-cell concn. CH. ABS. (p)

**Correlation between excess calories and excess urinary nitrogen in the specific dynamic action of protein in animals.** H. BORSOOK (Proc. Nat. Acad. Sci., 1935, 21, 492—498).—The relation between the cal. and urine-N in excess of the basal in the sp. dynamic action of proteins (A., 1931, 648) is confirmed, contrary to the conclusions of Aubel and Schaeffer.

The steady state is attained 4 hr. after ingestion and is maintained for 20 hr. H. G. R.

**Production of amino-acids from keto-acids and of urea in the liver.** M. NEBER (Z. physiol. Chem., 1935, 234, 83—96).—Surviving liver (but not liver pulp) in presence of  $O_2$  produces  $NH_2$ -acid and urea from  $AcCO_2H$  (I) and  $NH_3$  in amounts which depend on the concn. of (I), urea production predominating when this concn. is low. The temp. coeff. of the process is high. After 6 hr. production of urea begins to decrease, but that of  $NH_2$ -acid continues at undiminished rate. In  $N_2$ , production of urea ceases but that of  $NH_2$ -acid continues. Added ornithine (II) has no effect on the  $NH_2$ -acid production but increases urea production if the concn. of (I) is low (e.g., in liver from fasting animals). (II) shifts the equilibrium between  $NH_2$ -acid production and decomp. (to give urea). Lactic acid (III) and  $NH_3$  in liver yield  $NH_2$ -acid only after (III) is converted into (I). There is no increase in  $NH_2$ -acid production when glucose, quinol, cysteine, or ascorbic acid is added. In kidney (I) +  $NH_3$  yield  $NH_2$ -acid. W. McC.

**Perfusion of the stomach. V. Lactic acid formation from *d*-alanine.** K. WAKASUGI. VI. Uricolytic processes. T. TSUTSUI. VII. Formation of ketonic substances. T. NAGAO. VIII. Fission of arginine. S. MURAOKA. IX, X, XI. Creatine. Y. HONGO. XII. Urease (II). S. SUMIDA (J. Biochem. Japan, 1935, 21, 243—248, 249—258, 259—269, 271—277, 279—287, 289—293, 295—299, 301—308).—V. *d*-Alanine added to blood perfused through the dog's stomach is decomposed, a small part being converted (mainly in the mucosa) into lactic acid. The  $NH_3$ -N of the mucosa and urea-N of the muscular layer increase.

VI. Added uric acid is decomposed to allantoin especially in the mucosa.

VII. The ketonic substances, especially  $CH_3Ac \cdot CO_2H$ , of perfused normal blood are diminished. Addition of leucine and fatty acids with an even no. of C atoms, however, produces an increase in ketonic substances on perfusion, indicating that  $\beta$ -oxidation occurs in the stomach wall.

VIII. Arginine is decomposed with formation of ornithine, urea, and histidine, unchanged arginine and its decomp. products appearing in the blood, gastric juice, mucosa, and, more especially, muscle.

IX. Perfused creatine is decomposed (mainly in the muscle), partly forming creatinine and partly by an unknown reaction.

X. Arginine in the perfusing blood is partly converted into creatine in the mucosa.

XI. Betaine and urea are not converted into creatine on perfusion (in blood) through the dog's stomach.

XII. Urease occurs in the stomach-tissues (dog) the cardiac and fundus regions having an activity > that of the pylorus. It is absent from the duodenal mucosa. F. O. H.

**Nitrogen metabolism of the isolated tissues of the rat.** H. BORSOOK and C. E. P. JEFFREYS (J. Biol. Chem., 1935, 110, 495—509).—Surviving slices of the isolated liver, kidney, diaphragm, spleen,



and small intestine of the rat were used in Ringer's solution. In every case there was an increase in non-heat-coagulable sol. N, free  $\text{NH}_2\text{-N}$ , and  $\text{NH}_3$ ; uric acid, without any allantoin, was formed in every case except liver. Allantoin was formed only in liver and creatine in all the tissues except spleen. Deamination of  $\text{NH}_2$ -acids occurred at approx. the same rate in liver and kidney. Urea is formed in the small intestine from arginine, and in liver probably from histidine. Liver quantitatively converts uric acid into allantoin. J. N. A.

**Determination of glutathione in the tissues in the reduced form and in the oxidised form.** L. BINET and G. WELLER (Compt. rend. Soc. Biol., 1935, 119, 939—941).—Glutathione (I) is extracted from the tissue with aq.  $\text{CCl}_3\text{-CO}_2\text{H}$  and reduced (I) determined by pptn. with Cd lactate, oxidation with I, and titrating excess of I with  $\text{Na}_2\text{S}_2\text{O}_3$ . Oxidised (I) is reduced with NaCN in neutral solution and total (I) then determined similarly, oxidised (I) being found by difference. R. N. C.

**Effect of starvation on the glutathione of the tissues: rôle of the liver in glutathione metabolism.** L. BINET and G. WELLER (Compt. rend. Soc. Biol., 1935, 119, 941—943).—The glutathione (I) level in all tissues of the guinea-pig is maintained during starvation except in the liver, where it falls steadily, suggesting that the liver acts as a reserve store of (I) for the other organs. Reduced (I) generally follows total (I). R. N. C.

**Cystinuria. IV. Metabolism of homocysteine and homocystine.** E. BRAND, G. F. CAHILL, and R. J. BLOCK (J. Biol. Chem., 1935, 29, 399—410; cf. this vol., 775).—A cystinuric is fed with homocystine (I) or homocysteine (II) and the urinary total and urea-N, creatine,  $\text{SO}_4^{--}$  fractions, cystine (III), and (I) are determined. 18% of (I) fed is excreted as such, and the rest as inorg.  $\text{SO}_4^{--}$ ; 50% of (II) is excreted as (III), 24% as (I), and the remainder as inorg.  $\text{SO}_4^{--}$ . It is suggested that in the conversion of methionine into cysteine, (II) must be maintained in the reduced state. H. D.

**Influence on metabolism of addition of small amounts of cystine to protein-deficient diets.** L. LORENTE (Biochem. Z., 1935, 279, 76—81).—Determinations of N balance, C, and "vacate-O" vals. of the urine of rats fed on a diet deficient in quality and quantity of proteins indicate that small amounts (e.g., 0.0075 g. daily) of cystine influence the deoxidative metabolism (cf. A., 1930, 1613). F. O. H.

**Tyramine and blood perfusion through the kidney.** H. J. WOLF and H. A. HEINSEN (Arch. exp. Path. Pharm., 1935, 179, 15—23).—When the chief blood supply to one kidney in dogs (including those receiving protein-free diet) is cut off, outflow of blood being allowed to continue, tyramine (I) appears in the blood and the blood-pressure is increased. (I) is produced in the kidney from which the blood has been cut off. W. McC.

**Uric acid synthesis in the bird. III. A purine synthesis.** W. SCHULER and W. REINDEL (Z. physiol. Chem., 1935, 234, 63—82; cf. A., 1934, 104).—The kidney of the pigeon converts purines into

uric acid (I), but the pancreas and liver do not. A method of determining nucleosides, purines, and (I) in 4 c.c. of blood-serum is described. The precursor of (I) is enzymically produced in the liver (not in the kidney): it is not a mononucleotide or lactic, tartronic, mesoxalic, malonic, glutamic, aminomalonic, or  $\beta$ -hydroxyglutamic acid or hydantoin, glycerol, *d*-glucose, *d*-ribose, urea, carnosine, guanidine, creatine, creatinine, glycine, alanine, serine, glycylalanine, ornithine, arginine, histidine, cystine, reductone, or uracil. In the pigeon enzymic deamination of  $\text{NH}_2$ -acids occurs chiefly in the liver but also in the kidney (not in pancreas and muscle). In the kidney the N thus liberated appears as  $\text{NH}_3$  and (I) but in the liver part of it appears as  $\text{NH}_3$  and the rest neither as (I), precursor, nor urea. The liver produces (I), the C source being the precursor, the N source  $\text{NH}_2$ -acid (from  $\text{NH}_3$ ). W. McC.

**Nutritive value of Indian vegetable foodstuffs. V. Nutritive value of ragi (*Eleusine coracana*).** S. P. NIYOGI, N. NARAYANA, and B. G. DESAI (Indian J. Med. Res., 1934, 22, 373—382).—4% NaCl or hot 70% EtOH removes about 20% of the total N of ragi, the remainder being inextractable. Analytical figures are given for eleusinins; it is a prolamine, sol. in EtOH, and containing S and P. The cystine, tyrosine, and tryptophan contents are > those of wheat gliadin. Prolonged hydrolysis causes little deamination. There is no relation between free  $\text{NH}_3\text{-N}$  and the lysine-N of the prolamine. Ragi-proteins have biological vals. > those of rice and oats. The diastatic activity of ragi-malt is equal to that of barley-malt. R. N. C.

**Nutritive value of the protein of cabbage and of sweet potato.** H. C. KAO, W. H. ADOLPH, and H. C. LIAU (Chinese J. Physiol., 1935, 9, 141—148).—Using Mitchell's method on a 10% protein basis, the biological vals. for cabbage- and sweet potato-protein are 76 and 72, respectively. The proteins contain arginine-N 13.0 and 11.8, histidine-N 3.1 and 2.1, lysine-N 8.3 and 5.3, tyrosine-N 2.2 and 2.4, tryptophan-N 1.2 and 1.8, cystine-N 1.1 and 1.8%, respectively. H. G. R.

**"Digestibility" of common foodstuffs as determined by radiography.** W. C. D. MAILE and K. J. L. SCOTT (Lancet, 1935, 228, 1500—1501).—Boiling is the only method found to shorten the stomach emptying-time for milk. Sugar is more rapidly absorbed from the stomach when fluid is drunk with it, and glucose disappears from the stomach more slowly than sucrose. L. S. T.

**Biological value of proteins. VI. Balance-sheet method.** H. CHICK, J. C. D. HUTCHINSON, and H. M. JACKSON. **VII. Influence of variation in level of protein in diet and of heating protein on its biological value.** H. CHICK, M. A. B. FIXSEN, J. C. D. HUTCHINSON, and H. M. JACKSON (Biochem. J., 1935, 29, 1702—1711, 1712—1719; cf. A., 1932, 182).—VI. The balance-sheet method of studying the biological val. for maintenance of N equilibrium in rats of proteins is examined. The excretion of endogenous N in the urine diminishes with the time the rat is on a N-deficient diet; the N excretion on a N-free diet during 4 days after a preliminary period of 2—3 days gives a measure of the endogenous



N output. Only an approx. proportionality exists between food intake and faecal N output. Results on rats with food intake  $< 6$  g. per day are excluded.

VII. The biological vals. of whole wheat, white flour, wheat germ, maize endosperm, whole milk, lactalbumin (I), and caseinogen (II) are determined. With the exception of whole milk the biological vals. decrease with increased level of intake. Heating (II) at  $150^\circ$  for 66 hr. decreases its biological val. and digestibility; heating (I) at  $120^\circ$  for 72 hr. lowers its biological val. slightly and its digestibility considerably. H. D.

**Fate of ethynal in animals and men.** S. TSUNOO (J. Biochem. Japan, 1935, 21, 409—416).—Ingested "ethynal" (furylacrylyl-*p*-hydroxyphenylurea) is hydrolysed in the organism to furylacrylic acid [excreted both free and conjugated with glycine (dog, rabbit, man) or as the oxidation product, furoic acid (man)] and *p*-hydroxyphenylurea [excreted as glucuronate (dog, rabbit)]. F. O. H.

**Fate of  $\gamma$ -phthalimido- $\beta$ -hydroxybutyronitrile in animals.** T. KAWADA (J. Biochem. Japan, 1935, 21, 417—421).—The compound fed to rabbits is hydrolysed (approx. 85%) to phthalic acid (approx. 11% excreted as such, the remainder oxidised to BzOH and excreted as hippuric acid) and  $\gamma$ -amino- $\beta$ -hydroxybutyronitrile, which is converted into and excreted as SCN compounds and a thioaminopurine,  $C_5H_7N_5S_2$  or  $C_5H_7O_2N_5S$ . F. O. H.

**Fate of hydroxymethylfurfuraldehyde and of pyrrole in frogs.** K. KUSUI (J. Biochem. Japan, 1935, 21, 449—451).—Subcutaneously injected hydroxymethylfurfuraldehyde is excreted as the corresponding hydroxymethylfuroic acid; with pyrrole no base can be isolated from the urine. F. O. H.

**Nutrition and biochemical equilibrium in alimentary régime.** L. RANDOIN (Chim. et Ind., 1935, 34, 10—21).—A review indicating applications of results to maintenance of balanced diets. W. McC.

**Relation of food to regularity of nutritional response.** H. C. SHERMAN and H. L. CAMPBELL (Proc. Nat. Acad. Sci., 1935, 21, 434—436).—The coeff. of variability for rats at various stages on diets *A* and *B* are given. Diet *B* is superior to *A* in every respect and indicates the presence of an enrichment in an already adequate diet. H. G. R.

**Metabolism trials with suckling pigs.** G. SCHOLZ (J. Landw., 1935, 83, 107—156).—The S : N ratio of sow's milk averaged 1 : 11—12. Colostrum was relatively high in both elements but vals. reached normal after 3—4 days. The quantities of N and S eliminated in urine and faeces of piglings increased up to the age of 4 weeks and subsequently declined. The N : S ratio of the carcasses was 1 : 13.5 at birth and 1 : 14.0 at 4 weeks of age. The ratio varied considerably in the various organs. A. G. P.

**Influence of the spleen on sulphur metabolism.** K. IWABUCHI (Japan. J. Med. Sci., IV, 8; Proc. Japan. Pharmacol. Soc., 1933, 20—21).—Splenectomy increased all forms of urinary S and the total N in female dogs. Administration of 0.1 mg. of adrenaline caused further increases. CH. ABS. (p)

**Influence of the spleen on inorganic mineral metabolism.** H. KANEKO (Japan. J. Med. Sci., IV, 8; Proc. Japan. Pharmacol. Soc., 1934, 123—125).—Laparotomy had little effect on the composition of blood or urine in rabbits. Extirpation of the spleen decreased the erythrocytes, leucocytes, haemoglobin, K, Ca, and Mg in the blood and decreased the Ca and increased the K in urine. CH. ABS. (p)

**Availability of calcium from some typical foods.** M. L. FINCKE and H. C. SHERMAN (J. Biol. Chem., 1935, 110, 421—428).—The Ca of kale is nearly as well utilised as that of milk, but the Ca of spinach is utilised very poorly, if at all. This is due largely to the oxalate present in the spinach, and not to the presence of fibre. J. N. A.

**Relation of vitamin-D to calcium and phosphorus retention in cattle as shown by balance trials.** G. C. WALLIS, L. S. PALMER, and T. W. GULLICKSON (J. Dairy Sci., 1935, 18, 213—228).—Mineral retention was not increased by supplementary feeding of mineral matter with a vitamin-D-deficient ration. Administration of -D, however, increased the Ca retained to 14-fold and the P to 11-fold. The normal daily retention averaged 6.50 g. of Ca and 3.25 g. of P. The ratio of Ca : P retained was unaffected by the mineral content of the ration and was unchanged by -D deficiency. Calves store -D which may subsequently be utilised under adverse conditions. A. G. P.

**Utilisation of different magnesium salts.** J. C. FORBES and F. P. PRITS (J. Amer. Pharm. Assoc., 1935, 24, 450—452).—The average weekly Mg absorption and retention (by rats) of different Mg salts over a period of 5—6 weeks was approx. the same for each salt, i.e., 29—41% of the intake (av. 32.5%). Linseed meal, lucerne,  $MgCl_2$ , and Mg lactate were the sources of Mg. Addition of  $\geq 2\%$  of  $Na_2CO_3$  to the diet had no unfavourable effect on the Ca, P, or Mg utilisation. E. H. S.

**Biological action of metals irradiated with a mercury-quartz lamp. II. Effect of irradiated iron on the growing organism.** J. M. GOLDBERG (Acta med. Scand., 1934, 83, 573—595; Chem. Zentr., 1935, i, 919).— $Fe(OH)_3$  solution irradiated with a Hg-quartz lamp increases the rate of growth of chickens and children. R. N. C.

**Iodine content of Indian foodstuffs.** M. PATNAIK (Indian J. Med. Res., 1934, 22, 249—262). R. N. C.

**Environmental selection of the fresh-water sponges (*Spongillidae*) of Michigan.** M. C. OLD (Trans. Amer. Microscop. Soc., 1932, 51, 129—136).—Species distribution is examined in relation to  $pH$  ranges. Only *S. fragilis* tolerated the whole range examined ( $pH$  4.2—9.2). Sponges occurred in  $H_2O$  having free  $CO_2$  0—33, alkalinity to phenolphthalein of 0—22 (as  $CaCO_3$ ) and to Me-orange 19—270 p.p.m. (as  $CaCO_3$ ). All Michigan species preferred  $H_2O$  containing no carbonates. CH. ABS. (p)

**Alcoholism. IV. Modification of blood-alcohol after intravenous administration of alcohol.** R. FLEMING and D. REYNOLDS (J. Pharm. Exp. Ther., 1935, 54, 236—245).—Diathermic increase



in body-temp. appears to increase the rate of disappearance of EtOH from blood in man. Administration of adrenaline, insulin, caffeine, CO<sub>2</sub>, O<sub>2</sub>, olive oil, 0.9% aq. NaCl, or MgSO<sub>4</sub> is without effect.

F. O. H.

[Physiological effects of] cholesterol. S. MINOVICI and M. VANGHELOVICI (J. Chem. Educ., 1934, 11, 637—639).—Physiological effects are discussed. A biochemical synthesis of cholesterol from oleic acid by enzymes of liver or spleen is indicated.

CH. ABS. (p)

Lipin metabolism. I. Variation in cholesterol content of blood and of different organs in pigeons consequent on administration of chloroform. N. C. DATTA (Indian J. Med. Res., 1934, 22, 353—364).—Repeated inhalation of CHCl<sub>3</sub> in pigeons produces an increase in blood-cholesterol (I) during the first 2 months, followed by a fall. Body-wt. falls as blood-(I) rises. (I) in brain, lungs, heart, and kidney is not affected; liver-(I) falls slightly. Adipose tissue-fat is not formed during CHCl<sub>3</sub> administration. There is no definite relation between blood-(I) and the red-cell count, which remains const. as (I) increases, but falls considerably with (I).

R. N. C.

Relation of  $p_H$  and surface tension to the activity of local anaesthetics. J. H. GARDNER and J. SEMB (J. Pharm. Exp. Ther., 1935, 54, 309—319).—Although both the lowering of  $\gamma$  and the anaesthetic activity vary with  $p_H$ , no correlation was observed between these two factors for individual compounds (morpholine derivatives, procaine, cocaine).

H. G. R.

Relative anaesthetic effects of various carbamides. J. S. BUCK, A. M. HJORT, and E. J. DE BEER (J. Pharm. Exp. Ther., 1935, 54, 188—212; cf. this vol., 118).—With aliphatic carbamides the hypnotic potency decreases in the following order: monoalkyl-, *s*-dialkyl- (Me series) (methyl-*n*-propyl, m.p. 61°; -*n*-butyl-, m.p. 72°; -*n*-amyl, m.p. 79°), *as*-dialkyl- (ethyl-*n*-propyl, m.p. 54°; *di*-*n*-amyl, *s*-dialkyl- (Et series) (ethyl-*n*-propyl, m.p. 80°; -*n*-butyl-, m.p. 61°; -isobutyl-, m.p. 53°; -*n*-amyl, m.p. 59°), and trialkyl-carbamides ( $\alpha$ -dimethylethyl-, m.p. ca. 58°; methyl- $\alpha$ -diethyl-, m.p. 49°; methyl- $\alpha$ -*di*-*n*-propyl-, m.p. 63°; ethyl- $\alpha$ -*di*-*n*-propyl-, m.p. 63°; methyl-, b.p. 134°/0.7 mm., and ethyl- $\alpha$ -*di*-*n*-butyl-, b.p. 123°/0.65 mm.). Mol. wt. is a determining factor with alkyl- but not aryl- (*m*-anisyl, m.p. 133°; 3:4-dihydroxy-, m.p. 171°, and 4-dimethylamino- $\beta$ -phenylethyl, m.p. 129°) or alkylaryl-carbamides ( $\alpha$ -ethyl- $\beta$ -*m*-tolyl, m.p. 101°;  $\alpha$ -ethyl- $\alpha$ -*p*-tolyl, m.p. 97°;  $\alpha$ -ethyl- $\beta$ -phenylethyl, m.p. 79°;  $\alpha$ -*di*-*n*-butyl- $\beta$ -phenyl, m.p. 86°).

$\gamma$ -Hydroxypropyl-, m.p. 123°, *as*-*di*- $\beta$ -hydroxyethyl-, m.p. 80°, cyclopentyl-, m.p. 197°, butanedi-, m.p. 226° (decomp.), *as*-*di*- $\gamma$ -hydroxypropyl-, m.p. 148°, and 6:7-dimethoxytetrahydroisquinolyl-carbamide, m.p. 195°, are described.

F. O. H.

Cocaine, alcohol, dinitrophenol, and methylene-blue in experimental poisoning by barbiturics. A. ALLEGRI (Boll. Soc. Ital. Biol. sperim., 1935, 10, 48—51).—Cocaine and C<sub>6</sub>H<sub>5</sub>(NO<sub>2</sub>)<sub>2</sub>·OH show slight therapeutic effects in guinea-pigs, and

EtOH in rabbits, poisoned by barbiturics; methylene-blue is without effect.

R. N. C.

Thiobarbiturates. E. MILLER, J. C. MUNCH, and F. S. CROSSLEY (Science, 1935, 81, 615).—Some thiobarbiturates show promise as sedatives, being free from the side actions and after-effects observed with their O analogues.

L. S. T.

Local anaesthetics. Phenylprocaine. W. BRAKER and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1935, 24, 358—363).—Phenylprocaine hydrochloride (I) is considerably more active than cocaine hydrochloride and novocaine in the guinea-pig and on the rabbit's cornea. (I) is the most active in a series of analogous Ph derivatives of procaine, although, owing to pptn. on the addition of buffers and irritation in corneal and intradermal tests, it does not appear to be of practical therapeutic val. 5-Nitro-2-cyanodiphenyl, m.p. 131—133° (from the 2-NH<sub>2</sub>-carboxylic acid, reduced to the NH<sub>2</sub>-compound (II), the hydrochloride, m.p. 230°, of which is converted into the 2- $\beta$ -diethylaminoethyl ester dihydrochloride (I), hygroscopic, and the 2-dibutylaminopropyl ester, an oil (hydrochloride). (II) yields a chloride, b.p. 175—183°/2—3 mm., an *N*-Bu derivative (converted into the 2- $\beta$ -diethylaminoethyl ester hydrochloride), and the 4-Cl-derivative, the 2- $\beta$ -diethylaminoethyl ester of which was obtained as dihydrochloride, hygroscopic. 4-Amino-2- $\beta$ -diethylaminoethylcarbamyl-diphenyl hydrochloride was comparatively, and  $\beta$ -diethylaminoethyl 4-aminodiphenyl-2'-carboxylate was completely, inactive.

M. T.

[Pharmacological] activity of cocaine salts. J. RÉGNIER and R. DAVID (J. Pharm. Chim., 1935, [viii], 22, 16—22).—The anaesthetic activities of cocaine salts increase in the order hydrochloride, formate, acetate, salicylate, benzoate, phenylacetate. Salts of org. acids are more active than those of inorg. acids.

H. G. R.

Cardiac automaticity effects of caffeine and nicotine. Influence of (I) caffeine, (II) nicotine, and (III) caffeine-nicotine antagonism on the sino-aortic strip response. R. H. CHENEY (J. Pharm. Exp. Ther., 1935, 54, 213—221, 222—229, 230—235).—I. Low concns. of caffeine increase the amplitude of contractions in sino-aortic strips (frog); higher concns. diminish it and produce irregularities in rhythm.

II. Nicotine (0.2%) in Ringer's solution decreases frequency and amplitude and increases tonus. Only a slight stimulation occurs with a concn. of 0.05%.

III. The antagonism is investigated with reference to the automaticity of the strip and its physiological characteristics. Complete antagonism exists between 95 c.c. of 0.2% caffeine and 5 c.c. of 2.0% nicotine.

F. O. H.

Action of caffeine-containing and caffeine-free coffee on basal metabolism. E. MEYER (Z. Unters. Lebensm., 1935, 69, 563—570).—Ordinary coffee caused in six normal subjects and in four subjects suffering from hyperthyroidism or hypertonia a marked increase in basal metabolism, whilst caffeine-free coffee caused little or no increase.

