

# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

OCTOBER, 1933.

### General, Physical, and Inorganic Chemistry.

**Emission spectrum of molecular hydrogen in the extreme ultra-violet.** C. R. JEPPESEN (Physical Rev., 1933, [ii], 44, 165—184).—Using a new grazing-incidence vac. spectrograph, > 2200 lines in the emission spectrum of  $H_2$  in the range 1375—810 Å. were photographed. The known spectrum was extended about 200 Å. towards shorter wave-lengths, and 1400 new lines were found. Full data, analyses, and mol. and rotational consts. are given. N. M. B.

**Photo-excitation of Balmer series of hydrogen canal rays in relation to conditions of the discharge.** F. ZIMMER (Ann. Physik, 1933, [v], 17, 553—580).—The intensities of the  $\beta$ ,  $\gamma$ , and  $\delta$  Balmer lines of H canal rays have been studied at different discharge potentials and different pressures; the variation of the intensities under different conditions is discussed and the data are compared with theoretical predictions. W. R. A.

**Attempt to extend the helium spectrum by exciting both electrons.** A. H. ROSENTHAL (Z. Physik, 1933, 84, 794—798).—The result is doubtful. A. B. D. C.

**Wave-lengths of the vacuum spark spectrum of carbon, nitrogen, and oxygen.** B. EDLÉN (Z. Physik, 1933, 85, 85—106).—The region tabulated is from 104 to 1923 Å. A. B. D. C.

**Term tables of the atomic spectra of carbon, nitrogen, and oxygen.** B. EDLÉN (Z. Physik, 1933, 84, 746—766).—Tables of spectral terms are given for C I to C IV, N II to N V, and C II to C VI, including the extreme ultra-violet. A. B. D. C.

**Second positive group of the nitrogen spectrum.** D. COSTER, F. BRONS, and A. VAN DER ZIEL (Z. Physik, 1933, 84, 304—334).—Rotation lines are analysed, and from intensity perturbations and predissociation mol. terms are shown to dissociate thus:  $X^1\Sigma$  to  $^4S+^4S$ , 9,  $a^1\Pi$  to  $^2D+^2D$ , 5.2,  $A^3\Sigma$  to  $^4S+^2D$ , 3.56,  $B^3\Pi$  to  $^2D+^2P$ , 5.95, and  $C^3\Pi$  to  $^2D+^2P$ , 2.30 volts. This isotope effect gives a mass 15 assuming the normal atom to be 14. A. B. D. C.

**Rotation structure and Zeeman effect of NH bands.** H. BATSCHE (Ann. Physik, 1933, [v], 18, 81—96).—Numerous weak lines were found in the NH spectrum between 3360 and 3370 Å., in addition to the strong triplets. The effect of a magnetic field showed that these were partly lines of the (1,1) band, and partly lines of the subsidiary transition. In a magnetic field the lines between the intensity

max. of the Q branch undergo the greatest change. With the principal lines no splitting was observed, but only a change in the triplet distance which varied with the square of the field strength. Subsidiary lines show a widening proportional to field strength as demanded by theory. A. J. M.

**Hyperfine structure in the arc spectrum of fluorine.** J. S. CAMPBELL (Z. Physik, 1933, 84, 393—401).—The nuclear moment of F is  $\frac{1}{2}$ . A. B. D. C.

**Fine structure and natural width of spectral lines by self-absorption.** E. LAU, O. REICHENHEIM, and J. JOHANNESSEN (Ann. Physik, 1933, [v], 18, 97—106; cf. A., 1932, 208).—The asymmetry of the reversed lines of Ne is due to the difference in temp. of the emitting and absorbing gas, and also to the isotopic nature of Ne. The natural half-width of the lines is obtained. There are two groups of lines of which the natural half-widths are in the ratio 1:2, the lines of the first group being derived from a non-metastable, and those of the second from a metastable, ground term. The Hg line 5461 Å. shows three non-absorbed satellites, and the Hg line 4358 Å. one. The principal line of Hg 5769 is not simple. A. J. M.

**Spectrum of doubly-ionised neon in the extreme ultra-violet.** V. VON KEUSSLER (Z. Physik, 1933, 85, 1—3). A. B. D. C.

**Optical determination of the diffusion constant for sodium.** L. A. GINSEL and L. S. ORNSTEIN (Z. Physik, 1933, 84, 276—281).—Intensity measurements in a Na flame gave a diffusion const. corresponding with a gas kinetic radius of 2.4 Å. for the atom. A. B. D. C.

**New band systems of aluminium hydride.** W. HOLST (Nature, 1933, 132, 207—208).—Details of a new band system at 3800 Å. are recorded and a new system at 3600 Å. is reported. L. S. T.

**Variation with temperature of the continuous absorption spectrum of diatomic molecules. I. Experimental; absorption spectrum of chlorine.** G. E. GIBSON and N. S. BAYLISS. II. Theoretical. G. E. GIBSON, O. K. RICE, and N. S. BAYLISS (Physical Rev., 1933, [ii], 44, 188—192, 193—200).—I. A photographic method used in the temp. range 18—765° showed that rise of temp. decreased the absorption coeff. at the max., and broadened the region of continuous absorption. Analysis of results gave the contributions of individual vibrational levels to the total absorption.



II. The absorption from a single vibrational level is practically independent of temp.; the temp. effect is due to the changing distribution of the absorbing mols. among the various levels. The electric moment corresponding with the absorption from the lower state for  $\text{Cl}_2$  corresponds with the displacement of one electronic charge through 0.016 Å. N. M. B.

**Wavy emission continuum of potassium hydride.** T. HORI (Japan. J. Physics, 1933, 8, 151—163; cf. this vol., 660).—The spectrum of an arc between K electrodes in  $\text{H}_2$  shows, besides the  $^1\Sigma-^1\Sigma$  band structure, a wavy continuum, which can also be attributed to the KH mol. It is interpreted as due to transition from the unstable  $^1\Pi$  state to the stable  $^1\Sigma$  ground-state. NaH shows a similar but feebler continuum, whilst no analogue is observed with LiH. J. W. S.

**Fine structure and predissociation in the spectrum of calcium hydride.** B. GRUNDSTRÖM and E. HULTHÉN (Nature, 1933, 132, 241—242). L. S. T.

**Hyperfine structure of the resonance lines of Sr II.** H. SCHÜLER and H. WESTMEYER (Naturwiss., 1933, 21, 561—562).—The hyperfine structure of the resonance lines of  $\text{Sr}^{87}$  provides another example of inverted terms. The nuclear moment is  $> 0.5$ .  $\text{Sr}^{87}$  is an isotope of odd at. wt. and even at. no., whilst isotopes of odd at. wt. and odd at. no. possess regular terms.  $\text{Sr}^{87}$  is an isobar of  $\text{Rb}^{87}$ , but for the latter the terms are regular. A. J. M.

**Band spectrum of barium hydride.** G. FUNKE (Z. Physik, 1933, 84, 610—628).—An investigation between 5950 and 7500 Å. is described. A. B. D. C.

**Arc spectrum of rhenium between 2500 and 2320 Å. at normal pressure.** S. PIÑA DE RUBIES and J. DORRONSORO (Anal. Fis. Quím., 1933, 31, 412—415).—200 lines between 2500 and 2320 Å. are recorded ( $\pm 0.01$  Å.); 14 are visible with  $5 \times 10^{-4}$  g. of Re, and 3 with  $5 \times 10^{-5}$  g., whilst a line at 2428.58 Å. is visible with  $10^{-5}$  g. H. F. G.

**Principal series  $^1S_0-m^1P_1$  and  $^1S_0-m^3P_1$  of the mercury arc spectrum (Hg I).** Perturbation term  $^1P_1(5d)^9(6s)^26p$ . H. BEUTLER (Z. Physik, 1933, 84, 289—303). A. B. D. C.

**Abnormal increase in intensity of the mercury triplet 5461, 4358, 4057, in highly dried hydrogen and other gases.** A. GÜNTHER-SCHULZE and H. BETZ (Z. Physik, 1933, 84, 402—411).—The intensity ratio of green : yellow increases rapidly with exciting electron velocity and gas pressure for  $\text{H}_2$ , less rapidly for  $\text{N}_2$  and A, and not at all for He and Ne. A. B. D. C.

**Magnetic transition of the hyperfine structure of mercury.** D. R. INGLIS (Z. Physik, 1933, 84, 466—473).—Theoretical investigation of the Paschen-Back effect in hyperfine structure. A. B. D. C.

**Band spectra superimposed on the continuous spectra of mercury in the visible region.** J. OKUBO and E. MATUYAMA (Sci. Rep. Tôhoku, 1933, 22, 383—392).—The spectrum of Hg vapour excited by a high-frequency current of  $3 \times 10^7$  cycles in a

tube of the reflux condensation type shows two bands, at 4340—4078 and at 4047—3650 Å.

A. R. P.

**Polarisation of fluorescence of mercury vapour.** A. KASTLER (Compt. rend., 1933, 197, 442—444).—The deduction that when Hg vapour is illuminated by a beam of light containing the lines 2537 and 4358 Å., the fluorescence lines 4358 and 4046, when observed perpendicularly to the incident beam, should be polarised rectilinearly perpendicular to each other is the more nearly satisfied the narrower and more accurately parallel is the incident beam, the lower the temp., and the more fully compensated the terrestrial magnetic field. C. A. S.

**Prohibited lines due to nuclear spin.** R. EINAUDI (Atti R. Accad. Lincei, 1933, [vi], 17, 552—557).—Theoretical. The intensities of the lines  $^1S_0 \rightarrow ^3P_2$  and  $^1S_0 \rightarrow ^3P_0$  for a bivalent element are calc., and applied to the calculation of the 2270 and 2655 lines of Hg. O. J. W.

**Possibility of the introduction of very high potentials in discharge tubes.** M. SITNIKOV (Z. tech. Physik., 1932, 13, 460—464; Chem. Zentr., 1933, i, 825). L. S. T.

**Positive column in the Hittorf dark space.** A. GÜNTHER-SCHULZE and H. BETZ (Z. Physik, 1933, 84, 740—745). A. B. D. C.

**Electrical clean-up of gases.** W. VON MEYEREN (Z. Physik, 1933, 84, 531—540).—The clean-up of air and  $\text{H}_2$  between  $10^4$  and  $10^6$  mm. was studied with a discharge tube designed to give high electron densities. A. B. D. C.

**Re-striking of the electric arc as a discharge in highly ionised gases.** G. TIMOSHENKO (Z. Physik, 1933, 84, 783—793). A. B. D. C.

**Temperature of the beginning of grey glow radiation of metals, oxides, and sulphides.** G. TAMMANN and W. BOEHME (Ann. Physik, 1933, [v], 17, 863—868; cf. this vol., 117).—The temp. at which grey glow appears for metals, salts, and oxides is lowered by pulverisation, not from diminution of the particle size, but because of cold-working. The effect disappears after the powders have been heated for some time. J. W. S.

**Interpretation of nova spectra.** D. H. MENZEL and C. H. PAYNE (Proc. Nat. Acad. Sci., 1933, 19, 641—648).—The bright-line spectra of novæ are interpreted in terms chiefly of rapidly rising temp., rapidly falling pressure, and rapidly increasing dilution of radiation. C. W. G.

**Electrostatic theory of the plasma.** D. GÁBOR (Z. Physik, 1933, 84, 474—508).—Electrostatic forces between ions are taken into account in determining the condition of plasma. A. B. D. C.

**Vacuum discharges with internal high-voltage sources.** W. KOSSEL and A. ECKARDT (Ann. Physik, 1933, [v], 17, 543—552).—Description of necessary apparatus. W. R. A.

**Precision of the measurement of the Lo Surdo-Stark effect patterns.** Y. ISHIDA and T. TAMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 21, 158—177).—The main difficulty of the Lo Surdo

method is attributed to inaccuracy due to the inclination and chromatic variation; methods for correcting these are suggested. The effect of variation of the field strength with the cathode distance is discussed, and errors introduced by the method are compared critically with the probable error of reading. J. W. S.

**Stark effect by the perturbation theory.** W. VON KOPPEL (Z. Physik, 1933, 84, 694—700).—The relevant equation is solved for first-order perturbations. A. B. D. C.

**Absolute determination of scattering intensity of Cu  $\alpha$  radiation in argon.** G. HERZOG (Naturwiss., 1933, 21, 607—608).—The apparatus is described. The observed scattering in A at 2 atm. and at angle  $40^\circ$  was  $2.88 \times 10^{-7} \pm 5\%$ , agreeing with the Hartree at. model. A. J. M.

**Atom factor determination in the region of anomalous dispersion.** R. GLOCKER and K. SCHÄFER (Naturwiss., 1933, 21, 559—560).—The determination of the at. factor on the short-wave side of the  $K$ -absorption edge of Fe gives anomalous results. A. J. M.

**Effect of lattice binding forces on the fine structure of the carbon  $K\alpha$  line.** R. GLOCKER and H. KIESSIG (Naturwiss., 1933, 21, 593—594).—Photographs have been obtained showing the difference between the C  $K\alpha$  lines from graphite (I) and diamond (II), and consequently the effect of lattice forces on the lines. The components of the (I) line lie on the short-wave side of the max. in contrast to those of (II). SiC shows a fine structure similar to that of (II). A. J. M.

**X-Ray line intensities and cathode-ray retardation in thick targets of Ag.** D. L. WEBSTER, W. W. HANSEN, and F. B. DUVENECK (Physical Rev., 1933, [ii], 44, 258—264).—Measurements of  $K$  lin intensities for voltages up to 180 kv. and emergence angles  $1$ — $25^\circ$  were made in order to determine the voltage for max. efficiency of line emission at any emergence angle, and to extend quant. relations on cathode-ray retardation. N. M. B.

**Structure of X-ray  $K$  absorption limits of the elements manganese to zinc.** A. H. BARNES (Physical Rev., 1933, [ii], 44, 141—145).—The main absorption edges of Mn, Fe, Co, Ni, Cu, but not Zn, and of  $Mn_2O_3$ ,  $Fe_2O_3$ ,  $Co_2O_3$ ,  $Ni_2O_3$ , CuO, but not ZnO, showed definite structure. The oxide edges were all displaced towards shorter wave-length. The observed width of the edges varied from 15 volts for Zn to 23 volts for Fe. N. M. B.

**Relative intensities and transition probabilities of the  $K$ -series lines of the elements 24—52 by the ionisation chamber method.** J. H. WILLIAMS (Physical Rev., 1933, [ii], 44, 146—154).—The ionisation current ratios produced by X-ray lines of wave-lengths 2.29, 1.93, and 1.66 Å. entering a double ionisation chamber filled with MeI, MeBr, A, air, and  $SO_2$  were practically const. The method was applied to measurement of the relative intensities of the  $K$ -series of 20 elements from Cr (24) to Te (52).

Results, transition probabilities, and the absorption coeffs. of mica, cellophane, MeBr, and MeI are given. N. M. B.

**Structure of  $K$  lines of light atoms.** M. MORAND and A. HAUTOR (Compt. rend., 1933, 197, 520—522).—The  $K$  line of O, 23.6 Å., is 0.1—0.15 Å. wide (cf. A., 1930, 1502; this vol., 548); that of N,  $31.8 \pm 0.2$  Å., is wider. The components of  $K$  of C are 44.5, 44.1, and 43.5 Å.; the width of that of B is 2.5 Å., and its max. intensity at 66.55—67.55;  $K$  of Be is 9 Å. wide, sharp edge towards short  $\lambda$  at 112.6 Å. Results agree with theory (cf. this vol., 201, 440, 760). C. A. S.

**Intensity of the linear X-ray spectrum of tungsten.** L. PINCHERLE (Atti R. Accad. Lincei, 1933, [vi], 17, 560—564).—Theoretical. The intensities of the  $K$  and  $L$  lines of W are calc. O. J. W.

**Excitation of X-ray lines of the second kind.** D. COSTER and W. J. THIJSSSEN (Z. Physik, 1933, 84, 686—693).—Excitation of the  $K\alpha_{2,1}$  line of S is described. A. B. D. C.

**Magnitude of the  $L$ -absorption discontinuities.** I. BACKHURST (Phil. Mag., 1933, [vii], 16, 310—312).—Review of existing data suggests that the only relationship between absorption coeffs. which can be regarded as established is  $J(L_3/M_1) = 2^{-1/2}(E_3/E)$ , where  $E_3$  and  $E$  are the vals. of the  $L_3$  and  $M_1$  energy levels, respectively. J. W. S.

**Removal potential and atomic separation.** W. DISTLER and G. MÖNCH (Z. Physik, 1933, 84, 271—275).—The potential required to remove an electron from glowing Ni, 4.63 volts, agrees with Schottky's formula (*ibid.*, 1923, 14, 73), whilst that for Fe, 4.04 volts, does not. A. B. D. C.

**Ionisation potential and formation of the hydrogen molecule.** J. SAVARD (Compt. rend., 1933, 197, 397—399).—Comparison of the total energies of  $H_2^+$  and  $H_2$  as calc. by Hylleraas (cf. A., 1931, 1206) with the ionisation potentials as determined shows that the energy of formation of the normal mol. from normal atoms is double the difference between the ionisation potentials of the mol. and atom. C. A. S.