E. C. S.



**Action of drugs on liver-glycogen.** Y. AOYAMA (Japan. J. Med. Sci., IV, 1933, 7, 21—22).—Perfusion of male toads with adrenaline, pilocarpine, or eserine increased sugar mobilisation, ergotoxine was without action, atropine caused slight inhibition, and choline a definite decrease. CH. ABS. (p)

**Action of papaverine on blood-sugar of rabbits.** A. RO (Japan. J. Med. Sci., IV, 1933, 7, 9—10).—Small doses of papaverine stimulate the adrenal gland, causing hyperglycaemia; larger doses inhibit adrenal action and induce hypoglycaemia. CH. ABS. (p)

**Micro-determination of morphine in the brain.** I. KABASAWA (Japan. J. Med. Sci., IV, 8; Proc. Japan. Pharmacol. Soc., 1934, 97—98).—Minced tissue is decomposed by papain at 65—70° for 20—80 min. Morphine (I) is extracted with dil. HCl, Et<sub>2</sub>O-sol. matter is removed, and the tissue warmed with 3% HCl on a water-bath for 6 hr. After addition of NH<sub>3</sub> to pH 8.3 (I) is extracted (Soxhlet) with CHCl<sub>3</sub>-EtOH mixture. (I) is recovered from the extract with dil. HCl and the vol. of the liquid adjusted to about 25 c.c. and to contain approx. 0.005N-HCl. The concn. of (I) is adjusted to approx. 1 mg. per c.c. and sufficient I solution is added so that after pptn. of (I) iodide 1 c.c. of the filtrate requires >1.1 c.c. of 0.005N-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The temp. must be < 30°. CH. ABS. (p)

**Hyperglycaemic action of opium alkaloids.** H. GYOKU (Japan. J. Med. Sci., IV, 1933, 7, 101—103; cf. this vol., 528).—When injected intravenously into rabbits (2—50 mg. per kg.) morphine, codeine, and heroin were more potent hyperglycaemics than thebaine, although all contain the phenanthrene nucleus. *iso*Quinoline derivatives, papaverine, narceine, and narcotine had a much weaker action. Pantopon produced the greatest response. CH. ABS. (p)

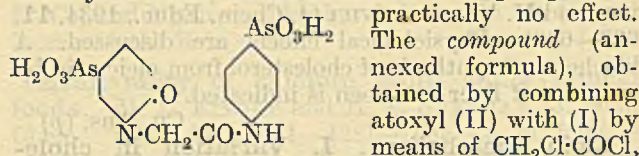
**Action of opium alkaloids on the rabbit uterus *in situ*.** S. HORIKOSHI (Japan. J. Med. Sci., IV, 1933, 7, 103—104).—Morphine (I), heroin (II), and codeine stimulated the uterus more strongly than did thebaine. Pantopon had a weaker action than (I) or (II). Narcotine and narceine were without effect (cf. preceding abstract). CH. ABS. (p)

**Pharmacology of arecoline.** K. KYU (Japan. J. Med. Sci., IV, 1933, 7, 7—9).—The potency of arecoline was equal to that of acetylcholine and > that of pilocarpine, eserine, or muscarine. CH. ABS. (p)

**Sedative action of antipyretics.** T. YAO (Japan. J. Med. Sci., IV, 1934, 7, 103).—In experimentally induced toothache (electrical stimulation) antipyrene sedatives were more effective than those of the salicylic acid type. Na salicylate and salipyrine increased the stimulation threshold. CH. ABS. (p)

**Biochemistry and medicinal significance of new pyridine derivatives.** A. BINZ (Angew. Chem., 1935, 48, 425—429).—3-Iodopyridine, pyridine-3-antimony chloride, and, especially, pyridine-3-arsinic acid are more toxic than C<sub>5</sub>H<sub>5</sub>N. The hydroxypyridines, although more toxic than C<sub>5</sub>H<sub>5</sub>N, are not as toxic as PhOH; when they are condensed with CH<sub>2</sub>Cl·CO<sub>2</sub>H, the resultant pyridoneglycines,

and the corresponding I-derivatives, are (unexpectedly) very slightly toxic. 2-Pyridone-5- (I) and 4-pyridone-3-arsinic acids have an exceptionally high tolerance but 2-pyridone-5-stibinic acid is less stable and more toxic. N-Alkylation of (I) greatly increases the toxicity but the introduction of ·CH<sub>2</sub>·CO<sub>2</sub>H has



has twice the tolerance of (II). 3-Amino-2-pyridone-5-arsinic acid is similar to (I), but 2-amino-, 2-ethylamino-, and 2-diethylamino-pyridine-5-arsinic acids (from the 2-chloroarsinic acid and the alkylamine) are 0.5, 5, and 50 times as toxic as C<sub>5</sub>H<sub>5</sub>N, respectively. The therapeutic properties of the iodopyridones and the pyridonearsinic acids are discussed. S. C.

**Toxicology of pyridine and its homologues (Wernicke encephalitis).** H. LUDWIG (Arch. Gewerbepath. Gewerbehyg., 1934, 5, 654—664).—Symptoms are described. R. N. C.

**Urobilinuria: false Ehrlich reaction caused by pyridium medication.** J. W. FARTHING and J. S. P. BECK (J. Lab. Clin. Med., 1934, 20, 61—62).—The false positive reaction with Ehrlich's reagent given by urines containing pyridium is due to the action on this of HCl used in preparing the reagent. Urines giving a positive test should be treated with HCl alone to detect the dye. CH. ABS. (p)

**Adrenolytic action of phenoxyamines in the rabbit.** J. LÉVY and L. ŒLSZYCKA (Compt. rend. Soc. Biol., 1935, 119, 899—902).—Phenoxyamines, ergot, and yohimbine—the so-called "sympatholytics"—antagonise, but do not invert, the pressor action of adrenaline. R. N. C.

**Substances affecting the circulation in "eutonon" liver extract.** H. A. HEINSEN (Klin. Woch., 1934, 13, 1597—1599; Chem. Zentr., 1935, i, 918).—"Eutonon" can be separated into a pressor and a depressor fraction by making strongly alkaline with Na<sub>2</sub>CO<sub>3</sub> and extracting with C<sub>5</sub>H<sub>11</sub>·OH. The C<sub>5</sub>H<sub>11</sub>·OH fraction contains tyramine, and the H<sub>2</sub>O fraction choline. R. N. C.

**Action of certain new histamine derivatives.** A. VARTIAINEN (J. Pharm. Exp. Ther., 1935, 54, 265—282).—All the alkylhistamines substituted in the NH<sub>2</sub> show some histamine-like activity. That of the Me<sub>1</sub> derivative is weaker on the blood-vessels but stronger on the uterine and intestinal muscles. The Me<sub>2</sub> derivative has 1/5—2/5 of the activity of histamine and a weak nicotine-like action, which becomes predominant in the NMe<sub>3</sub> base. The Et<sub>1</sub> derivative has 1/20 of the activity of histamine and hydroxyethylgloxaline a weak stimulating action on plain muscle. H. G. R.

**Interaction between acetylcholine and sterols in tissues.** G. S. CARTER and L. W. MAPSON (Nature, 1935, 136, 143—144).—Addition of a sterol or of acetylcholine (I) to the gastrocnemius muscle of a frog in the resting winter condition leads to a prolonged contraction. When added together in the



correct proportion, which, however, varies with different sterols, only a normal twitch is observed even when concn. is increased. Like (I), sterols weaken and retard the beat of the frog's heart, but when added together in the correct proportion the effect on the heart is reduced or disappears. The results suggest that sterols play a part in the same chemical processes as those in which (I) is concerned. L. S. T.

**Occurrence of unstable choline esters in invertebrates.** Z. M. BACQ (Nature, 1935, 136, 30—31).— $\text{CCl}_3\cdot\text{CO}_2\text{H}$  extracts of various tissues of *Octopus vulgaris* contain a substance, probably acetylcholine, which possesses the physiological properties of unstable choline esters. In some invertebrates, at least, conditions for cholinergic nervous action appear to be realised. L. S. T.

**Action on the rabbit's isolated intestine of an acetylcholine-sensitising substance formed in the trunk of the pneumogastric nerve by electric excitation.** C. NOCHIMOWSKI (Compt. rend. Soc. Biol., 1935, 119, 943—946).—Extracts of the peripherally or centrally excited pneumogastric of the dog increase the effect of acetylcholine on the isolated rabbit's intestine. Previous isolation of the nerve before excitation does not inhibit formation of the sensitising substance. R. N. C.

**Colour changes in the catfish *Ameiurus* in relation to neurohumours.** G. H. PARKER (J. Exp. Zool., 1934, 69, 199—233).—The nature of these secretions and their action on the chromatophores are examined. CH. ABS. (p)

**New active principle of ergot.** H. W. DUDLEY and J. C. MOIR (Science, 1935, 81, 559—560).—Concerning nomenclature. L. S. T.

**New active principle(s) of ergot.** M. S. KHARASCH and R. R. LEGAULT (Science, 1935, 81, 614—615).—A reply to the above. L. S. T.

**New active principle of ergot.** M. R. THOMPSON (Science, 1935, 81, 636—639).—Concerning nomenclature and priority (cf. preceding abstract). L. S. T.

**New active principle of ergot.** M. R. THOMPSON (Science, 1935, 82, 62—63).—A correction (cf. preceding abstract) and a reply to criticism. Pure ergotetrine, m.p. 161—163° (decomp.), is dextrorotatory in  $\text{H}_2\text{O}$ ,  $\text{EtOH}$ , and  $\text{CHCl}_3$ . L. S. T.

**Pharmacological effects of ergometrine, a new alkaloid of ergot.** RAYMOND-HAMET (Compt. rend., 1935, 201, 176—179).—The pharmacological effects are compared with those of other ergot alkaloids. H. G. R.

**Ergobasine, a water-soluble alkaloid from ergot of rye.**—See this vol., 995, 1137.

**Action of ergoclavine and sensibamine.** A. VARTIAINEN (J. Pharm. Exp. Ther., 1935, 54, 259—264).—The pharmacological activities of these alkaloids are identical with those of ergotoxine and ergotamine. H. G. R.

**Vegetable extracts and blood-sugar.** P. S. JORGENSEN and E. V. LYNN (J. Amer. Pharm. Assoc., 1935, 24, 389—392).—Contrary to previous reports no evidence could be found of activity of plant

extracts in reducing normal or high blood-sugar levels. M. T.

**Some common [Indian] indigenous remedies.** R. N. CHOPRA and S. GHOSH (Indian J. Med. Res., 1934, 22, 263—270).—The chemical composition, pharmacological actions, and therapeutic properties of a no. of plant extracts are described. R. N. C.

**Phloridzin diabetes. II.** E. S. LONDON, N. KOTSCHNEV, F. I. RIVOSCH, L. I. KRIZANOVSKAJA, R. R. PADVE, and N. B. MANUSSOVA (Arch. exp. Path. Pharm., 1935, 178, 700—718; cf. A., 1933, 746).—Continuous subcutaneous or single intravenous injection of phloridzin (I) into dogs produces disturbances in carbohydrate metabolism in which the kidney is not the only organ involved. Liberation of sugar occurs in the liver and retention in kidney, intestine, and muscle, whilst liberation of glycogen into the blood by the kidney is initiated. The arterial blood- $\text{AcCO}_2\text{H}$  and  $\text{-AcCHO}$  decrease, whilst lactic acid increases. Determinations of P fractions in the blood from various vessels indicate that phosphorylation and dephosphorylation processes are significantly modified by (I); *in-vitro* experiments are misleading (cf. Lundsgaard, A., 1933, 1076). The blood- $\text{PO}_4'''$  of young dogs (normal or phloridzinised) is  $>$  that of adult dogs. (I) increases the blood contents of  $\text{NH}_2$ -acid- and polypeptide-N and total glutathione. These and data from other tissues indicate that (I) diabetes is exclusively neither of renal origin nor concerned with P fractions, but is a general intoxication one symptom of which is glycosuria. F. O. H.

**Pharmacological action of taxin.** C. S. LIM (Japan. J. Med. Sci., IV, 1934, 8, 121—122).—Doses of 4 mg. per kg. decreased the normal blood-sugar and glucose-hyperglycæmia but did not affect adrenaline-hyperglycæmia. 50—200 p.p.m. of taxin caused depression of the isolated heart and tissue constriction in toads. CH. ABS. (p)

**Active constituents of *Podophyllum plectanthum*, Hance.** S. To (Japan. J. Med. Sci., IV, 1933, 7, 15—16).—The active constituent resembles podophyllotoxin. Analytical data are given. CH. ABS. (p)

**Polarimetric determination of physiological activity of hemp resin.** M. N. GHOSE and S. N. BHATTACHARJEE (Analyst, 1935, 60, 313—316).—The physiological activity of charas and ganja, as estimated by a panel of experienced smokers from the degree of intoxication produced,  $\propto$  the  $[\alpha]_D$  of the  $\text{CCl}_4$  extract of the drug. E. C. S.

**Relative toxicities of pyrethrins I and II.** J. RIPERT and O. GAUDIN (Compt. rend., 1935, 200, 2219—2220).—Staudinger's method of isolating pyrethrins gives degraded products. The pure substances are best obtained by preferential extraction of pyrethrin II from ligroin by 82%  $\text{MeOH}$ . Pyrethrin I causes only slow paralysis of fish, but pyrethrin II causes also a preliminary excitation. Doses of pyrethrins I and II and a 1:1 mixture thereof which give a 50% mortality when injected into snails are 0.8, 0.75, and 0.66 mg. per kg. body-wt., respectively. R. S. C.



**Action of cardiotonics on frog hearts.** T. TAKABE (Japan. J. Med. Sci., IV, 1934, 8, 138—141).—In dynamic tests, digitalis, camphor (I), hexetone (II), and coramine (III) strengthened the abs. contractions and increased the beat vol., digitalis acting chiefly on the abs. contractile power. Cardiazole slightly affected the beat vol. Strophanthin, strychnine, and caffeine had a weak stimulative action on contractile power. (III) decreased, and digitalis and (I) increased, the rate, whereas (II) had no action. CH. ABS. (p)

**Biological assay of digitalis preparations in the tropics.** V. Potency of lanadigin (glucoside of *D. lanata*) and its relation to the standard powder (B.P. 1932). R. N. CHOPRA, J. S. CHOWHAN, and S. LAL (Indian J. Med. Res., 1934, 22, 279—283).—Lanadigin shows the same physiological potency as the glucosides of *D. purpurea*; it can be sterilised by boiling, and deteriorates less rapidly in the tropics than the *D. purpurea* glucosides.

R. N. C.

**Potency of Oregon digitalis.** D. K. LEE and E. T. STUHR (J. Amer. Pharm. Assoc., 1935, 24, 367—369).—A comparative study of seasonal physiological activity of wild *D. purpurea*, L.

M. T.

**Bioassay of digitalis. III. Diuretic, oliguric cat method.** J. H. DEFENDORF (J. Amer. Pharm. Assoc., 1935, 24, 369—374).

M. T.

**Action and toxicity of retrorsine.** K. K. CHEN, A. L. CHEN, and C. L. ROSE (J. Pharm. Exp. Ther., 1935, 54, 299—305).—Retrorsine has a depressor and a hyperglycæmic action and contracts the guinea-pig uterus. The guinea-pig is less susceptible than the mouse, the min. lethal dose being 0.32 g. per kg., whereas 0.2 g. per kg., injected intravenously, causes death in the mouse.

H. G. R.

**Blood changes caused by ophidian venoms. III. Variations in alkaline reserve.** J. VELLARD and M. MIGUELOTE-VIANNA (Ann. Inst. Pasteur, 1935, 55, 148—152; cf. this vol., 398).—A much smaller decrease in the alkaline reserve of the blood of dogs is observed on injection of *Naja tripudians* venom than with venoms from *Crotalinae*. This is attributed to the curarising effect of the former.

E. A. H. R.

**Variations in the reaction of different parts of the central nervous system as influenced by depressant and stimulating drugs.** D. E. JACKSON (J. Lab. Clin. Med., 1934, 20, 1—13).—The varied effects of metrazole on dogs anaesthetised with  $\text{Et}_2\text{O}$ , evipal, and with  $\text{C}_2\text{HCl}_3$  are recorded.

CH. ABS. (p)

**Influence of bile acids on phosphorylation of adenylic acid in liver and muscle.** K. WATANABE (J. Biochem. Japan, 1935, 21, 203—209).—Phosphorylation of adenylic acid to adenylypyrophosphoric acid occurs in liver and muscle *in vitro* and is enhanced, especially in muscle, by 0.1% Na cholate. This agrees with the respective dephosphorylating activities (A., 1911, ii, 412).

F. O. H.

**Influence of bile acids on urinary ammonia excretion.** Y. KAWADA (J. Biochem. Japan, 1935, 21, 213—218).—Intravenous or oral administration of cholic acid to dogs produces a transient decrease in

the  $\text{NH}_3$  content and sp. gr. of the urine; the vol. excreted tends to increase.

F. O. H.

**Bile acids and calcium metabolism. X. Urine- and bile-calcium in normal and thyro-parathyroidectomised dogs.** S. TUZIOKA (J. Biochem. Japan, 1935, 21, 219—241).—Excretion of Ca in urine and, more especially, in bile is increased in dogs by subcutaneous and, to a greater extent, oral administration of cholic acid. Thyro-parathyroidectomy diminishes the vol. of bile and Ca excretion in bile and urine; subsequent administration of cholic acid increases the vals. but not to normal levels. Following the operation, tetany occurs more readily in dogs with biliary fistulæ than in normal dogs, but is offset by injection of cholic acid. Thus tetany is related to liver function.

F. O. H.

**Salt and water losses in diuretin diuresis and their relation to serum-non-protein-nitrogen and -electrolyte concentrations.** E. KERPEL-FRONIUS and A. M. BUTLER (J. Exp. Med., 1935, 61, 157—172).—Losses are shown of Na, K, Cl, N, and  $\text{H}_2\text{O}$  together with changes in serum-Na, -Cl, -non-protein-N, and -total protein following administration of diuretin to rabbits. No relationship is apparent between the occurrence of azotæmia and the coincident hypo-chloræmia. Administration of  $\text{H}_2\text{O}$  without salt prevents N retention and lowers the serum-electrolyte and -protein. The efficiency of NaCl in preventing the withdrawal of K, Na, and Cl after diuretin treatment is examined.

CH. ABS. (p)

**Effect, in the dog, of sinus blockage on the adrenaline, sugar, and calcium content of blood, and on the oxygen requirements.** U.S. VON EULER and G. LILJESTRAND (Skand. Arch. Physiol., 1934, 71, 73—84).—Blockage of both carotids of anaesthetised dogs caused rise of blood-pressure,  $\text{O}_2$  consumption, and adrenaline content of the blood. Blood-sugar and -Ca were unchanged. After extirpation of adrenals, blockage still caused rise of blood-pressure, but almost no rise in  $\text{O}_2$  consumption.

G. H. F.

**Effect of iodoacetic acid on rabbit muscle.** Y. NISHITA (Japan. J. Med. Sci., IV, 1934, 8, 117).—Subcutaneous injection of 5% solution of  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$  in  $\text{NaHCO}_3$  (50 mg. per kg. wt.) into rabbits increased the blood-sugar (I) and -lactic acid (II) and decreased the  $\text{CO}_2$ -combining power. Section of both splanchnic nerves lowered the alteration in blood-(I) and -(II) but did not affect that of the  $\text{CO}_2$ -combining power.

CH. ABS. (p)

**Iodoacetic acid and glycosuria.** G. PERETTI (Boll. Soc. Ital. Biol. sperim., 1935, 10, 77—79).—Small doses of  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$  injected into rats or rabbits produce variable increases of urinary sugar. Injection of one kidney only with  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$  in the dog produces no difference between the sugar contents of the urine excreted from the two kidneys.

R. N. C.

**Does methylene-blue form methæmoglobin?** M. M. BROOKS (Proc. Soc. Exp. Biol. Med., 1934, 31, 1134—1137; cf. A., 1934, 912).—With rats and dogs, intravenous injection of methylene-blue (I) did not produce detectable amounts (spectrophotometer) of methæmoglobin (II). Only oxyhæmoglobin



was found. Hence recovery of HCN- and CO-poisoned animals treated with (I) is not due to formation of (II), but probably results from the catalytic action of (I) in transferring  $O_2$ . CH. ABS. (p)

Basal metabolism and the dyestuffs methylene-blue, neutral-red, and malachite-green (in rats). A. H. ROFFO and R. L. RAMÍREZ (Rev. Asoc. Med. Argentina, 1932, 46, 901—904).—Intravenous injection of methylene-blue reduces basal metabolism. Neutral-red and malachite-green have no action. CH. ABS. (p)

Action of hexenol from tea leaves. I. S. MURAKAMI (Japan. J. Med. Sci., IV., 1934, 8, 136—137).— $\Delta^6$ -Hexen- $\alpha$ -ol obtained by distillation of raw leaves resembled hexyl alcohol in its action on the frog heart and in lowering the blood-pressure in rabbits. CH. ABS. (p)

Resistance of fixed tissue cells to the toxic action of certain chemical substances. W. DE B. MACNIDER (Science, 1935, 81, 602—605).—A lecture. L. S. T.

Influence of bromobenzene on the glutathione content of tissues. K. FUJII (Japan. J. Med. Sci., IV, 1933, 7, 84—86).—Following injection of PhBr (4500 mg. per kg.) into frogs, mice, and rats, the glutathione content was increased in heart, lungs, spleen, and pancreas and decreased in liver, kidneys, muscle, and testicles. CH. ABS. (p)

Excretion of sodium salicylate. C. MEI (Japan. J. Med. Sci., IV, 1933, 7, 98).—Acidosis delays and alkalosis increases excretion of Na salicylate (I). Injection of (I) lowers HCl-acidosis and delays excretion, but has no effect on  $NaHCO_3$ -alkalosis although excretion is hastened. Administered alone (I) increases the plasma- $pH$  over a 6-hr. period. CH. ABS. (p)

Toxicology of phenols. C. GERIN (Boll. Chim. farm., 1935, 74, 465—468).—With tissue-protein PhOH forms a compound which is decomposed by  $Na_2CO_3$  but not by acids. Factors (e.g., putrefaction) influencing the content of phenolic substances in normal tissue and urine are discussed and a method for their determination in viscera etc. is described. F. O. H.

Anthelmintic properties of certain alkylphenols. P. D. LAMSON, H. W. BROWN, and P. D. HARWOOD (Amer. J. Trop. Med., 1934, 14, 467—478).—Comparison is made of *o*- and *p*-alkylphenols, 4-alkylresorcinols, and 6-alkylresols by the *Ascaris* method *in vitro*. The lower and higher members of each series were inactive whereas those having 4—7 C in the side-chain were active. With increasing length of the side-chain toxicity decreased, but irritation of the alimentary tract increased. *o*-Heptylphenol and hexyl-*m*-cresol gave best results *in vitro*, but on man infected with *Ascaris* and hookworm were disappointing. CH. ABS. (p)

Effect of 2:4-dinitrophenol on oxygen consumption, blood-sugar, and cholesterol. V. EMMER (Compt. rend. Soc. Biol., 1935, 119, 1137—1140).—Administration of 2:4- $C_6H_3(NO_2)_2 \cdot OH$  to patients causes a rise of  $O_2$  consumption, which reaches its max. in 4—5 hr. Blood-sugar rises steadily,

whilst cholesterol varies irregularly, diminishing in most cases. R. N. C.

Vago-inhibitory effects on the respiratory metabolism of the heart after treatment with dinitrophenol. W. E. GARREY and J. T. BOYKIN (Amer. J. Physiol., 1935, 111, 196—200).—The respiratory metabolism of resting cardiac muscle is augmented by  $C_6H_3(NO_2)_2 \cdot OH$  *in vitro*,  $O_2$  consumption being increased approx. 3 times. Vagus inhibition is still effective, stimulation causing a decrease of  $O_2$  consumption in resting turtle's auricles, which is of the same order of magnitude as for normal resting auricles. R. N. C.

Spleen and experimental hyperthermia. M. RUBINSTEIN (Med. Doswiad. Spol., 1934, 19, 91—113).—Splenectomy diminished the fever response to 2:4-dinitrophenol (I). The glutathione content of the spleen of febrile dogs was < normal, the alkali reserve of the blood was lowered, and the red-cell-Cl increased. Alkaline solutions of (I) induced more intense fever than did neutral solutions. CH. ABS. (p)

Toxicology of aromatic nitro-compounds. I. 2:4-Dinitrophenol. A. I. TSCHERKESS, V. F. MELNIKOVA, and S. M. DUBASCHINSKAJA (Arch. exp. Path. Pharm., 1935, 179, 1—14).—The lethal dose of 2:4-dinitrophenol (I) (administered orally, subcutaneously, through the skin, or by inhalation) for dogs, cats, rabbits, pigeons is 15—50 mg. per kg. body-wt. The symptoms produced by lethal or nearly lethal doses are accelerated respiration, high fever (temp. up to 42—45°), hyperglycaemia, and increase of lactic acid and ketone contents with decrease in the alkali reserve of the blood, increased  $O_2$  consumption, and increased  $CO_2$  production. These results, which are not affected by preceding administration of drugs [ $CCl_3 \cdot CH(OH)_2$ , luminal, salicylate] which act on the central nervous system, indicate that (I) acts by stimulating tissue-oxidations. W. McC.

Effect of dinitro- $\alpha$ -naphthol on blood-cholesterol in man. L. F. GRANT and P. G. SCHUBE (J. Lab. Clin. Med., 1934, 20, 56—61).—Daily oral administration of dinitronaphthol causes a temporary increase of blood-cholesterol followed by a decline to < initial vals. and a slow return to normal. CH. ABS. (p)

Metabolism of naphthalene in adult and growing dogs. J. A. STEKOL (J. Biol. Chem., 1935, 110, 463—469).— $\alpha$ -Naphthylmercapturic acid was isolated from the urine; the latter also contained an ethereal sulphate, possibly a naphthol conjugation product with  $H_2SO_4$ . There was an increased output of glycuronic acid in the urine after administration of  $C_{10}H_8$ . J. N. A.

Curative action of 2:4-diamino-4'-sulphonamidoazobenzene hydrochloride and similar derivatives in experimental streptococcal infection. C. LEVADITI and A. VAISMAN (Compt. rend. Soc. Biol., 1935, 119, 946—949).—The curative action of rubiazol is sp. for streptococcal infections. Azoi-4 is the most therapeutically active azo-derivative against streptococci. Rubiazol and prontosil are equally effective, whilst Na 4-sulphonamido-



benzeneazo-7-acetamido- $\alpha$ -naphthol-3:6 disulphonate is least effective. The action of azo-compounds is to inhibit encapsulation of the streptococci, and to facilitate phagocytosis. R. N. C.