**Effect of temperature on the emission of electron field currents from tungsten and molybdenum.** A. J. AHEARN (Physical Rev., 1933, [ii], 44, 277—286).—Thermionic emission measurements were made for fields of range  $5 \times 10^5$  to  $1 \times 10^6$  volt per cm., and temp. range 300—2000° abs. Down to about 1600° abs. the thermionic currents masked the field currents. Below 1600° abs. thermionic emission vals. were obtained by extrapolation. Field currents were independent of temp. to within 5% in the range 300—1400° abs., above which data indicate that the current consists of a thermionic current plus a current which is independent of temp. N. M. B.

**Gravitational field of an electron.** J. GHOSH (Nature, 1933, 132, 170, and Z. Physik, 1933, 85, 511—513). L. S. T.

**Electrostatic deviation and specific charge of positive electron.** J. THIBAUD (Compt. rend., 1933, 197, 447—448).—Examination of the magnetic

spectrum (field 10,000 gauss) given by Ra in a Ag tube or of Ra-Th in Pb shows a strong emission of positive electrons. Such electrons are unaffected by interposition of 0.04 mm. of Ag, but greatly absorbed by 0.5 mm. of Al, and almost entirely by 1.0 mm. Superimposition of an electric field shows that the mass of the positive is at least approx. identical with that of the negative electron. C. A. S.

**Electron-microscopic images with secondary electrons.** M. KNOLL and G. LUBSZYNSKI (Physikal. Z., 1933, 34, 671—674).—By means of a new form of electrical electron lens it is possible to obtain images of metallic nets with secondary electrons. The apparatus will permit quant. determinations of secondary emission from metals and insulators. A. J. M.

**Mott's polarisation effect for the scattering of electrons at atoms.** F. SAUTER (Ann. Physik, 1933, [v], 18, 61—80; cf. A., 1929, 861; 1932, 441).—Mott's results can be derived in a simpler and more general manner by the use of the Born-Dirac collision method. A. J. M.

**Effect of exchange on the scattering of slow electrons from atoms.** P. M. MORSE and W. P. ALLIS (Physical Rev., 1933, [ii], 44, 269—276).—Mathematical. The treatment of states involving one or more unbound electrons scattered by an atom is developed. N. M. B.

**Diffraction of slow electrons at single crystals of tungsten.** R. VON MEIBOM and E. RUPP (Ann. Physik, 1933, [v], 18, 107—120).—The electrons were of velocities 25—600 volts. The apparatus is described, and the inner potentials corresponding with the various reflexion max. are obtained. 127 max. were measured, of which 87 can be assigned integral order nos. A. J. M.

**Anomalies in mirror reflexion and diffraction of molecular rays at crystal cleavage surfaces.** I. R. FRISCH and O. STERN. II. R. FRISCH (Z. Physik, 1933, 84, 430—442, 443—447).—I. Reflexion and diffraction curves for H<sub>2</sub> and He by LiF and NaF show characteristic min. (saddles) in the Maxwell distribution curve, probably due to adsorption of the mol. ray by the crystal.

II. The characteristic min. of the intensity curves are shown to occur when the reflected or diffracted rays have definite components of momentum relative to the crystal axes; for these momenta the rays are most readily adsorbed by the doubly periodic force field of the crystal surface. A. B. D. C.

**Mobility of positive ions in gases.** T. EDQVIST (Physikal. Z., 1933, 34, 618—623).—The mobility of positive ions in a gas is calc. on Lenard's formula with respect to pressure, temp., and field strength; conclusions agree with experiment. A. J. M.

**Electrical diffusion of ions in gases of bipolar charge.** N. VOLODKEVITSCH (Z. Physik, 1933, 84, 593—609).—An extension of Townsend's equation for the time distribution of charge density around an ion in a gas containing ions of one charge and one mobility to that of an ion in a gas with positive or negative ions of various mobilities. A. B. D. C.

**Determination of mobilities of ions in gases.** A. STEPANOVA and T. TZAREVA (J. Exp. Theor. Phys., Russia, 1932, 2, No. 5—6, 339—352).—Vals. in air and saturated vapours of HCO<sub>2</sub>H, AcOH, EtCO<sub>2</sub>H, PrCO<sub>2</sub>H, Bu<sup>n</sup>CO<sub>2</sub>H, camphor, and Et<sub>2</sub>O are recorded. CH. ABS.

**Fundamental at. wts. XII. Revision of at. wt. of potassium.** Analysis of potassium chloride and potassium bromide. O. HÖNIG-SCHMID and R. SACHTLEBEN (Z. anorg. Chem., 1933, 213, 365—376).—From the ratios KCl : Ag, KCl : AgCl, KBr : Ag, and KBr : AgBr vals. of 39.096, 39.097, 39.097, and 39.094, respectively, were obtained. The mean of 39 determinations was 39.096. H. J. E.

**Revision of at. wt. of potassium.** G. P. BAXTER and W. M. MACNEVIN (J. Amer. Chem. Soc., 1933, 55, 3185—3190).—From determinations of the ratio KCl : Ag with K from various sources the at. wt. of K is 39.094, which accords with Richards' vals., but is 0.01 unit < that recorded by Hönigschmid and Goubeau (A., 1929, 370). J. G. A. G.

**At. wt. of less volatile potassium prepared by Hevesy.** G. P. BAXTER and C. M. ALTER (J. Amer. Chem. Soc., 1933, 55, 3270—3271).—From determinations of the ratio KCl : Ag, the at. wts. of ordinary K and heavy K conc. by ideal distillation (cf. A., 1928, 684) are 39.096 and 39.109, respectively; the heavy K contains 7.3% K<sup>41</sup> (cf. A., 1929, 370). J. G. A. G.

**Relative abundance of hydrogen isotopes.** W. BLEAKNEY and A. J. GOULD (Physical Rev., 1933, [ii], 44, 265—268).—The abundance ratio H<sup>2</sup> : H<sup>1</sup> determined by the mass-spectrograph for H<sub>2</sub> liberated in the electrolysis of rain-H<sub>2</sub>O varied between 1 : 4500 and 1 : 6500. N. M. B.

**Isotopes of cobalt by the magneto-optic method.** T. R. BULL and S. S. COOPER (J. Amer. Chem. Soc., 1933, 55, 3207—3210).—Two new isotopes of Co, probably of masses 57 and 58, have been discovered. Co<sup>59</sup> is by far the most abundant, followed in order by 57 and 58, in keeping with the at. wt. 58.94. Earlier data (A., 1930, 1541) are revised. J. G. A. G.

**Mass ratio of the lithium isotopes from the spectrum of Li<sub>2</sub>.** A. MCKELLAR (Physical Rev., 1933, [ii], 44, 155—164).—Wave nos. of all the lines of the blue-green absorption bands of the Li<sup>7</sup>Li<sup>7</sup> and Li<sup>6</sup>Li<sup>7</sup> systems are given. Vibrational, rotational, and electronic consts. are calc. N. M. B.

**Packing effect.** A. SOMMERFELD (Conv. Fis. nucl., 1932, 1, 155—157; Chem. Zentr., 1933, i, 1078).—Aston's and Stefan Meyer's curves do not differ essentially. The bifurcation of Aston's curve has no physical basis. The packing effect exhibits a periodicity parallel with that of the outer at. shell. A. A. E.

**Energy levels of radium-C'.** G. BECK (Conv. Fis. nucl., 1932, 1, 167—172; Chem. Zentr., 1933, i, 1079).

**Artificial transformation of magnesium with polonium  $\alpha$ -rays.** W. BOTHE and H. KLARMANN (Naturwiss., 1933, 21, 639—640).—The Rutherford-

Geiger counter was used in the investigation of nuclear transformation of Mg with Po  $\alpha$ -rays of various ranges. The absorption curves of protons were obtained. For the longer ranges (3.87 cm.) there are four distinct proton groups, but this no. decreases with the range until for ranges  $< 2.84$  cm. there is only one group. Some of the proton groups possess a narrow excitation interval with regard to  $\alpha$ -ray range. A. J. M.

**Nuclear radii and atomic disintegration efficiency for heavy elements.** G. KIRSCH (Naturwiss., 1933, 21, 640).—For Ra-C absorption, elements with odd at. no., especially In and Sb, show, contrary to expectation, concave absorption curves; even elements, e.g., Te, Sn, and Cd, show a step in the absorption curve.  $\alpha$ -Particles within a certain velocity range were not reflected. A no. of experiments give results apparently incompatible with the Gamow nuclear model. A. J. M.

**$\alpha$ -Particles, artificial nuclear transformation and excitation, isotopes.** W. BOTHE (Conv. Fis. nucl., 1932, 1, 83—106; Chem. Zentr., 1933, i, 1078—1079).

**Theory of  $\beta$ -emission.** K. SITTE (Physikal. Z., 1933, 34, 627—630).—Dirac's theory is applied to  $\beta$ -emission. A. J. M.

**$\beta$ -Radiation of radium-E and of active deposit of actinium.** M. LECOIN (Compt. rend., 1933, 197, 405—407).— $H_p$  for 600  $\beta$ -rays from active deposit of Ac, 250 from Ac'', and 400 from Ra-E have been measured. The (no. of rays)- $H_p$  curves are: for Ac'' bell-shaped, max. at about 3000  $H_p$ , ending at about 6500; and for Ac-B max. about 1000, ending at 3000—3500. That for Ra-E seems to end or change direction at about 5800. Ra-E emits  $< 1$  positive electron per 2000  $\beta$ -rays. C. A. S.

**Energy law and reversibility of elementary processes.** G. BECK (Z. Physik, 1933, 84, 811—813).—The relation of the energy law to reversibility is discussed for elementary processes, particularly for  $\beta$ -ray disintegration. A. B. D. C.

**Radioactivity of potassium.** D. BOCCIARELLI (Atti R. Accad. Lincei, 1933, [vi], 17, 830—836).—Absorption measurements show that the radiation from K is made up of (a) a relatively soft  $\beta$  component forming 60% of the total intensity with a velocity 0.83  $c$ , (b) a harder  $\beta$  component (nearly 40%) with velocity 0.93  $c$ , and (c) a very hard  $\gamma$ -radiation forming 1.08% of the total. O. J. W.

**$\beta$ - and  $\gamma$ -rays.** C. D. ELLIS (Conv. Fis. nucl., 1932, 1, 107—117; Chem. Zentr., 1933, i, 1079—1080).—A discussion. A. A. E.

**Inner photo-effect with  $\gamma$ -rays.** L. MEITNER and K. C. WANG (Naturwiss., 1933, 21, 594).—The intensity of  $\beta$ -ray groups emitted from Th-B+C+C'' was determined in a magnetic field by a Geiger-Müller counter. Agreement is shown between the results of this method and the photographic method of Ellis. A. J. M.

**Internal conversion [of  $\gamma$ -rays].** J. SOLOMON (Compt. rend., 1933, 197, 401—403; cf. this vol.,

110, 111).—Mathematical; the probability of the occurrence of these transitions is calc. C. A. S.

**Absorption of very penetrating  $\gamma$ -rays.** W. GENTNER (Compt. rend., 1933, 197, 403—405).—The absorption of  $\gamma$ -rays of great energy is attributed to (a) Compton effect, (b) photo-electric absorption, (c) nuclear diffusion, and (d) excitation of positive electrons. (a) obeys Klein and Nishina's formula; (b) is determinable by Gray's method. The coeff. of absorption of Pb for  $\gamma$ -rays of  $\lambda 4.7$ — $9.3$  X experimentally determined, compared with the coeff. deduced from (a) and (b), gives by difference the effect due to (c). Its effect begins at  $\lambda=12$  X, and increases as  $\lambda$  diminishes (cf. A., 1932, 671, 791).

C. A. S.

**Passage of penetrating corpuscular rays through a ferromagnetic.** C. F. VON WEIZSÄCKER (Ann. Physik, 1933, [v], 17, 869—896).—Theoretical. J. W. S.

**Spin and statistics of the neutron.** T. SEXL (Nature, 1933, 132, 174). L. S. T.

**Existence of a neutron of mass 2.** H. WATKE (Nature, 1933, 132, 242—243).—Certain anomalies in recent measurements in disintegration experiments can be explained by assuming the existence of a neutron of mass 2 with an energy of  $16 \times 10^6$  electron volts. L. S. T.

**Theory of the neutron.** J. J. PLACINTEANU (Z. Physik, 1933, 84, 370—379).—The model consisting of a proton and an electron of negative kinetic energy fits known empirical data for the neutron (cf. this vol., 660). A. B. D. C.

**Constitution of neutrons, positive electrons, and protons: existence of negative protons.** J. J. PLACINTEANU (Compt. rend., 1933, 197, 549—552; cf. this vol., 660, 683, and preceding abstract).—It is shown that photons of energies  $< 10^6$  and  $10^9$  ev. should be decomposable into a negative and a positive electron, and a negative and a positive proton, respectively; non-detection of the negative proton is probably due to the great energy required. C. A. S.

**Interaction of neutrons and protons.** G. C. WICK (Z. Physik, 1933, 84, 799—800).—Heisenberg's hypothesis of neutron and proton interchange (A., 1932, 1074) is applied to scattering of these particles. A. B. D. C.

**Theory of atomic nuclei. IV, V.** E. N. GAPON (Z. Physik, 1933, 84, 509—519, 520—530).—IV. Mass defects are determined for nuclear protons, neutrons, and  $\alpha$ -aggregates; binding energies for nuclei of  $\alpha$ -particles and neutrons and the diameter of the  $\alpha$ -particle are also calc.

V. A scheme is given representing the transformation of light nuclei by  $\alpha$ -particles, neutrons, and proton, and the  $\alpha$ - and  $\beta$ -disintegration of radioactive elements. A. B. D. C.

**Ultra-corpuscular radiation.** W. BOTHE (Conv. Fis. nucl., 1932, i, 153—154; Chem. Zentr., 1933, i, 1080).

**Disintegration of various substances by ultra-radiation.** E. G. STEINKE, A. GASTELL, and H. NIE (Naturwiss., 1933, 21, 560; cf. A., 1932, 556,

791).—With some exceptions, there is proportionality between collision impact and normal ionisation. There is comparatively high collision frequency with Fe and Al compared with Pb. A. J. M.

**Interaction between cosmic rays and matter.** B. ROSSI (Nature, 1933, 132, 173—174).—The showers of secondary particles produced when cosmic rays pass through matter occur more frequently in elements of high at. no. For Pb, Fe, and Al, the ratio is 4:2:1. The radiation which causes the showers has a mean range of a few cm. in Pb and cannot be identical with the primary cosmic rays. The shower-producing rays are more readily absorbed by elements of high at. no. Absorption of secondary rays by an element and the no. of showers produced depend similarly on at. no. L. S. T.

**Diminution of cosmic-ray intensity by transmission through various materials.** E. G. STEINKE and H. TIELSCH (Z. Physik, 1933, 84, 425—429).—Comparison of absorption by Pb, Fe, and Al indicates that only orbital electrons reduce the intensity of the beam. A. B. D. C.

**Secondary and tertiary particles produced by cosmic rays.** J. H. SAWYER, jun. (Physical Rev., 1933, [ii], 44, 241—245).—Counts of triple coincidences by means of Geiger counters, as a function of the thickness of plates of Pb, Sn, and Al as scatterers, give curves which can be explained by assuming that the effect is due to tertiary particles generated in the metal by light element secondaries produced in the regions above the scatterers. N. M. B.

**Mechanism of the Geiger-Müller counter.** W. CHRISTOPH and W. HANLE (Physikal. Z., 1933, 34, 641—645).—The normal form of the charge in the Geiger-Müller counter is a photon charge. The no.-potential characteristics are explained. A. J. M.

**Application of the FP-54 pliotron to atomic disintegration studies.** L. R. HAFSTAD (Physical Rev., 1933, [ii], 44, 201—213).—Investigation of the resonance disintegration of Al gave 20 protons of range 30—50 cm. per  $10^8$   $\alpha$ -particles. Evidence of groups of ranges 30 and 60 cm., and a strong group 45—50 cm., was obtained. N. M. B.

**Quantum theoretical treatment of radiation problems.** L. ROSENFELD (Conv. Fis. nucl., 1932, 1, 131—135; Chem. Zentr., 1933, i, 1075—1076).—A review. A. A. E.

**Subdivision of the series of transition elements.** W. BILTZ and W. KLEMM (Z. Elektrochem., 1933, 39, 597—598; cf. this vol., 110).—A discussion of the electron arrangement in the elements between Ca and Zn. H. J. E.

**Charge distributions in fluorine and neon.** F. W. BROWN (Physical Rev., 1933, [ii], 44, 214—223).—Mathematical. Energy parameters of electrons are calc. by a modified Hartree field method. N. M. B.

**Dissociation of diatomic molecules with  $p$ - $p$  binding.** H. LESSHEIM and R. SAMUEL (Z. Physik, 1933, 84, 637—656).—By comparison of electron configurations of mol. terms and of the energies of

bound and separated atoms, the influence of the electrons of the individual atoms on the strength of the linking is deduced. The results are applied to BeO, NO, PO, BeF, MgF, CaF, SrF, AlO, PbO, and SnCl. A. B. D. C.

**Theory of the nucleus.** G. WATAGHIN (Atti R. Accad. Lincei, 1933, [vi], 17, 645—647).—Certain aspects of Heisenberg's theory of the at. nuclear structure are discussed in the light of the discovery of the positive electron. O. J. W.