**Combinations of different qualities of taste as a method of investigating the chemical sense of the earthworm.** O. MANGOLD (Naturwiss., 1935, 23, 472—474).—Earthworms prefer pure gelatin (I) to (I) containing NaCl, quinine, or dulcitol, but (I) containing  $\text{H}_2\text{C}_2\text{O}_4$  is preferred to pure (I). Combinations of the four taste substances exert in general an additive effect except that the preference for  $\text{H}_2\text{C}_2\text{O}_4$  is specially effective in such combinations. W. O. K.

**Fate of oxalic acid in dogs.** G. ORZECOWSKI, P. GÖMÖRI, and M. HUNDRIESER (Arch. exp. Path. Pharm., 1935, 178, 739—748).— $\text{H}_2\text{C}_2\text{O}_4$  fed to dogs is excreted unchanged, no decomp. occurring in the organism. F. O. H.

**[Fate of oxalate in] oxalate-poisoned dogs.** W. HEUBNER and R. HÜCKEL (Arch. exp. Path. Pharm., 1935, 178, 749—754).—Histological appearance of the kidney and oxalate content of various organs in dogs poisoned with  $\text{Na}_2\text{C}_2\text{O}_4$  are recorded. The prolonged retention of oxalate by the kidney is noteworthy. F. O. H.

**Toxicology of petrol.** L. M. FRUMIN and S. S. FAINSTEIN (Zentr. Gewerbehyg. Unfallverhütg., 1934, 21, 161—165; Chem. Zentr., 1935, i, 1087).—The toxic effects of petrol vapours on workers in the rubber industry are described. R. N. C.

**Propeptan therapy.** E. URBACH and S. KITAMURA (Klin. Woch., 1934, 13, 1573—1578).—Egg-propeptan induces contraction of uterus from guinea-pig sensitised with it; the reaction is sp. Anaphylactic shock in guinea-pigs can be prevented by administration of minimal doses of antigen, or of the sp. propeptan. G. H. F.

**Relationship between anaphylaxis and magnesium chloride.** C. Y. CHOI (J. Chosen Med. Assoc., 1934, 24, 1249—1257).—Injection of 0.25 c.c. of 1% aq.  $\text{MgCl}_2$  into guinea-pigs either before sensitisation with or before re-injection of horse-serum did not prevent anaphylaxis. The latter was inhibited by use of 0.25—0.5 c.c. of 3% aq.  $\text{MgCl}_2$ . CH. ABS. (p)

**Methylene-blue, methæmoglobin, and cyanide poisoning.** W. B. WENDEL (J. Pharm. Exp. Ther., 1935, 54, 283—298).—The author's previous conclusions are confirmed (cf. A., 1934, 1400). H. G. R.

**Importance of moisture in poisoning with carbon dioxide and with illuminating gas in mice.** L. DI BELLA (Boll. Soc. Ital. Biol. sperim., 1935, 10, 14—16).—The toxicities of the gases increase  $\propto$  their solubilities in  $\text{H}_2\text{O}$  when they are inhaled together with  $\text{H}_2\text{O}$  vapour. R. N. C.

**Anæsthetic properties of carbon monoxide and other gases in relation to plants, insects, and centipedes.** P. W. ZIMMERMANN (Contr. Boyce Thompson Inst., 1935, 7, 147—155).—Min. anæsthetic concns. of  $\text{CO}$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_4\text{H}_8$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ , and  $\text{CO}_2$  for various insects and centipedes are recorded.  $\text{C}_4\text{H}_8$

was the most and  $\text{C}_2\text{H}_4$  the least effective. Insects remained normal in  $\text{N}_2$  or He mixtures with the  $\text{O}_2$  content reduced to 2%.  $\text{C}_2\text{H}_4$  was the most efficient plant anæsthetic, and retarded growth to extents  $\propto$  the concn. and differing with the plant species.  $\text{C}_2\text{H}_2$  and  $\text{C}_3\text{H}_8$  were equally active and approx. 10 times as active as  $\text{CO}$ . A. G. P.

**Purpura hæmorrhagica caused by gold and arsenical compounds.** E. H. HUDSON (Lancet, 1935, 229, 74—77).—Two cases due to administration of allochrysine and sulpharsphenamine are recorded. L. S. T.

**Effect of mercury vapour on the upper air passages.** A. STOCK (Naturwiss., 1935, 23, 453—456).—The effects of Hg poisoning by breathing the vapour are described and discussed. A. J. M.

**Lead content of human tissues and excreta.** S. L. TOMPSETT and A. B. ANDERSON (Biochem. J., 1935, 29, 1851—1864).—Pb in bone tissue and excreta may be separated by ashing and extracting with  $\text{Et}_2\text{O}$  the complex of Pb with Na diethyldithiocarbamate. Pb in the extract after destruction of org. matter is determined colorimetrically with diphenylthiocarbazon in  $\text{CCl}_4$ . A special modification is given for blood requiring 20 c.c. The mean concns. in mg. of Pb per kg. for adults not exposed to Pb were: liver 1.73, kidney 1.34, spleen 1.68, brain 0.5, rib 8.55, vertebra 7.09. Fœtal tissues gave vals. considerably below those for normal adults. The mean normal daily excretion in urine was 0.05 mg. and in fæces 0.22 mg. The blood-Pb in normals varied from  $40\text{--}70 \times 10^{-6}$  g. per 100 c.c. with a mean of  $55 \times 10^{-6}$  g. per 100 c.c. The blood-Pb but not the excretion of Pb was markedly increased in a case of plumbism. W. O. K.

**Retrobulbar neuritis due to thallium poisoning.** W. MAHONEY (Yale J. Biol. Med., 1933—1934, 6, 583—597).—Effects of TI poisoning from depilatory preps. are described. CH. ABS. (p)

**Toxicity of aluminium. I. Slight cumulative poisoning by ingestion of food prepared in aluminium cooking-vessels.** L. TOCCO (Boll. Soc. Ital. Biol. sperim., 1935, 10, 65—66).—Prolonged contact of food with Al vessels in presence of warm  $\text{NaHCO}_3$  solution, followed by cooking without washing, results in contamination of the food with Al, which is cumulatively toxic, producing a gastro-intestinal syndrome. R. N. C.

**Effect of feeding high amounts of soluble iron and aluminium salts.** H. J. DEOBALD and C. A. ELVEHJEM (Amer. J. Physiol., 1935, 111, 118—123).—Addition of large amounts of sol. Fe or Al salts to the normal diet in chicks produces severe rickets with fatal results in 3 weeks. Fe and Al levels equiv. to 50% and 75% of the amount necessary to convert the total P in the diet into  $\text{FePO}_4$  and  $\text{AlPO}_4$  reduce bone-ash to 25% and blood-P to 2—4 mg. per 100 c.c. of serum. Addition of sufficient  $\text{Na}_2\text{HPO}_4$  to unite with the Fe and Al allows normal growth and bone formation. Blood-P falls 5 days after addition of Fe or Al, reaching 1.5—1.7 mg. per 100 c.c. of serum in 4 days. R. N. C.



**Influence of sodium fluoride on the phosphate metabolism of rabbit muscle.** M. MIYOSHI (Japan. J. Med. Sci., IV, 1933, 7, 86—87).—Subcutaneous injection of NaF (80—120 mg. per kg.) induced hyperglycemia and changed the proportions of various P compounds in the muscles.

CH. ABS. (p)

**Urine of phosphorus-poisoned men.** T. KAWADA and F. YAMASAKI (J. Biochem. Japan, 1935, 21, 423—425).—Urine from P-poisoned men contained  $\gamma$ -butyrobetaine, tyrosine, and other  $\text{NH}_2$ -acids.

F. O. H.

**Action of mineral water on composition of the blood. IV. Karlsbad water and serum-anions.** E. STRANSKY (Arch. exp. Path. Pharm., 1935, 178, 724—730; cf. A., 1934, 1254).—Continuous drinking of Karlsbad  $\text{H}_2\text{O}$  by rabbits produces no marked change in serum-Cl, -Na,  $-\text{HCO}_3'$ , or -total  $\text{SO}_4''$ . Inorg. P and K increase in some cases, Ca increases by  $<0.001\%$ , and Mg correspondingly decreases, changes due to all and not merely one of the mineral constituents. The bearing of the data on those from men is discussed.

F. O. H.

**Germicidal and antiseptic activity of some mercury compounds.** E. MONESS, S. E. HARRIS, and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1935, 24, 386—389).— $\beta$ -4 : 4' - *Dihydroxydiphenylpropane*, b.p. 225—230°/4 mm., m.p. 144° (from  $\text{PhOH}$ ,  $\text{COMe}_2$ , and  $\text{POCl}_3$ ), was converted into the 3 : 3-( $\text{NO}_2$ )<sub>2</sub>-derivative, m.p. 132° [which furnishes the 5 : 5'-( $\text{OAcHg}$ )<sub>2</sub>-compound (I)], and also into the 3 : 3'-*di*-bromo-5 : 5'-*di*-acetoxymercuri-compound (II), m.p. 250° (decomp.). A Hg derivative (III) of *di*-bromo-resorcinoldiphenene was also prepared. (I), (II), and (III) all show germicidal activity.

M. T.

**Effect of amœbicidal drugs on tissue culture cells (arsenious trithiosalicylic acid, carbarsone, kurchi bismuth iodide, proparsamide, vioform).** M. J. HOGUE (Amer. J. Trop. Med., 1934, 14, 443—456).—Toxic effects of the drugs are compared on tissues of the digestive tract of 8-day chick embryos *in vitro* at  $p_{\text{H}}$  6.3—6.8.

CH. ABS. (p)

**Influence of radon on internal secretion.** N. P. KOCHNEVA (Ann. Roentgenol. Radiol. U.S.S.R., 1934, 13, 243—248).—Increased retention of blood-sugar by the kidneys during insulin action is accelerated by intravenous injection of 20—25 millicuries of Rn and diminished by 1 millicurie. During absorption of protein derivatives Rn decreases the sugar level in renal and peripheral blood. In fasting dogs Rn does not accelerate the general hypoglycemic action of insulin, but augments sugar retention by kidneys, probably by decreasing the retention by other organs.

CH. ABS. (p)

**Emission of radiation in chemical and biological phenomena.**—See this vol., 1055.

**Specificity of enzyme catalysis.**—See this vol., 940.

**Kinetics of heterogeneous catalysis and of enzyme action.**—See this vol., 1084.

**Enzyme catalysis of the exchange of deuterium with water.**—See this vol., 1084.

**Methods and applications of enzyme studies in histological chemistry of the Linderström-Lang-Holter technique.** D. GLICK (J. Chem. Educ., 1935, 12, 253—259).

L. S. T.

**Vitazymes and hormozymes.** H. VON EULER (Arkiv Kemi, Min., Geol., 1935, 11, B, No. 45, 6 pp.).—It is suggested that animal and plant co-enzymes of carbohydrate decomp. have a common prosthetic group, adenosylphosphoric acid, and differ only in their ligatory group. Flavin (I) when bound to a protein is a typical vitazyme. The occurrence of light-stable (I) in green leaves is attributed to the protecting influence of chlorophyll and its colloidal carrier. Methylene-blue (II) may play a similar protective rôle in the photo-reduction of (I) by yeast extract and EtOH, which proceeds without lumiflavin formation, as the max. activation of this reaction is brought about by  $\lambda$  corresponding with the absorption bands of (II).

E. A. H. R.

**Potentiometric study of catalase action.** R. ITOH (J. Biochem. Japan, 1935, 21, 329—334).—Purified catalase preps. from horse erythrocytes added to dil. aq.  $\text{H}_2\text{O}_2$  have an oxidation potential (Pt electrode)  $>$  that of the aq.  $\text{H}_2\text{O}_2$  alone. A periodicity in the potential- $[\text{H}_2\text{O}_2]$  curve is related to the oxidation and reduction functions of  $\text{H}_2\text{O}_2$  in presence of catalase.

F. O. H.

**Chemical studies on enzymes. II.** H. VON EULER (Arkiv Kemi, Min., Geol., 1935, 11, B, No. 42, 6 pp.).—In the pig, dehydrogenase (I) activity of the mucosa of the small intestine is accelerated (slightly) by EtOH, glucose, and  $\text{HCO}_2\text{Na}$ , and (greatly) by Na succinate. A-avitaminosis in rats increases (I) activity and the mucosa of the small intestine, and B<sub>2</sub>-avitaminosis also increases it. B<sub>2</sub>-avitaminosis in chickens has little action on the (I) activity of the small intestine. In the guinea-pig C-avitaminosis decreases (I) activity, suggesting that the influence of vitamin-C (II) is connected with enzymic activity. Phosphatase activity of the small intestine of the pig is inhibited by (II), whilst phosphatase activity is inhibited by cysteine and not by (II).

E. A. H. R.

**Characterisation of three co-enzymes concerned in biological oxidation-reduction processes.** H. VON EULER, E. ADLER, F. SCHLENK, and G. GÜNTHER (Arkiv Kemi, Min., Geol., 1935, 11, B, No. 52, 6 pp.).—Adenyl pyrophosphate cannot function as a co-enzyme for EtOH-dehydrogenase (I) nor for hexose monophosphate-dehydrogenase (II). Cozymase (III) is identical with the activator of yeast-(I). Warburg's "co-ferment II" is a better activator of (II) than is (III), but does not activate (I); it is more thermolabile than (III).

E. A. H. R.

**Dehydrogenation of succinic acid by charcoal. Model of the mode of reaction of succinodehydrase.**—See this vol., 940.

**Influence of the yellow respiratory enzyme on the dehydrogenation of lactacidogen and hexose-diphosphoric acid by yeast-dehydrogenase.** A. HAHN, H. NIEMER, and B. FREYTAG (Z. Biol., 1935, 96, 453—458).—The addition of the yellow enzyme (I) reduces the time of decolorisation of methylene-



blue (II) by lactacidogen (III) and hexosediphosphoric acid (IV) in the presence of yeast-dehydrogenase (V) to about one third. (I) has no influence on the rate of dehydrogenation of lactic acid (VI) by (II) and (V). Aerobically (I) does not accelerate the oxidation of (VI), but the  $O_2$  uptake in the presence of (III) is about doubled. (IV) shows such a small  $O_2$  uptake that its acceleration by (I) would not be significant.

E. A. H. R.

**Citric acid dehydrase of liver.** L. REICHEL [with A. NEEFF] (Naturwiss., 1935, 23, 391).—COMe<sub>2</sub>-dried preps. from liver (man, calf, pig, horse) contain a citric acid dehydrase for which  $O_2$ , methylene-blue, and lactoflavin do not function as intermediary acceptor. HCO<sub>2</sub>H is the only true fission product, the formed acetonedicarboxylic acid being degraded by another enzyme system or non-enzymically. *p*-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>3</sub>H is introduced as a deproteinising agent.

F. O. H.

**Active group of co-enzyme from erythrocytes.** O. WARBURG, W. CHRISTIAN, and A. GRIESE (Biochem. Z., 1935, 279, 143—144).—The C<sub>5</sub>H<sub>5</sub>N component (I) of the co-enzyme (this vol., 121, 249, 400), acting in a system converting hexose monophosphate into phosphohexonic acid, takes up 2 H. The hydrogenated (I) thus formed is oxidised not by  $O_2$  alone, but by  $O_2$  in presence of the alloxazine from yellow enzyme which acts as H<sub>2</sub> carrier. With Pt+H<sub>2</sub>, 1 mol. of (I) takes up 3 H<sub>2</sub>, the product being inactive.

F. O. H.

**Identity of xanthine-oxidase and Schardinger enzyme.** V. H. BOOTH (Biochem. J., 1935, 29, 1732—1748).—The identity of xanthine-oxidase (I) and the Schardinger enzyme (II) is claimed for the following reasons. With both aldehyde and purine substrates together only competition is observed; (I) is inhibited by the oxidation products of (II); activity ratios for the milk- and liver-enzymes are similar; in yolk-sac and whole embryo the first appearances of the two are coincident; no preferential destruction is caused by heat etc.; mixed dismutation occurs between uric acid and salicylaldehyde whereby the former is converted into hypoxanthine, no respiratory carrier being necessary. The change in the activity ratio of the two enzymes after adsorption (A., 1930, 248) is not due to preferential adsorption of one component, but to the removal of an equal quantity of both, and to the fact that the relation between enzyme concn. and activity is not linear for either substrate. The change in ratio due to added protein is the result of preferential adsorption of one substrate.

H. D.

**Action of hydrocyanic acid on oxidase of gum arabic.** V. ZANOTTI (Giorn. Farm. Chim., 1934, 83, 385—388; Chem. Zentr., 1935, i, 1255).—Gaseous HCN inactivates the enzyme, which recovers its activity after aeration. Brief exposure to HCN may induce a stimulative effect and prolonged treatment (120 hr.) permanently destroys the enzyme.

A. G. P.

**Enzymic hydrolysis *in situ* of intracellular tissue.** H. COLIN and A. CHAUDUN (Compt. rend., 1935, 201, 407—409).—Hydrolysis (by snail's hepato-

pancreatic juice) of pectin substances (I), determined by changes in the ratio of  $[\alpha]$  to reducing val., in beetroot tissue indicates that a part of (I) adheres firmly to the cellulose walls; this agrees with the conception of a pecto-cellulose membrane.

F. O. H.

**Activation of glycolysis by heat-inactivated cozymase preparations.** H. VON EULER and G. GÜNTHER (Svensk Kem. Tidskr., 1935, 47, 189).—Cozymase preps. heated for 1 hr. at 100° and  $p_H$  3.5 almost completely lose their activity on apozymase in fermentation, but retain their activity as indicated by lactic acid formation in extract of rat's muscle.

F. O. H.

**Liver-amylase: effect of nutrition and of hormones.** F. H. SCHARLES, P. D. ROBB, and W. T. SALTER (Amer. J. Physiol., 1935, 111, 130—137).—Liver-amylase in mice is determined by incubation of glycogen (I) with liver extract at 45°. Amylase activity after feeding varies widely. Insulin (II) depresses the activity of the amylase to the fasting val. Thyroxine (III) increases the activity in the fasting state, but feeding of thyrotoxic animals causes a temporary fall in activity. Adrenaline does not affect the activity. (II) and (III) both lower liver-(I). In general, amylase activity increases when liver-(I) varies, but remains low when this is steady.

R. N. C.

**Adsorption of malt  $\alpha$ -amylase on calcium phosphate.** O. HOLMBERGH (Arkiv Kemi, Min., Geol., 1935, 11, A, No. 20, 12 pp.).—Pptn. of impurities from a crude malt extract with Ca(OAc)<sub>2</sub> and successive amounts of EtOH (final concn. 45%) gives a solution containing nearly all the amylase activity of the extract, which retains its activity unchanged at 0° for 2 months. Further impurities are adsorbed by Al subacetate. The optimum conditions for adsorption of  $\alpha$ -amylase on rice-starch are temp. 2°,  $p_H$  5.3, and time of adsorption 1 hr. 4% tannin ppts. the majority of  $\alpha$ - and  $\beta$ -amylase at  $p_H$  5.7 from malt extract to which acetate has been added. Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> as a selective adsorbent for  $\alpha$ -amylase (cf. A., 1933, 1330) is prepared as follows. A lukewarm solution of 32 g. of Na<sub>2</sub>HPO<sub>4</sub> in 200 c.c. of H<sub>2</sub>O is added slowly to 29 g. of CaCl<sub>2</sub>·6H<sub>2</sub>O in 200 c.c. of H<sub>2</sub>O, 40 c.c. of 4N-NH<sub>3</sub> are added, and after 1 day the Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> is centrifuged off and washed. The ppt. obtained by increasing the EtOH concn. in malt extract to 80% is redissolved in H<sub>2</sub>O and treated with a suspension of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> (0.025 g. per c.c.) at  $p_H$  5.7, when 73% of the  $\alpha$ -amylase is adsorbed. The adsorbate is washed with 0.0005N-H<sub>3</sub>PO<sub>4</sub> and eluted with dil. aq. NH<sub>3</sub>.

E. A. H. R.

**Amylosynthase. II. Rice amylosynthase.** T. MINAGAWA (Bull. Agric. Chem. Soc. Japan, 1935, 11, 62—65).—Polished and unpolished rice yield amylosynthase (I), which differs from that obtained from yeasts, and it can be pptd. by EtOH or COMe<sub>2</sub> from aq. solution as a highly active powder. A similar enzyme has been detected in corn, millet, potato, and seed of panic-grass.

J. N. A.

**Salt activation. I. Influence of neutral salts on the enzymic hydrolysis of starch.** K. V. GRI and J. G. SHRIKHANDE (J. Indian Chem. Soc., 1935,



12, 273—286).—The effect of neutral salts (NaF, NaCl, Na<sub>2</sub>SO<sub>4</sub>, NaNO<sub>3</sub>) on the hydrolysis of starch by sweet-potato amylase is dependent on the  $p_H$  of the medium and on the concn. of the salt. At  $p_H$  6.0 the salts do not affect the activity of the enzyme. At  $p_H > 6.0$  the reaction is retarded at high salt concn., whereas below 6.0 it is accelerated to an extent  $\propto$  the acidity of the system. The accelerating effect at  $p_H$  4.0 decreases in the order NaF > NaCl > Na<sub>2</sub>SO<sub>4</sub> > NaNO<sub>3</sub>. O. J. W.

**Secretion of diastase and invertase by *Empoasca solana*, De Long (*Rhynchota*, *Homoptera*, *Jassidae*).** G. V. B. HERFORD (Ann. Appl. Biol., 1935, 22, 267—278).—Adults and nymphs eject diastase into the feeding medium. The insect also secretes an enzyme which inverts sucrose. A. G. P.

**Water relations of enzymes. II. Water concentration required for invertase action.** Z. I. KERTESZ (J. Amer. Chem. Soc., 1935, 57, 1277—1279).—Hydrolysis of sucrose (I) in a solid reaction mixture [(I) 75%; invertase (II) 1%; dry apple pomace 20%; phosphate buffer 4%] by (II) occurs in presence of 4.75—5% H<sub>2</sub>O at 25°. No enzyme action occurs with smaller concns. of H<sub>2</sub>O, but with >5% hydrolysis is faster and more regular. H. B.

**Emulsin. XX. Effect of neutral salts on the activity of almond-emulsin.** B. HELFERICH and E. SCHMITZ-HILLEBRECHT (Z. physiol. Chem., 1935, 234, 54—62; cf. this vol., 783).—The rate of hydrolysis of phenol- $\beta$ -D-glucoside by the emulsin is not appreciably altered by cations, but anions, in accordance with their position in the lyotropic series, increase it, in some cases greatly (e.g., ClO<sub>4</sub>' threefold). The concn. of substrate is immaterial, but increasing concn. of salt causes corresponding increase until a max. is reached. Thereafter the rate remains const. or decreases. No change occurs in the form of the hydrolysis curve, the reaction remaining unimol. The increase in rate also varies with the  $p_H$ , being greatest at the  $p_H$  optimum. Emulsin damaged by O<sub>3</sub> behaves like undamaged. The extent of increase varies with the substrate chosen, being sometimes very slight with substrates which are very rapidly hydrolysed. W. McC.

**Fission of  $\alpha$ -L-arabinosides by almond emulsin.**—See this vol., 1110.

[Esterase model.] S. C. J. OLIVIER (Rec. trav. chim., 1935, 44, 599—600).—A reply to Langenbeck (this vol., 784). H. W.

**Destruction of acetylcholine by various organs of the guinea-pig, frog, and snail.** N. HALPERN and E. CORTEGGIANI (Compt. rend. Soc. Biol., 1935, 119, 1049—1052).—The blood and organs of the guinea-pig, frog, and snail all contain a thermolabile substance that destroys acetylcholine, the action being inhibited by eserine. R. N. C.

**Correlation between the splitting of fats and their oxidation.** E. FREUDENBERG (Klin. Woch., 1934, 13, 723—724).—The lipase-zymogen of human milk is activated (reversibly) by bile acids, and (irreversibly and to a smaller extent) by COMe<sub>2</sub> and naturally-occurring products of fat oxidation, e.g.,

$\beta$ -hydroxybutyric acid, CH<sub>3</sub>Ac-CO<sub>2</sub>H. If milk-fat or triolein is oxidised by shaking, the products can activate the pro-enzyme (I): on the contrary, cod-liver oil after shaking damages (I). Shaking does not activate (I) directly. G. H. F.

**Proteins of foods. IV. Digestibility by proteolytic enzyme from viscera of eel.** T. TOMIYAMA (J. Biochem. Japan, 1935, 21, 367—369).—Protein from soya bean is more readily hydrolysed at  $p_H$  7.3 and 37° than that from sardine or silk-worm pupæ. F. O. H.

**Proteolytic digestion in the ammocœte larva.** E. J. W. BARRINGTON (Nature, 1935, 136, 145).—Extracts of certain parts of the intestine and of the skin of brook-lamprey larva show strong proteolytic activity of the tryptic type, optimum  $p_H$  approx. 8. The intestinal extract is stronger than that of the skin. The proteolytic digestion is similar to that of the *Ascidacea*. L. S. T.

**Natural activators of papain.** W. GRASSMANN (Biochem. Z., 1935, 279, 131—136).—Phytokinase in papain preps. does not owe its activity to glutathione, but to a peptide consisting largely of cystine (and/or cysteine) and glutamic acid (cf. A., 1931, 328, 393; this vol., 122). F. O. H.

**Glutathione and autolysis.** S. LÁNG (Z. physiol. Chem., 1935, 234, 127—130; cf. A., 1934, 925).—The livers of fasting dogs poisoned with P do not contain increased amounts of reduced glutathione (I). During autolysis (I) passes from the reduced into the oxidised form. It is improbable that reduced (I) is the activator the protease which causes autolysis. W. McC.

**Coli-tryptophan-indole reaction. I. Enzyme preparations and their action on tryptophan and indole derivatives.** F. C. HAPPOLD and L. HOYLE (Biochem. J., 1935, 29, 1918—1926).—Preps. of certain strains of *B. coli* killed by CHCl<sub>3</sub> contain an enzyme ("tryptophanase"), active at  $p_H$  5.0—10.0 (optimum 8.5), which converts tryptophan (I) into indole (cf. this vol., 663). The enzyme occurs in *B. coli* grown on (I)-free media, but to a far greater extent when the media have a high (I) content or, more especially, when (I) is the sole source of N. Tryptophanase does not produce indole from indolyl-propionic, -acrylic, or -pyruvic acid, indole-carboxylic acid or -3-aldehyde. F. O. H.

**Enzymic histochemistry. XV. Micro-determination of arginase.** K. LINDERSTRØM-LANG, L. WEIL, and H. HOLTER (Compt. rend. Trav. Lab. Carlsberg, 1935, 21, No. 2, 7—14).—In presence of COMe<sub>2</sub>-EtOH in high concn., arginine (I) at  $p_H$  9.5 behaves as a strong base, whereas ornithine and urea are scarcely ionised. The enzymic cleavage of (I) can therefore be followed by the increase in the amount of base (0.05N-NMe<sub>4</sub>OH) used in titrating to a standard  $p_H$ . This method is more convenient and rapid than a modified urease method also described, except that it cannot be used in the presence of excess of urease. Both methods give comparable results. E. A. H. R.

**Ultrafiltration of ureases of different origin through membranes of graduated permeability.**



P. GRABAR and A. RIEGERT (Compt. rend. Soc. Biol., 1935, 119, 1004—1006).—Commercial urease (Squibb) contains particles of varying sizes; cryst. urease is more homogeneous. Soya and *Canavallia* ureases differ greatly in particle dimensions, although prepared by identical methods. All ureases are retained by membranes non-permeable to particles  $>15 \mu$ .

R. N. C.

**Ultrafiltration of urease after partial digestion by activated trypsin.** P. GRABAR and A. RIEGERT (Compt. rend. Soc. Biol., 1935, 119, 1006—1007).—The active material of a urease solution partly digested by trypsin is retained by a membrane with  $15 \mu$  pores. Hence the activity of urease is associated with the cryst. globulin isolated by Sumner, the digestion products of which are inactive.

R. N. C.

**Enzymic fission of yeast-nucleic acid.** A. CONTARDI and C. RAVAZZONI (R. Ist. lombardo Sci. Lett. Rend., 1934, 67, 503—517; Chem. Zentr., 1935, i, 1075).—Hydrolysis of the acid cannot be followed by changes in  $\alpha$  of the Na salt, since observations are complicated by mutarotation. An enzyme system occurring in aq. extracts of rice chaff consists of a phospho-diesterase (optimum  $p_H$  4.0) and a monoesterase ( $p_H$  5.5). All P in nucleic acid is converted into inorg. forms by this system. The diesterase is not identical with choline-phosphatase.

A. G. P.

**Enzymic conversion of glyceraldehyde- into dihydroxyacetone-phosphoric acid.** O. MEYERHOF and W. KIESSLING (Biochem. Z., 1935, 279, 40—48).—Dialysed muscle extracts rapidly convert (indicated iodometrically) 50% (i.e., the biologically active optical isomeride) of *dl*-glyceraldehydephosphoric acid (I) into dihydroxyacetonephosphoric acid (II). This supports the theory of the reaction chain  $(I) \rightleftharpoons (II) \rightleftharpoons$  hexosediphosphoric acid.

F. O. H.

**Alkaline phosphomonoesterase of the mammary gland.** S. J. FOLEY and H. D. KAY (Biochem. J., 1935, 29, 1837—1850).—The phosphatase (I) of guinea-pig mammary glands hydrolyses  $Na_2PhPO_4$  (II) in glycine buffer at a rate dependent on  $p_H$  and (II) concn., being max. at  $p_H$  10.0 and at a (II) concn. of 0.009*M*. At low (II) concns. the behaviour of (I) follows the theory of Michaelis with  $K_m=0.0006$  at  $p_H$  10.0, whilst at higher concns. the data are in agreement with the theory put forward by Haldane to explain inhibition by high substrate concns. (I) is unstable in alkaline solution, has a marked stability max. at  $p_H$  7.0, is activated by small concns. of  $Mg^{++}$ , and is able to synthesise glycerophosphate from glycerol and inorg.  $PO_4^{---}$ . Its properties agree closely with those of kidney-phosphatase, with which it is probably identical. W. O. K.

**Phosphatase of the long bones during growth in the rat.** J. ROCHE and A. LEANDRI (Compt. rend. Soc. Biol., 1935, 119, 1141—1144).—Phosphatase (I) increases rapidly in all parts of the bone in the initial period of development, but falls steadily after the animals have reached 80 g. wt. In the adult rat, (I) is  $\alpha$  bone-protein. The diaphysis shows an exceptionally high (I) content. R. N. C.

**Phosphatase of the red corpuscles.** J. ROCHE and M. LATREILLE (Compt. rend. Soc. Biol., 1935, 119, 1144—1147).—The crude phosphatase of the red corpuscles shows a preferential action on  $\alpha$ -glycerophosphates at an optimum  $p_H$  of 6.5. It can be adsorbed on kaolin at  $p_H$  6.0 and eluted with 0.05*N*- $NH_3$ ; the purified product, however, shows a preferential action on  $\beta$ -glycerophosphates at an optimum  $p_H$  of 8—9, similar to the other animal phosphatases. The corpuscles contain a mixture of sp.  $\alpha$ - and  $\beta$ -glycerophosphatases, and kaolin preferentially adsorbs the  $\beta$ -enzyme. R. N. C.

**Urine- and blood-phosphatase.** A. DMOCHOWSKI and D. ASSENHAJIM (Naturwiss., 1935, 23, 501).—Human urine contains a phosphatase (I) with an optimum activity at  $p_H$  5.4—5.6 which is strongly inhibited by KCN,  $Cu^{++}$ , and NaF, more weakly by cysteine, and very slightly by phloridzin. Mg salts have no activating effect. It is partly inhibited by conc. urine, but with diluted or dialysed urine the inhibition is less marked. Urinary (I) is probably not derived from blood-(I), but from the kidney cells.

W. O. K.

**Development of enzymes in malt.** H. LÜERS (Woch. Brau., 1935, 52, 249—254).—A lecture.

E. A. H. R.

**Synthesis of reserve carbohydrate by yeast.**  
**I. Synthesis from glucose and maltose and influence of phosphate thereon.** R. A. MCANALLY and I. S. MACLEAN (Biochem. J., 1935, 29, 1872—1876).—Yeast, incubated at 25° for 2 days, is examined for total carbohydrate, glycogen (I), insol. carbohydrate (II), and yeast-gum (III). With glucose or maltose media addition of  $HPO_4^{--}$  causes increased formation of (I), (II), and (III). The (I) produced on a maltose medium is much  $>$  that on a glucose medium.

H. D.

**Yeasts capable of fermenting trioses.** C. NEUBERG and E. HOFMANN (Naturwiss., 1935, 23, 484—486).—Three varieties of yeast, *Schizosaccharomyces Pombe*, *Hansenula (Willia) javanica*, and *Willia anomala* (Hansen), fermented dihydroxyacetone (50—80%) and glyceraldehyde ( $\approx 33\%$ ) with the formation of EtOH and  $CO_2$ .

W. O. K.

**Velocity of fermentation of sugar by zymase and the origin of the first fermentation equation of Harden and Young.** O. MEYERHOF and W. KIESSLING (Naturwiss., 1935, 23, 501—502).—Phosphopyruvic acid (I) is fermented (to  $CO_2$  and MeCHO)  $\frac{1}{2}$ — $\frac{1}{10}$  as rapidly as is glucose (II), but addition of (II) to the yeast extract with NaF, which inhibits the fermentation of (II), results in an increase of the fermentation rate of (I) up to 10 times the original. The phosphate of (I) with an equal amount of inorg. phosphate combines in ester formation with (II), half appearing as hexose diphosphate (III) and half as phosphoglyceric acid (IV), whilst EtOH and not MeCHO is formed:  $2(II) + 2(I) + 2H_3PO_4 \rightarrow (III) + 2(IV) + 2CO_2 + 2EtOH$ . When the system is poisoned with  $CH_2I \cdot CO_2H$  instead of NaF the velocity of fermentation of (I) remains high, showing that the reaction limiting the velocity is not the oxidation of (IV) but the phosphorylation of hexose:  $(II) + 2(I) \rightarrow (III) + 2CO_2 + 2MeCHO$ . [NaF inhibits con-



version of  $\alpha$ -(IV) into (I) and  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$  inhibits oxidation of triosephosphoric acid to (IV).] When various sugars are employed as  $\text{PO}_4'''$  acceptors in the fermentation of (I) the velocities correspond with the known velocities of fermentation of these sugars. The latter are therefore conditioned by their velocities of esterification. In yeast fermentation  $\text{MeCHO}$  is not reduced by the stable (III) esters but by an unstable ester formed from (II) in presence of (III). In the yeast extracts the reduction of  $\text{MeCHO}$  is sufficiently slow to allow a quantity of the (III) esters to assume the stable form instead of being oxidised to (IV). Extra (II) must then be esterified. W. O. K.

**Fat and lipin metabolism of yeast. IV. Accumulation of sterols and fat in bottom yeast.** M. SOBOTKA, W. HALDEN, and F. BILGER (*Z. physiol. Chem.*, 1935, 234, 1—20; cf. A., 1934, 1035).—It is the removal of  $\text{H}_2\text{O}$  which initiates and controls the increase in production of lipins and sterols, the predominating cause being the treatment of the yeast with  $\text{EtOH}$  vapour in a moderate supply of air. Better yields are obtained when the medium contains glucose than when no nutrient matter is present, apparently because of the action of the  $\text{EtOH}$  produced during the consequent fermentation. The yield of lipin is related to the dry wt. of the yeast, the yield of sterol, and the duration of the process, but not to the total N content of the yeast, which decreases owing to autolysis and removal of  $\text{H}_2\text{O}$ , loss of N beginning when the  $\text{H}_2\text{O}$  content has fallen to 73% of its initial val. The accumulation of lipin does not interfere with N equilibrium. W. McC.

**Oligodynamic action of oxygen on the multiplication of yeast-cells.** W. LIBBRECHT and L. MASSART (*Compt. rend. Soc. Biol.*, 1935, 119, 1193—1194).—The development of yeast-cells is accelerated by an  $\text{O}_2$  pressure of  $10^{-6}$  atm. R. N. C.

**Phytochemical reduction of anthradiquinone.** A. VERCELLONE (*Biochem. Z.*, 1935, 279, 137—139).—Yeast-sugar mixtures convert 1:4:9:10-anthradiquinone into quinizarin to an extent of approx. 80% when fermenting and approx. 30% when fermentation is inhibited by heating at  $90^\circ$  for 10 min. F. O. H.

**Phytochemical reduction of *dl*-lactaldehyde.** C. NEUBERG and A. VERCELLONE (*Biochem. Z.*, 1935, 279, 140—144).—*dl*-Lactaldehyde added to fermenting sucrose-yeast mixtures is converted into  $\alpha\beta$ -propylene glycol,  $[\alpha]_D +5.53^\circ$ . F. O. H.

**Action of ethylene on cell processes.** F. H. SHAW (*Austral. J. Exp. Biol.*, 1935, 13, 95—102).— $\text{C}_2\text{H}_4$  increases the rates of fermentation and inversion by living yeast but not by dead yeast or cell-free enzyme preps. The stimulating action of  $\text{C}_2\text{H}_4$  is due to increased production of enzyme and not to changes in cell permeability (cf. A., 1929, 1200; 1931, 468). F. O. H.

**Activation of enzymic reactions. I.** H. VON EULER and T. SVENSSON (*Arkiv Kemi, Min., Geol.*, 1935, 11, B, No. 47, 6 pp.).—If dried brewer's yeast be mixed with fructose and  $\text{KH}_2\text{PO}_4$  within 6—7 hr. the greater part of the free  $\text{PO}_4'''$  is consumed (phosphatase action), after which the free  $\text{PO}_4'''$  again

increases up to nearly its original concn. (phosphatase action). The latter is accelerated by ascorbic acid and inhibited by  $\text{Cu}^{++}$  and cysteine. When  $[\text{Cu}^{++}]$  is  $> 10^{-3}N$  phosphatase and phosphatase action cannot be separated; both are strongly inhibited. The latter is accelerated by vitamin-D. E. A. H. R.

**Oxidation-reduction potential of yeast suspensions.** C. FROMAGEOT and P. DESNUELLE (*Biochem. Z.*, 1935, 279, 34—39).—Fermenting top yeast in buffered anaerobic suspension at  $p_H$  6.4 or in unbuffered suspension at  $p_H$  6.4—4.5 has  $r_H=6.6$ —8.0. The significance of this val. is discussed with reference to the formation of lactic acid from  $\text{AcCO}_2\text{H}$  and to the non-formation of alanine from lactate and added  $\text{NH}_3$ . F. O. H.

**Changes in the flavin content of yeast.** L. B. PÉRT (*Arkiv Kemi, Min., Geol.*, 1935, 11, B, No. 53, 6 pp.).—Yeast grown in a medium containing inorg. salts, glucose, and a trace of marmite develops flavin (I). A certain amount of  $\text{PO}_4'''$  ( $> 4$  g. per litre) must be present for normal (I) development.  $\text{CN}'$  produces a (I) content much  $>$  normal. During autolysis very little (I) disappeared. Impoverishment of yeast-glycogen reserves by shaking with  $\text{O}_2$  leads to a rapid reduction of the (I) content. E. A. H. R.

**Changes in the concentration of cozymase, Z-factor, and flavin during the germination of peas.** A. W. H. VAN HERK (*Arkiv Kemi, Min., Geol.*, 1935, 11, A, No. 22, 11 pp.).—The cozymase content of germinating peas is initially large and remains so for 4 days, but after 7 days it has fallen to  $1/5$ — $1/6$  of its original val. The Z-factor remains const. for the first 2 days and then decreases, reaching a min. after 4 days, after which it again increases, reaching  $1\frac{1}{2}$  times its original concn. in 2 weeks. The flavin (I) content remains const. for 2 days and then increases to 3 times its original val. In the etiolated plant (I) synthesis ceases after 12 days but increases again on exposure to light. A temporarily higher (I) content of the etiolated plant may be due to (I) destruction by light in the green plant. E. A. H. R.

**Temperature stability and formation of cozymase.** H. VON EULER and G. GÜNTHER (*Arkiv Kemi, Min., Geol.*, 1935, 11, B, No. 50, 6 pp.).—Cozymase (I) preps. from yeast, horse-muscle, and peas vary considerably in thermostability. The (I) activity of rat-muscle is not appreciably increased by creatine feeding, nor is it affected by A-avitaminosis or -hypervitaminosis. E. A. H. R.

**Distribution of growth-promoting factor (bios) in normal animal tissues and tumours.** C. DITTMAR (*Biochem. Z.*, 1935, 279, 99—105).—Growth-promoting action on yeast in Reader's solution indicates that tissues contain the factor in relatively approx. const. amounts for the same species, the contents giving the series: kidney  $>$  adrenal  $>$  liver  $>$  spleen, muscle, etc.  $>$  blood. The content of any tissue (excepting blood) is independent of the animal's age and of the type of nutrition. Tumour implants have a content = that of kidney. Large necrosing growths have a very high content, indicating a relation between growth and content of growth factor. F. O. H.



**Culture and physiology of marine dinoflagellates.** H. A. BARKER (Arch. Mikrobiol., 1935, 6, 157—181).—Dinoflagellates examined are characterised by an adaptation to very poorly nutritive media. The P and N requirements are low. Org. compounds cannot be utilised to replace or supplement autotrophic nutrition. With 0.1 p.p.m. of N, max. rate of division occurs. A. G. P.

**Nitrogen and carbon nutrition of *Polytomella agilis*.** A. LWOFF (Compt. rend. Soc. Biol., 1935, 119, 974—976).—*P. agilis* grows very feebly with asparagine as the only N source, but readily in peptone at  $p_H$  4.5—8.4. It can utilise as C source AcOH, propionic, *n*- or *iso*-butyric, *n*-valeric, or *n*-hexoic acid, or starch. R. N. C.

**Photosynthesis in diatoms.** H. A. BARKER (Arch. Mikrobiol., 1935, 6, 141—156).—Photosynthesis in *Nitzschia closterium* and *N. palea* is essentially similar to that in green plants. A. G. P.

**Method for the study of crystals found in amoeba by means of X-rays.** C. FOWLER (Science, 1935, 82, 45). L. S. T.

**Cultivation of a sterile amoeba on media without solid food.** K. REICH (J. Exp. Zool., 1934, 69, 497—500).—The culture of *Mayorella palestinensis* is examined. N is obtained from complex substances which cannot be replaced by  $NH_3$ -acids. Sugars (glucose, fructose, sucrose, or lactose) are essential for good growth. The  $O_2$  requirement is small. The organism develops at 12—27° (optimum  $p_H$  6.8) and liquefies gelatin. CH. ABS. (p)

**Decomposition of formic to oxalic and carbonic acids by various moulds.** T. CHRZĄSZCZ and M. ZAKOMORNY (Biochem. Z., 1935, 279, 64—75).—Various moulds develop normally in media containing 2.5% of formate, which is decomposed with formation of  $H_2C_2O_4$  and  $CO_2$  to an extent varying with the species of mould; this is an alternative route to direct decomp. to  $CO_2$  and  $H_2O$  (cf. A., 1934, 536, 982; this vol., 406). F. O. H.

**Lactic acid formation by a fungus of the *Rhizopus* species.** E. KANEL (Microbiol. [U.S.S.R.], 1934, 3, 259—265).—The organism, related to *R. japonicus*, produced a 40% yield of lactic acid on a medium containing 10% of sugar and 4% of chalk. CH. ABS. (p)

**Starch formation in moulds.** T. HIDA (J. Shanghai Sci. Inst., 1934, [iv], 1, 85—116).—Of 22 varieties of *Aspergillus* investigated, only 9 produced starch (I), acid also being generally developed. The most convenient variety is *A. niger*. (I) formation takes place only in strongly acid culture media; with *A. niger* the  $p_H$  must be < 2.2 for (I) to accumulate, but the optimum conditions for (I) formation are not those for the growth of *A. niger*. The accumulation of (I) in acid cultures is probably due to an inhibition of a diastatic factor rather than to a greater rate of (I) synthesis in acid solution.  $O_2$  is essential for (I) formation and poisons which inhibit the respiration and rate of growth also inhibit (I) formation to the same extent. The best yields of (I) are obtained with a culture medium in which the source of C is glucose or sucrose. More carbohydrate is consumed during the

growth of *A. niger* than can be accounted for by the formation of (I) and other polysaccharides.

E. A. H. R.

**Formation of fatty acids from glucose by *Aspergillus niger*.** C. F. SCHMIDT, jun. (J. Biol. Chem., 1935, 110, 511—520).—A strain of *A. niger* in a glucose medium synthesised fatty acids under conditions in which further growth could not take place. The fatty acid content of the mycelium increased approx. 100% during 3 days. This increase is independent of  $p_H$  between 2.4 and 8.2. There is no relationship between  $p_H$  and degree of unsaturation of the acids. Formation of fatty acids takes place under aerobic and, to a smaller degree, under anaerobic conditions. J. N. A.

**Sulphopeptidase of moulds. I. *Aspergillus niger*. II. Separation of sulphopeptidase from protease. III. Comparison of animal and plant sulphopeptidase. IV. Presence of sulphopeptidase in various species of moulds.** H. OTANI (Acta Schol. Med. Univ. Kyoto, 1934, 17, 242—248, 249—259, 260—268, 269—287).—I. 2-Naphthalenesulphonylglycylglycine (I) was hydrolysed by a glycerol extract of mycelium of *A. niger*. Optimum  $p_H$  was 7.1—7.3. Naphthalenesulphonylglycine (II) is an end-product.

II. Sulphopeptidase (III) and erepsin were adsorbed at  $p_H$  4 by animal C, kieselguhr, kaolin, and  $Al_2O_3$ , and at  $p_H$  5 by  $Al_2O_3$  only. The two enzymes could not be separated. Protease was pptd. by acidification to  $p_H$  5.

III. Heating at 70° destroyed (III) in 1 hr. Glycine inhibited the action of (III) from *A. niger*, whilst (II) and leucine were most effective against the (III) from pigs.

IV. Nine species of fungi hydrolysed (I) and *o*-toluene- and benzene-sulphonylglycine but not (II).

CH. ABS. (p)

**Formation of hydroxylamine in cultures of *Aspergillus niger* in a medium containing ammonium nitrate.** M. LEMOIGNE and R. DESVEAUX (Compt. rend., 1935, 201, 239—241).—Comparison of cultures of *A. niger* in an ordinary Czapek medium and also with 16 times the usual amount of  $NH_4NO_3$  shows that in the latter case there is definite formation of  $NH_2OH$  with retardation of growth after 120—144 hr. F. R. G.

**Nutritional requirements of *Aspergillus niger*.** R. A. STEINBERG (Bull. Torrey Bot. Club, 1935, 62, 81—90).—Fe, Zn, Cu, and Mn are essential for normal growth and sporulation. CH. ABS. (p)

**Gluconic fermentation. XI. Influence of iron on the gluconic fermentation of *Penicillium crustaceum* (L.), Fries.** A. ANGELETTI and D. PONTE (Annali Chim. Appl., 1935, 25, 217—221).—Increasing small amounts of Fe (as  $FeCl_3$ ) cause increasing retardation of the formation of gluconic acid from sucrose by *P. crustaceum* (cf. A., 1934, 1405).

T. H. P.

**Utilisation of growth factors by micro-organisms. Biological synthesis of growth factors.** W. H. SCHOPFER (Arch. Mikrobiol., 1935, 6, 196—207).—Vitamin- $B_1$  is absorbed by fungi from nutrient medium, which gradually loses its ability to activate



other media. Extracts of *Phycomyces* grown on an active medium can activate other media. This property is manifest as soon as a trace of  $-B_1$  is added to the original culture. *Phycomyces* probably synthesises another growth factor in proportion to the supply of  $-B_1$ . Active extracts of *Phycomyces*, active cultures of *Mucorineæ*, and both, can activate *Sacc. cerevisiae*. A. G. P.

**Chitinivorous bacteria.** A. G. BENTON (J. Bact., 1935, 29, 449—465).—Numerous organisms are described and some biochemical reactions are recorded. A. G. P.

***Bacillus cellulose dissolvens* and thermophilic fermentation of cellulose.** Y. KHOUVINE and K. SOETERS (Compt. rend. Soc. Biol., 1935, 119, 1036—1037).—Certain strains grow only at 50—55°, and are responsible for the destruction of cellulose (I) in heaps of vegetable debris where the internal temp. has been raised by fermentation. The yellow pigment produced from (I) fermentation is not a carotenoid. R. N. C.

**Products of the fermentation of glucose and arabinose by butyric acid anaerobes.** A. F. LANGLYKKE, W. H. PETERSON, and E. MCCOY (J. Bact., 1935, 29, 333—347).—In yeast- $H_2O$  media and with many strains of organisms, low yields of neutral products are associated with high final acidity in the cultures. The yield of BuOH is lowered when  $Pr^{\beta}OH$  replaces  $COMe_2$  in the products. The formation of EtOH during fermentation proceeds more easily than that of BuOH or  $COMe_2$ . Fermentation of arabinose by nearly all cultures was poor. Acid production was high and yields of neutral substances relatively low. A. G. P.

**Carbonic acid assimilation by red sulphur bacteria.** II. H. GAFFRON (Biochem. Z., 1935, 279, 1—33; cf. A., 1934, 698).—Addition of NaSH to cultures of *Thiocystis* produces storage of S with concomitant loss of colour; lactate has the same effect, marked changes occurring in cell metabolism. The evolution of  $CO_2$  by pure strains in  $NaHCO_3$ -media in the dark is increased by addition of  $SO_4^{--}$ , butyrate, malate, pyruvate, or lactate; in the light assimilation of  $CO_2$  occurs. With S-loaded cells, a marked evolution of  $CO_2$  occurs in the light, probably due to storage of org. assimilation products coincidental with that of S. Formation of  $H_2S$  in the dark occurs at the expense of reserve material in the cell and is not sensitive to PhMe (A., 1934, 453) (which increases  $CO_2$  formation).  $CO_2$  is not assimilated by cultures in  $CO_2+H_2$  in the dark; exposure to light increases absorption of  $H_2$  and initiates that of  $CO_2$ . The action of CO, HCN, and thymol was also investigated. The bearing of the data on the metabolism of S bacteria is discussed and the results of Roelofsen (this vol., 406) are criticised. F. O. H.

**Nitrifying bacteria.** T. Y. K. BOLTJES (Arch. Mikrobiol., 1935, 6, 79—138).—Winogradsky's medium prepared from pure substances is unsatisfactory for the growth of nitrifying bacteria owing to deficiency of Ca. The use of cooking-salt in place of pure NaCl brings improvement and substitution of tap- $H_2O$  for distilled  $H_2O$  permits optimum growth. The

injurious effects of peptone on the organism are due to certain  $NH_2$ -acids present therein. A. G. P.