**Frequency of the elements and constitution of the nucleus of atoms. II. Twenty years in the history of an observation and of a hypothesis.** G. ODDO (Gazzetta, 1933, 63, 355—380; cf. A., 1914, ii, 239).—The development of the theory that the nuclei of all atoms contain He atoms is discussed. O. J. W.

**Quantum theory of nuclear structure.** G. GAMOW (Conv. Fis. nucl., 1932, 1, 65—81; Chem. Zentr., 1933, i, 1077).—Units of nuclear structure are distinguished as (a) heavy (protons and agglomerations, e.g.,  $\alpha$ -particles) and (b) light (electrons). Processes involving (a) which can be treated by non-relativistic quantum mechanics are considered. A. A. E.

**Theoretical optics of the hydrogen molecule.** B. MROWKA (Z. Physik, 1933, 84, 448—465).—The mean polarisability of the mol., taking into account zero point vibration of the nuclei, is calc., and used to determine intensity of Raman lines, degree of depolarisation, and variation of refractive index with wave-length. A. B. D. C.

**Charge distributions for the normal atoms from boron to neon.** F. W. BROWN, J. H. BARTLETT, jun., and C. G. DUNN (Physical Rev., 1933, [ii], 44, 296—299).—Mathematical. N. M. B.

**Stability of the atom and the laws of conservation.** N. BOHR (Conv. Fis. nucl., 1932, 1, 119—130; Chem. Zentr., 1933, i, 1077).—A discussion. A. A. E.

**Magnetic moment of the proton. I.** ESTERMANN, R. FRISCH, and O. STERN (Nature, 1933, 132, 169—170).—Deflexion experiments with para-H at room temp. give a rotational moment of 0.8—0.9 nuclear magneton per unit quantum no. This result together with deflexion experiments with ortho-H gives a val. of 2.5 nuclear magnetons, and not 1, as would be expected, for the moment of the proton. L. S. T.

**Magnetic deviation of hydrogen molecules and the magnetic moment of the proton. I. R. FRISCH and O. STERN. II. I. ESTERMANN and O. STERN (Z. Physik, 1933, 85, 4—16, 17—24).—I.** Para-H gave deviations corresponding with approx. one nuclear magneton (1/1840 Bohr magneton) per rotational quantum. Ortho-H gave the magnetic moment of the proton between 2 and 3 nuclear magnetons.

II. More accurate measurements gave the moment of the proton as 2.5 nuclear magnetons, with a possible error  $< 10\%$ , and the rotational moment as 0.8—0.9 nuclear magneton per rotational quantum. A. B. D. C.

**Magnetic moment of a rotating hydrogen molecule.** G. C. WICK (Z. Physik, 1933, 85, 25—28).—Introduction of circulation of the electronic cloud around the nuclei due to rotation of the mol. gives 0.36 and 0.925 as the limits of the magnetic rotational moment in nuclear magnetons (cf. preceding abstract).  
A. B. D. C.

**Impulse corona in water.** Y. TORIYAMA and U. SHINOHARA (Nature, 1933, 132, 240). L. S. T.

**Colour of precipitated cadmium sulphide.** W. J. MÜLLER and G. LÖFFLER (Angew. Chem., 1933, 46, 538—539).—X-Ray examination shows that the variation in colour of CdS pptd. by  $H_2S$  from solutions containing differing amounts of  $H_2SO_4$  is due solely to the differing size of the crystals.  
H. W.

**Colour centres of alkali halide crystals.** E. MOLLWO (Z. Physik, 1933, 85, 56—67).—Quant. investigation of the production of centres by heating in presence of metal vapours shows that for each temp. there is a definite concn. of centres, and the v.p. of the cation metal at any temp. gives the lower limit of this concn. The principal optical properties of the centres were also determined, and show the width of the absorption band and its max. to depend on the thermal energy of the lattice. A. B. D. C.

**New type of diffuse molecular spectrum. Optical absorption and photochemical decomposition of chromyl chloride vapour.** R. DE L. KRONTG, A. SCHAAFSMA, and P. K. PEERLKAMP (Z. physikal. Chem., 1933, B, 22, 323—332).—In the absorption spectrum of  $CrO_2Cl_2$  five diffuse absorption bands without edges are repeated some 15 times at a const. interval of  $136\text{ cm.}^{-1}$  from  $6000\text{ Å.}$  towards the violet. Light absorption is accompanied by dissociation, probably into  $CrO_2$  and  $Cl_2$ , a dust appearing. Assuming this dissociation to correspond with passage of the mol. into an electronic state in which the interaction of the two groups of atoms is described by a repulsion curve, the spectrum may be interpreted as a Condon diffraction band.  
R. C.

**Extension of ultra-violet absorption spectrum of ozone towards greater wave-lengths.** D. CHALONGE and (MME.) L. LEFEBVRE (Compt. rend., 1933, 197, 444—447).—An arrangement enabling a tube  $245 \times 3.5\text{ cm.}$  to be filled with  $O_3$  containing 22%  $O_3$  is described. The absorption spectrum of  $O_3$  has been examined from  $\lambda\ 3385$  to  $3660$ , and the bands at  $3439$ ,  $3515$ , and  $3575$  are shown to be due to  $O_3$  (cf. A., 1925, ii, 998).  
C. A. S.

**New band system of beryllium oxide and the structure of the  $BeO$  molecule.** L. HERZBERG (Z. Physik, 1933, 84, 571—592).—The electron configurations, dissociation energies, and other mol. constns. are deduced for various electron levels.  
A. B. D. C.

**New bands in the spectrum of vanadium monoxide.** G. PICCARDI (Atti R. Accad. Lincei, 1933, [vi], 17, 836—838).—Twelve visible new bands of VO are recorded.  
O. J. W.

**Spectrum of molybdic anhydride.** G. PICCARDI (Atti R. Accad. Lincei, 1933, [vi], 17, 654—656).—

The light emitted when  $MoO_3$  is heated in the Bunsen and  $O_2-H_2$  flames gives a continuous spectrum between  $6600$  and  $4840\text{ Å.}$ , with intensity max. at  $5520$  and  $6300\text{ Å.}$  The arc spectrum between Ag electrodes is almost wholly linear, but shows a few weak bands at  $6100-6500\text{ Å.}$  The continuous spectrum may represent a new type of pre-dissociation spectrum, due to the group MoO.  
O. J. W.

**3600 Å. doublet band of the carbon dioxide spectrum.** R. SCHMID (Z. Physik, 1933, 84, 732—739).  
A. B. D. C.

**Influence of halides on the extinction coefficients, and its bearing on the constitution, of silver halides in fusion.** G. S. FORBES and H. B. ELKINS (J. Amer. Chem. Soc., 1933, 55, 3272—3276).—The extinction coeffs.,  $K$ , of molten AgCl and AgBr at  $\lambda\ 5460\text{ Å.}$  are greatly diminished by small quantities of the chlorides and bromides, respectively, of Li, K, Rb, Ba, Sr, and Pb. The data are consistent with the presence of the complex cation  $Ag_2Cl^+$  in equilibrium with AgCl, of which the dissociation const. is  $3 \times 10^{-4}$ . With mixtures of Ag halides,  $\log K$  is almost a linear function of the mol. fraction of one constituent. J. G. A. G.

**Spectrophotometry of short-lived intermediate products.** H. SCHMID and E. GASTINGER (Z. Elektrochem., 1933, 39, 573—576; cf. A., 1930, 1395).—Aq.  $Na_2S_2O_3$  and aq. HCl were mixed by a continuous-flow method in an absorption cell, and the extinction coeff. of the unstable  $HS_2O_3'$  ion between  $2800$  and  $2300\text{ Å.}$  was measured.  
H. J. E.

**Absorption spectra of the samarium ion in solids. III. Absorption of  $Sm(BrO_3)_3 \cdot 9H_2O$  and a partial energy level diagram for the  $Sm^{+++}$  ion as it exists in crystalline  $Sm(BrO_3)_3 \cdot 9H_2O$ .** F. H. SPEDDING and R. S. BEAR (Physical Rev., 1933, [ii], 44, 287—295; cf. A., 1932, 1188).—Data on the energy levels were obtained from a study of the absorption spectra in the temp. range  $20-298^\circ$  abs. Low-temp. splitting may be due either to actual removal of degeneracy or to development of two types of  $Sm^{+++}$  ion, differing in crystal environments, either effect being caused by small changes of crystal dimension and symmetry. N. M. B.

**Ultra-violet absorption of the amino-group and other groups in simple gaseous molecules.** G. HERZBERG and R. KÖLSCH (Z. Elektrochem., 1933, 39, 572—573).— $NH_2Me$ ,  $NH_2Et$ , and  $NH_2Pr$  vapours show absorption bands between  $2500$  and  $2100\text{ Å.}$  resembling those of  $NH_3$ . The band spacings for the amines and for  $NH_3$  are approx.  $650$ ,  $900\text{ cm.}^{-1}$ , respectively, interpreted as a vibration frequency of the excited  $NH_2$  group. For  $NHMe_2$ ,  $NMe_3$ , and  $NHET_2$  similarly placed but diffuse bands occur.  $NH_2Ph$  also has an absorption band at  $2400\text{ Å.}$   $HCO \cdot NH_2$  vapour shows neither bands due to C:O nor those of  $NH_2$ .  
H. J. E.

**Absorption spectra of mixed fatty acids from cod-liver oil.** W. J. DANN and T. MOORE (Biochem. J., 1933, 27, 1166—1169).—The mixed fatty acids (I) obtained by brief hydrolysis (aq. EtOH-KOH)

of cod-liver oil show only relatively low absorption (ultra-violet region) without fine structure. The acids obtained by more prolonged hydrolysis [or by further treatment of (I) with EtOH-KOH] show much more intense absorption, and definite signs of fine structure are evident. The absorption spectra of stearic and oleic acids are unaffected by treatment with KOH; the absorption of linoleic acid (II) increased about fourfold. There is no significant change in the degree of unsaturation (I vals.) of (I) or (II), indicating that increased absorption may be related to an isomeric change involving the double linkings of the more highly unsaturated acids.

H. B.

**Low-temperature absorption spectrum of pepsin.** G. I. LAVIN, J. H. NORTHRUP, and H. S. TAYLOR (J. Amer. Chem. Soc., 1933, 55, 3497—3498).—The absorption band of pepsin at 2600—2900 Å. is resolved into sharp narrow bands by cooling to  $-100^{\circ}$ . Serum- and ov-albumin have narrow bands at low temp.

J. G. A. G.

**Infra-red radiations from small particles.** A. H. PFUND (J. Opt. Soc. Amer., 1933, 23, 270—272; cf. A., 1932, 212).—Powder films of quartz,  $\text{BaSO}_4$ , and  $\text{K}_2\text{CO}_3$ , the particle size of which is small compared with the wave-length, show pronounced emission max. within the region of selective absorption. The behaviour of quartz powder is the inverse of that of a polished plate.

N. M. B.

**Influence of H' and OH' ions in concentrated acids and alkalis on the infra-red absorption spectrum of water.** R. SUHRMANN (Z. Elektrochem., 1933, 39, 642; cf. A., 1932, 1188).—Aq.  $\text{H}_2\text{SO}_4$  (2.80, 1.40N), HCl (5.50, 2.75N), and KOH (10.9, 5.47, 2.73N) show a lowering of the normal absorption max. of  $\text{H}_2\text{O}$  at 0.98, 1.20, and 1.96  $\mu$ , respectively. The absorption on the long wave-length side of the band at 1.45  $\mu$  is increased. This result is attributed to association of  $\text{H}_2\text{O}$  mols. with the ions.

H. J. E.

**Infra-red dispersion of carbon dioxide.** A. PARTS and A. TUDEBERG (Anal. Fis. Quím., 1933, 31, 319—324).—A dispersion formula is derived which yields a val. of  $1.00 \times 10^{-18}$  for the dipole moment of the C:O linking.

H. F. G.

**Resolution of the two difference bands of  $\text{CO}_2$  near 10  $\mu$ .** E. F. BARKER and A. ADEL (Physical Rev., 1933, [ii], 44, 185—187).—The rotational structure of the two absorption bands at 9.4 and 10.4  $\mu$  is completely resolved; both bands have positive and negative, but no zero, branches. The moment of inertia is  $70.6 \times 10^{-40}$  g.-cm.<sup>2</sup>

N. M. B.

**Measurements of the rotation spectrum of water vapour.** J. KÜHNE (Z. Physik, 1933, 84, 722—731).—A vac. grating spectrometer was used to investigate this spectrum between 30 and 90  $\mu$ .

A. B. D. C.

**Rotation-vibration bands of ammonia.** E. FERMI (Nuovo Cim., 1932, [ii], 9, 277—283; Chem. Zentr., 1933, i, 1244—1245).—Theoretical.

A. A. E.

**Vibration structure of the carbon tetrachloride spectrum.** J. HORIUTI (Z. Physik, 1933, 84, 380—

392).—Resonance of the combination tone (315+457)  $\text{cm}^{-1}$  and the fundamental 774  $\text{cm}^{-1}$  is investigated, and fits the empirical vibration spectrum.

A. B. D. C.

**Raman effect and its application to mineral chemistry.** H. VOLKRINGER (Bull. Soc. chim., 1933, [iv], 53, 445—468).—A lecture.

**Applications of the Raman effect to organic chemistry.** M. BOURGUEL (Bull. Soc. chim., 1933, [iv], 53, 469—505).—A lecture.

**Rotation Raman spectrum of  $\text{O}_2$  at high pressures.** B. TRUMPY (Z. Physik, 1933, 84, 282—288).—The rotation Raman spectrum of  $\text{O}_2$  showed lines up to 60 atm. pressures; at 15 atm. the intensity of the lines agreed with theory.

A. B. D. C.

**Relation between the Raman spectra of different halides.** O. REDLICH (Z. Elektrochem., 1933, 39, 571; cf. this vol., 113).—For  $\text{H}_2\text{SnBr}_6$ , 5 lines were observed; only 3 were expected.

H. J. E.

**Existence of  $\text{NaHSO}_3$  in solution.** P. FADDA (Nuovo Cim., 1932, 9, 227—230; Chem. Zentr., 1932, ii, 3838).—In the Raman spectra of solutions of  $\text{NaHSO}_3$  only  $\text{S}_2\text{O}_5''$  and not  $\text{HSO}_3'$  frequencies occur, showing that  $\text{NaHSO}_3$  does not exist in solution. The lines 571 and 1054 ascribed to  $\text{S}_2\text{O}_5''$  belong to  $\text{HSO}_4'$ .

L. S. T.

**Nuclear vibration spectrum of acetylacetone.** K. W. F. KOHLRAUSCH [with A. PONGRATZ and J. KÖPPL] (Anal. Fis. Quím., 1933, 31, 315—318).—The oscillation frequencies of the CO group in a no. of aldehydes, ketones, acids, and esters are recorded; for each class of compound the variations from the mean are small. In symmetrical compounds containing 2 CO groups only 1 line due to CO appears (in the range  $< 2000 \text{ cm}^{-1}$ ), and its frequency is increased by conjugation of the CO groups. In unsymmetrical mols. 2 lines appear; e.g.,  $\text{AcCO}_2\text{H}$  exhibits the lines characteristic of ketones and of acids.  $\text{CH}_2\text{Ac}_2$  exhibits the ketone line (1719  $\text{cm}^{-1}$ ), and 2 lines (1593 and 1655  $\text{cm}^{-1}$ ) characteristic of the C:C linking. The substance therefore exists as a tautomeric mixture of 1 keto- and 2 enol forms.

H. F. G.

**Raman spectra of cis- and trans-1:2-dimethylcyclohexanes.** O. MILLER and L. PIAUX (Compt. rend., 1933, 197, 412—414).—The Raman spectra of the isomerides (cf. this vol., 815) are radically different, having out of 24 lines measured between 315 and 2975  $\text{cm}^{-1}$  only 5 the same; substances previously obtained were probably mixtures (cf. A., 1932, 213, 1240).

C. A. S.

**Predissociation in fluorescence emission spectra: fluorescence of acetone vapour.** H. G. CRONE and R. G. W. NORRISH (Nature, 1933, 132, 241).—With the Hg line 3340 Å. as excitant, visible fluorescence of  $\text{COMe}_2$  is accompanied by considerable emission in the ultra-violet extending down to the exciting line. The visible fluorescence consists of diffuse bands, whilst the ultra-violet fluorescence consists of a series of fine, sharp lines. This is the first example of predissociation associated with fluorescence, and represents a transition from an

upper excited level to a lower metastable level. Predicted absorption in the near infra-red and a region of discrete structure in the ultra-violet absorption have been verified. L. S. T.

**Conservation of kinetic moment and the rules of polarisation in spectroscopy. Application to the diffusion of light and to fluorescence.** A. KASTLER (J. Phys. Radium, 1933, [vii], 4, 406—420).—Mathematical. N. M. B.

**Polarisation of fluorescent light.** (MLLE.) J. CAHEN (J. Chim. phys., 1933, 30, 420—428).—The degree of polarisation,  $p$ , of light emitted by solutions of fluorescent org. compounds in  $H_2O$  and in aq. and anhyd. glycerol, increases with increasing viscosity of the solvent, approaching a limiting val. for each substance as  $\eta \rightarrow \infty$ . This val. varies considerably with the wave-length of the exciting light, each absorption band giving a different val. of  $p$ . D. R. D.

**Destruction of zinc sulphide phosphors by  $\alpha$ -rays. II.** P. M. WOLF and N. RIEHL (Ann. Physik, 1933, [v], 17, 581—586).—The mechanism of the change in ZnS phosphors by  $\alpha$ -rays is explained and the relation between the change in the phosphor and the part played by impurities is considered. W. R. A.

**Temperature dependence of scintillation processes and the destruction of phosphors.** N. RIEHL (Ann. Physik, 1933, [v], 17, 587—592).—The relation between the brightness of the scintillation of ZnS and the temp. has been investigated between  $-252^\circ$  and  $600^\circ$ . Above  $200^\circ$  (but not below) the luminescence on exposure to  $\alpha$ -rays diminishes gradually to  $500^\circ$ , where it disappears. Similar behaviour results from photo-excitation and by breaking the crystals. None of the known inorg. phosphors is luminescent above  $500^\circ$ ;  $\alpha$ -rays, therefore, increase or decrease the luminescence according to the temp. W. R. A.

**Mechanisms of luminescence phenomena in the burning of combustible gases in air.** PIETRE (Ann. Office nat. Combust. liq., 1932, 7, 699—719; Chem. Zentr., 1933, i, 1260).—A summary and discussion. A. A. E.

**Solarisation of luminiferous calcite.** S. IIMORI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 21, 220—231; cf. this vol., 661).—Theoretical relations, confirmed by experiment, are developed for the rate of growth of the radiator of photoluminescence during excitation and for the rate of its decay after cessation of excitation. J. W. S.

**Stopping layer of rectifiers.** W. JUSÉ (Nature, 1933, 132, 242).—Rectification depends on the thickness of the contact layer between a semi-conductor and a metal within narrow limits ( $10^{-5}$  to  $10^{-6}$  cm.). L. S. T.

**Crystal photo-effect.** A. JOFFÉ and A. F. JOFFÉ (Nature, 1933, 132, 168—169).—The assumption that the equilibrium of electrons in an illuminated crystal is dynamic, and consists of a continuous circulation of electrons between the bright and dark parts of a crystal, agrees with experimental facts. L. S. T.

**Influence of metal surface on the position of selectivity of the external photo-electric effect.** F. HLÚČKA (Z. Physik, 1933, 84, 364—366).—The condition of the metal surface, although determining the long wave-length limit of sensitivity, does not displace the selective max. A. B. D. C.

**Selectivity of the external photo-electric effect of alloys.** F. HLÚČKA (Z. Physik, 1933, 84, 367—369).—Spectral selectivity for alloys is additive of the constituent metals. A. B. D. C.

**Internal photo-electric effect in amorphous substances.** D. N. NASLEDOV, L. M. NEMENOV, and P. V. SHARAVSKI (J. Exp. Theor. Phys., Russia, 1932, 2, 97—101). CH. ABS.

**Photo-electric effect with the carborundum detector.** P. SPECHT (Physikal. Z., 1933, 34, 640).—The SiC detector shows a photo-potential with small contact pressures. For instantaneous currents, the photo-active places exhibit towards others a strong rectifying action. There was direct proportionality between photo-potential and unipolar conductivity. Experiments on the dependence of the photo-effect on the radiated energy gave no linear current curve. The potential and current reach saturation vals. A. J. M.

**External photo-electric effect of alkali halide crystals.** R. FLEISCHMANN (Z. Physik, 1933, 84, 717—721).—The dependence of photo-electric effect sensitivity on wave-length is examined for KBr; for the alkali halides, particularly KBr, illumination with short-wave ultra-violet light gives a new absorption region which is photo-electrically effective. A. B. D. C.

**Thermal and photo-electric emission of caesium-caesium oxide cathodes, and the effect of caesium atoms in the dielectric.** P. GÖRLICH (Z. Physik, 1933, 85, 128—130).—An alternative method for getting Cs atoms in the dielectric is described (cf. de Boer and Teves, this vol., 887). A. B. D. C.

**Behaviour of electrons and "holes" in cuprous oxide.** A. JOFFÉ, D. NASLEDOV, and L. NEMENOV (Nature, 1933, 132, 239—240). L. S. T.

**Photo-electric effect in the contact layer under the action of ultra-violet light.** D. N. NASLEDOV and L. M. NEMENOV (J. Exp. Theor. Phys., Russia, 1932, 2, 179—182).—In  $Cu_2O$ -Zn, ultra-violet light drives the electrons from  $Cu_2O$  to Zn. CH. ABS.

**Photo-electric effect in single crystals of cuprite.** G. MÖNCH and R. STÜHLER (Z. Physik, 1933, 85, 131—134).—Polemical, against Deaglio (this vol., 554). A. B. D. C.

**Electrical conduction in solids with high field strengths.** A. VON HIPPEL (Z. Elektrochem., 1933, 39, 506—512; cf. A., 1932, 565).—The field strengths necessary for the passage of a spark through crystals of halides of Li, Na, K, and Rb were measured. Vals. between  $3.2$  and  $0.4 \times 10^6$  volt per cm. were observed, decreasing for a given halide in the order  $Li \rightarrow Rb$ , and for a given alkali metal in the order  $F \rightarrow I$ . For NaCl breakdown took place most easily along the [110] plane. Results are correlated with lattice structure. H. J. E.

Dependence of transport characteristics on temperature and the mechanism of the reverse voltage in solid ionic conductors. A. SNEKAL (Z. Elektrochem., 1933, 39, 542—543).—A discussion.

H. J. E.

Electron and lattice disarrangement in crystalline polar compounds as basis for electronic and ionic conduction. C. WAGNER (Z. Elektrochem., 1933, 39, 543—545).—The changes in conductivity of ZnO, CdO, Cu<sub>2</sub>O, NiO, and CuO between 500° and 1000° with the O<sub>2</sub> pressure of the surrounding atm. are correlated with changes in electron distribution and lattice structure in the solids.

H. J. E.

Transport of matter in solid bodies. G. VON HEVESY (Z. Elektrochem., 1933, 39, 490—500).—A survey of recent work on conduction and diffusion in solids.

H. J. E.

Electrical conduction and diffusion in non-metallic solids. C. TUBANDT (Z. Elektrochem., 1933, 39, 500—506).—A summary.

H. J. E.

Dependence of electrical conductivity and self-diffusion in crystals on the crystallographic direction. W. SEITH (Z. Elektrochem., 1933, 39, 538—542; cf. A., 1929, 1136).—The conductivity of solid PbI<sub>2</sub> was measured parallel and perpendicular to the *c* axis at temp. between 200° and 400°. The contribution of the Pb and I ions in the two cases is discussed. The self-diffusion of Pb in PbI<sub>2</sub>, measured with Th-B as radioactive indicator, was independent of the crystallographic direction. For Bi, with Th-C indicator, the val. parallel to the *c* axis was very small, but, perpendicular, it had an abnormally high temp. coeff.

H. J. E.

Relation between the electrical conductivity of glass and the strain. E. G. BACKER (Z. Elektrochem., 1933, 39, 554—555).—The electrical conductivity of glass may be used to measure the strain of heat-treatment.

H. J. E.

Electrical conduction in zeolites. E. RABINOWITSCH and W. C. WOOD (Z. Elektrochem., 1933, 39, 562—566).—Natural zeolites had sp. resistances between approx. 0.1 and 100 ( $\times 10^8$ ) ohms. The val. for chabasite (I) increased with progressive dehydration. Treatment of the partly dehydrated material with NH<sub>3</sub> lowered the resistance. In the electrolysis of (I), H<sub>2</sub> is liberated according to Faraday's law. The resistance of (I) falls rapidly on raising the temp. The mechanism of electrolysis is discussed.

H. J. E.

Electrical conductivity of Cu<sub>3</sub>Pd and Cu<sub>3</sub>Pt alloys at low temperatures with disordered and ordered atomic distributions. H. J. SEEMAN (Z. Physik, 1933, 84, 557—564).—Unlike Cu<sub>3</sub>Au, Cu<sub>3</sub>Pd and Cu<sub>3</sub>Pt show only small increases in the resistance drop due to a fall in temp. when ordered replaces disordered at. distributions. X-Rays reveal no differences in these alloys, but magnetic measurements suggest that the difference between the Au and Pd or Pt alloys is due to a difference in behaviour of the valency electrons.

A. B. D. C.

Electrical conductivity of cuprous oxide. V. ZHUSE and B. KURCHATOV (J. Exp. Theor. Phys.,

Russia, 1932, 2, No. 5—6, 309—318).—The electrical conductivity of Cu<sub>2</sub>O increases with the O content; that of pure Cu<sub>2</sub>O at 12° is  $2.7 \times 10$  mho per cm. The computed work of dissociation of the electron is 0.72 volt. The work of dissociation in well-conducting samples is 0.134—0.129 volt.

CH. ABS.

Electrical and optical behaviour of semi-conductors. IX. Mechanism and origin of the "dark" current and the electrical conductivity of cuprous oxide. E. ENGELHARD (Ann. Physik, 1933, [v], 17, 501—542).—The influence of heat-treatment in O<sub>2</sub> and in vac. on the electrical conductivity and the Hall const. of Cu<sub>2</sub>O has been investigated between —70° and room temp.

W. R. A.

Transitions in solidified gases. K. CLUSIUS (Z. Elektrochem., 1933, 39, 598—601; cf. A., 1930, 1103).—Theoretical. In gases with high dipole moment (*e.g.*, HF, H<sub>2</sub>O, NH<sub>3</sub>) free rotation in the solid state is hindered, and transition points are not observed. With lower dipole moments (HCl, HBr, HI, H<sub>2</sub>S, PH<sub>3</sub>), and when the dispersion effect is more marked, transition points occur.

H. J. E.

Dielectric constant of Volkenroda. H. LÖWY (Physikal. Z., 1933, 34, 674—676).—The dielectric const. of minerals in the Volkenroda potash mines is < normal. This supports the view that such decrease in dielectric const. is due to the presence of mineral oil.

A. J. M.

Calculation of dielectric constant of a salt from a single determination with a salt mixture. D. A. G. BRUGGEMAN (Naturwiss., 1933, 21, 577—578).—A formula derived for the dielectric const. of a pure salt from that of an isotropic mixture is tested with Pb(NO<sub>3</sub>)<sub>2</sub>. This can exist in octa- or tetrahedral crystals, and otherwise fulfils the conditions, satisfactory agreement being obtained.

A. J. M.

Variation of the dielectric constants of bromine and iodine chloride vapours with temperature and pressure. K. F. LUFT (Z. Physik, 1933, 84, 767—782).—Br has zero moment, ICl  $0.5 \times 10^{-18}$  e.s.u.

A. B. D. C.

Dipole moment and association. G. BERGER (Z. physikal. Chem., 1933, B, 22, 283—297).—B.-p. elevation measurements with C<sub>6</sub>H<sub>6</sub> solutions of various aromatic compounds have shown that there is no general parallelism between dipole moment and association. Probably the latter is determined by group moments of substituents, as well as by the total moment. With position isomerides of disubstituted C<sub>6</sub>H<sub>6</sub> derivatives and with various monosubstituted compounds the association is approx. proportional to the dipole moment. In some instances the latent dipoles of the C<sub>6</sub>H<sub>6</sub> and C<sub>10</sub>H<sub>8</sub> nuclei probably contribute to association. The association of phenols, anilines, alcohols, and acids is abnormally high, which is attributed to the moment of the polar group increasing with concn.

R. C.

Dielectric constants and water of crystallisation of alums. [J.] ERRERA and H. BRASSEUR (Compt. rend., 1933, 197, 480—482; cf. this vol., 663).—The dielectric const.,  $\epsilon$ , of the Al alums of

Cs, Rb, NH<sub>4</sub>, K, and Tl<sup>I</sup>, and the NH<sub>4</sub> alums of Cr and Fe (respectively 5.2, 5.7, 6.0, 6.6, 7.1, 7.0, and 7.9) increases approx. with decreasing at. vol. of the metal and m.p. of the alum. Only NH<sub>4</sub> Fe alum shows dispersion of  $\epsilon$  at room temp.;  $\epsilon$  increases slightly with temp. between 20° and the m.p., more so for greater wave-lengths. It is thus smaller the more strongly the H<sub>2</sub>O is bound, and its relation to at. vol. suggests that the metal atoms are in the neutral rather than the ionic state. C. A. S.

**Association of some salicylic esters and deformation of their molecules deduced from their dipole moments.** C. HRYNAKOWSKI and C. KALINOWSKI (Compt. rend., 1933, 197, 483—484).—The dipole moments of Ph, Et, and Me salicylate are respectively 3.15, 2.88, and  $2.41 \times 10^{-18}$  e.s.u.; the association (at 40.2°) is respectively 71.56, 62.37, and 51.70% (55.86 at 13.2°). The unusually large difference between the moments of the Et and Me esters is due to the greater length of the former mol. and its deformation due to the OH group in the *o*-position. C. A. S.

**Measurements of dielectric losses in castor oil.** J. L. SNOEK (Physica, 1932, 12, 234—238; Chem. Zentr., 1932, ii, 3841).—Dielectric losses in relation to frequency and viscosity have been determined from 20° to 90°. The results agree with Debye's theory. The dielectric const. of castor oil Me ester is only slightly > that of the oil itself, and the losses are smaller owing to the smaller viscosity. L. S. T.

**Refractive index. III.** A. M. TAYLOR and (Miss) D. A. DURFEE (J. Opt. Soc. Amer., 1933, 23, 263—269; cf. this vol., 765).—The distance of penetration of light into the second medium at total reflexion was measured interferometrically, and the intensity of the superficial wave relative to the state of polarisation was obtained. Discrepancies in the laws of reflexion, as found with saturated aq. KMnO<sub>4</sub>, are explained in terms of adsorbed surface layers. N. M. B.

**Abbé's number and the constitution of liquid organic compounds.** W. BIELENBERG (Physikal. Z., 1933, 34, 632).—Abbé's no.,  $v = (n_D - 1)/(n_F - n_C)$  for dispersion, is a constitutive property. Rules for its use in the case of hydrocarbons are given. The no. can be derived from Drude's formula involving the characteristic frequencies of atoms and groups. A. J. M.

**Dispersion measurements for potassium bromide and iodide in the infra-red.** K. KORTH (Z. Physik, 1933, 84, 677—685).—Refractive indices for KI are given between 14 and 21  $\mu$ , and for KBr between 14 and 20  $\mu$ . The method of prep. of these crystals artificially is given. A. B. D. C.

**Rotatory dispersion of organic compounds. XXII. Borotartrates and bromomalates.** B. JONES (J.C.S., 1933, 951—955).—The prep. of NH<sub>4</sub>, K Et, and K Me borotartrates, and K boromalate (I) is described. The rotatory dispersion of solutions of each compound has been measured for 20 different wave-lengths, ranging from  $\lambda$  6708 to 3590. Crystallographic data are given for (I). E. S. H.

**Magnetic rotatory power of gases and vapours.** P. GABIANO (Ann. Physique, 1933, [x], 20, 68—131).—Using a special magneto-polarimeter, data are obtained for 24 gases and vapours, and are compared for the gaseous and liquid states. Verdet consts. and sp. at. rotations are calc. N. M. B.

**Kerr effect with isomeric benzene derivatives.** G. OTTERBEIN (Physikal. Z., 1933, 34, 645—646; cf. A., 1931, 669).—It is possible to calculate the Kerr const. of substitution products of C<sub>6</sub>H<sub>6</sub> knowing the increments due to the substituting groups. PhCl and the three C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> are taken as examples. A. J. M.

**Two different states of liquid carbon disulphide.** M. WOLFFKE and J. MAZUR (Acta phys. Polonica, 1932, 1, 63—69; Chem. Zentr., 1932, ii, 3828). L. S. T.

**Structure of amines of platinous chloride.** F. W. PINKARD, H. SAENGER, and W. WARDLAW (J.C.S., 1933, 1056—1060).—The prep. of the following compounds is described:  $\alpha$ -chloroamminodipyridino- and  $\alpha$ -chlorodiamminopyridino-platinous chloride,  $\beta$ -chloroamminodipyridinoplalinous chloroplatinite,  $\alpha$ -hydroxylamino-amminodipyridinoplalinous chloride and -tripyridinoplalinous chloroplatinite,  $\alpha$ -dihydroxylamino-dipyridinoplalinous chloride, and -amminopyridinoplalinous chloride. A study of the decomp. of these compounds by HCl and of the action of C<sub>2</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> on  $\alpha$ -platinous diammines suggests that the  $\alpha$ -diammines have a *trans*-planar configuration, and that amine groups in *trans* positions are always eliminated by HCl from the tetrammines. It is suggested that the theoretical basis for Werner's hypothesis of *trans* elimination may be *trans* pairing when Pt has a covalency of 4. E. S. H.

**Stereochemistry of crystal compounds. XI. Structural formulæ of crystal compounds, especially of silicates.** P. NIGGLI (Z. Krist., 1933, 86, 121—144).—Various methods of formulating silicates are discussed, with special reference to possible replacements of an element by one of another valency. Constitutional formulæ are suggested to show linkings between atoms. Graphical formulæ are proposed, somewhat similar to those of Rheinhold (cf. A., 1931, 1217), to indicate co-ordination nos. and the X-ray structure of the unit cell. C. A. S.