**Nitrogen-assimilating bacteria.** II. Fixation of atmospheric nitrogen by *Azotobacter*. G. ENDRES (Annalen, 1935, 518, 109—126).—The fixation of  $N_2$  in the form  $>C:N\cdot OH$  by *Azotobacter* is proved by the following data. Oxidation of the culture solution, after removal of the bacteria by centrifuging, with I affords  $HNO_2$ . Under similar conditions only solutions containing free  $NH_2OH$  or oximes (of  $AcCO_2H$ ), but not solutions containing  $N_2H_4$ ,  $NH_3$ , or alanine, afford  $HNO_2$ . As the  $O_2$  consumption and wt. increase  $Q_{O_2}$  decreases and approx. 10% of the total fixed  $N_2$  occurs as  $>C:N\cdot OH$ , but increase of the latter with growth varies with different substrates. The concentrate (1:40) of the culture solution (method described) contains no  $NH_3$ ,  $HNO_2$ , or  $NH_2OH$ , but affords  $NH_2OH$  ( $1-3 \times 10^{-4}$  mol. per litre) after hydrolysis. Addition of  $NH_2OH$  in amounts  $>2 \times 10^{-5}$  mol. has a growth-inhibiting effect on *Azotobacter*, which is greater the greater is  $[NH_2OH]$ ; the effect begins at approx. the same concn. as that of HCN but increases more slowly with increasing concn. Oximes have a similar but smaller effect. In presence of  $NH_2OH$  growth of *Azotobacter* occurs only in presence of  $NH_4^+$ : when  $[NH_2OH]=10^{-5}$  mol. per litre, growth occurs only at the expense of  $NH_4^+$ , but at  $10^{-4}$  mol. per litre  $NH_3$  assimilation is also inhibited. In the absence of  $N_2$  (80%  $A-20\% O_2$ ) neither growth nor oxime formation occurs; hence the latter is definitely associated with  $N_2$  fixation. J. W. B.

**Influence of ultra-violet rays on the physiological activities of *Azotobacter*.** II. Stimulation of *A. chroococcum* by ultra-violet rays. A. ITANO and A. MATSUURA (Ber. Ohara Inst. landw. Forsch., 1935, 6, 561—573).—The greatest no. of bacteria was found after 1 min. exposure to the Hg arc lamp; longer exposure caused increased acidity of the medium and a diminution in the no. of bacteria. The conductivity,  $[H^+]$ , and osmotic pressure were affected  $>$  viscosity and surface tension, but these phenomena had little influence on bacterial growth. P. G. M.

**Pantothenic acid and the nodule bacteria-legume symbiosis.** C. H. MCBURNEY, W. B. BOLLEN, and R. J. WILLIAMS (Proc. Nat. Acad. Sci., 1935, 21, 301—304).—Pantothenic acid is one of the substances which passes from bacteria to host in symbiosis and effects the growth of plants. It is not alone responsible for N fixation but is an important factor in the carbohydrate anabolism. H. T.

**Effect of temperature on bacterial ammonification of urea.** S. P. TANDON (Proc. Acad. Sci. Agra and Oudh, 1934—1935, 4, 169—172).—Formation of  $NH_3$  from urea by bacteria of tropical soils is optimum at approx. 40° and does not occur at temp.  $> 50-55^\circ$ . Hence ammonification in these soils cannot be of bacterial origin during summer. F. O. H.

**Synergic gas production by bacteria.** N. ATKINSON (Austral. J. Exp. Biol., 1935, 13, 67—73).—Symbiotic gas ( $H_2+CO_2$ ) formation (A., 1928, 797) from xylose or mannitol occurs with *B. Morgani* and



*B. typhosus* especially in presence of  $\text{CaCO}_3$ . Old cultures of *B. typhosus* contain a stable intermediate substance which liberates gas in presence of *B. Morgani*. A similar phenomenon occurs with gas production from lactose by *B. Morgani* and a hæmolytic or non-hæmolytic streptococcus. The possibility of  $\text{HCO}_2\text{H}$  being the precursor of the gas is discussed.

F. O. H.

**Vitality of the typhoid bacillus in butter as a function of the acidity.** J. BRISOU (Compt. rend. Soc. Biol., 1935, 119, 1221—1222).—The bacillus can grow in fresh or rancid butter containing  $>1\%$  of  $\text{PrCO}_2\text{H}$ . In peptone broth or peptone- $\text{H}_2\text{O}$  it is destroyed by  $p_{\text{H}} < 6.0$ , and in  $\text{H}_2\text{O}$  by  $p_{\text{H}} 4.0$ . The increased resistance in butter is due to the buffers present.

R. N. C.

**Cultural requirements of bacteria. V. Diphtheria bacillus.** J. H. MUELLER (J. Bact., 1935, 29, 515—530).—The utilisation of certain energy sources and  $\text{NH}_2$ -acids by a certain strain of the organism is examined.

A. G. P.

**Diphtheria formol toxoid and the Moloney test.** R. SWYER (Lancet, 1935, 229, 22).—The test is not an accurate index of the reactions to be expected in adults after the injection of formol toxoid.

L. S. T.

**Existence of "complete" and "residual" antigens in various bacteria.** A. BOIVIN and L. MESROBEANU (Compt. rend., 1935, 201, 168—170).—Extraction of capsulated bacteria (*Pneumococcus* type II) with  $\text{CCl}_3\cdot\text{CO}_2\text{H}$  yields a sp. polysaccharide but no "complete" antigen. Digestion of the bacillus with trypsin prior to the extraction indicates that the complex is probably present in a very labile state.

H. G. R.

**Immunising substances in *Pneumococci*. II. Separation of the organism into acid-soluble and -insoluble fractions.** L. D. FELTON (J. Immunol., 1934, 27, 379—393).—Organisms of types I and II retain their antigenicity after drying with  $\text{COMe}_2$  and desiccation in vac. The immunising agent occurs in the acid-sol. fraction of the cells, is pptd. (90%) by  $\text{EtOH}$  or  $\text{COMe}_2$ , and is largely sp. A small amount of immunising substance occurring in the acid-insol. fraction produces heterologous immunity in mice.

CH. ABS. (p)

**Chemo-immunological studies on the soluble specific substance of *Pneumococcus*. II. Chemical basis for immunological relationship between capsular polysaccharides of types III and VIII *Pneumococcus*.** W. F. GOEBEL (J. Biol. Chem., 1935, 110, 391—398).—The constitution of the sp. polysaccharide (I) of *Pneumococcus* VIII is examined in relation to its immunological cross-reaction with type III. (I), prepared by an earlier method (A., 1931, 267), gives glucose and an aldobionic acid of which the hepta-acetate, m.p.  $249-250^\circ$ ,  $[\alpha]_{\text{D}}^{25} +40.0^\circ$  in  $\text{CHCl}_3$ , of the Me ester gives no depression of m.p. with that of the (I) obtained from type VIII.

H. D.

**Antigenic structure of *Vibrio cholerae*. VII. Two acid-soluble protein fractions.** R. W. LINTON and B. N. MITRA (Indian J. Med. Res., 1934, 22, 295—308; cf. this vol., 787).—Two acid-sol.

protein substances, A and B, were extracted from a no. of vibrios. A was extracted by  $0.025N\text{-HCl-EtOH}$ ; amide-N was double, and humin-N half, that of the total protein. A occurred in the pseudo- and eu-globulin fractions of the protein, and appeared to increase when the whole protein was kept in  $\text{H}_2\text{O}$  at  $10^\circ$  for 2 weeks; it was destroyed by attempted extraction with  $0.125N\text{-HCl}$ . B was extracted after the removal of A by boiling in  $75\%$   $\text{EtOH}$ , dilution with  $0.9\%$   $\text{NaCl}$ , and making  $0.05N$  with  $\text{HCl}$ . B was present in greater amount in the euglobulin fraction, and did not increase in  $\text{H}_2\text{O}$  at  $10^\circ$ . Neither fraction showed any dependence on the strain of the vibrio. B was chemically similar to the residual protein and the whole protein.

R. N. C.

**Structure of cholera and cholera-like vibrios.** R. W. LINTON, D. L. SHRIVASTAVA, and B. N. MITRA (Indian J. Med. Res., 1934, 22, 309—312; cf. this vol., 786).—Elementary analytical figures are given for a no. of vibrios. The polysaccharide of *Vibrio* W880 contains arabinose (I) and an aldobionic acid complex of galactose (II) and glycuronic acid. In cholera vibrios (I) is replaced by (II).

R. N. C.

**Scarlet fever. II. Toxins produced by hæmolytic streptococci of scarlatinal origin.** S. B. HOOKER and E. M. FOLLENSBY (J. Immunol., 1934, 27, 177—193).—Two toxins are demonstrated. These may be distinguished by immunological and chemical criteria. A single toxigenic strain of organisms may produce either toxin, both, or neither.

CH. ABS. (p)

**Respiratory mechanism of the *Streptococci*.** M. A. FARREL (J. Bact., 1935, 29, 411—435).—*Streptococci* contain no catalase, but a heat-stable peroxidase (differing from plant-peroxidase) is intimately associated with the dehydrase mechanism of the cell. Cytochrome and indophenol-oxidase could not be detected in the organism. The ability of *Streptococci* to activate a large no. of org. substances is examined.

A. G. P.

**Formation of precipitin for the group A specific carbohydrate of *Streptococcus hæmolyticus* in rabbits injected intravenously and subcutaneously.** D. SEEGAL, M. HEIDELBERGER, and E. L. JOST (J. Immunol., 1934, 27, 211—214).—Rabbits injected intravenously with heat-killed *S. hæmolyticus* rapidly developed precipitin for the bacterial nucleoprotein (I) and the group A-sp. carbohydrate (II). Subcutaneous injection produced the precipitin for (I) in all cases, but that for (II) was less often obtained. Animals failing to produce the (II) precipitin after subcutaneous injection developed the antibody after intravenous injection.

CH. ABS. (p)

**Amino-acids and *Staphylococcus* toxin.** O. GENGOU (Ann. Inst. Pasteur, 1935, 55, 129—147).—*Staphylococcus* in culture media containing peptone utilises the protein of the medium in the development of its toxin. The toxin is still produced when certain  $\text{NH}_2$ -acids replace the peptone, but only with arginine (I) is the development of the toxin immediate. The toxin produced in a medium containing (I) is identical with that formed in a bouillon-peptone medium.

E. A. H. R.



**Crystal-violet-agar as a differential medium for *Staphylococci*.** G. H. CHAPMAN and C. BERENS (J. Bact., 1935, 29, 437—448).—The colour of the growths on this medium differentiates the organisms with the same order of accuracy as the hæmolytic and coagulase tests and animal inoculations.

A. G. P.

**Plurality of antigens of *Clostridium welchii*.** A. SORDELLI and J. FERRARI (Folia biol., 1931, 10—12).—Extracts of high fixative val. are obtained from suspensions of *C. welchii* at  $p_H$  7.0. The antigen is not destroyed by boiling at  $p_H$  8.6. Addition of 10%  $Na_2SO_4$  to the boiling antigen causes pptn. Antigenic activity is destroyed by EtOH or  $COMe_2$ . Differentiation between fixation antigen and precipitinogen is described.

CH. ABS. (p)

**Prozone phenomenon in specific bacterial agglutination.** F. S. JONES and M. ORCUTT (J. Immunol., 1934, 27, 215—233).—When suitable proportions of agglutination-inhibitory sera [sp. to *Br. abortus*] are added to a strong *Br. abortus* agglutinin, agglutination is inhibited or a prozone developed. Failure to agglutinate is attributed to the deposition on the surface of the globulin film of a substance which interferes with the cohesive properties of specifically sensitised organisms.

CH. ABS. (p)

**Factors influencing the rate of thermal destruction of the tetanus antitoxin of antitetanic horse plasma at 60—66°.** T. D. GERLOUGH and W. WHITE (J. Immunol., 1934, 27, 367—377).—Destruction of the antitoxin is accelerated by addition of neutral salts, up to a max. corresponding with an ionic concn. of 0.6—0.9. Further additions decrease the effect. The  $p_H$  of max. stability is at or near neutrality. The rate of destruction is markedly increased by PhOH, the increase being  $\propto [PhOH]^2$ .

CH. ABS. (p)

**Comparative value of fresh and aged tetanus toxoid as an immunising agent.** H. L. WILCOX (J. Immunol., 1934, 27, 195—198).—Fresh toxoid has approx. 50% higher antigenic val. than that stored for 3 years.

CH. ABS. (p)

**Decomposition of organic matter in sea-water by bacteria.** I. Bacterial multiplication in stored sea-water. II. Influence of addition of organic substances on bacterial activities. S. A. WAKSMAN and C. L. CAREY (J. Bact., 1935, 29, 531—543, 545—561).—I. The  $[O_2]$  of the  $H_2O$  has an important influence on bacterial activities. With a reduced  $[O_2]$  org. matter is attacked with considerable difficulty. A close parallelism exists between bacterial multiplication,  $O_2$  consumption, and the liberation of N in an available form. Sea- $H_2O$  contains sufficient dissolved org. matter to support an extensive bacterial population.

II. The bacterial population developing in sea- $H_2O$  varies with the nature and quantity of org. matter present. The decomp. of N-free org. matter, e.g., glucose (I), added to the  $H_2O$  is controlled by the amount of available N. The latter may be determined directly (as  $NH_3$ ) or indirectly by the amount of (I) decomposed.

A. G. P.

***Escherichia*-*Aerobacter* intermediates. I. Cultural characteristics.** R. P. TITSLER and L. A.

SANDHOLZER (J. Bact., 1935, 29, 349—361).—The heterogeneity of this group of organisms is demonstrated by the varied ability of different members to ferment carbohydrates, notably cellobiose and  $\alpha$ -methylglucoside, and other materials. A system of classification is described.

A. G. P.

**Fermentation of  $\alpha$ -methylglucoside by bacteria.** R. P. TITSLER and L. A. SANDHOLZER (J. Bact., 1935, 29, 363—368).—Relatively few species characterise the glucoside. The use of this substance in characterising certain species of the *Escherichia*-*Aerobacter* group is considered (see preceding abstract).

A. G. P.

**Specificity of hexosidases. Comparison of activity of *E. coli* and *E. communior*.** M. HOTCHKISS (J. Bact., 1935, 29, 391—398).—All preps. of *E. coli* contained maltase but not invertase. In a no. of cultures of *E. communior*, either or both enzymes appeared.

A. G. P.

**Growth of *B. coli* on alanine.** E. AUBEL and K. SOETERS (Compt. rend. Soc. Biol., 1935, 119, 1035—1036).—*B. coli* grown in a medium containing alanine decolorises methylene-blue, Nile-blue, or cresyl-violet, the last also being decolorised in a medium containing  $AcCO_2H$ .

R. N. C.

**Lipoid hapten of aqueous extracts of living tubercle bacilli.** G. SANDOR and C. NINNI (Ann. Inst. Pasteur, 1935, 55, 38—45).—Aq. extracts of tubercle bacilli yield a lipid hapten sol. in EtOH and then insol. in  $H_2O$  which is responsible for its power of absorbing complement in presence of antiserum. Its presence in the aq. extract is apparently due to its forming loose combinations with the proteins and allied substances.

W. O. K.

**Residual antigens of *B. tuberculosis*.** G. SANDOR and W. SCHAEFER (Ann. Inst. Pasteur, 1935, 55, 163—174).—Polysaccharides (I) and proteins pptd. from filtrates of *B. tuberculosis* cultures by  $(NH_4)_2SO_4$  have the same antigenic effect on anti-BCG horse-serum. A very active hapten-like fraction is obtained by fractional pptn. of (I) with MeOH. This fraction has a very variable chemical constitution and the hapten-like substance can be present only in very small concn.

E. A. H. R.

**Chemistry of tubercle bacilli. Presence in the "smooth" variety of a precipitation hapten that does not exist in the "rough" variety.** M. A. MACHEBOEUF and J. DIERYCK (Compt. rend. Soc. Biol., 1935, 119, 917—919).—EtOH extracts of "smooth" tubercle bacilli, shaken, after removal of EtOH, with  $H_2O$  and  $Et_2O$ , give a three-phase mixture, a thick opaque emulsion-like layer appearing between the  $H_2O$  and  $Et_2O$  phases; extracts of the "rough" bacilli do not give this substance. The emulsion is purified by repeated pptn. from tepid EtOH solution with  $H_2O$  (the last pptn. at 0°), followed by pptn. with  $Et_2O$ . The ppt. contains no P or N, and is hydrolysed by acid or alkali into an  $Et_2O$ -sol. fraction containing sp. fatty acids, and a  $H_2O$ -sol. fraction, which is not a reducing sugar. It is pptd. by "anti-smooth," but not by "anti-rough," sera. It does not fix alexin, and is hence a pptn. hapten.

R. N. C.



**Development of precipitins for protein, lipin, and carbohydrate fractions of *S* and *R* forms of tubercle bacilli.** C. E. RICE (J. Immunol., 1935, 28, 19—30).—Precipitin tests show small differences in the proteins (I) and carbohydrates (II) of *S* and *R* types. Lipin fractions show no type-specificity. During immunisation with killed *S* bacilli there is an increase in precipitins for (I) and (II) from *S* organisms over that of precipitins for (I) and (II) of *R* forms. *S*-antisera reacted more strongly with purified globulin and polysaccharide preps. from virulent cultures of human types than did *R*-antisera. The latter were the more reactive toward purified albumin.

CH. ABS. (p)

**Properties of the tuberculin extracted from bacilli by serum and organic liquors.** A. BOQUET and R. LAPORTE (Compt. rend. Soc. Biol., 1935, 119, 1038—1040).

R. N. C.

**Action of dilute heavy water on tubercle bacilli.** M. ITOH, K. INOSHITA, and T. TITANI (Bull. Chem. Soc. Japan, 1935, 10, 260).—The growth of tubercle bacilli of types *bobinus* and *Kamike* in Long's medium is increased both by decrease of  $[H^+]$  from  $p_H$  5.83 to 7.25 and by increase of  $D_2O$  from 0.08% to 2.24% [D].

F. R. G.

**Metabolism of residual nitrogen and curves of elimination of glycine in rabbits inoculated with *BCG*.** F. PEZZANGORA (Compt. rend. Soc. Biol., 1935, 119, 964—966).—The metabolism of residual N is scarcely affected by injection of *BCG*. The elimination curves of residual N after injection of glycine are slightly disturbed, becoming normal again 4 weeks after the *BCG*-inoculation.

R. N. C.

**Cultural requirements of bacteria. IV. Quantitative determination of bacterial growth.** J. H. MUELLER (J. Bact., 1935, 29, 383—387).—Micro-determinations of bacterial N serve as a measure of growth. The cells are separated and subsequently washed (centrifuge) with dil. AcOH.

A. G. P.

**Micro-method for determining the utilisation of carbohydrates and polyhydric alcohols by micro-organisms.** F. H. JOHNSON (Science, 1935, 81, 620—621).—The change in colour of phenol-red to yellow is the basis of the method.

L. S. T.

**Agar. II. Physico-chemical properties of agar and their influence on the growth of micro-organisms.** A. ITANO and Y. TSUJI (Ber. Ohara Inst. landw. Forsch., 1935, 6, 575—586; cf. B., 1934, 475).—Good-quality agar is more sol. and contains less total N than other grades. Grade III agar is more efficient than grade I for the growth of *B. subtilis*, *Azotobacter chroococcum*, and *Saccharomyces cerevisiae*. Grade I agar has a lower  $p_H$ .

P. G. M.

**Inactivation of bacteriophage by oxidation.** I. LOMINSKI (Compt. rend. Soc. Biol., 1935, 119, 952—954).—Bacteriophage is inactivated by  $KMnO_4$  at relatively low concns. The min. concn. for inactivation is  $\propto$  the reducing power of the medium, and inversely  $\propto$  the temp., suggesting that the inactivation is due to oxidation.

R. N. C.

**Comparative sensitivity of bacteriophages and homologous bacteria to oxidation.** I. LOMINSKI

(Compt. rend. Soc. Biol., 1935, 119, 1090—1092).—Bacteriophages are more sensitive to oxidation by  $KMnO_4$  than the homologous bacteria, which is in contrast to their behaviour with most physical and chemical agents. The fact permits the removal of bacteriophages from cultures containing them.  $KMnO_4$  appears to act only on the extracellular bacteriophages.

R. N. C.

**Antibacteriophagic properties of human sera.** R. BIGLIERI and A. FISCHER (Folia biol., 1931, 21—24).—Certain human and rabbit (but not horse or guinea-pig) sera possessed marked antibacteriophagic properties in presence of *Staphylococcus* of human origin.

CH. ABS. (p)

**Bactericidal action of water exposed to the combined action of metallic silver and electrolysis.** N. METALNIKOV (Compt. rend., 1935, 201, 411—412).—Marked bactericidal activity ( $\propto$  area of anode and *I* and not destroyed by boiling) in  $H_2O$  is produced by mild electrolysis (e.g., 3—4 milliamp. at 1.5—4.5 volts) with Ag anode and C cathode. The product is not toxic to mice.

F. O. H.

**Gonococcicidal action of mallophen in urine.** R. D. HERROLD (J. Lab. Clin. Med., 1934, 20, 53—55).—Mallophen (I) in urines (1:2000—3000) at  $p_H$  4.9—7.0 kills gonococci. At dilutions of 1:4000 (I) is not effective in nearly neutral urines, but prevents growth in acid samples. All urines having  $p_H < 5.4$  have some gonococcicidal action.

CH. ABS. (p)

**Bactericidal power of blood.** R. OTTENBERG (J. Lab. Clin. Med., 1934, 20, 70—74).—The bactericidal power of blood is not decreased by presence of Na citrate. Disappearance of streptococci during incubation with blood is more marked when the latter is drawn from patients infected with homologous strains. Defibrination removes large nos. of bacteria from serum.

CH. ABS. (p)

**Action of X-rays on certain bacteria.** A. T. PUGSLEY, T. H. ODDIE, and C. E. EDDY (Proc. Roy. Soc., 1935, B, 118, 276—298).—*Sarcina lutea*, *B. coli*, and *Phytomonas medicaginis* are killed by X-rays, the ratio of sensitivities being 0.3:1:3. For equal doses, the longer  $\lambda$  are more effective and it appears that the medium is affected similarly to the production of a toxin. After consideration of the survival rate of bacteria singly and in colonies, the one-quantum-hit-to-kill theory of Crowther is considered the most satisfactory explanation of the mode of killing.

H. G. R.

**Hormones.** O. RIDDLE (Endocrinol., 1935, 19, 1—13).—An address.

R. N. C.

**Biological effects of thymus extract (Hanson).** L. G. ROWNTREE, J. H. CLARK, and A. STEINBERG (Arch. Int. Med., 1935, 56, 1—29).—A detailed account of work already noted (A., 1934, 1266).

**Determination of thyroxine in thyroid substance.** N. F. BLAU (J. Biol. Chem., 1935, 110, 351—363).—Greater yields of thyroxine (I) are obtained by acidification of the tissue hydrolysate to  $p_H$  5 before extraction with BuOH; the time of hydrolysis with NaOH may be shortened by this treatment.



Only 4% loss is sustained by boiling (I) with  $\text{Ba}(\text{OH})_2$  for 6 hr.; this is increased to 10% if proteins are present. The method of determining (I) described earlier (A., 1933, 1209) is modified accordingly.

H. D.

**Determination of thyroxine-iodine by hydrazine.** H. PAAL and G. MOTZ (Biochem. Z., 1935, 279, 106—107).—Aq. preps. (equiv. to 1—2 mg. of thyroxine) are refluxed with  $\text{N}_2\text{H}_4$  (1—2 drops) and  $\text{N-NaOH}$  (1—2 c.c.) for 1 hr. and the liberated I is pptd. as  $\text{AgI}$  and determined electrochemically.

F. O. H.

**Thyroxine and tissue metabolism.** A. H. SCOTT (Amer. J. Physiol., 1935, 111, 107—117).—Thyroxine (I) *in vivo* accelerates metabolism in the blood of the alligator. Glucose consumption and lactic acid (II) production are increased, and intermediate products other than (II) decreased; the R.Q. is lowered *in vivo* and *in vitro*. Metabolism increases in early summer. (I) *in vivo* produces an initial acidosis followed by a progressive alkalosis, due probably to increased  $\text{CO}_2$  production and increase of the buffering power of the blood. (I) is destroyed only slowly, increased metabolism persisting after 6 months. (I) *in vitro* increases  $\text{O}_2$  consumption in some cases, but does not increase  $\text{CO}_2$  production.

R. N. C.

**Compounds that affect basal metabolism in man.** W. O. THOMPSON, P. K. THOMPSON, S. G. TAYLOR, S. B. NADLER, and L. F. N. DICKIE (Endocrinol., 1935, 19, 14—20).—Thyroxine (I) is more active calorigenically than any other known compound. Basal metabolism is also affected by *N*-acetylthyroxine, adrenaline, di-iodothyronine (II),  $\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{OH}$  (III), and di-iodotyrosine, in decreasing order of activity; thyronine is apparently inert. The activity of (I) is greatly reduced by slight changes in the mol., the  $(\text{C}_6\text{H}_5)_2\text{O}$  and  $\text{NH}_2$  and all four I being important. The calorogenic response to (II) is of shorter duration than that to (I); the response to (III) lasts only a few days as compared with 70—90 days for (I). Attempts to determine the (I) content of desiccated thyroid have resulted in the destruction of most of its calorogenic activity. Peptic digestion of thyroid produces an acid-insol. I fraction, the activity of which per mg. I is  $>$  that of the whole gland, and an acid-sol. fraction, the activity of which per mg. I is  $<$  that of the whole gland. Subcutaneous injection of pituitary growth-hormone and of "phy-one" to cases of various types has produced in many of them a definite increase of basal metabolism.

R. N. C.

**Action of diuresis and thyroxine on protein metabolism.** G. SCOZ (Boll. Soc. Ital. Biol. sperim., 1933, 8, 1718—1720; Chem. Zentr. 1935, i, 917).—Total N excretion is temporarily increased by thyroxine; a longer retention period follows for N and S. Diuresis appears through increase of urea- $\text{NH}_3$  and  $\text{NH}_2$ -acids, whilst allantoin, creatine, and creatinine fall. Hence thyroxine increases exogenous, and lowers endogenous, protein metabolism.

R. N. C.

**Phospholipin content of liver, skeletal muscle, and whole blood, as affected by thyroxine injections.** L. H. SCHMIDT (Amer. J. Physiol., 1935,

111, 138—144).—Injection of thyroxine in rabbits produces decrease of phospholipin fatty acids and increase of non-phospholipin fatty acids in liver, whilst in skeletal muscle the former are increased and the latter are decreased. Both are increased in blood.

R. N. C.

**Inhibition of thyroid activity by animal blood.** EITEL and LOESER (Klin. Woch., 1934, 13, 1742—1744).

G. H. F.

**Biochemical basis of thyroid function.** C. R. HARRINGTON (Lancet, 1935, 228, 1199—1204, 1261—1266).—Lectures.

L. S. T.

**Use of rabbits in the standardisation of parathyroid hormone.** F. J. DYER (Quart. J. Pharm., 1935, 8, 197—212).—The method of Hamilton and Schwartz has been modified, using groups of rabbits and analysing the average blood samples. The variations in the normal val. and in those after injection admit of qual. work only.

H. G. R.

**Vasopressin content of the pituitary of the normal guinea-pig, and after injections of folliculin or thyroxine.** J. A. SCHOCKAERT and A. LEJEUNE (Compt. rend. Soc. Biol., 1935, 119, 1197—1199).—The vasopressin content of the posterior pituitary of the male guinea-pig is remarkably const., and is not affected by folliculin or thyroxine.

R. N. C.

**Presence of a substance antagonistic to vasopressin in the serum of pregnant women.** J. A. SCHOCKAERT and J. LAMBILLON (Compt. rend. Soc. Biol., 1935, 119, 1194—1197).—The effect of vasopressin in cats is reduced by simultaneous injection of pregnancy serum, but not by normal serum.

R. N. C.

**Effect of the pituitary growth-hormone on mice with hereditary dwarf growth.** T. KEMP (Klin. Woch., 1934, 13, 1854—1855).—Injection of ox anterior pituitary into dwarf mice with hereditary anterior pituitary defect (lack of eosinophils) resulted in harmonious growth of all organs. There was excessive growth of the thymus (3—4 times normal wt.).

G. H. F.

**Maternal behaviour in male rats.** M. McQUEEN-WILLIAMS (Science, 1935, 82, 67—68).—Such behaviour can be induced in male rats by chronic administration of bovine pituitary implants or by complete thyroidectomy. In both cases the pituitaries are considerably enlarged. No mammary development occurs in the latter case.

L. S. T.

**Action of the anterior pituitary-like substance of urine on the metabolism of dogs.** O. H. GAEBLER (Endocrinol., 1935, 19, 63—68).—Metabolism is not affected by large doses of the anterior pituitary-like substance of pregnancy urine. In some cases  $\text{H}_2\text{O}$  and N storage occurs similar to that produced by growth-hormone preps.

R. N. C.

**Effect of antuitrin-S on the male lizard, *Anolis carolinensis*.** L. T. EVANS (Anat. Rec., 1935, 62, 213—221).

R. N. C.

**Response of the isolated gall-bladder to cholecystokinin.** F. T. JUNG and H. GREENGARD (Amer. J. Physiol., 1933, 103, 275—278).—Chole-



cystokinin caused contraction of the gall-bladder of the guinea-pig, was active between  $pH$  5.0 and 8.5, and was destroyed by alkali and heat. It still produced contraction, after atropine had rendered both pilocarpine and acetylcholine ineffective.

CH. ABS. (p)

**Effect of incretin on the glycogen reserve of the liver in the rabbit.** J. LA BARRE and G. HOUSSA (Compt. rend. Soc. Biol., 1935, 119, 1179—1181).—Intravenous injection of small quantities of incretin in young rabbits produces an increase in liver-glycogen. The hypoglycæmic effect of duodenal extracts is probably due to this action.

R. N. C.

**Plant secretions.** J. SKUJA (Skand. arch. Physiol., 1934, 70, 126—132; Chem. Zentr., 1935, i, 912).—By the method previously described (A., 1933, 319) secretins were detected in fresh tomato sap, in fermenting cabbage, sour cucumbers, silage, and in spontaneously soured milk.

A. G. P.

**Action of the pancreatropic hormone of anterior pituitary origin on blood-sugar.** E. ZUNZ and J. LA BARRE (Compt. rend. Soc. Biol., 1935, 119, 1174—1177).—Intravenous injection of pancreatropic hormone in dogs produces a fall of blood-sugar by stimulating insulin secretion. Thyroidectomy does not affect the action.

R. N. C.

**Influence of various hormones on intestinal absorption. III. Amino-acid.** S. ISAWA (J. Chosen Med. Assoc., 1934, 24, 1332—1342; cf. this vol., 540).—Absorption of 0.5% glycine solution (in 0.9% NaCl) was accelerated by insulin, retarded by pituglandol and adrenaline, and unaffected by thyroxine.

CH. ABS. (p)

**Insulin-inhibiting agency in the duodenum.** A. B. MACALLUM (Nature, 1935, 136, 32).—Extracts from the duodenum of rabbits contain a component antagonistic to insulin.

L. S. T.

**Influence of adrenaline and insulin on carbohydrate metabolism of snails (*Helix pomatia*, L.).** G. WOLF-HEIDEGGER (Biochem. Z., 1935, 279, 55—63).—The blood-sugar of snails in summer is  $0.022 \pm 0.008\%$ , this val. being reduced by approx. 50% in winter. Adrenaline produces a depigmentation but neither adrenaline nor insulin has any apparent effect on the carbohydrate metabolism (blood-sugar and glycogen levels).

F. O. H.

**Increase in insulin secretion following injections of adrenaline and its relation to the high liver-glycogen values obtained.** J. L. CHIDSEY and J. A. DYE (Amer. J. Physiol., 1935, 111, 223—229).—Adrenaline (I) is more effective in raising the blood-sugar of a depancreatized dog given sufficient insulin (II) to keep the blood-sugar normal, than that of a normal dog. Glycogen (III) is high in the liver and low in the muscles of a normal dog several hr. after (I) administration, but low in both liver and muscles in the depancreatized dog given (II). (I) stimulates (II) secretion in normal dogs, the increase being responsible both for the slower rise in blood-sugar and the high (III) vals.

R. N. C.

**Effects of adrenaline injection in moderate work.** D. B. DILL, H. T. EDWARDS, and R. H. DE

MEIO (Amer. J. Physiol., 1935, 111, 9—20).—A fasting man expends 5000 kg.-cal. of energy in 24 hr., about 1.5% of which is derived from protein, and about 50% of the total from carbohydrate in the early stages, but < 10% in the last 2 hr. Adrenaline (I) does not affect protein metabolism, but increases carbohydrate utilisation. Excretion of ketones always falls after (I), showing that carbohydrate oxidation in moderate activity is facilitated. The effects of (I) on blood-sugar resemble those in resting subjects.

R. N. C.

**Continuous injection of adrenaline and adrenaline secretion.** J. MALMÉJAC, V. DONNET, and E. DESANTI (Compt. rend. Soc. Biol., 1935, 119, 1152—1154).—Continuous injection of small quantities of adrenaline in the dog reduces adrenaline secretion for the period of injection, the reduction being sufficient to cause a considerable fall of blood-sugar.

R. N. C.

**A mechanism by which continuous injection of adrenaline reduces adrenaline secretion.** J. MALMÉJAC, V. DONNET, and E. DESANTI (Compt. rend. Soc. Biol., 1935, 119, 1155—1157).—Adrenaline (I) secretion is not reduced by continuous injection of (I) in the dog if the depressors have been cut. Perfusion of a vascularly isolated carotid sinus with Ringer's solution containing (I) reduces (I) secretion; hence this action is one of the mechanisms by which (I) secretion is reduced.

R. N. C.

**Modifications in distribution of phosphorus in rabbit livers by changes in blood-sugar and liver-glycogen.** T. TAKAHISA (Japan. J. Med. Sci., IV, 1934, 8, 117—119).—Subcutaneous injection of adrenaline hydrochloride (0.2 mg. per kg.) increased the blood-sugar and decreased liver-glycogen (I). Inorg.  $PO_4'''$  was slightly increased, but other constituents were scarcely affected. Administration of insulin (1 unit per kg.) caused hypoglycæmia and a slight increase in (I). Inorg. P, phosphagen, N, and total phosphates increased. Intravenous injection of phloridzin (300 mg. per kg.) produced no change in blood-sugar, but increased (I) and lactacidogen phosphate. Oral administration of glucose (10 g. per kg.) increased inorg., phosphagen-, and lactacidogen-phosphate.

CH. ABS. (p)

**Influence of amino-acids on the action of adrenaline.** K. TERAI (Japan. J. Med. Sci., IV, 1933, 7, 111—112).—Adrenaline inactivated by storage in darkness at  $pH$  8.0 became active (perfusion through rabbit ears) on addition of  $NH_2$ -acids (histidine, lysine, etc.). The degree of action was paralleled by the amount of acid added.

CH. ABS. (p)

**Adrenaline-sensitising action of alanine.** M. KATÔ (Japan. J. Med. Sci., IV, 1934, 8, 130).—The action of *d*- was > that of *l*-alanine in sensitising the constrictor action of adrenaline on the isolated rabbit ear.

CH. ABS. (p)

**Influence of dihydroxyphenylalanine on adrenaline glycogenolysis.** J. HORIMI (Japan. J. Med. Sci., IV, 1933, 7, 112).—Dihydroxyphenylalanine (I) exhibited a glycogenolytic action on toad liver resembling that of adrenaline (II). (I) potentiated the action of (II).

CH. ABS. (p)



**Effect of sympathol and adrenalone on the action of adrenaline.** M. KATÔ and S. AIBARA (Japan. J. Med. Sci., IV, 1933, 7, 113).—Administration of sympathol or adrenaline (1–2 mg. per kg.) increased the pressor action of adrenaline (I) on rabbits and also the depressant action on intestinal motility. Larger doses weakened the action of (I). CH. ABS. (p)

**Effect of adrenalone on blood-sugar and lactic acid.** T. ASADA (Japan. J. Med. Sci., IV, 1934, 8, 119–120).—Injection of adrenalone (I) increased blood-sugar and lactic acid to extents  $\propto$  the dosage. (I) was less effective than adrenaline and its action was partly antagonised by pituitrin or  $\text{CaCl}_2$ . CH. ABS. (p)

**Some factors affecting adrenal insufficiency in the rat.** F. J. AGATE, jun., and R. L. ZWEMER (Amer. J. Physiol., 1935, 111, 1–8). R. N. C.

**Adrenal cortex and vitamin-A content of the blood.** J. MALMEJAC, A. CHEVALLIER, and Y. CHORON (Compt. rend. Soc. Biol., 1935, 119, 1158–1160).—Splanchnic excitation in the dog increases blood-vitamin-A by stimulation of the adrenal cortex. R. N. C.

**Adrenaline content of adrenal glands of grown rats.** H. ENDO (Japan. J. Med. Sci., IV, 7; Proc. Japan. Pharmacol. Soc., 1933, 82–83).—Monthly determinations are recorded. The average val. for the year was 0.09 g. per kg. body-wt. Subcutaneous administration of adrenaline lowered the amount in the gland. CH. ABS. (p)

**Specificity of the Viale reaction for detecting adrenaline in the urine.** F. DOMENICI (Boll. Soc. Ital. Biol. sperim., 1935, 10, 53–55).—The reaction is sp. for adrenaline. R. N. C.

**Effect of ultra-violet light on some sympathomimetic substances.** P. L. EWING (J. Lab. Clin. Med., 1934, 20, 16–33).—The normal physiological activity of adrenaline is destroyed by exposure to ultra-violet light. The decomp. products, which have no pressor action, are similar to those formed by the action of  $\text{H}_2\text{O}_2$ . The activity of synephrine (I) salts and of *p*-hydroxyphenylpropanolamine is increased by moderate and destroyed by excessive irradiation. The free (I) base is unaffected. CH. ABS. (p)

**Padutin.** R. SIVÓ and E. VON DOBOZY (Klin. Woch., 1934, 13, 1602–1605; Chem. Zentr., 1935, i, 917).—Padutin (callicrein), injected intramuscularly, abolishes the cyanosis and gangrene of the comb produced by ergotin in cocks. It also neutralises the constrictor effect of adrenaline (I) in the Lâwen-Trendelenburg frog prep. It does not antagonise the midriatic effect of (I) on the enucleated frog's eye, but inhibits its hyperglycæmic action in normal man, without affecting the blood-sugar *per se*. R. N. C.

**Effect of the circulation hormone padutin on the resorption of intracutaneous sodium chloride wheals.** H. FRENKEL (Klin. Woch., 1934, 13, 1749–1751; Chem. Zentr., 1935, i, 917–918).—The rate of resorption of NaCl injected into the skin of rabbits is increased by intravenous injection of

padutin (I). The same effect appears in human patients, and  $\text{COMe}_2$  and  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{H}$  disappear from the urine. Intramuscular injection of (I) also accelerates resorption. (I) probably causes dilatation and increased permeability of the intradermal vessels. R. N. C.

**Chemistry of œstrogenic substances.** E. FRIEDMANN (Nature, 1935, 136, 108).—A criticism (cf. this vol., 1033). L. S. T.

**Nature of the œstrogenic substance in human male urine and bull testis.** R. I. DORFMAN, T. F. GALLAGHER, and F. C. KOCH (Endocrinol., 1935, 19, 33–41).—Theelol (I) is more effective than theelin (II) in causing vaginal introitus in the rat, whilst (II) is more effective in causing uterine hypertrophy. The œstrogenic substance in the total  $\text{C}_6\text{H}_6$  extract of normal male urine does not cause either of these effects; that in the alkali-sol. fraction of the  $\text{C}_6\text{H}_6$  extract is biologically identical with (II). The alkali-insol. fraction probably contains a substance that enhances the action of (II) on the uterus and vagina, but is neither (I) nor (II). R. N. C.

**Effect of œstrin injections on the developing ova of mice and rabbits.** H. O. BURDICK and G. PINCUS (Amer. J. Physiol., 1935, 111, 201–208).—Daily injections of œstrin from the day of mating result in retention of the ova in the Fallopian tubes, followed by degeneration from the fourth day. R. N. C.

**Prolonged administration of theelin and theelol to male and female rats and its bearing on reproduction.** N. J. WADE and E. A. DOISY (Endocrinol., 1935, 19, 77–87).—Prolonged administration of theelin or theelol (I) to male rats lowers body-wt. and the wts. of the testes, prostates, and Cowper's glands; fertility is somewhat reduced. Female rats given (I) show reproduction < normal and an interference with lactation. R. N. C.

**Structural and functional features of rabbits' uteri following prolonged œstrin administration.** S. R. M. REYNOLDS (Anat. Rec., 1935, 62, 269–277).—The uterus loses its motility and the endometrium undergoes progressive involution. The uterus is still responsive to progesterin, and hence the involution is not due to the development of an anti-hormone against œstrin. R. N. C.

**Effect of œstrin and male hormone injected separately and simultaneously on the smooth muscle and epithelium of the seminal vesicle in the albino rat.** M. D. OVERHOLSER and W. O. NELSON (Anat. Rec., 1935, 62, 247–267).—Prolonged administration of œstrin to normal or castrated rats stimulates the growth of the smooth muscle of the seminal vesicle, and also the seminal vesicle epithelium in castrated animals. Œstrin and the male hormone act synergistically on the smooth muscle and the epithelium when administered simultaneously. R. N. C.

**Destruction of folliculin in the animal body.** B. ZONDEK (Skand. Arch. Physiol., 1934, 70, 1933–1967).—When  $\alpha$ -folliculin (I) is injected into male and female rats even in excessive doses, only about 0.2% can be recovered from the urine. In man (male



and female) approx. 3% is recovered. On extraction of whole rats < 2%, and after acid hydrolysis up to 20%, can be recovered. Loss of the remainder is due to inactivation in the liver. 95% of (I) is destroyed *in vitro* by liver extract. Folliculin benzoate is not thus inactivated. The enzyme action probably results in esterification, attacking the phenolic OH (the action being partly reversible by acid hydrolysis); in the benzoate mol., this position is already occupied by the Bz. (I) is adsorbed by striped muscle-tissue. G. H. F.

**Hormones from cases of toxæmias of pregnancy.** K. HEIM (Klin. Woch., 1934, 13, 1614).—The folliculin and prolan contents of urine in cases of toxæmias of pregnancy are much > normal and are comparable with those in cases of hydatidiform mole and chorioepithelioma. Increased secretion of folliculin in twin pregnancies is in agreement with the known relationship between multiple births and eclampsia. G. H. F.

**Experimental production of hermaphrodites by injecting folliculin into chicken embryos.** E. WOLFF and A. GINGLINGER (Compt. rend., 1935, 200, 2118–2120).—Folliculin injected into chicken embryos prior to the 7th day of incubation inhibits the development of males. After the 7th day, hermaphrodite tendencies are lessened. J. L. D.

**Comparative luteinising capacity of the urine of pregnancy and of the menopause.** A. LIPSCHÜTZ (Endocrinol., 1935, 19, 42–50).—The coeff. of luteinisation in the infantile rat of the urine of pregnancy tends to diminish as the quantity of urine injected is increased. In the urine of the menopause it is relatively low. R. N. C.

**Luteinising hormone and cholesterolaemia.** L. CIOGLIA and D. TORE (Boll. Soc. Ital. Biol. sperim., 1935, 10, 75–77).—Injection of progestin (I) in rabbits provokes an increase of blood-cholesterol (II). (I) combined with folliculin (III) provokes a smaller and less prolonged fall of (II) than (III) alone. (I) and antelobin (IV) combined do not affect (II). Hence (I) antagonises (III) and (IV). R. N. C.

**Steric inversion of carbon 3 of sterols and male sexual hormones.**—See this vol., 1125.

**Sexual hormones.** V, VI.—See this vol., 1125.

**[Preparation of the male sexual hormone.]** B. FRATTINI and M. M. MAINO (Ber., 1934, 68, [B], 677–679, 1264–1265). K. TSCHERNING (*ibid.*, 679–681).—A further discussion regarding priority (cf. A., 1930, 505; 1931, 398; 1934, 781).

**Biological activity of derivatives of the male hormone androsterone.** R. K. CALLOW and R. DEANESLY (Lancet, 1935, ii, 77–78).—Dihydroandrosterone produces normal growth of the accessory glands of the pre-puberally castrated rat; the seminal vesicles grow equally with prostate. Androsterone benzoate is inactive with respect to castrated rats, probably owing to its slow rate of hydrolysis. L. S. T.

**Assay of crystalline male sexual hormone (androsterone).** V. KORENCHESKY and M. DENNISON (Biochem. J., 1935, 29, 1720–1731; cf. A.,

1934, 1269).—Using castrated rats and doses of 200–900 × 10<sup>-6</sup> g. in olive oil solution the dose of synthetic androsterone (I) ∝ % increase in wt. of prostate or prostate vesicles. For higher doses the increase is less. The relation between the average activity of (I) and the rat unit is determined; 1 rat unit of comb-growth activity = 162–169 and of whole male sexual activity is 165–172 × 10<sup>-6</sup> g. The effects of (I) on the wt. of penis and preputial glands are not so regular. H. D.

**Water retention and vitamin-A.** G. DOMINICI and G. OLIVERA (Deut. med. Woch., 1934, 60, 1955).—Administration of vitamin-A increased the daily output of urine in cases of cirrhosis of liver, and slightly increased output in precirrhosis; it had no effect on normals, or on a cancer case with liver metastases. G. H. F.

**Hypervitaminosis-A.** K. STRAUSS (Beitr. path. Anat., 1934, 94, 345–352; Chem. Zentr., 1935, i, 1260).—White rats fed with large excess of vitamin-A show symptoms of poisoning after 4 weeks, even though the amount of vitamin-D given is < the toxic limit. R. N. C.

**Histology of avitaminosis-A.** I, II. T. H. DE RUYTER (Acta Brev. neerl. Physiol., 1934, 4, 122–124, 124–126; Chem. Zentr., 1935, i, 1260–1261).—I. The metaplastic epithelium of rats cured of avitaminosis-A is compensated, the lymphatic and recticular apparatus and the thymus recover, and glycogen reappears in the liver. There is no indication of a relation between vitamin-A deficiency and tumour formation.

II. Avitaminosis-A reduces the resistance of rats to spontaneous lung infections. Fat resorption is more rapid than in normal animals. There is no difference in the lipin-P of the blood. R. N. C.

**Antagonism of vitamin-A and -C.** H. WENDT and H. SCHROEDER (Z. Vitaminforsch., 1935, 4, 206–212).—Administration of vitamin-C to guinea-pigs or rats inhibits the symptoms of hypervitaminosis, growth retardation, and hepatic storage of vitamin-A due to excessive doses of -A. F. O. H.

**Influence of vitamins on growth of normal and tumour tissue.** T. GORDONOFF and T. LUDWIG (Z. Vitaminforsch., 1935, 4, 213–223).—The growth of embryonic heart fibroblasts and tumour transplants in plasma from rats suffering from avitaminosis-A is < that in normal plasma which, in turn, is < that in plasma from rats receiving excess of vitamin-A. The same technique indicates that vitamin-D has no influence, and -C a retarding action, on growth. F. O. H.

**Plural nature of vitamin-B.** A. G. HOGAN and L. R. RICHARDSON (Nature, 1935, 136, 186).—EtOH extracts of rice, wheat-germ oil, and flavins differ in their ability to cure dietary deficiencies in rats, and provide additional evidence for the plural nature of vitamin-B. L. S. T.

**"Oryzotoxin" and experimental beri-beri in the pigeon.** G. SOLARINO (Boll. Soc. Ital. Biol. sperim., 1935, 10, 11–14).—Intramuscular or oral administration of EtOH extracts of rice, autoclaved grain, or starch to starved pigeons produces poly-



neuritis leading to death. In birds fed with maize, larger doses and longer treatment are necessary. The extracted rice or autoclaved grain also provokes beri-beri, the toxic action being > that of the unextracted material.  $\text{Et}_2\text{O}$  extracts a further quantity of "oryzotoxin" from the residue, but does not lessen the toxic action. R. N. C.

**Avitaminosis.** Toxic substance extracted from polished rice. L. TOCCO and S. BRUNO (Boll. Soc. Ital. Biol. sperim., 1935, 10, 67—68).—A substance producing polyneuritis in pigeons is extracted from polished rice with slightly acid  $\text{H}_2\text{O}$  and pptd. from the extract by neutralisation with  $\text{NH}_3$ .

R. N. C.

**Growth factors.** Influence of vitamin- $B_1$  and wheat-germ oil on *Mucorineae*. W. H. SCHOPFER (Z. Vitaminforsch., 1935, 4, 187—206).—Various genera of *Mucorineae* do not grow in a synthetic medium free ( $< 1 \times 10^{-6}$  g.) from vitamin- $B_1$ . Wheat-germ extracts contain a similar growth factor which is not identical with vitamin- $B_1$  (cf. this vol., 544, 663).

F. O. H.

**Crystalline vitamin- $B_1$  as growth-hormone for micro-organisms (*Phycomyces*).** W. H. SCHOPFER (Arch. Mikrobiol., 1935, 6, 139—140).—Effects previously ascribed (this vol., 534) to vitamin- $B_2$  are now recorded as due to certain impurities, probably  $B_1$ .

A. G. P.

**Vitamin- $B_1$ . I. Solubility as present in the international standard preparation. II. Isoelectric point as determined by electrophoresis of solutions made from the international standard preparation.** G. SANKARAN and N. K. DE (Indian J. Med. Res., 1934, 22, 215—232, 233—247).—I. The solubility of vitamin- $B_1$  is min. at  $p_H$  3.5; the rate of increase as  $p_H$  rises is > as  $p_H$  falls. The relation between  $p_H$  and  $\lambda_{\text{max. abs.}}$  is linear,  $\lambda$  increasing with  $p_H$ . The prep. of standard solutions at all  $p_H$  vals. is described.

II. Vitamin- $B_1$  behaves as an amphoteric electrolyte in electrophoresis, migration being bipolar over a range of two  $p_H$  units. The isoelectric point is approx. 3.0.

R. N. C.

**Electrical transference of vitamin- $B_1$  in aqueous solution.** B. N. GHOSH and B. C. GUHA (Current Sci., 1935, 3, 554).—Electrodialytic migration of vitamin- $B_1$  to the cathode (A., 1931, 1338) is confirmed at  $p_H$  8.2, in refutation of the criticisms of Sankaran and De (see above).

E. W. W.

**Oryzanin "antineuritic vitamin." IV. Activity and thermostability of oryzanin hydrochloride.** S. ODAKE and T. YAMAGISHI (Bull. Agric. Chem. Soc. Japan, 1935, 11, 51—61).—The yield of oryzanin hydrochloride (I) from rice polishings and yeast has been improved. 0.001 mg. is the min. dose for curing young rats of vitamin- $B_1$  deficiency and for maintaining normal growth. The activity of (I) is destroyed by heating the aq. solution for 1 hr. at  $140^\circ$ , or by heating the crystals for 1 hr. at  $180^\circ$ .