**Stereochemistry of crystal compounds. X. Molecular and crystalline configuration.** P. NIGGLI and W. NOWACKI (Z. Krist., 1933, 86, 65—99).—A discussion on the connexion between the possibilities of formation of a mol. and of a crystal lattice by the resultant mols., with special reference to the combining and co-ordination nos. of the constituent atoms. C. A. S.

**General formula for lattice energy of crystals of any structure.** A. KAPUSTINSKI (Z. physikal. Chem., 1933, B, 22, 257—260).—The equation  $U = 256 \cdot 1 \Sigma n \eta_1 \eta_2 / (r_K + r_A)$  has been deduced for the energy,  $U$ , of any heteropolar lattice, where  $\Sigma n$  is the no. of ions in the mol., and  $r$  and  $\eta$  are the effective ionic radii and valencies. R. C.

**Crystal lattice energies and the Born-Haber cycle.** A. KAPUSTINSKI and B. VESELOVSKI (Z.

physikal. Chem., 1933, B, 22, 261—266).—The energies calc. by Kapustinski's formula (cf. preceding abstract) agree with the vals. derived from experimental data by the cycle process as well as do those calc. by Born's formula. R. C.

**Diamagnetism of thin films of bismuth.** A. GOETZ (Nature, 1933, 132, 206—207).—An explanation of the discrepancy between the results of Lane (this vol., 114) and those of other workers is advanced. L. S. T.

**Diamagnetism of thin films of bismuth.** S. R. RAO (Nature, 1933, 132, 207; cf. preceding abstract).—A criticism (cf. this vol., 114). L. S. T.

**Variation with temperature of the diamagnetic constant of water.** B. CABRERA and H. FAHLENBRACH (Anal. Fis. Quím., 1933, 31, 401—411).—The susceptibilities of H<sub>2</sub>O and ice, respectively, at 0° are  $-7.177 \times 10^{-4}$  and  $-7.019 \times 10^{-7}$ . For both the susceptibility varies linearly with temp. (between 0° and 100°, and 0° and  $-60^\circ$ , respectively). The results are discussed in relation to the association of H<sub>2</sub>O. H. F. G.

**Diamagnetism and temperature.** B. CABRERA and H. FAHLENBRACH (Compt. rend., 1933, 197, 379—381).—The deviations from the law of additivity of mol. susceptibility are due to structural deformations in the outer portions of the atoms.  $\chi$  is approx. independent of temp. in the solid and in the liquid state, but shows a sudden change on fusion, due to deformations caused by the cryst. forces. C. A. S.

**Magnetic investigation of single electron linkings in compounds of the type tellurium dimethyl dihalide.** S. S. BHATNAGAR and T. K. LAHIRI (Z. Physik, 1933, 84, 671—675).—Investigation of the susceptibility of TeMe<sub>2</sub>X<sub>2</sub> (X=Cl, Br, I, or NO<sub>3</sub>) indicates that the single electron linking assumed by Lowry and Gilbert (A., 1929, 127) is not established. A. B. D. C.

**Paramagnetism of salts.** C. J. GORTER (Physica, 1931, 11, 171—181; Chem. Zentr., 1933, i, 1256).—A discussion. A. A. E.

**Paramagnetism and the molecular field of neodymium.** P. W. SELWOOD (J. Amer. Chem. Soc., 1933, 55, 3161—3177; cf. A., 1931, 788).—Magnetic susceptibility data in the range  $-190^\circ$  to  $100^\circ$  are recorded for NdF<sub>3</sub>, Nd(NO<sub>3</sub>)<sub>3</sub>, Nd(ClO<sub>4</sub>)<sub>3</sub>, Nd<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Nd<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.8H<sub>2</sub>O, 0.5—41 wt.-% Nd(NO<sub>3</sub>)<sub>3</sub> in 90% EtOH, H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, Pyrex glass, Nd<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, and mixtures of 2—50 wt.-% of Nd<sub>2</sub>O<sub>3</sub> with La<sub>2</sub>O<sub>3</sub>. Although the results are in general accord with Van Vleck's quantum mechanical theory of paramagnetism, important discrepancies exist. The prep. of anhyd. Nd(ClO<sub>4</sub>)<sub>3</sub> is described. J. G. A. G.

**Susceptibilities of paramagnetic solutions.** E. VOGT (Physikal. Z., 1933, 34, 687—688).—Criticisms of the papers by Gorter (this vol., 664) and Fahlenbrach (this vol., 340). A. J. M.

**Molecular volumes of ammonium phosphates.** W. BILTZ and L. LE BOUCHER (Anal. Fis. Quím., 1933, 31, 427—433).—Anhyd. (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub> is prepared by treating dehydrated (over H<sub>2</sub>SO<sub>4</sub>) (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> with liquid NH<sub>3</sub> under pressure for several days;

it has  $d^{78}$  1.480. If (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>.3H<sub>2</sub>O is used the ratio NH<sub>4</sub>:PO<sub>4</sub> in the product is  $> 2.6$ . The densities of (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>H<sub>2</sub>PO<sub>4</sub>, NH<sub>4</sub>PO<sub>3</sub>, and (NH<sub>4</sub>)<sub>4</sub>P<sub>2</sub>O<sub>7</sub> at temp. down to  $-195^\circ$  are recorded. The calc. zero vols. of the anions are normal, but  $<$  those for the free acids; for HPO<sub>4</sub>' and H<sub>2</sub>PO<sub>4</sub>' the zero vols. lie between those of PO<sub>4</sub>' and H<sub>3</sub>PO<sub>4</sub>. H. F. G.

**Determination of the parachor by the drop-weight method.** I. G. SEMERANO. II. G. SEMERANO and G. FABBRANI (Atti Accad. Veneto-Trentino-Istria, 1932, 23, 17—32, 33—44; Chem. Zentr., 1933, i, 1915).—I. A discussion.

II. Vals. have been determined for methylsuccinimide in C<sub>5</sub>H<sub>5</sub>N and PhNO<sub>2</sub>, and for succinimide and pyruvimide in C<sub>5</sub>H<sub>5</sub>N and H<sub>2</sub>O. The linear relation describing the contribution of the solvent and solute to the parachor of a solution is strictly valid only when the components have the same surface tension. A. A. E.

**Liquid drops on the surface of the same liquid.** L. D. MAHAJAN (Z. Physik, 1933, 84, 676; cf. this vol., 223).—Further observations show that between the drop and the surface there exists a layer of air or equiv. surrounding medium. A. B. D. C.

**Surface tension of molten metals and alloys.** IV. Alteration with time of the surface tensions and the drop method of measurement at high temperatures. F. SAUERWALD and B. SCHMIDT (Z. anorg. Chem., 1933, 213, 310—318).—The surface tension of Hg in high vac. lies between the initial and end vals. in air. The val. for Sn is independent of the time under a pressure of  $5 \times 10^{-5}$  mm., whereas that for Tl increases with time at  $10^{-5}$  to  $10^{-4}$  mm. A. R. P.

**Capillary ascent or depression of liquids in cylindrical tubes.** A. W. PORTER (Trans. Faraday Soc., 1933, 29, 702—707).—Tables for the capillary correction  $h_0$  are given supplementing those of Cawood and Patterson (this vol., 367). J. S. A.

**Dependence of focussing effect obtained with curved crystals in X-ray spectroscopes on the bending mechanism of the crystal.** E. CARLSON (Z. Physik, 1933, 84, 801—810). A. B. D. C.

**Non-crystallographic point-groups.** W. NOWACKI (Z. Krist., 1933, 86, 19—31). C. A. S.

**Crystal lattice and spontaneous striction.** A. PERRIER (Helv. phys. Acta, 1932, 5, 306—310; Chem. Zentr., 1933, i, 742).—The extent to which a lattice-like arrangement of magnetic dipoles brings about a spontaneous striction is discussed. L. S. T.

**Scattering of X-rays from powdered crystals at low temperatures.** G. E. M. JAUNCEY and F. PENNELL (Physical Rev., 1933, [ii], 44, 138—140).—Indication of a slight change (cf. this vol., 115, 558) in the true atom form factor was found by scattering at  $295^\circ$  and  $103^\circ$  abs. for KCl, but not for NaF. N. M. B.

**Diffuse scattering of X-rays from sylvine.** IV. Scattering at high temperatures. G. G. HARVEY (Physical Rev., 1933, [ii], 44, 133—137; cf. this vol., 666).—Intensity measurements at  $630^\circ$  and

1020° abs. are in good agreement with the general expression previously found. N. M. B.

**Vicinal faces and the work of Parker.** G. KALB (Z. Krist., 1933, 86, 1—7; cf. A., 1932, 682).

C. A. S.

**Effect of temperature and use of monochromatic radiation in the scattering of X-rays in carbon tetrachloride vapour.** W. VAN DER GRINTEN (Physikal. Z., 1933, 34, 609—618).—Apparatus for the investigation of scattering of X-rays by gases at high temp. is described, and is applied in the determination of the scattering curves of CCl<sub>4</sub> vapour at 100° and 350°. The effect of at. oscillations on X-ray interference in gases and crystals is compared. The use of monochromatic radiation gives for CCl<sub>4</sub> satisfactory agreement with theory.

A. J. M.

**Liquid metal single crystals.** I. E. DONAT and O. STIERSTADT (Ann. Physik, 1933, [v], 17, 897—914).—An improved method of preparing single Bi crystals is described. When such a crystal is heated to  $\approx 10^\circ$  above its m.p. it shows the same orientation after re-solidifying, suggesting that the melt itself is cryst. No asymmetry is observed in the conductivity of the melt, but this has no significance, as the passage of current disturbs the orientation of the melt. A method for expressing the anisotropy of any physical property of crystals is developed.

J. W. S.

**X-Ray examination of electrolytic chromium deposits.** G. R. LEVI and M. TABELT (Atti R. Accad. Lincei, 1933, [vi], 17, 647—653).—From X-ray measurements data are obtained regarding the size of the particles in Cr deposits prepared by the electrolysis of solutions of Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, CrO<sub>3</sub>, and NH<sub>4</sub> chromioxalate, respectively, and also of Cr obtained by thermal reduction.

O. J. W.

**Amorphous-crystalline transformation of arsenic and of antimony.** G. R. LEVI and D. GHIRON (Atti R. Accad. Lincei, 1933, [vi], 17, 565—569).—X-Ray measurements show that the change of amorphous As to the cryst. form is accelerated by various catalysts, particularly by conc. HI. There is no definite transition point, and the change may occur as low as 180°. Amorphous Sb can be obtained in presence of SbCl<sub>3</sub>. Reduction of Sb compounds in the absence of SbCl<sub>3</sub> gives cryst. Sb. The change of amorphous to cryst. Sb may take a few min. to several hr. in the temp. range 250—100° and does not require a catalyst. No amorphous preps. of Bi could be obtained.

O. J. W.

**Crystal structure of LaSn<sub>3</sub> and LaPb<sub>3</sub>.** A. ROSSI (Atti R. Accad. Lincei, 1933, [vi], 17, 839—846).—The following data are obtained by the powder method: LaSn<sub>3</sub>,  $a$  4.77 Å.,  $d$  7.15—7.20,  $d_{\text{calc.}}$  7.516; LaPb<sub>3</sub>,  $a$  4.893,  $d$  10.50,  $d_{\text{calc.}}$  10.71.

O. J. W.

**X-Ray proof of [existence of] ZrW<sub>2</sub>.** A. CLAASSEN and W. G. BURGERS (Z. Krist., 1933, 86, 100—105).—X-Ray examination of a W wire on which, when incandescent, Zr had been deposited from its vapour showed the presence of a face-centred cubic compound, ZrW<sub>2</sub>, with  $a$  7.61 Å., 8 mols. in unit cell, Zr—W=3.15 Å.,  $d_{\text{calc.}}$  13.78. The structure resembles

that of MgCu<sub>2</sub> (cf. A., 1928, 109). ZrW<sub>2</sub> was prepared by volatilising Zr on to W and heating for 20 hr. at 1800°; it contained a slight excess of Zr, and had  $d$  12—13.5, m.p.  $> 2200^\circ$ . C. A. S.

**Constitution of anodically deposited Ta<sub>2</sub>O<sub>5</sub> layers.** P. O. SCHUPP (Z. Physik, 1933, 84, 412—424).—Study of the formation of Ta in non-aq. solutions indicates that the high potential across the Ta<sub>2</sub>O<sub>5</sub> layer is due to work required to remove electrons from the layer to the electrolyte, and not to electrical resistance of the layer (cf. Günther-Schulze and Betz, A., 1932, 214); during formation the layer is first porous and finally non-porous.

A. B. D. C.

**Crystal structure of rhombic chromium carbide.** K. HELLBOM and A. WESTGREN (Svensk Kem. Tidskr., 1933, 45, 141—150; cf. A., 1927, 279).—Rotation and powder diagrams of Cr<sub>3</sub>C<sub>2</sub> were obtained. The space-group is  $V_1^h$ . The crystal probably consists of parallel long-chain mols.

R. P. B.

**Crystal structure of nitrides and phosphides of bivalent metals.** M. VON STACKELBERG and R. PAULUS (Z. physikal. Chem., 1933, B, 22, 305—322).—Crystals of Mg<sub>3</sub>P<sub>2</sub> have a cubic structure with 16 mols. in the unit cell and the space-group  $T_1^h$ . The P atoms form a somewhat deformed closest-packed cubic lattice, and the Mg atoms occupy three quarters of the tetrahedral interstices. Be<sub>3</sub>P<sub>2</sub>, Be<sub>3</sub>N<sub>2</sub>, Mg<sub>3</sub>N<sub>2</sub>, and  $\alpha$ -Ca<sub>3</sub>N<sub>2</sub> have the same structure. The lattices of a second form of Ca<sub>3</sub>N<sub>2</sub>, Sr and Ba nitrides, and Ca, Sr, and Ba phosphides are not cubic. Zn<sub>3</sub>P<sub>2</sub>, Cd<sub>3</sub>P<sub>2</sub>, and Zn<sub>3</sub>As<sub>2</sub> crystallise in the cubic system, but not with the Mg<sub>3</sub>P<sub>2</sub> lattice, and have 16 mols. in the unit cell; they are metallic in character.

R. C.

**Crystal structure of zinc hydroxide.** R. B. COREY and R. W. G. WYCKOFF (Z. Krist., 1933, 86, 8—18; cf. A., 1928, 350; 1932, 214).—Zn(OH)<sub>2</sub> cryst. from aq. NH<sub>3</sub> (cf. A., 1927, 731) is orthorhombic with  $a$  5.16,  $b$  8.53,  $c$  4.92 Å., and 4 mols. in the unit cell, space-group  $V^4$ . Each Zn is surrounded by 4 OH forming a distorted tetrahedron in which Zn—O=1.95 Å., and OH—OH is  $> 3$  Å.; in adjacent tetrahedra OH—OH=2.83 Å.

C. A. S.

**Structure and polymorphism of the hydrogen halides.** G. NATTA (Gazzetta, 1933, 63, 425—439).—The existence of a face-centred cubic form of solid HBr is confirmed, with 4 mols. per unit cell,  $a$  5.76—5.78 Å.,  $v$  191—193  $\times 10^{-24}$  c.c.,  $d_{\text{calc.}}$  2.76—2.80. The form of HBr stable below 100° abs. is face-centred rhombic, with 4 mols. per unit cell,  $a$  5.555,  $b$  5.64,  $c$  6.063  $\pm$  0.01 Å.,  $v$  190  $\times 10^{-24}$  c.c.,  $d_{\text{calc.}}$  2.81, space-group  $V^7$  or  $V_2^h$ . The cubic form of HCl, stable above 98° abs., has  $a$  5.46 Å.,  $v$  162.8  $\times 10^{-24}$  c.c.,  $d_{\text{calc.}}$  1.48. The face-centred rhombic form of HCl, stable below 98° abs., has 4 mols. per unit cell,  $a$  5.03,  $b$  5.35,  $c$  5.71  $\pm$  0.02 Å.,  $v$  154.7  $\times 10^{-24}$  c.c.,  $d_{\text{calc.}}$  1.55, space-group  $V^7$  or  $V_2^h$ .

O. J. W.

**Crystal structure of anhydrous magnesium and calcium iodides.** H. BLUM (Z. physikal. Chem., 1933, B, 22, 298—304).—These compounds are isomorphous with CdI<sub>2</sub> (type C6). MgI<sub>2</sub> has  $a_0$  4.14  $\pm$  0.02,  $c_0$  6.88  $\pm$  0.03 Å., and CaI<sub>2</sub> has  $a_0$  4.48  $\pm$  0.02,  $c_0$  6.96  $\pm$  0.03 Å.

R. C.

**Crystal structure of cadmium iodide.** O. HASSEL (Z. physikal. Chem., 1933, B, 22, 333—334).—A modification of Bozorth's structure (A., 1922, ii, 851) is proposed. R. C.