J. N. A.

**Growth-promoting action of synthetic flavins.** P. GYÖRGY (Z. Vitaminforsch., 1935, 4, 223—226).—The identity of synthetic 6 : 7-dimethyl-9- $\alpha$ -l'-ribityl-

isalloxazine (A., 1934, 1233; this vol., 359, 631, 760) (and the non-identity of the corresponding arabinoseflavin) with lactoflavin from milk is confirmed by growth-promoting experiments on rats.

F. O. H.

**Photochemical phenomena involved in vitamin- $B_2$  studies.** G. C. SUPPLEE, S. ANSBACHER, and R. C. BENDER (J. Biol. Chem., 1935, 110, 365—374).—Vitamin- $B_2$  (I), prepared by a slight modification of Kuhn's method (A., 1933, 847), is subjected to irradiation with various  $\lambda$  and its growth-promoting power assayed. Exposure to light produces a progressive change in the fluorescence from yellow-green to blue-green, running parallel with decreases in (I) activity; light of  $> 310 \text{ m}\mu$  is responsible for the change.

H. D.

**Effect of administration to children of extra vitamin- $B_2$ .** M. ISHII (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 608—617).—Addition of the vitamin to the diet of children receiving typical Japanese food had only a very slight favourable effect on the normal gain in body-wt.

W. McC.

**Avitaminosis- $B_2$  and pellagra in rats. Biological investigation of vitamins.** W. VON DRIGALSKI (Z. Vitaminforsch., 1935, 4, 177—187).—Diets deficient in vitamin- $B_2$  produce pellagra-like skin lesions in rats, the effect not being influenced by natural or artificial irradiation. No antagonism exists between  $B_1$  and  $B_2$  (cf. A., 1934, 208). Considerable storage of  $B_2$  occurs in healthy rats. A basal diet supplemented with all the known vitamins produces growth < that with a diet of bread, milk, and kitchen scraps.

F. O. H.

**Occurrence of cataract in rats fed on diets deficient in vitamin- $B_2$ .** M. C. BOURNE and M. A. PYKE (Biochem. J., 1935, 29, 1865—1871).—Only 20—31% of young rats, fed on a vitamin- $B_2$  (I)-deficient diet, developed cataract; on the diet + cystine and on one containing caseinogen, salts, and maize-starch no cataract developed. Dermatitis is a better characteristic of (I) deficiency than cataract.

H. D.

**Effect of the growth-promoting, appetite-stimulating, or "physin" factor on the live-weight increase of swine.** G. DUNLOP (J. Agric. Sci., 1935, 25, 445—459).—Physin has a stimulative effect on the growth of pigs and customary rations are deficient in this factor. It stimulates appetite and general growth without enhancing the net energy val. of the ration. The physin content of foodstuffs is in the descending order, liver, liver meal, dried whole milk, whey, green food, fish meal, meat meal, soya-bean meal.

A. G. P.

**Discovery, isolation, and synthesis of vitamin-C.** K. TAUFEL (Z. Unters. Lebensm., 1935, 70, 7—16).—A lecture.

**Galacturonic acid as a precursor of ascorbic acid.** R. JOHNSTIN and K. S. POTTER (J. Biol. Chem., 1935, 110, 279—284).—Guinea-pigs on a vitamin-C-deficient diet given *d*-galacturonic acid (I) orally, subcutaneously, and intraperitoneally show no differences from those on the diet without (I).

H. D.



**Vitamin-C and thiosulphate in the urine.** M. VAN EEKELLEN (*Acta Brev. neerl. Physiol.*, 1934, 4, 137—139; *Chem. Zentr.*, 1935, i, 1262).—Normal human urine, after pptn. with  $\text{Hg}(\text{OAc})_2$ , shows only half of its original reducing power against dichlorophenol-indophenol, which corresponds with its vitamin-C (I) content; the ppt. contains other reducing substances. Administration of (I) in large quantities increases urinary (I). The reducing action of urine is increased by hydrolysis with 5%  $\text{H}_2\text{SO}_4$  in  $\text{CO}_2$ ; the effect is possibly due to reduction of dehydroascorbic acid or formation of reductic acid from glycuronic acid. A reducing substance, probably  $\text{Na}_2\text{S}_2\text{O}_3$ , is found in the urine of diabetics, cats, and dogs, and in normal human urine in small quantities.

R. N. C.

**Ascorbic and dehydroascorbic acids in the urine of normal and scorbutic guinea-pigs.** E. MARTINI and F. PINOTTI (*Boll. Soc. Ital. Biol. sperim.*, 1935, 10, 58—60).—The scorbutic index of the urine of scorbutic guinea-pigs rises to 5 times the normal val. Injection of dehydroascorbic acid produces a fall of the scorbutic index.

R. N. C.

**Ascorbic and dehydroascorbic acids in the aqueous humour under the action of light.** A. BONSIGNORE (*Boll. Soc. Ital. Biol. sperim.*, 1935, 10, 62—65).—Illumination of the normal eye causes a lowering of the dehydroascorbic/ascorbic acid ratio of the aqueous humour. In the atropinised eye the ratio rises.

R. N. C.

**Behaviour of the ascorbic acid of the tissues in inanition.** E. MARTINI and A. BONSIGNORE (*Boll. Soc. Ital. Biol. sperim.*, 1935, 10, 60—62).—The scorbutic index of the adrenals of guinea-pigs is not affected in starvation, but rises in scurvy.

R. N. C.

**Ascorbic acid and adrenaline.** A. BONSIGNORE and F. PINOTTI (*Boll. Soc. Ital. Biol. sperim.*, 1935, 10, 55—58).—Oxidised adrenaline is reduced by ascorbic acid to a physiologically inactive compound.

R. N. C.

**Depigmenting effect of vitamin-C.** F. TECHNER (*Klin. Woch.*, 1934, 13, 1614).—Pigmentation occurring in a pregnant woman was not diminished by feeding lemon-juice; pigment faded naturally after delivery. Animal experiments have shown that vitamin-C is ineffective in reducing pigmentation caused by ovarian substances.

G. H. F.

**Influence of vitamin-C on pigmentation.** H. A. SCHADE (*Klin. Woch.*, 1935, 14, 60—61).—Administration of vitamin-C to man inhibited both the erythema and pigmentation caused by artificial sun rays. Vitamin-C also caused leucopenia and lymphocytosis, but was without effect on the oxidase reaction of leucocytes.

G. H. F.

**Distribution of vitamin-C in organs of the fox.** G. BOURNE (*Austral. J. Exp. Biol.*, 1935, 13, 113—125).—Reduction of  $\text{AgNO}_3$  (in dil.  $\text{AcOH}$ ) indicates the presence of vitamin-C (I) in almost every tissue of foxes. The high concns. of (I) in the anterior lobe of the pituitary gland, adrenals, corpus luteum, and interstitial cells of the gonads indicate the possibility of (I) being concerned in the production of the respective hormones.

F. O. H.

**Formation, origin, and distribution of vitamin-C in plant tissues.** R. STROHECKER (*Z. Unters. Lebensm.*, 1935, 70, 76—81).—The reduction of 2:6-dichlorophenol-indophenol by extracts of fruits and leaves is not due to vitamin-C (I). (I) is formed in germinating barley and in birch leaves at the beginning of development, whilst the reducing power of hawthorn berries is at a max. when the red pigment appears. Birch and robinia leaves are rich in (I). The glands of the former contain a reducing substance.

E. C. S.

**Vitamin-C content of cucumbers and fruits of *Ziziphus sativa* and *Sorbus domestica*.** E. CASERIO (*Z. Vitaminforsch.*, 1935, 4, 173—177).—In each case the amount in mature or immature fruit is  $\approx$  approx. 20% of that of lemon-juice.

F. O. H.

**Vitamin-C in lower organisms.** G. BOURNE and R. ALLEN (*Nature*, 1935, 136, 185—186).—Staining with  $\text{AcOH-AgNO}_3$  reveals small black granules scattered in the protoplasm in the cells of protozoa, bacteria, moulds, lichens, and algae. This reducing agent is possibly vitamin-C, which may be essential for the existence of living protoplasm, probably as an integral part of an oxidation-reduction system.

L. S. T.

**Determination of ascorbic acid by titration.** M. VAN EEKELLEN (*Nature*, 1935, 136, 144—145).—Data for the amount of vitamin-C (I) extracted from the potato under various conditions indicate that the increase in (I) recorded by McHenry and Graham (this vol., 903) is due to the destruction by cooking of an oxidase present in some vegetables, and not to the liberation of more (I) from an ester. The oxidase can be activated in 3%  $\text{CCl}_3\text{-CO}_2\text{H}$  solution. In determining (I) in blood, reduction with  $\text{H}_2\text{S}$  must follow the  $\text{Hg}(\text{OAc})_2$  pptn., since, in presence of erythrocytes, (I) is reversibly oxidised when blood is pptd. by  $\text{CCl}_3\text{-CO}_2\text{H}$ .

L. S. T.

**Constitution of calciferol (vitamin-D).**—See this vol., 1120.

**Properties and physiological significance of biosterol.** IX. Condensation of biosterol with maleic and citraconic anhydrides. Z. NAKAMIYA (*Bull. Inst. Phys. Chem. Res. Japan*, 1935, 14, 584—607).—Biosterol (I) from *Stereolepis ischinagi* is accompanied by a triacontane ("stereolepisane"),  $\text{C}_{30}\text{H}_{62}$ , m.p. 65°. (I) with citraconic anhydride gives biosterol-citraconic acid,  $\text{C}_{25}\text{H}_{34}\text{O}_4$ , m.p. 207° (perhydro-derivative,  $\text{C}_{25}\text{H}_{42}\text{O}_4$ , m.p. 65—66°; bromide,  $\text{C}_{25}\text{H}_{34}\text{O}_4\text{Br}_6$ , m.p. 186—188°; hydrochloride,  $\text{C}_{25}\text{H}_{34}\text{O}_4\text{HCl}$ ), and with maleic anhydride gives the substance (II),  $\text{C}_{27}\text{H}_{36}\text{O}_8$ , m.p. 247°, which with  $\text{AcCl}$  in  $\text{C}_5\text{H}_5\text{N}$  yields an isomeride, m.p. 227°. Bromination of crude (II) in  $\text{CHCl}_3$  followed by fractional pptn. with  $\text{MeOH}$  yields the compounds  $\text{C}_{27}\text{H}_{36}\text{O}_8\text{Br}_3$ , m.p. 247.5°,  $\text{C}_{27}\text{H}_{36}\text{O}_8\text{Br}_4$ , m.p. 230°,  $\text{C}_{27}\text{H}_{36}\text{O}_8\text{Br}_5$ , m.p. 215°, and  $\text{C}_{27}\text{H}_{36}\text{O}_8\text{Br}_6$ , m.p. 160—170°. W. McC.

**Biochemical standardisation of vitamin-D or irradiated ergosterol.** N. K. BASU (*Indian J. Med. Res.*, 1934, 22, 199—202).—The standard vitamin dose is the min. quantity that can raise  $[\text{Ca}]\times[\text{P}]$  in the blood of rabbits from 27 to 40 mg. in 7—10 days, or to 60 mg. in 15—18 days.

R. N. C.



Calcium and phosphorus contents of the offspring after feeding vitamin-D to the mother rat. W. W. SWANSON and L. V. IOB (Amer. J. Dis. Children, 1935, 49, 43—46).—Administration of cod-liver oil or viosterol to the mother increased the Ca and P contents of the young. CH. ABS. (p)

Prevention of injury from excess vitamin-D by feeding vitamin-A. C. GROSS-SELBECK (Klin. Woch., 1935, 14, 61—62).—Harmful effects of overdoses of vitamin-D on growth and condition of growing rats were prevented by feeding large amounts of -A. G. H. F.

Carr-Price reaction of the fatty acids of cod-liver oil after vigorous saponification. A. EMERIE (Nature, 1935, 136, 183—184).—The effect on the Carr-Price reaction of the saponification of the fatty acids of cod-liver oil and the method of concn. of the substance responsible for the reaction are described. L. S. T.

Vitamin-E. II. Eutrophic action and vitamin-E activity of rice-husk oil. III. Influence on fertility. L. SCHIOPPA (Z. Vitaminforsch., 1935, 4, 162—167, 167—173).—II. Wheat- and rice-germ oil have a marked eutrophic action in rats fed on a vitamin-E-deficient diet (this vol., 670).

III. Addition of small amounts of vitamin-E to a diet of bread, green vegetables, and mineral salts increases the fertility and the size and viability of the young of rats. F. O. H.

Chlorophyll and hæmoglobin—two natural pyrrole pigments. E. M. DIETZ (J. Chem. Educ., 1935, 12, 208—216).—A review. L. S. T.

Chlorophyll derivatives. L. MARCHLEWSKI and W. URBANCZYK (Bull. Acad. Polonaise, 1935, A, 146—155).—Blood-hæmatin and  $\alpha$ - and  $\beta$ -phyllhæmatin (formed by dissolution of the respective hæmins in NaOH) have similar absorption curves, as have the corresponding hæms (formed by action of  $H_2S$  on the hæmatin) and the hæmatochromogens (produced by action of  $N_2H_4 \cdot H_2O$  on the hæm). J. W. S.

Variations in chlorophyll content of leaves. N. T. DELEANO and J. DICK (Biochem. Z., 1935, 279, 49—54).—Determinations of Mg (A., 1934, 465, 1044) in leaves of *Salix fragilis* and *Populus alba* indicate that storage of chlorophyll continues for approx. 70 and 40 days, respectively. The content increases during growth, remains const. during the assimilation period (110—120 days), and decreases rapidly during the last 20—25 days; small amounts occur in the yellowed leaves. Florescence and fructification do not influence storage. F. O. H.

Causes of the irregular course of photosynthesis during the day. Diurnal course of respiration in sugar-beet leaves. A. KURSANOV and P. UGRUMOV (Bull. Soc. nat. Moscow, Sect. biol., 1934, 43, 159—166).—Physical causes, e.g., variation in the absorptive capacity of living tissue for  $CO_2$ , may operate to cause fluctuations. CH. ABS. (p)

Influence of deuterium oxide on the rate of photosynthesis. J. CURRY and S. F. TRELEASE (Science, 1935, 82, 18).—Measurements of the rate of  $O_2$  evolution at  $25.7^\circ$  by *Chlorella* suspended in

$CO_3^{--}HCO_3'$  buffer show that the rate of photosynthesis with 99.9%  $D_2O$  is approx. 0.41 of that with  $H_2O$ . L. S. T.

Assimilation of carbon dioxide by plants. P. KLASON (Svensk Pappers-Tidn., 1934, 37, 572—573; Chem. Zentr., 1935, i, 1077).—Assimilated  $CO_2$  is converted directly into sugars and only to a minor extent into  $CH_2O$ . Lignin is produced exothermically from xylose (I) independently of  $O_2$ . The mol. ratio (I):hexoses is 1:1 in conifers and becomes 3:2 in broad-leaved plants if to the (I) content is added a further amount of (I) corresponding with the lignin present. A. G. P.

[Chlorophyll fluorescence and assimilation of carbonic acid.] H. KAUTSKY (Naturwiss., 1935, 23, 389).—The contention of Franck (cf. this vol., 681, 794) that his theory of the mechanism of  $CO_2$  assimilation is supported by the author's experimental data (cf. *ibid.*, 263) is refuted. F. O. H.

[Chlorophyll fluorescence and assimilation of carbonic acid.] J. FRANCK (Naturwiss., 1935, 23, 389—390).—A reply to the above. F. O. H.

Carbon dioxide storage. VIII. Chemical changes in potato tubers resulting from exposure to carbon dioxide. N. C. THORNTON (Contr. Boyce Thompson Inst., 1935, 7, 113—118).—Exposure of tubers to atm. containing 20%  $O_2$  and varying proportions of  $CO_2$  resulted in increased respiratory activity, increased sp. conductivity of tissue leachings, and higher catalase activity,  $p_n$ , sucrose, and reducing sugar contents in the extracted juice. A. G. P.

Physiology of development and ripening in the strawberry. C. W. CULPEPPER, J. S. CALDWELL, and H. H. MOON (J. Agric. Res., 1935, 50, 645—696).—Fruit at the petal-fall stage shows max. total and insol. solids and "total astringency" ( $KMnO_4$ -reducing power). Titratable acidity and sol. solids are high but  $<$  max. Of the sol. solids, 30—40% is sugar, 60—99% of which comprises reducing sugars. In the stage of rapid development the  $H_2O$  content increases markedly. The corresponding decline in total solids occurs principally in the insol. fraction. The sugar val. remains practically unchanged, acidity increases, and astringency declines. With the approach of the "whitening" stage changes in acidity, total solids, and sugars are small. In the "whitening" period  $H_2O$  contents and acidity reach max., and sol. solids increase, mainly as a result of sugar formation. Insol. solids and astringency decrease less rapidly. The transition to full ripeness is marked by a further increase in total solids, the rate of sugar formation being  $>$  the decline in insol. matter. From 70 to 80% of the sol. solids is now represented by sugars (mainly reducing). Titratable acidity decreases rapidly and astringency more slowly. Varieties are grouped according to chemical characteristics, which are discussed in relation to adaptability to different methods of preservation. A. G. P.

Trend of organic food reserves in lucerne roots as affected by cutting practices. C. O. GRANFIELD (J. Agric. Res., 1935, 50, 697—709).—The carbohydrate and N contents of roots decline



rapidly during early spring growth and after each cutting, min. vals. being reached approx. 20 days after each cut. Max. vals. occur at the full-bloom stage. Early and frequent cutting tends somewhat to lower the winter reserves of carbohydrate and N. The extent of winter accumulation is largely influenced by the amount of growth permitted after the final cutting. Spring growth is improved by permitting the aftermath to remain during winter. A. G. P.

**Nutrient intake and transport in the leaves of *Drosera capensis*, L.** J. OUDMAN (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 650—662).—Plants developed normally in nutrients containing sufficient N. In N-free media N was assimilated from compounds [e.g., asparagine (I)] applied to the leaves or from insects. The intake of (I) occurred through tentacles or through the underside of leaves, and increased with rising temp. or with increasing concns. applied. The influence of temp. and concn. was most marked > 6 hr. after treatment. Assimilation of caffeine was > that of (I). Glands of the outer tentacles facilitated N absorption. Synthesis of protein from (I) in leaves was very small. N thus absorbed was probably utilised in other organs of the plant. A. G. P.

**Effect of temperature on growth anatomy and metabolism of apple and peach roots.** G. T. NIGHTINGALE (Bot. Gaz., 1935, 96, 581—639).—Growth responses at different temp. are examined in relation to the  $p_H$  of the tissues and to carbohydrate and N metabolism. The absorption of  $\text{NO}_3^-$  was limited to current roots in both species and was but little affected by the temp. of the medium. The reduction of  $\text{NO}_3^-$  to  $\text{NH}_3$  and the production of  $\text{NH}_2$ -acids increased, within limits, with rising temp. Max. root growth is associated with max. abs. reduction of  $\text{NO}_3^-$  at 18.3°. The distribution of carbohydrates in the various tissues is examined in relation to differences in temp. A. G. P.

**Physiological significance of ammonium salts in relation to the composition changes of nutrient solutions.** I. G. DIKUSAR (Lenin Acad. Agric. Sci. Ged. Inst. Fert., 1934, No. 3, 67—76).—In sand cultures of sugar-beet, cabbage, and flax,  $\text{NH}_4^+$  gave somewhat better yields at  $p_H$  7.0 and  $\text{NO}_3^-$  was the more effective at  $p_H$  5.0. The response of flax to  $\text{NH}_4\text{Cl}$  was favoured by increasing the proportions of Ca, Mg, and K in the nutrient. An increase in Mg in place of Ca decreased the yield and prevented seed formation. The cation content (especially K) of plants was decreased and the  $\text{PO}_4^{3-}$  content increased by  $\text{NH}_4^+$ , whereas  $\text{NO}_3^-$  favoured the reverse changes. Toxic effects of Al in media may be counteracted by increasing the concn. of Ca, Mg, and K. CH. ABS. (p)

**Effect of a controlled nitrogen supply with different temperatures and photo-periods on the development of the potato plant.** H. O. WERNER (Nebraska Agric. Exp. Sta. Res. Bull., 1934, No. 75, 132 pp.).—Carbohydrates (I) accumulated (with tuber formation) in conditions in which N assimilation was inhibited, viz., low temp., short days, deficient N supply. With high temp. excessive respiration

prevented the accumulation of (I). Reverse conditions favoured vegetative growth. The effect of various growth conditions and of different levels of N supply on the distribution of N and of (I) in the plant system, and on the collateral morphological and physiological responses of the plant, is examined. A. G. P.

**Effect of potassium on the respiration of plants.** G. RÖHDE (Z. Pflanz. Düng., 1935, 39, 159—170).—The action of K in facilitating aerobic and retarding anaerobic (intermol.) respiration is related to its ability to improve the distribution of Fe within the plant. A. G. P.

**Effect of the rate of flow of air on assimilation and of fluids on other natural fluids.** A. H. BURGESS (Ann. Bot., 1935, 49, 567—578).—The effect of the rate of air-flow on the drying of hops, on the absorption of  $\text{CO}_2$  by alkalis, and on the rate of absorption of  $\text{CO}_2$  by plant leaves during photosynthesis depends on the same principles as the effect of the rate of flow of  $\text{H}_2\text{O}$  on the dissolution of  $\text{Na}_2\text{CO}_3$ ,  $\text{CuSO}_4$ , and rock-salt crystals. The rates  $\propto v^{0.39}$  ( $v$ =velocity of fluid-flow). Hence the thickness of the "stagnant film" of fluid at the boundary surface  $\propto 1/v^{0.39}$ . A. G. P.

**Changes in hydrogen-ion concentration of culture solutions containing nitrate- and ammonium-nitrogen.** S. F. TRELEASE and H. M. TRELEASE (Amer. J. Bot., 1935, 22, 520—542).—The growth of plants tended rapidly to decrease the  $p_H$  of media (initial  $p_H$  4.3—6.0) having a low  $\text{NO}_3^- : \text{NH}_4^+$  ratio and to increase the  $p_H$  of those having a high ratio. The extreme vals. approached were  $p_H$  3.0 and 6.5, respectively. By suitable adjustment of  $\text{NO}_3^-$  and  $\text{NH}_4^+$ , media may be obtained the  $p_H$  of which remain substantially const. during 8 days' growth. The ability of plants to change the reaction of media varied with age. A. G. P.

**Influence of light on certain plant processes.** P. P. LAZAREV and L. N. FORMOZOVA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 414—418, 419—421).—A mathematical relationship is derived expressing the variation in  $\text{H}_2\text{O}$  content of pea plants with light intensity. No significant differences in  $\text{H}_2\text{O}$  content could be attributed to the use of various light filters. Lighting did not affect the amount of sol. minerals in the plants. A. G. P.

**Metabolism of calcareous algæ. II. Seasonal variation in certain metabolic products of *Corallina squamata*, Ellis.** P. HAAS, T. G. HILL, and W. K. H. KARSTENS (Ann. Bot., 1935, 49, 609—619; cf. A., 1934, 121).—The incrustation of *C. squamata* consists of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  and shows seasonal variations in amount (max. in winter, min. in spring). The ratio of the bases also varies, Ca being max. in January and July, and Mg max. in November and min. in March. The N fractions fluctuate considerably with season. Floridoside (I) contents are high in May and low in January. A reciprocity between (I) and  $\text{NH}_2\text{-N}$  is apparent during the active growth season, thus supporting the view that the presence of peptides results from a lack of balance between C and N metabolism. A. G. P.



Production of ethylene by plant-tissue as indicated by the epinastic response of leaves. F. E. DENNY and L. P. MILLER (Contr. Boyce Thompson Inst., 1935, 7, 97—102).—Emanations from various fruits and other plant-tissues caused epinasty in young potato plants, probably due to the presence of  $C_2H_4$ . A. G. P.

Wood. I. The cell-wall. II. Water content of certain Canadian trees and changes in the water-gas system during seasoning and flotation. III. Physiology of the tree with special reference to the ascent of sap and the movement of water before and after death. R. D. GIBBS (Canad. J. Res., 1935, 12, 715—726, 727—760, 761—787).—I. A review of lit. on the nature of the cell-wall and a description of attempts to separate lignin (I) and cellulose (II) by the use of solvents. For (I) lactic acid containing 0.1% HCl and for (II) 72% aq.  $H_2SO_4$  and  $CCl_3 \cdot CO_2H$  are effective except for the material of the torus, pit membrane, and bordered pits, which are more resistant.

II. Diurnal and seasonal variations in the  $H_2O$  content of paper birch, poplar, jack pine, white spruce, and balsam fir trees are studied.  $H_2O$  decreases during the morning and increases later in the day, whilst in hard woods a max. is reached in spring and a min. in summer. No seasonal variation in the  $H_2O$  content of soft wood occurs. The distribution of  $H_2O$  and the seasonal changes in corresponding parts of the tree vary from year to year, but are const. for each species. The effects of girdling on  $H_2O$  content and the changes in the rate of penetration of  $H_2O$  into logs due to differences in length, barking, and painting are described. Whilst  $H_2O$  penetration is chiefly through the ends, gas escape is in a radial direction, so that seasoning followed by end-painting leads to slow  $H_2O$  entry.

III. The seasonal and diurnal variations in the  $H_2O$  and gas content of trees are in accordance with the demands of the tension hypothesis for the ascent of sap. The reasons for the observed differences in the  $H_2O$  content of the various species and the problem of log flotation are discussed. A. L.