**Structure and polymorphism of silver cyanide.** G. NATTA and O. VECCHIA (Gazzetta, 1933, 63, 439—448).—The stable form of AgCN is rhombohedral, with 2 mols. per unit cell,  $a$   $5.99 \pm 0.01$  Å.,  $c/a$  0.877, mol. vol. 46.8,  $d_{\text{calc.}}$  4.72, space-group  $C_{3v}^2$ . The cubic form, observed only as a solid solution in AgBr, has 4 mols. per unit cell,  $a$   $5.69 \pm 0.03$  Å., mol. vol. 46.0,  $d_{\text{calc.}}$  4.80, space-group  $T'$  or  $Td'$ . The physical properties of AgCN and of the Ag halides, especially the solubility, are related to the apparent contraction of the anion due to the polarising action of the cation. O. J. W.

**Crystal structure of boron phosphate and boron arsenate.** G. E. R. SCHULZE (Naturwiss., 1933, 21, 562).—The crystal structures of  $BPO_4$  and  $BAsO_4$  are similar, being of the  $SiO_2$  type, with O arranged tetrahedrally around P, As, and B, each O atom belonging to two tetrahedra. The space-group is  $S_6^2$ . The unitary cells contain 2 mols. and have respectively  $a$   $4.334 \pm 0.008$ ,  $4.459 \pm 0.006$ ;  $c$   $6.636 \pm 0.008$ ,  $6.796 \pm 0.006$  Å.;  $c/a$  1.534, 1.524. A. J. M.

**Crystal structure of carbonatotetramminocobaltic sulphate.** L. W. SROCK (Z. Krist., 1933, 86, 42—52).— $[Co(NH_3)_4CO_3]SO_4 \cdot 3H_2O$ , prepared according to Jørgensen's method (cf. A., 1898, ii, 592), is monoclinic,  $a : b : c = 1.1132 : 1 : 0.7030$ ,  $\beta$   $98^\circ 39'$ ,  $d^{22}$  1.8816 (Jaeger's orthorhombic substance,  $d$  1.807, appears to have been another substance, or at least another modification),  $n_a$  1.5973,  $n_\beta$  1.6210,  $n_\gamma = n_a$  0.248, for  $\lambda$  6702 Å. X-Ray examination: unit cell with  $a$  11.80,  $b$  10.60,  $c$  7.42 Å.,  $\beta$   $98^\circ 39'$ , containing 2 mols., space-group  $C_2$ . C. A. S.

**Crystal structure of hydrohalides of *d*-ephedrine and *l*-ephedrine.** B. GOSSNER and H. NEFF (Z. Krist., 1933, 86, 32—41; cf. this vol., 892).—The following data are given for  $d$ ,  $a$ ,  $b$ ,  $c$  (in Å.),  $\beta$  (if not  $90^\circ$ ), no. of mols. in unit cell, and space-group: *d*-ephedrine hydrochloride, 1.198, 25.49, 6.48, 6.91, 4,  $V^4$ ; hydrobromide 1.410, 24.68, 6.93, 6.78, 4,  $V^4$ ; hydriodide, 1.581, 11.39, 6.83, 15.62, 4,  $V^4$ ; all three are rhombic disphenoidal; *l*-ephedrine hydrochloride 1.208, 12.64, 6.15, 7.34,  $102^\circ 6'$ , 2,  $C_2^2$ ; hydrobromide 1.399, 12.74, 6.20, 7.62,  $100^\circ 48'$ , 2,  $C_2^2$ , both are monoclinic sphenoidal; hydriodide 1.607, 25.66, 7.33, 19.14, 12,  $V^3$ , rhombic disphenoidal. The relationships with the corresponding *r*-compounds are discussed. C. A. S.

**Structure of edingtonite.** W. H. TAYLOR and R. JACKSON (Z. Krist., 1933, 86, 53—64).—Edingtonite,  $BaAl_2Si_3O_{15} \cdot 4H_2O$ , although apparently tetragonal, is probably orthorhombic; its unit cell has (approx.)  $a$  9.7,  $c$  6.6 Å., and contains 2 mols. The framework is identical with that of natrolite (cf. this vol., 451), the  $Ba^{++}$  ions and  $H_2O$  mols. being situated in the channels between the strings of  $(AlO_4)$  and  $(SiO_4)$  tetrahedra. C. A. S.

**New type of transformation in alkali salts of higher fatty acids.** P. A. THIESSEN and E. EHRLICH

(Z. physikal. Chem., 1933, 165, 453—463; cf. this vol., 116).—Near the m.p. of the free acid the vol.-temp. curve of Na palmitate and stearate changes in slope and there is a halt on the cooling curve. X-Ray fibre diagrams show that two kinds of change occur, one beginning near the m.p. of the fatty acid, and that these salts exist in two stable forms which have different temp. limits, are able to co-exist over a wide temp. interval, and are present in approx. equal amounts at the m.p. of the corresponding fatty acid. The suggested explanation is that the chains rotate about their long axis at comparatively low temp., and this rotation, which initiates a transformation, is followed by a directed oscillation of the chains, which sets in near the m.p. of the acid. R. C.

**Crystal structure of a new type of molecular compound.** E. HERTEL and G. H. RÖMER (Z. physikal. Chem., 1933, B, 22, 280—282).—The compound of 2 : 4 : 6- $C_6H_2Cl(NO_2)_3$  (I) with 2 : 4 : 6- $C_6H_2Me(NO_2)_3$  (II) has a pseudorhombic lattice with  $I_a$  40.5,  $I_b$  6.19,  $I_c$  15.2 Å. and space-group  $C_{3h}^2$ . The lattice is equiv. to that of (II) with every second mol. replaced by a mol. of (I). R. C.

**Fine structure of trinitrobenzene derivatives.** E. HERTEL and G. H. RÖMER (Z. physikal. Chem., 1933, B, 22, 267—279).—The X-ray analysis of the crystal structure of various monosubstituted derivatives is reported. R. C.

**Crystallography of the hydrates of phenylmethylethyl and phenylmethylpropyl betaine.** (MME.) GUAISNET-PILAUD (Compt. rend., 1933, 197, 419—420).—Mono- and di-hydrated phenylmethyl-ethyl betaine (cf. this vol., 387) are doubtful and monoclinic, respectively, and both have  $n_a$  1.549,  $n_\beta$  1.585; the latter after melting at  $79.5^\circ$  resolidifies, remelts at  $100^\circ$ , and decomposes at  $145$ — $150^\circ$ . The mono- and di-hydrates of phenylmethyl-propyl betaine (cf. this vol., 948) are respectively probably orthorhombic and doubtful; both have  $n_a$  1.555 and  $n_\beta$  1.595. C. A. S.

**Crystal structure of fibrin.** J. R. KATZ and A. DE ROOY (Naturwiss., 1933, 21, 559).—Fibrin spun into threads shows cryst. structure when examined with X-rays. The identity period along the thread axis is 6.7 Å. There are two  $NH_2$ -acid residues in this direction in the elementary cell. The polypeptide cell is almost straight, with slight crumpling and twisting. Fibrin agrees almost completely with stretched keratin ( $\beta$ -keratin), although the two consist of different  $NH_2$ -acids. A. J. M.

**Contact potential differences between different faces of copper single crystals.** H. E. FARNSWORTH and B. A. ROSE (Proc. Nat. Acad. Sci., 1933, 19, 777—780).—A p.d. exists between the (111) and (100) faces of a Cu crystal, the (111) face being positive when the crystal is outgassed at high temp. The p.d. is increased by outgassing and has a max. val. of 0.463 volt. E. S. H.

**Absolute saturation of cubic cobalt.** R. I. ALLEN and F. W. CONSTANT (Physical Rev., 1933, [ii], 44, 228—233).—Magnetisation for given temp. but increasing field strengths was measured, and

calc. for infinite field. Extrapolation gave the saturation intensity. The important influence of crystal structure is indicated. N. M. B.

**Magnetic after-effects.** P. C. HERMANN (Z. Physik, 1933, 84, 565—570).—Magnetic after-effects investigated for soft Fe show a limit between eddy current and hysteresis effects. A. B. D. C.

**Properties of gelatin in an electric field.** (MLLE.) S. VEIL (J. Phys. Radium, 1933, [vii], 4, 362—367).—Under the influence of an electric field gelatin underwent a complex mechanical deformation and the conductivity decreased, the substance becoming approx. a dielectric; Ohm's law was obeyed only for weak fields. Deformations were observed by impregnation with coloured indicators. Changes of  $[H^+]$  in the zones of deformation were observed. Similar results were obtained for agar-agar. N. M. B.

**Crystal cohesion and crystal plasticity.** A. SMEKAL (Physikal. Z., 1933, 34, 633—639).—Experiments on the deformation of synthetic rock-salt are described. There can be no deformation by ideal slipping along crystallographic slip planes. The deformed crystal is converted into a conglomerate of crystallites. Self-diffusion of crystals is considered. A. J. M.

**Plasticity in single crystals.** W. G. BURGERS (Physikal. Z., 1933, 34, 623—624).—A criticism of Schlechtweg's theory (this vol., 667). A. J. M.

**Plasticity in single crystals.** H. SCHLECHTWEG (Physikal. Z., 1933, 34, 624).—A reply to Burgers (see above). A. J. M.

**Optical crystallography of acetaldehyde-2:4-dinitrophenylhydrazone.** W. M. D. BRYANT (J. Amer. Chem. Soc., 1933, 55, 3201—3207; cf. A., 1932, 1109).—The stable modification obtained by crystallisation yields, on cooling the melt, a metastable form which exhibits crossed axial-plane dispersion. Both modifications are pleochroic; refractive indices are recorded. J. G. A. G.

**Effect of water on the rigidity of rock-salt.** N. N. DAVIDENKOV and M. V. KLASSEN-NEKLUDOVA (J. Exp. Theor. Phys., Russia, 1932, 2, No. 5—6, 412—420).— $H_2O$  does not penetrate into the crystal. Solidity occasioned by surface dissolution disappears on drying. CH. ABS.

**Remanence of single iron crystals.** S. KAYA (Z. Physik, 1933, 705—716).—The remanence is inversely proportional to the sum of the direction cosines of the direction of the field with respect to the cubic edges. A. B. D. C.

**Fixed and variable electrical resistances of graphite.** J. GUZMÁN (Anal. Fis. Quím., 1933, 31, 169—171).—The variable resistance described resembles the liquid type; one of the conducting wires moves up or down in a uralite tube containing finely-divided graphite. For high max. resistance the graphite is mixed with  $SiO_2$ . Fixed resistances may be constructed in a similar manner. H. F. G.

**Self-consistent field for bound electrons; superconductivity.** L. BRILLOUIN (J. Phys. Radium, 1933, [vii], 4, 333—361).—Mathematical.

Hartree's self-consistent field is applied to bound electrons in various metal crystal lattice structures. The energy curves for the face-centred cubic lattice permit the formation of electron groupings metastable at very low temp., and having a permanent current; this indicates a possible explanation of superconductivity. N. M. B.

**Explanation of the discontinuity of superconductivity.** U. DEHLINGER (Naturwiss., 1933, 21, 607).—The reason for the sudden occurrence of superconductivity as temp. is lowered is considered from the point of view of lattices of alloys. A. J. M.

**Frequency dependence of superconductivity and ferromagnetism.** R. SÄNGER (Physical Rev., 1933, [ii], 44, 302—307).—Mathematical. An explanation of the frequency dependence as a further consequence of the skin effect, assuming the existence of a surface layer which shows neither superconductive nor ferromagnetic properties, is proposed. N. M. B.

**Effect of pressure on the electrical resistance of single metal crystals at low temperatures.** P. W. BRIDGMAN (Proc. Amer. Acad. Arts Sci., 1933, 68, 95—123).—Zn, Cd, Sn, Bi, Sb, As, and Te were examined. Vals. in different directions were determined. CH. ABS.

**Heat capacity curves of the simpler gases. III. Heat capacity, entropy, and free energy of neutral OH from near 0° abs. to 5000° abs.** H. L. JOHNSTON and D. H. DAWSON (J. Amer. Chem. Soc., 1933, 55, 2744—2753).—The heat capacity curve of OH in the ideal gas state is computed from spectroscopic data to have a sharp max. at 0.06° abs., and a broad max. at 90° abs. The vibrational component which starts at about 600° abs. attains equipartition val. at about 3500° abs., whilst the rotational component which enters at 16° abs. attains equipartition val. at room temp. At 5000° abs. the rotational stretching and the anharmonic character of the oscillations contribute 0.18 and 0.5 g.-cal., respectively, to the mol. heat. Vals. of the entropy and free energy are tabulated. Villars' calculations are criticised (A., 1930, 1121). J. G. A. G.

**Calculation of gas radiation at high temperatures.** S. UCHIDA (J. Soc. Chem. Ind. Japan, 1933, 36, 337—338B).—Vals. of the radiation from  $H_2O$  vapour at high temp. calc. by Schack's method agree with Schmidt's experimental data. A. G.

**Thermal conductivity of water at temperatures up to 270°.** E. SCHMIDT and W. SELL-SCHOPP (Forsch. Ingenieurwes., 1932, A, 3, 277—286; Chem. Zentr., 1933, i, 742).—The thermal conductivity-temp. curve is practically a symmetrical parabola, and not linear as hitherto assumed, above 75°. The thermal conductivity no. of Cu is 320 kg.-cal. per m. per hr. per degree. L. S. T.

**Vapour tension of BaO, SrO, and CaO and their mixtures deduced from measurements of the rates of evaporation.** E. PRESTON (J. Soc. Glass Tech., 1933, 17, 118—121T; cf. this vol., 344).—Vals. of the v.p., obtained from data on the rates of evaporation by means of the Herz-Knudsen equation, are:

BaO (at 1475° abs.)  $33 \times 10^{-6}$ ; SrO (1635°)  $4.0 \times 10^{-6}$ ; CaO (1728°)  $1.8 \times 10^{-6}$  mm. Hg. It is concluded that volatilisation losses of the oxides in glass-making would be negligible. A. L. R.

**Vapour pressure and b.p. of methylacetylene.** G. B. HEISIG and C. D. HURD (J. Amer. Chem. Soc., 1933, 55, 3485—3487).—The v.p. of pure CMe:CH are recorded from  $-79.5^\circ$  to  $-23.5^\circ$ .  $\log p_{\text{mm.}} = -1247.95/T + 7.877$ . The calc. b.p. is  $-23.1^\circ$ . R. S. C.

**V.p. of *n*-butyl chloride.** C. W. LENTH (J. Amer. Chem. Soc., 1933, 55, 3283).—The v.p. between  $12.5^\circ$  and  $77.5^\circ$  is given by  $2.303 \log P_{(\text{cm.})} = -8090/1.99T + 6.912$ , from which the latent heat of vaporisation is 8090 g.-cal. per mol. J. G. A. G.

**Preparation and purification of methyl borate and ethyl borate.** S. H. WEBSTER and L. M. DENNIS (J. Amer. Chem. Soc., 1933, 55, 3233—3235).—Modifications of existing methods are described. The v.p. of  $\text{Me}_3\text{BO}_3$ , m.p.  $-29.3^\circ$ , b.p.  $68.75^\circ/760$  mm., between  $-27^\circ$  and  $70^\circ$  is given by  $\log P = -1785.3/T + 8.1073$ . From the v.p. equation  $\log P = -2298.0/T + 8.8553$ , the calc. b.p. of  $\text{Et}_2\text{BO}_3$ , m.p.  $-84.8^\circ$ , is  $111.8^\circ$ ; decomp. occurs above  $65^\circ$ . J. G. A. G.

**Compressibilities and pressure coefficients of resistance of elements, compounds, and alloys, many of them anomalous.** P. W. BRIDGMAN (Proc. Amer. Acad. Arts Sci., 1933, 68, 27—93).—Vals. at  $> 12,000$  atm. at  $30^\circ$  and  $75^\circ$  were determined for Nb, Rh, Ru, Cr, As, Be,  $\text{MnCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Cu}_5\text{Cd}_8$ , Ag—Au, Co—Fe—W, gulonolactone, rhamnose, and sucrose. CH. ABS.

**Pressure-volume-temperature relations of fifteen liquids.** P. W. BRIDGMAN (Proc. Amer. Acad. Arts Sci., 1933, 68, 1—25).— $\text{N}(\text{OEt})_3$ , PrCl, PrBr, PrI, BuCl, BuBr, BuI,  $\text{C}_5\text{H}_{11}\text{Cl}$ ,  $\text{C}_5\text{H}_{11}\text{Br}$ ,  $\text{C}_5\text{H}_{11}\text{I}$ , octan- $\gamma$ -ol,  $\beta$ -methylheptan- $\gamma$ - and  $-\varepsilon$ -ol,  $\gamma$ -methylheptan- $\alpha$ - and  $-\delta$ -ol were examined.  $\text{C}_5\text{H}_{11}\text{Cl}(\text{Br}, \text{I})$  are about 0.8 as compressible as  $\text{C}_5\text{H}_{12}$ . The effect of a halogen in decreasing compressibility is about the same as that of an OH group. A  $\text{CH}_2$  group increases the molal vol. 15.36—17.09 at 1 atm. and 11.18—13.69 at 12,000 atm. The difference in vol. between Br and Cl is  $<$  that between I and Br. The difference between the vols. of the halides is much  $>$  that calc. from the space lattices of the solid elements. No significant differences in vols. or compressibilities of the five isomerides were observed. CH. ABS.