Catalase activity as a measure of viability of tree seeds. H. I. BALDWIN (Amer. J. Bot., 1935, 22, 635—644).—Conifer seed of high germinative capacity showed a marked increase in catalase activity due to stimulation in the germinator. The quotient,  $O_2$  evolved by stimulated seed  $\div$   $O_2$  evolved by resting seed was  $> 1$  in nearly all cases of high viability. A. G. P.

Distribution of enzymes in dormant and germinating wheat seeds. I. Dipeptidase and protease. II. Lipase. L. B. PETT (Biochem. J., 1935, 29, 1898—1904).—I. Dipeptidase (I) and protease (II) activity decrease on drying the seed; the optimum  $p_H$  was 7.5 and 5.0, respectively. The small quantities of (I) and (II) in the hull and endosperm are not increased on germination, whereas those in the scutellum and embryo increased greatly. After 12 hr. germination the embryo enzymes decrease and only after 36 hr. do those in the scutellum also.

II. Lipase occurs chiefly in the scutellum and decreases rapidly on germination. The lipase in the

endosperm and embryo passes through a max. 12 hr. after germination. H. D.

Action at a distance of metals on germinating seeds. G. A. NADSON and C. STERN (Compt. rend., 1935, 201, 159—161).—At short distances small metal discs retard the germination of white mustard seeds in the dark. The effect is almost independent of the thickness of the discs, but increases with increasing at. no. of the metal and with increasing surface of the disc, large discs having an effect at greater distances. The effect depends strongly on the radio-activity of the surrounding air, being considerably increased when this contains radon. The radio-activity of the air is regarded as producing a secondary radiation (chiefly  $\beta$ -electrons) from the discs and this retards the growth of the seeds. H. G. M.

Influence of the micro-elements on the distribution of calcium, magnesium, and phosphates in plants. A. P. SCHTSCHERBAKOV (Z. Pflanz. Düng., 1935, 39, 129—140).—Flax grown in cultures to which the micro-elements (B, F, I, Mn, Zn, Al, Cu) were added produced greater growth, higher chlorophyll accumulation, and less leaf dry matter per unit length of stem than when these elements were omitted. Addition of micro-elements increased the % of Ca and Mg in the dry matter of leaves and decreased that in stems. The intake of Mg and  $PO_4'''$  per plant was lowered. Differences in distribution of Ca and Mg corresponding with presence or absence of micro-elements are attributable to differences in the form of combination of the bases within the plant, org. compounds predominating when micro-elements are supplied, and inorg. compounds when they are omitted. A. G. P.

Kinetics of penetration. X. Guanidine. A. G. JACQUES (Proc. Nat. Acad. Sci., 1935, 21, 488—492).—Similarly to  $NH_3$  (cf. this vol., 671) guanidine enters *Valonia* cells in combination with an acidic constituent of the sap. H. G. R.

Spectrographic determination of calcium in plant ashes. K. WAY and J. M. ARTHUR (Contr. Boyce Thompson Inst., 1935, 7, 103—112).—Apparatus and technique are described. Accuracy within 5% of that of chemical methods is attainable. A. G. P.

Phosphorus content of marine algæ. P. HAAS and B. RUSSELL-WELLS (Biochem. J., 1935, 29, 1915—1917).—Data for total P of the plant and of aq. extracts are given for *Chondrus crispus*, *Poly-siphonia fastigiata*, and *Dilsea edulis*. With aq. extracts, P occurs mainly as esters of  $H_3PO_4$  and varies slightly with the month of collection. F. O. H.

Determination of molybdenum in plants and soils. K. E. STANFIELD (Ind. Eng. Chem. [Anal.], 1935, 7, 273—274).—When  $> 5$  mg. Mo is present it is determined gravimetrically as Pb molybdate by pptn. with  $Pb(OAc)_2$  in presence of AcOH and  $NH_4OAc$ . For smaller amounts of Mo a colorimetric method is described, based on extraction of the red-coloured Mo thiocyanate by BuOAc. E. S. H.

Gold in *Zea mays*. B. NĚMEC (Ber. deut. bot. Ges., 1935, 53, 560—562).—Plants from W. Czechoslovakia contain about 0.0001% of Au and As equiv.



to about 0.7% of  $\text{As}_2\text{O}_3$ . Beans (*Vicia faba*) grown in the same district contain no Au. W. McC.

**Chemical composition of the loquat (*Eriobotrya japonica*).** C. G. CHURCH and D. G. SORBER (Fruit Products J., 1935, 14, 335—340).—Analyses of loquats (Japanese medlar) are compared with those made by other authors and with analyses of apples. E. B. H.

**Constituents of the bark of *Nerium odorum*, Soland.** G. P. PENDSE and S. DUTT (Bull. Acad. Sci. Allahabad, 1934, 3, 209—214).—The dried bark does not contain alkaloids but yields 13.5% of ash (78% of  $\text{H}_2\text{O}$ -sol., 22% of  $\text{H}_2\text{O}$ -insol.). An EtOH extract deposits a white ppt. which, recrystallised from EtOH, has m.p. 97° (carnaubyl coccerate?). Conc. of the EtOH filtrates yielded an essential oil, a tannin, m.p. 240° (decomp.), a phlobaphen, m.p. 120—122°, and a red amorphous pigment. From the mother-liquors after pptn. with EtOH-Pb(OAc)<sub>2</sub>, there were obtained *neriodorin*,  $\text{C}_{22}\text{H}_{32}\text{O}_7$ , m.p. 86—87° (sol. in EtOAc), and *neriodorein*,  $\text{C}_{23}\text{H}_{34}\text{O}_{11}$ , m.p. 106—107° (insol. in EtOAc), glucosides of which the aglucosones have, respectively, m.p. 68° and 70°. P. G. M.

**Surface composition of certain latex particles.** L. S. MOYER (Amer. J. Bot., 1935, 22, 609—627).—Latex particles from various plant species varied widely in their resistance to wetting by oil. In *Euphorbia* a protein surface of the latex is associated with high resistance to passage through an oil interface. The phenomena of wetting is discussed in relation to the chemical nature of the particle surface. A. G. P.

**Composition of the latex of *Asclepias cornuti* (Syriaca, L.).** I. K. MATZUREVITSCH (J. Appl. Chem. Russ., 1935, 8, 476—487).—The latex contains rubber, inorg. salts, reducing substances (not sugars), esters of aliphatic (AcOH,  $\text{PrCO}_2\text{H}$ , palmitic, cerotic, and erucic acids) and OH-acids with unidentified alcohols ( $\text{C}_{20}\text{H}_{35}\text{OH}$ , m.p. 137°;  $\text{C}_{25}\text{H}_{43}\text{OH}$ , m.p. 158—160°;  $\text{C}_{28}\text{H}_{47}\text{OH}$ , m.p. 180—181°), lecithin, and  $\alpha$ - and  $\beta$ -myrrin. R. T.

**Components of Shaohsing-Chiu.** Y. WANG (Bull. Agric. Chem. Soc. Japan, 1935, 11, 70).—Formic, acetic, lactic, and succinic acids and histidine have been obtained. J. N. A.

**Seeds of *Plantago ovata* (Isabghol).** G. P. PENDSE and S. DUTT (Proc. Acad. Sci. Agra and Oudh, 1934—1935, 4, 133—140).—The seeds (5% ash) are free from enzymes and alkaloids and contain 5% of a semi-drying oil having  $d$  0.9212,  $n_D^{25}$  1.4737, sap. val. 181.8, Ac val. 37.7, I val. 116 [oleic acid, 37%; linoleic, 48%; linolenic, trace; saturated acids, 12.5%; unsaponifiable fraction (containing sitosterol), 1.8—2.0%]. F. O. H.

**Seed kernels of *Caesalpinia bonducella*.** N. GHATAK (Proc. Acad. Sci. Agra and Oudh, 1934—1935, 4, 141—146).—The kernels are free from alkaloids and contain oil (23.9%), amylase, starch, sucrose, a substance, m.p. 107—109°, a bitter principle ("bonducin"),  $\text{C}_{20}\text{H}_{28}\text{O}_8$ , m.p. 119—120°,  $[\alpha] +25.6^\circ$  in EtOH, which is hydrolysed to glucose and a non-bitter substance, m.p. 127—128°. F. O. H.

**Presence of sterols in vesicular cryptogams.** E. MONTIGNIE (Bull. Soc. chim., 1935, [v], 2, 1219).—Sterols are obtained from *Equisetum arvense* and, in small amounts, from *Scolopendrium officinale*, L., and *Cetraria Islandica*. R. S. C.

**Non-heptane constituents of digger pine (*Pinus sabinana*).** A. H. UHL (J. Amer. Pharm. Assoc., 1935, 24, 380—382).—*n*-Oct., *n*-non., *n*-dec., and *n*-myrist-aldehydes have been isolated. The presence of *n*-lauric and other aldehydes is indicated. M. T.

**Separation of *n*-nonacosane from myrrh.** F. TROST and B. DORO (Annali Chim. Appl., 1935, 25, 227—229).—0.14% of *n*-nonacosane may be obtained by distilling the Et<sub>2</sub>O extract in a current of superheated steam. T. H. P.

**Carotenoid content of peaty soils.** O. BAUDISCH and H. VON EULER (Arkiv Kemi, Min., Geol., 1935, 11, A, No. 21, 10 pp.).—The exhaustive extraction of various peaty soils with org. solvents is described. Chalk-containing layers adsorb xanthophyll specifically, whilst carotene (0.6 mg. per g. of org. material) is almost exclusively found in other layers. E. A. H. R.

**Pigmentation of the ripening gourd blossom (*Cucurbita pepo*).** L. ZECHMEISTER, T. BÉRES, and E. UJHELYI (Ber., 1935, 68, [B], 1321—1323).—Ripening of the blossoms is accompanied by increase in carotenes and, particularly, in polyene alcohols. The amount of lutein (I) is greatly diminished and that of zeaxanthin (II) is very greatly increased. The isolation of (I), (II), and cryptoxanthin is described. H. W.

**Substance with a blue fluorescence from carrots.** F. H. COHEN (Chem. Weekblad, 1935, 32, 441—442).—The aq. extract of carrots containing lactoflavin (I) is acidified (3% HCl) and adsorbed twice on franconite. The second adsorbate when extracted with  $\text{H}_2\text{O}$ -EtOH- $\text{C}_5\text{H}_5\text{N}$  (4:1:1) affords a substance (II) with a strong blue fluorescence, especially in alkaline solution, destroyed reversibly by  $\text{Na}_2\text{S}_2\text{O}_4$  and irreversibly by 0.1*N*-NaOH (24 hr.) but not by heating to 60°, which is not due to quinine,  $\alpha$ -sculin, or salicylic acid. (II) gives no ppt. with  $\text{Pb}(\text{OAc})_2$  or  $\text{KI-HgI}_2$  and is not a decomp. product of (I). S. C.

**Yellow colouring matter from the wood of *Adina cordifolia*, Hook.**—See this vol., 1129.

**Gum of the lemon tree.** E. PARISI (Annali Chim. Appl., 1935, 25, 230—236).—Hydrolysis of the gum yields arabinose, galactose, small amounts of a methylpentose, and a uronic acid, but no glucose or xylose. T. H. P.

**Mucilage of *Scaphium affine*, Pierre.** H. NAKAHARA (Bull. Agric. Chem. Soc. Japan, 1935, 11, 77—78).—Autoclaving of the mucilage (1.5 hr., 130°) rendered it completely sol. and addition of 95% EtOH pptd. a Ca-Mg salt of pectic acid. Hydrolysis of the free acid with  $\text{H}_2\text{SO}_4$  yielded galactose, arabinose, and galacturonic and acetic acids. No tetragalacturonic acid was obtained. J. N. A.

**Soluble sugars in *Mercurialis perennis*, L.** II. M. BOUILLENNE and R. BOUILLENNE (Bull. Acad.



roy. Belg., 1935, [v], 21, 642—659; cf. A., 1933, 1342).—The sucrose and maltose content of the male plants is greater during the period of growth, but lower during the flowering period, than that of the female plants. F. R. G.

**Decomposition in potatoes. III. Ascorbic acid, glutathione, and sugar.** E. PFANKUCH (Biochem. Z., 1935, 279, 115—130).—Press juice from normal potatoes contains 0.002—0.005% of glutathione and 0.015—0.020% of ascorbic acid; approx. the same vals. are obtained with diseased potatoes, the increased reducing power being therefore due to increased dehydrogenase activity. Enzymic hydrogenation of dehydroascorbic acid by press juice indicates the function of vitamin-C as an  $O_2$ -carrier. With virus-diseased tubers the ratio sucrose:reducing sugar is increased due to enzymic activity. F. O. H.

**Mono-amino-acids of soya-bean protein.** S. SASAKI (Bull. Agric. Chem. Soc. Japan, 1935, 11, 78).—The following  $NH_2$ -acids, expressed as wt.-% of protein, have been obtained: glycine (0.23), alanine (4.12), valine (2.56), leucine (10.02), isoleucine (2.38), proline (3.94), phenylalanine (5.21), tyrosine (3.82), aspartic (15.09), glutamic (16.50), and  $\beta$ -hydroxyglutamic (13.20) acids. J. N. A.

**Proteins of Indian foodstuffs. VI. Globulins of the cowpea (*Vigna catiang*).** K. BHAGOAT (J. Indian Inst. Sci., 1935, 18, A, 39—47).—Determinations of N distribution in four preps. of the globulins of cowpea obtained by dialysis and by  $(NH_4)_2SO_4$  pptn. indicate the presence of two cystine-rich fractions. Fractionation of the globulins by  $(NH_4)_2SO_4$  pptn. and heat-coagulation is described. A. L.

***Butea frondosa* flowers. Isolation of a crystalline glucoside of butin.** J. B. LAL and S. DUTT (J. Indian Chem. Soc., 1935, 12, 262—267).—In addition to a phlobaphen, m.p. 115° (Proc. C.S., 1903, 19, 133), and butein (*ibid.*, 134; J.C.S., 1904, 85, 1463), a diglucoside, *butrin* (I),  $C_{27}H_{32}O_{15} \cdot 2H_2O$ , m.p. 193.5°, has been extracted from the dried flowers. (I) loses  $2H_2O$  at 120° and is hydrolysed (dil.  $H_2SO_4$ ) to glucose and butin (*loc. cit.*). (I) is a flavanone derivative. H. G. M.

**Isomerisation of cyanogenic heterosides.**—See this vol., 1083.

**Amygdonitrile glucoside and amygdaloside in plants.** V. PLOUVIER (Compt. rend., 1935, 200, 2120—2122).—The glucosides are isolated and characterised by their glucose:HCN ratios. J. L. D.

**Hydrocyanic acid in *Pyrocydonia winkleri*.** L. D. M. CORNIER (Compt. rend., 1935, 200, 2031—2032).—HCN (0.09%) is extracted from the fresh leaves with  $H_2O$ ; *Cydonia vulgaris* contains 0.0116%. After 15 days' growth, the HCN content is 0.0421 and 0.0059%, respectively. J. L. D.

**Reaction for *Helvella esculenta* [distinction from other fungi].** G. REIF (Z. Unters. Lebensm., 1935, 69, 585—586).—*H. esculenta* reacts with  $H_2SeO_3$  in  $H_2SO_4$  to give a red colloidal solution of Se, and eventually a red ppt. The substance responsible is present in both pileus and stalk, and is sol. in  $H_2O$ .

Of 13 other species of fungi examined, including 3 species of morel, none gave the reaction. E. C. S.

**Sex reversal of *Melandrium album* by a fungus.** H. ERLÉNMEYER and M. GEIGER-HUBER (Helv. Chim. Acta, 1935, 18, 921—923).—Male sexual hormone could not be detected in the extract from a culture of *Ustilago violacea* although this is able to reverse the sex of female *M. album*. F. R. G.

**Biochemical factors of disease-resistance in plants.** A. V. V. IYENGAR (Current Sci., 1935, 4, 47—50).—A review.

**Pathological and physiological effects of *Erwinia tracheiphila*.** E. F. SMITH, on species of *Cucurbitaceae*. T. F. YU (Nanking J., 1933, 3, 47—128; Coll. Agric. and Forestry Univ. Nanking, Bull. 5, 82 pp.).—The organism produced acid but no gas from glucose, fructose, galactose, mannose, mannitol, sucrose, glycerol, dextrin, and, feebly, from inulin, starch, lactose, and raffinose. Xylose and arabinose were unattacked. The C but not the N of tyrosine, phenylalanine, and asparagine was utilised. Growth was optimum at  $p_H$  6.75—7.60 and ceased in old cultures at approx. 5.7. No artificial medium was as favourable as those prepared from plant or animal extracts. In beef broth the inhibitory action of NaCl was counteracted by additions of  $KH_2PO_4$  and  $MgSO_4$ . Neither alone was effective. No evidence was obtained of toxic substances produced by the organism in media or in diseased plants. The latter showed abnormally low transpiration rates and characteristic variations in osmotic pressure in leaves. CH. ABS. (p)

**Biochemistry of the spike disease of *Vigna rosea*.** A. V. V. IYENGAR (J. Indian Inst. Sci., 1935, 18, A, 61—67).—The stem and leaf-tissue of spiked *V. rosea* compared with that of healthy plants show reduced ash, Ca, and protein contents and increased  $NH_4^+$ , starch, and sugar contents and diastatic activity. The roots of the diseased plants have a reduced N and an increased Ca content. These findings are similar to those obtained in the case of spiked *Z. anoplia* and sandal. A. L.

**Changes in tobacco leaves due to "wild-fire" disease.** H. LEGATU and L. MAUME (Compt. rend., 1935, 201, 374—376).—The disease produces a decrease in mineral content ( $N+P_2O_5+K_2O$ ),  $K_2O:N$  ratio, and  $K_2O$  content, whilst the CaO level increases. F. O. H.

**Isolation of a crystalline protein possessing the properties of tobacco mosaic virus.** W. M. STANLEY (Science, 1935, 81, 644—645).—The cryst. protein, practically insol. in  $H_2O$  but sol. in dil. acid, alkali, or salt solutions, has been pptd. by 0.4-saturated  $(NH_4)_2SO_4$ , by saturated  $MgSO_4$ , or by safranine, EtOH,  $COMe_2$ ,  $CCl_3 \cdot CO_2H$ , tannic acid, phosphotungstic acid, and  $Pb(OAc)_2$  from the juice of infected tobacco plants. The mol. wt. of the protein is of the order of a few millions. 1 c.c. of a 1 to  $10^9$  dilution of the crystals is usually infectious. Injection of solutions of the crystals into animals causes the production of a precipitin which is active for solutions of the crystals and the juice of infected but not normal plants. Tobacco mosaic virus is regarded



as an autocatalytic protein which, for the present, may be assumed to require the presence of living cells for multiplication. L. S. T.

**Filtration of tobacco mosaic virus.** H. H. THORNBERRY (Phytopath., 1935, 25, 601—617).—Filtration through Berkefeld "W" candles depended on the  $p_H$  of the suspension, being complete at 8.5 and negligible at 1.5. The virus in acid media is adsorbed by the filter and after the filter surface is saturated the filtrate is as infectious as the original material. Such adsorbed virus is eluted by  $PO_4^{3-}$  buffer solutions at  $p_H$  8.5. Filtration of virus at  $p_H$  8.5 increased its infectivity by 66%. A. G. P.

**Effect of phosphate buffers on infectivity of tobacco mosaic virus.** H. H. THORNBERRY (Phytopath., 1935, 25, 618—627).—Infectivity was greatly increased by dibasic phosphates in 0.1M solution. The valency of anion or cation of salts examined was without influence. Optimum activity occurred at  $p_H$  7.0—8.5. Complete inactivation took place in suspensions at  $p_H$  10.6 in 4 hr. and at  $p_H$  11.2 in 5 min. The presence of  $Al_2(SO_4)_3$  reduced infection, but adjustment of the reaction to  $p_H$  8.5 restored full activity. A. G. P.

**Serological estimate of the absolute concentration of tobacco mosaic virus.** K. S. CHESTER (Science, 1935, 82, 17).—It is estimated that the concn. of virus in expressed virus sap is  $< 0.1$ — $1.0$  mg. per c.c. Assuming a mol. wt. of  $10^5$  for tobacco mosaic virus, 1 c.c. of virus sap will contain  $6.06 \times 10^{14}$ — $6.06 \times 10^{15}$  mols. of virus, and a single min. infective dose on *Nicotiana glutinosa* corresponds with  $6$ — $60 \times 10^7$  mols. of virus antigen. L. S. T.

**Rapid combined fixing and staining method for plant chromosome counts.** E. BACKMAN (Stain Tech., 1935, 10, 83—86).—Smears, made by Taylor's method, are fixed and stained with Bouin's solution in which picric acid is replaced by anthraquinone and alizarin-red S, with a metallic salt as mordant, is present. The smears are then dehydrated with concns. of aq. EtOH rising to 95%, differentiated in 95% EtOH saturated with picric acid and containing 0.5%  $H_2SO_4$ , washed, cleared, and mounted in xylene-balsam. Root-tips fixed in the above solution may be dehydrated in dioxan, infiltrated, embedded, and sectioned in the ordinary manner. H. W. D.

**Syringe hydrogen electrode.**—See this vol., 1097.

**Determination of bromine in biological material.** L. OLSZYCKA (Bull. Soc. Chim. biol., 1935, 17, 852—873).—A review of the methods for the determination of Br and a summary of recent literature on the metabolism of Br. A. L.

**Determination of iodine in biological material.** V. TREVORROW and G. J. FASHENA (J. Biol. Chem., 1935, 110, 29—38).—Biological material is digested with  $K_2Cr_2O_7$ ,  $Ca_2(SO_4)_3$ , and  $K_2Cr_2O_7$ — $H_2SO_4$ , the  $IO_3^-$  formed is converted into I by  $H_3PO_3$ , and the I is steam-distilled into  $K_2CO_3$ . To the  $K_2CO_3$ —KI solution  $NaHSO_3$  and Me-orange are added and  $H_2SO_4$

until just acid after boiling. Br is added and the solution is conc.; KI and starch are added and the free I is titrated with  $Na_2S_2O_3$ . The method has an error of approx. 10%. H. D.

**Determination of iodine in biological substances.** C. O. HARVEY (Med. Res. Coun., Spec. Rept. 201, 43 pp.).—A modification of Hurlley's method (Chem. and Ind., 1929, 1246; A., 1932, 1272) is described. The conditions for the destruction of the org. matter with KOH, extraction of the iodide from the ash with EtOH, destruction of nitrite with  $N_3H$ , oxidation with  $Br-H_2O$ , removal of Br, and titration of the I with  $Na_2S_2O_3$  solution have been studied and standardised. E. H. S.

**Conditions for precipitation of lead chromate in forensic analysis.** K. HÖLL (Z. anal. Chem., 1935, 102, 4—7).—Org. matter is destroyed by conc.  $HNO_3$ , excess of acid evaporated off,  $H_2O$  added, and  $H_2S$  passed in presence of  $Cu(NO_3)_2$ . The ppt. is dissolved in  $HNO_3$  and treated with  $NaOAc$ , dil. AcOH, and  $K_2Cr_2O_7$ . The  $PbCrO_4$  is centrifuged off and determined iodometrically. The necessary conditions are: the  $Pb^{++}$  solution must be added to the  $K_2Cr_2O_7$  and not *vice versa*, and must then be kept for 2 hr. with const. shaking; the concn. of  $NaOAc$  or AcOH may not exceed 5%, whilst that of  $K_2Cr_2O_7$  must be  $< 3\%$ . 0.02 mg. of Pb in 15 c.c. of solution can then be satisfactorily determined. S. J. G.

**Specific micro-determination of mercury in biological media.** M. RANGIER and H. RABUSIER (Compt. rend. Soc. Biol., 1935, 119, 1052—1054).—After destruction of org. matter with  $HCl-HNO_3$  and  $KClO_3$ ,  $Ca_3(PO_4)_2$  is added if not already present, and the Hg pptd. with NaOH, dissolved in dil. HCl, and, after addition of  $CdSO_4$ , pptd. with  $H_2S$ . The  $HgS$ — $CdS$  ppt. is dissolved in dil.  $HCl-HNO_3$ , nearly neutralised with NaOH, excess of KI is added, and NaOH till alkaline. After removal of  $Cd(OH)_2$ , Hg is determined colorimetrically with  $NH_3$ . R. N. C.

**Spectro-analytically detected elements adsorbed on ferromagnetic colloidal  $\gamma$ -ferric oxide as biological indicators.** O. BAUDISCH (Naturwiss., 1935, 23, 512).— $\gamma$ - $Fe_2O_3$  retains its ferromagnetic properties in the colloidal state, and may be used as a biological indicator, and for the magnetic separation of living cells of the reticulo-endothelial system. By adding spectrally pure  $(C_5H_5N)_4FeCl_2$  to solutions of  $Cu(NO_3)_2$ ,  $Zn(OAc)_2$ ,  $BeCl_2$ , and  $MnSO_4$ , colloidal  $\gamma$ - $Fe_2O_3$  with adsorbed Cu, Zn, Be, and Mn, respectively, is obtained. The use of these enables their location in tissues or isolated cells to be determined spectro-analytically. A. J. M.

**Determination of very small quantities of ethyl bromide in biological systems.** F. L. HAHN (Compt. rend., 1935, 201, 296—298).—EtBr in animal tissues is determined to within 5% by passing air and  $H_2O$  vapour through the heated system and then through a red-hot quartz tube; HBr in the condensate is neutralised, and Br liberated by  $NH_2Cl$  is determined colorimetrically (fluorescein). The method can also be applied to  $Pr^+Br$  and  $Pr^+Br$ . E. W. W.