**Hydrogen sulphide.** T. BATUECAS (J. Chim. phys., 1933, 30, 482—486).—A criticism of recent work on the  $d$  of  $\text{H}_2\text{S}$  and at. wt. of S (cf. this vol., 16). E. S. H.

**Thermodynamical theory of liquids.** N. DE KOLOSSOWSKI (Compt. rend., 1933, 197, 517—519).—From the thermodynamic potential are deduced an equation of state for the liquid, Mendeléev's law of dilatation for a liquid, Tait's expression for compressibility, the entropy, Schiff's rule regarding the mol. heat of a liquid (cf. A., 1887, 6), and an expression for the mol. latent heat, which applied to  $\text{C}_6\text{H}_6$  gives vals. agreeing closely with experiment. C. A. S.

**Molecular specific heats of some liquids.** N. DE KOLOSSOWSKI (Compt. rend., 1933, 197, 519—520).—To test the relation between mol. heat, thermodynamic potential, and entropy (see preceding abstract) the following sp. heats have been determined at the abs. temp. noted: limonene  $0.4380$ ,  $293.4^\circ$ ; sabinene  $0.4431$ ,  $297.04^\circ$ ; linalool  $0.5777$ ,  $293.15^\circ$ ; pulegone  $0.4320$ ,  $293.38^\circ$ ;  $\text{CH}_2\text{Ph}\cdot\text{OAc}$   $0.3983$ ,  $292.71^\circ$ ; Me salicylate  $0.3910$ ,  $295.20^\circ$ ; and those of 12 other org. liquids were redetermined. C. A. S.

**Viscosity of fused salts and Andrade-Sheppard formula for the viscosity of liquids.** B. PRASAD (Phil. Mag., 1933, [vii], 16, 263—268).—The viscosities of fused  $\text{NaNO}_3$ ,  $\text{KNO}_3$ , and  $\text{PbBr}_2$  follow the simple formula  $\log \eta = \alpha + \beta/T$ , where  $\eta$  = viscosity,  $\alpha$  and  $\beta$  are consts., and  $T$  = abs. temp. For  $\text{PbCl}_2$  the formula is  $\log \eta = \alpha + \beta/(T + \theta)$  ( $\theta$  = const.), this being attributed to the gradual increase in the dissociation of  $\text{PbCl}_2$  with temp. Neither formula holds for the viscosity of fused  $\text{K}_2\text{Cr}_2\text{O}_7$  at low temp., probably owing to decomp. into  $\text{K}_2\text{CrO}_4$  and  $\text{CrO}_3$ . J. W. S.

**Densities of hydrocarbon mixtures.** E. W. THIELE and W. B. KAY (Ind. Eng. Chem., 1933, 25, 894—898).—Curves are given for obtaining the density of hydrocarbon oils in the liquid state at various temp. and pressures when  $d^{15.5}$  and the viscosity at  $37.7^\circ$  are known. D. K. M.

**Viscosity of solutions of camphor.** A. CASTIGLIONI (Gazzetta, 1933, 63, 395—399).—The viscosity of solutions in  $\text{C}_6\text{H}_6$ ,  $\text{CHCl}_3$ , EtOH, and  $\text{Et}_2\text{O}$  increases with the concn. With solutions in vaseline, olive and sesamé oils, and in oleic acid  $\eta$  decreases up to the saturation concn. O. J. W.

**Diffusion in the solid state in the metal pairs gold-nickel, gold-palladium, and gold-platinum.** A. JEDELE (Z. Elektrochem., 1933, 39, 691—695).—The diffusion velocity increases as the difference between the temp. of diffusion and the m.p. of the alloy diminishes. The diffusion velocity of Au in Pt is  $<$  that of Pt in Au; at  $900^\circ$  the diffusion coeff.  $D$  is  $0.1 \times 10^{-5}$  sq. cm. per day for the Pt-rich solid solution and  $0.5 \times 10^{-5}$  sq. cm. per day for the Au-rich solid solution. In the Au-Pd system the vals. of  $D$  are  $0.2 \times 10^{-5}$  and  $2.0 \times 10^{-5}$  sq. cm. per day, respectively, for the Pd-rich and Au-rich solid solutions. In the Au-Ni system  $D = 0.3 \times 10^{-5}$  and  $5 \times 10^{-5}$  sq. cm. per day for the Ni-rich and Au-rich solid solutions, respectively. E. S. H.

**Relation between diffusion coefficients and concentrations of solid metals. Nickel-copper system.** C. MATANO (Japan. J. Physics, 1933, 8, 109—113; cf. A., 1932, 1195).—Analysis of Grube and Jedele's results at  $1025^\circ$  shows that the coeff. of diffusion decreases from about  $8 \times 10^{-5}$  sq. cm. per day for 0% Ni to  $1 \times 10^{-5}$  for 30% Ni, thereafter remaining const. up to 100% Ni. J. W. S.

**X-Ray analysis of alloys of mercury with silver, gold, and tin.** S. STENBECK (Z. anorg. Chem., 1933, 214, 16—26).—The results of Murphy and Preston (A., 1931, 1244) for Ag—Hg amalgams are confirmed. The lattice dimensions increase with the Hg concn. For Au—Hg amalgams, up to 80% Hg, five solid phases have been observed. In the

hexagonal  $\beta$ -phase the axial ratio is const. between 19.3 and 33.0% Hg (cf. Pabst, A., 1929, 98). The system Sn-Hg forms a hexagonal lattice (8% Hg;  $b$  3.193,  $c$  2.980 Å.), and a rhombic lattice (>14% Hg;  $a$  5.548,  $b$  3.196,  $c$  2.981 Å.) (cf. Simson, A., 1924, ii, 449). H. J. E.

**X-Ray investigations of the constitution of alloys.** A. WESTGREN (Assoc. Int. Essai Mat., 1932, 1, 484—499; Chem. Zentr., 1933, i, 844).—The X-ray method appears to be more trustworthy than thermal analysis or microscopical investigation for the identification of solid phases. Homogeneous fields also can generally be determined. The difference between intermetallic compounds and solid solutions is discussed. The best classification is not on chemical grounds, but on the basis of crystal structure. L. S. T.

**X-Ray study of iron-silicon alloys containing 0—15% Si.** E. R. JETTE and E. S. GREINER (Amer. Inst. Min. Met. Eng., 1933, No. 8, 15 pp.).—The graph of lattice const. as a function of at.-% Si consists of two straight lines intersecting at 4.7% (8.95 at.-%) Si. Two hypotheses of structure are discussed. CH. ABS.

**System beryllium-copper.** H. TANIMURA and G. WASSERMANN (Z. Metallk., 1933, 25, 179—181).—X-Ray analysis of well-annealed Be-Cu alloys shows that the solubility of Be in Cu decreases from 2.1% at the peritectic temp. (864°) to 1.8% at 700°, 0.4% at 400°, and 0.16% at 250°. Pptn. of a constituent from supersaturated solid solutions annealed at 150° can be detected. A. R. P.

**Electrical conductivity measurements of zinc-cadmium and lead-antimony systems, with reference to the establishment of stable equilibrium.** M. LE BLANC and H. SCHÖPEL (Z. Elektrochem., 1933, 39, 695—701).—In the system Zn-Cd the establishment of stable equilibrium is slow when the alloy contains < 10% of either constituent; in the system Pb-Sb a retardation is observed over the whole range. Temp.-resistance curves show that at 263° the solubility limits of the system Zn-Cd lie at 6 and 97.5 at.-% Zn, whilst in the system Pb-Sb the limits are 1.5 and 94.2 at.-% Pb at 249°. The results are confirmed by micrographic examination. E. S. H.

**Solubility of the compound MgZn<sub>2</sub> in aluminium in the solid state at different temperatures.** P. SALDAU and M. ZAMOTORIN (Z. anorg. Chem., 1933, 213, 377—382).—Between 15° and 300° the solubility increases from 1.58% to 3.57% MgZn<sub>2</sub>. The val. then increases rapidly to 30.0% MgZn<sub>2</sub> at the eutectic temp. (475°). H. J. E.

**Solubility curves of copper in solid aluminium.** P. J. SALDAU and N. G. ANISIMOV (Ann. Inst. Anal. Phys. Chem., 1933, 6, 69—79).—The solubility of Cu in solid Al is 2.7% from 15° to 300°, 3.12% at 400°, 5.55% at 500°, and 6.5% at the eutectic temp. (543°). The hardness of chilled alloys becomes > that of slowly cooled alloys when the Cu content exceeds 2.7%, and shows a max. at 6% Cu. R. T.

**Solubility of silicon in solid aluminium at various temperatures.** P. J. SALDAU and M. V.

DANILOVITSCH (Ann. Inst. Anal. Phys. Chem., 1933, 6, 81—89).—The solubility of Si in solid Al is 0.09% from 15° to 300°, 0.3% at 400°, 0.65% at 560°, and 1.32% at the eutectic temp. (570°). R. T.

**Densities of iron-nitrogen alloys.** A. SIEVERTS and H. HAGEN (Z. Elektrochem., 1933, 39, 735—736).—The val.  $d$  6.88 found for Fe<sub>2</sub>N agrees with that derived from X-ray measurements, but is 6% > Sieverts and Krüll's val. (A., 1930, 878). H. J. E.

**Crystal structure of phase A of the system Ag-Li.** H. PERLITZ (Z. Krist., 1933, 86, 155—158; cf. A., 1930, 1359).—Phase A, with 76.3—80.2 at.-% Li, has a cubic unit cell containing 52 atoms with  $a$  9.94 Å. C. A. S.

**Mode of combination of silicon in aluminium or aluminium-silicon alloys.** P. URECH (Z. anorg. Chem., 1933, 214, 111—112).—The amount of Si hydrides evolved on dissolution in H<sub>2</sub>SO<sub>4</sub> ( $d$  1.6) is independent of the Si content of the alloy between 0.2 and 12% Si. This is consistent with the absence of compound formation. H. J. E.

**Hardening transformation in manganese steels.** H. SCOTT and J. G. HOOP (Trans. Amer. Soc. Steel Treat., 1933, 21, 233—248).—The hardening transformation (Ar'') temp. has been determined in steels containing Mn 4.5—12.0, C 0.12—1.0%, all the C being retained in solid solution. Within certain composition limits, C in solid solution has 12 times the effect of Mn. Extrapolated vals. for Ar'' temp. in Fe-C alloys are recorded. CH. ABS.

**Equilibrium A3 and A cm points in pure carbon steels.** CHU-PHAY YAP (Trans. Amer. Soc. Steel Treat., 1933, 21, 260—268).—New vals. are: A3 (ordinary pure Fe) 900°; A1 720°; A cm line, straight line from 0.795 at 720° to 1.685% C at 1130°. CH. ABS.

**Influence of heavy metals on aluminium alloys. I. Solid solution formation in aluminium alloys.** P. RÖNTGEN and W. KOCH (Z. Metallk., 1933, 25, 182—185).—Micrographic examination of alloys of Ni, Cr, and Mo with Al (0.048% impurity) shows that the solubility of these metals in Al at 560° is > 0.02% and that addition of 2% Cu does not increase this solubility. A. R. P.

**System iron-cobalt-manganese.** W. KÖSTER and W. SCHMIDT (Arch. Eisenhüttenw., 1933—1934, 7, 121—126).—The temp. of the  $\gamma$ - $\epsilon$  and magnetic transformations of Co are reduced by addition of Mn, reaching 0° at about 30 and 38% Mn, respectively. The m.p. and the polymorphic and magnetic transformation points in Fe-Co-Mn alloys with > 50% Mn have been determined. At about 1400° all the alloys consist solely of  $\gamma$ -solid solution, but alloys with > 18% Mn and > 80% Co undergo an irreversible transformation into  $\alpha$ , the hysteresis of which increases with increasing Mn content. Alloys with 18—30% Mn are partly converted into  $\epsilon$  similar to the  $\epsilon$ -Co phase. The lattice parameter of the ternary  $\alpha$ -,  $\gamma$ -, and  $\epsilon$ -solid solutions with const. Mn content decreases linearly at first, then at an increasing rate with increasing Co. With const. Fe or Co content the at. distance increases linearly with the Mn content

and is greater in the ferromagnetic than in the paramagnetic state. A. R. P.

**Alloys of iron. XI. Constitution of iron-manganese alloys.** (Miss) M. L. V. GAYLER (Iron and Steel Inst., 1933, Sept., Advance copy, 48 pp.).—The Fe-Mn system has been investigated by thermal, micrographic, and X-ray methods using alloys made from distilled Mn and electrolytic Fe purified by melting in  $H_2$ . The liquidus has three branches: (a) from 0 to 7% Mn it is concave to the composition axis and falls from  $1527^\circ$  to  $1504^\circ$ ;  $\delta$ -Fe separates as primary crystals; (b) from 7 to 75% it falls linearly to  $1265^\circ$  and corresponds with the crystallisation of  $\gamma$ -Fe, and (c) with  $>75\%$  Mn primary crystals of  $\gamma$ -Mn separate at gradually falling temp. to  $1242^\circ$ . A peritectic reaction  $\delta + \text{liquid} \rightleftharpoons \gamma$  occurs at  $1504^\circ$  with 1–8% Mn and a second peritectic reaction  $\gamma\text{-Fe} + \text{liquid} \rightleftharpoons \gamma\text{-Mn}$  at  $1270^\circ$  with 65–74% Mn. The solidus runs almost parallel with the liquidus between 6 and 68% Mn ( $1504$ – $1270^\circ$ ), and there is a freezing range of only about  $10^\circ$  in alloys containing  $>68\%$  Mn. The  $\gamma$ - $\delta$  transformation of Fe is raised linearly from  $1400^\circ$  to  $1504^\circ$  with addition of Mn up to 6%. Typical martensitic structures are obtained by quenching alloys with 1.7–9.3% Mn from above  $780^\circ$ , but with  $>10\%$  Mn this treatment produces a finely-twinned structure which is unaffected by heat-treatment and cold work; the nature of this phase and of the complex changes which occur in alloys with  $<60\%$  Mn have not been elucidated. At the Mn end of the system the  $\gamma \rightleftharpoons \beta$ -Mn transformation, which occurs in pure Mn at  $1188^\circ$  on heating and at  $1195^\circ$  on cooling, is gradually depressed by addition of Fe to  $1036^\circ$  on heating and  $1021^\circ$  on cooling with 29% Fe, after which it cannot be detected. The transformation which occurs in pure Mn at  $1043^\circ$  on heating and  $1005^\circ$  on cooling is raised to  $1128^\circ$  and  $1129^\circ$ , respectively, by 14% Fe and then depressed to  $1088^\circ$  and  $1092^\circ$ , respectively, with 21.1% Fe, after which it merges into the other transformation. The  $\gamma$ -Mn-Fe phase in alloys with 64–72% Mn decomposes at  $1028^\circ$  into a mixture of  $\gamma$ -Fe +  $\beta$ -Mn and the  $\beta$ -Mn-Fe solid solution with 59–63% Mn decomposes at  $600^\circ$  into  $\gamma$ -Fe +  $\beta$ -Mn. The solubility of  $\beta$ -Mn in  $\gamma$ -Fe falls from 63.5% Mn at  $1028^\circ$  to 60% at  $600^\circ$ , and that of  $\gamma$ -Fe in  $\beta$ -Mn increases from 28% Fe at  $1028^\circ$  to 38% at  $600^\circ$ . The  $\alpha \rightleftharpoons \beta$  transformation in pure Mn occurs at  $742^\circ$  and a second energy change at  $682^\circ$ ; in the alloy with 94.2% Mn these transformations occur at  $729^\circ$  and  $682^\circ$ , respectively, and with more Fe the temp. gradually falls to  $600^\circ$ .

A. R. P.

**Ternary alloys of thallium with lead, cadmium, and tin.** N. S. KURNAKOV and I. I. KORENEV (Ann. Inst. Anal. Phys. Chem., 1933, 6, 47–68).—The fusion diagrams of the systems Tl-Pb-Cd and Tl-Pb-Sn afford no evidence of compound formation. The f.-p. curves deviate considerably from linearity as compared with those of the constituent binary systems. The dystectic point of the system Pb-Tl is displaced by addition of Cd or Sn. R. T.

**Heats of mixing of liquid Fe-Ni-C alloys.** F. SAUERWALD and F. FLEISCHER (Z. Elektrochem., 1933, 39, 686–687).—The heat of mixture of an

alloy containing Ni 46, Fe 49, and C 5 at.-% is 500 g.-cal. per g.-atom. Probably Fe-Ni compounds are formed in considerable amount. E. S. H.

**Rare gases. II. Diffusion of helium through crystalline substances and the molecular flow through rock masses.** W. D. URRY (J. Amer. Chem. Soc., 1933, 55, 3242–3249; cf. this vol., 20).—He at 23–200 mm. does not pass through Bi, Fe, or a single crystal of  $SiO_2$  at temp.  $<700^\circ$ , but excited He diffuses through Bi. The adsorption of He on steel is zero. The fractional rate of loss of He from ordinary rocks is extremely small compared with that from radioactive minerals, and thus an objection to the He method for determining ages of rocks is ill-founded. From the rate of flow of He through rock materials, structure consts. have been calc.

J. G. A. G.

**Solubilities of hydrogen chloride, carbon dioxide, and hydrogen in liquid chlorine.** ANON. (Trans. State Inst. Appl. Chem., Leningrad, 1932, No. 15, 3–7).—Vals. are low. Corrosion of metal cylinders by HCl is due to ionisation in presence of  $H_2O$  or org. compounds. CH. ABS.

**System aniline-acetone-water.** A. N. CAMPBELL and E. M. BROWN (Trans. Faraday Soc., 1933, 29, 835–837).—Composition of conjugate phases at  $30^\circ$  and temps. of homogeneity for mixtures of various compositions are given. F. L. U.

**Solubilities of sparingly soluble salts using large volumes of solvents. I. Solubility of lead sulphate.** R. B. PURDUM and H. A. RUTHERFORD, jun. (J. Amer. Chem. Soc., 1933, 55, 3221–3223).—The solubility at  $20^\circ$  in  $H_2O$  (43.5 mg.  $PbSO_4$  per litre) and in 0.001–0.05*N*- $H_2SO_4$  has been determined. J. G. A. G.

**Solubility of monopotassium phosphate in presence of phosphoric acid, potassium hydroxide, and potassium chloride.** A. I. KRASILSCHTSCHIKOV (Ann. Inst. Anal. Phys. Chem., 1933, 6, 159–168).—The solubility of  $KH_2PO_4$  (I) at  $0^\circ$  is greatly depressed in saturated aq. KCl, the solubility of which is only slightly reduced by (I). In the system  $P_2O_5$ - $K_2O$ -KCl- $H_2O$  addition of  $K_2O$  or  $P_2O_5$  depresses the solubility of KCl and increases that of K phosphate. R. T.

**Solubility of thallos iodate in solutions of sodium mellitate [at  $25^\circ$ ].** C. F. FALEY (J. Amer. Chem. Soc., 1933, 55, 3112–3116).—The unexpectedly large increase in the solubility, *S*, of  $TlIO_3$  in 0.0001–0.01*M*-Na mellitate is not related to the slight alkalinity of the solutions. The addition of a third salt to a solution with a const. concn. of Na mellitate depresses *S* to a min. which is much lower for Mg than for Na salts. The phenomenon of an activity coeff. first increasing and then decreasing on the addition of an electrolyte to a moderately dil. solution is contrary to the predictions of the principle of ionic strength and the theory of Debye. Mellitic acid buffers uniformly from  $p_H$  3 to  $p_H$  7, and the shape of the electrometric titration curve with NaOH is similar to that of a protein. J. G. A. G.

**Rare earths. XXXIII. [Relative] basicity.** G. R. SHERWOOD and B. S. HOPKINS. XXXIIIa.

Basicity of illinium and yttrium. XXXIX. Transference numbers of the chlorides of neodymium, samarium, and gadolinium. I. Purification of materials. G. HUGHES and B. S. HOPKINS. II. Measurement of transference numbers [at 25°]. D. HAAS and W. H. RODEBUSH. XL. Magnetic susceptibilities of europium, [gadolinium], and ytterbium salts. G. HUGHES and D. W. PEARCE (J. Amer. Chem. Soc., 1933, 55, 3117—3121, 3121—3123, 3236—3237, 3238—3242, 3277—3279).—XXXIII. The pptn. of rare earths by  $\text{NaNO}_2$  has been modified to increase the efficiency of fractionation and emphasise the differences in basicity. Omitting Sc, Y, Ce, and Th, the order of decreasing basicity is identical with the order of increasing at. no. The differences of basicity in the series  $\text{Sm} > \text{Eu} > \text{Gd}$  are extremely slight.

XXXIIIa. The basicities are in the order  $\text{Nd} > \text{Pr} > \text{Y} > \text{Sm}$ .

XXXIX (I). Nd, Sm, and Gd each containing < 0.1% of other rare earths have been obtained by fractional crystallisation.

XXXIX (II). The moving boundary method affords the transference nos. 0.442, 0.442, and 0.433, respectively, for Nd, Sm, and Gd in 0.1N solutions of the chlorides. However, it does not follow that the mobility of the Gd ion is < that of Nd or Sm.

XL. The susceptibility,  $7510 \times 10^{-6}$  per g.-atom, of Yb in  $\text{Yb}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  is much < previously recorded vals. Data for other salts are confirmed. The susceptibility of an earth in the bivalent state approaches that of the earth of the next higher at. no. in the trivalent state.

J. G. A. G.

Regularities in isomorphous separation of small amounts of substances with crystallising salts. A. RATNER, P. TOLMATSHEV, and A. POLESITSKI (Z. physikal. Chem., 1933, 165, 472—476).—The views of Käding, Mumbrauer, and Riehl (A., 1932, 1198) are criticised. A single explanation covering all the experimental data so far obtained is outlined (cf. *ibid.*, 14).

R. C.

Regularities in isomorphous separation of small amounts of substances with crystallising salts. R. MUMBRAUER (Z. physikal. Chem., 1933, 165, 477).—A reply to criticism (cf. preceding abstract).

R. C.

Discontinuity and thermodynamics of crystal growth. E. SOMMERFELDT (Zentr. Min., 1932, 321—329; Chem. Zentr., 1932, ii, 3829).

L. S. T.

Limits of fractionation of cellulose nitrates. J. DUCLAUX and J. BARBIÈRE (Bull. Soc. chim., 1933, [iv], 53, 564—565).—The viscosities of cellulose nitrate solutions in  $\text{CMe}_2$ , fractionally pptd. by  $\text{H}_2\text{O}$ , have been compared.

A. S. C. L.

Hantzsch-Landau rule. G. HERRERO (Anal. Fis. Quím., 1933, 31, 416—421).—The influence of concn. on the distribution of I between  $\text{H}_2\text{O}$  and  $\text{C}_2\text{HCl}_3$  and between  $\text{H}_2\text{O}$  and  $\text{C}_6\text{H}_6$  has been examined in reference to the above rule. The solubility of I in  $\text{C}_2\text{HCl}_3$  at 20° is 34.78 g. per litre.

H. F. G.

Distribution coefficients of monocarboxylic acids and esters between immiscible solvents. H. J. HENRIQUES (J. Amer. Chem. Soc., 1933, 55,

3284—3288).—Data are recorded for  $\text{HCO}_2\text{H}$ ,  $\text{AcOH}$ ,  $\text{Pr}^n\text{CO}_2\text{H}$ , heptonic (I), lauric (II), myristic, palmitic (III), and oleic (IV) acids between  $\text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CHMe}_2$  (V) and  $\text{OMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$  (VI); for the Me esters of (I), (II), (III), (IV), and linoleic acid between (V) and  $\text{MeOH}$ , and also for the esters from (VI) and (I), (II), (III), and (IV) between (V) and (VI), at 0° and  $-19.5^\circ$ .

R. S. C.

Surface evaporation of boiling liquids. M. STRUBIN (Chem. Appar., 1932, 19, 145—147, 157—161; Chem. Zentr., 1933, i, 744).—Theoretical.

A. A. E.

Adsorption layers at the surface of solutions. D. G. DERVICHIAN (J. Chim. phys., 1933, 30, 468—481).—Determination of surface tension by establishing equilibrium with the pressure of an air jet impinging on the surface has been applied to the study of dil. aq. solutions of fatty acids containing 4—11 C atoms. The results show that the surface film is comparable with that obtained by spreading insol. acids on the surface of the  $\text{H}_2\text{O}$ , for a marked change in properties occurs when a certain crit. mol. surface is exceeded.

E. S. H.

Adsorption of sulphurous acid by platinum, ferric oxide, and chromic oxide. II. B. NEUMANN and E. GOEBEL (Z. Elektrochem., 1933, 39, 672—682; cf. this vol., 773).—Reversible adsorption occurs up to 200°, but at higher temp., corresponding with the temp. attained in catalytic reactions, chemical change also occurs with formation of  $\text{PtS}$  or  $\text{FeSO}_4$ . At 600° chemical reactions are considered to play a greater part than adsorption in catalysis. The heats of adsorption of  $\text{SO}_2$  by  $\text{Fe}_2\text{O}_3$  or  $\text{Cr}_2\text{O}_3$  are approx. equal; for small amounts of adsorbed  $\text{SO}_2$  the val. is about 40,000 g.-cal. per mol., but the val. falls as the amount of adsorption increases and as the temp. rises.

E. S. H.

Absorbent power of zinc oxalate partly decomposed by heat with respect to methyl alcohol. G. HÜTTIG and A. MELLER (Chim. et Ind., 1933, Spec. no., 788—791).—A series of products represented by  $\text{ZnO} \cdot n\text{C}_2\text{O}_4$  ( $n=1-0$ ) has been prepared by heating  $\text{ZnC}_2\text{O}_4$ . The behaviour of these towards  $\text{MeOH}$  vapour at 20° has been examined.

C. I.

Degassing of tantalum. U. S. IVANOV (J. Exp. Theor. Phys., Russia, 1932, 2, 162—170).—Desorption of H on Ta at 105—1760° follows Grünberg's law. The desorbed atoms are adsorbed by the glass walls to  $> 3.6 \times 10^{15}$  atoms per sq. cm.

CH. ABS.

Adsorption of hydrogen by silica gel at elevated temperatures. L. H. REYERSON (J. Amer. Chem. Soc., 1933, 55, 3105—3108).—If appreciable quantities of  $\text{H}_2$  are adsorbed by  $\text{SiO}_2$  gel at 400—600°, the process must occur immediately and exclusively on admission of the gas, since no change of pressure occurs subsequently (cf. this vol., 572).

J. G. A. G.

Nature of spontaneous separation of polonium on silver in various acids. O. ERBACHER (Z. physikal. Chem., 1933, 165, 421—426).—The separation depends on the exchange of Ag atoms for Po ions and the formation of a solid solution of Po in the  $\text{Ag}_2\text{O}$  formed.

R. C.

**Theory of film formation.** B. F. H. SCHEIFELE (*Fettchem. Umschau*, 1933, 40, 141—144).—From a consideration of the cohesive and adhesive forces acting in a film, and the consequent orientation and deformative strains of the constituent (macro-)mols., it is suggested that the "ideal" mol. structure to impart film-forming properties should consist of a central nucleus bearing three radiating, thread-like groups. This structure is realised to some extent by mols. such as linolenodilinolein (I) or the cellulose esters. Since trielæostearin possesses three like fatty acid chains, it should be less stable than (I) under the deformative strain resulting from the unequal forces of cohesion in the film and adhesion to the base, and this may account for the defective adhesion of tung-oil films, and their tendency to wrinkle.

E. L.

**Surface films of cellulose derivatives on water and dyestuff solutions. II.** J. B. HARDING and N. K. ADAM (*Trans. Faraday Soc.*, 1933, 29, 837—844; cf. this vol., 222).—Measurements of the change in contact potential between solution and air caused by the presence of surface films of methyl-, acetyl-, and benzyl-cellulose confirm the conclusions reached from surface pressure measurements, viz., that the hexose rings lie flat in the surface at low compressions, but are tilted slightly on compression. With methyl-cellulose there is evidence of small gaps in the film at areas  $> 140 \text{ \AA}^2$  per hexose group.

F. L. U.

**Physico-chemical analysis and molecular surface energy. Heat of wetting and inversion of the composition-property diagram.** B. V. ILJIN, V. A. OSCHMAN, N. L. REBENKO, and N. K. ARCHANGELSKAJA (*Ann. Inst. Anal. Phys. Chem.*, 1933, 6, 91—96).—The heat of wetting-composition curve of the system  $\text{H}_2\text{O}-\text{Ac}_2\text{O}$  is nearly horizontal for hydrophobic colloids (charcoal) with a flat max. at 50 mol.-%; for hydrophilic colloids ( $\text{SiO}_2$  gel) a well-defined min. exists at this point.

R. T.

**Decrease in surface energy of solid bodies and the work of dispersion in the formation of an adsorption layer.** P. A. REBINDER and N. A. KALINOVSKAYA (*J. Tech. Phys.*, Russia, 1932, 2, 726—755).—The following systems have been studied: graphite- $\text{H}_2\text{O}$ -aliphatic acid; graphite-kerosene-aliphatic acid; graphite- $\text{H}_2\text{O}$ -tannin, gallic acid, or alizarin-red; witherite-paraffin oil-acid; fluorite-paraffin oil-oleic acid; garnet- $\text{H}_2\text{O}$  or kerosene-aliphatic acid; glass-paraffin oil-oleic or butyric acid; Cu or galena-kerosene-stearic acid; calcite- $\text{H}_2\text{O}$ -aromatic base or aliphatic acid; calcite-air; calcite-PhMe-camphor.

CH. ABS.

**Effect of curvature of surface on surface energy. Rate of evaporation of liquid droplets. Thickness of saturated vapour films.** D. J. WOODLAND and E. MACK, jun. (*J. Amer. Chem. Soc.*, 1933, 55, 3149—3161).—On the assumption that the rate of evaporation of droplets of  $\text{Bu}^a$  tartrate and phthalate (I) is directly proportional to droplet radius, the relative v.p. of droplets of 2.0—0.7  $\mu$  radius have been evaluated from observations with a Millikan oil-drop apparatus. Using the Kelvin equation, the calc. surface energies,  $\sigma$ , are 50—100-fold those for the

flat surface. The anomaly is removed by correcting for the thickness (0.6  $\mu$  approx.) of the saturated vapour film around the droplet. The data from which Shereshefsky concluded that  $\sigma$  increases at a concave surface (A., 1929, 128) admit an alternative explanation on kinetic grounds. The latter is supported by the constancy of  $\sigma$  (capillary rise) of  $\text{H}_2\text{O}$  in capillaries of radius  $> 6.7 \mu$ . The v.p. of (I) at 25° is  $3.1 \times 10^{-6}$  mm. by the Knudsen method.

J. G. A. G.

**Interaction between soot films and oil.** D. M. CARDING (*Nature*, 1933, 132, 317—318).—Two effects, the Blacktin effect (cf. A., 1932, 464) and the formation of gas bubbles (cf. this vol., 672), are distinguished and further observations recorded.

L. S. T.

**Velocity of permeation of electrolytes through a membrane.** S. MATUURA (*Sci. Rep. Hiroshima Higher Tech. School*, 1933, 2, 67—187).—The following relations hold for the permeation of a single electrolyte through a membrane: (1)  $(1/t) \log (C_0 - C_\infty) / (C - C_\infty) = \lambda A (V - v) / 2.3 V v = k$ ; (2)  $(1/t) \log (c_\infty - c_0) / (c_\infty - c) = \lambda A (V + v) / 2.3 V v = k$ ; (3)  $C_\infty = c_\infty = (C_0 V + c_0 v) / (V + v)$ , where  $C_0$  is the initial concn. of the inside solution (I),  $c_0$  is that of the outside solution (II),  $C$  the concn. of (I) at time  $t$ ,  $c$  that of (II) at time  $t$ ,  $C_\infty$  and  $c_\infty$  are the concns. of (I) and (II) at time  $\infty$ ,  $V$  and  $v$  the initial vols. of (I) and (II),  $A$  is the surface area of the membrane, and  $k$  a const. when  $V$ ,  $v$ , and  $A$  are const. The permeation velocities of various electrolytes are in the following order:  $\text{KCl} > \text{NH}_4\text{Cl} > \text{NaCl} > \text{LiCl}$ ;  $\text{BaCl}_2 > \text{CaCl}_2 > \text{MgCl}_2$ ;  $\text{KI} \geq \text{KBr} > \text{KCl} > \text{KNO}_3 > \text{K}_2\text{SO}_4$ ;  $\text{HCl} > \text{H}_2\text{SO}_4 > \text{AcOH} > \text{H}_3\text{C}_2\text{O}_4 > \text{H}_3\text{PO}_4$ ;  $\text{HCO}_2\text{H} > \text{AcOH} > \text{H}_3\text{BO}_3 > \text{CH}_2\text{Cl} \cdot \text{CO}_2\text{H} > \text{PrCO}_2\text{H} > \text{succinic acid} > \text{malic acid} > \text{tartaric acid}$ . The velocity of permeation varies linearly with temp.; the temp. coeff. is higher, the lower is the velocity of permeation. The experiments are extended to the case of two electrolytes having a common ion, (a) when both electrolytes are initially on the same side of the membrane, (b) when they are initially on opposite sides, (c) when one electrolyte is initially on one side and the other at equal concn. on both sides. The influence of non-electrolytes (EtOH, glycerol, glucose) is to decrease the velocity of permeation.

E. S. H.

**Galvanotropism of Traube's copper ferrocyanide cells.** FE. SCHEMINZKY and FR. SCHEMINZKY (*Z. Biol.*, 1933, 94, 78—85).—The growths formed by placing crystals of  $\text{K}_4\text{Fe}(\text{CN})_6$  in aq.  $\text{CuSO}_4$  incline towards the cathode when an electric current is applied horizontally. Galvanotropism is not shown by silicate growths, which do not suffer rupture of the membrane and thickening with age. The phenomenon is traced to more rapid rupture and re-formation of the ferrocyanide membrane on the anode side.

E. S. H.

**Behaviour of Traube's cells under the influence of the electric current.** R. WAGNER (*Z. Biol.*, 1933, 94, 86—89).—The direction of growth of the  $\text{Cu}_2\text{Fe}(\text{CN})_6$  membrane cells is towards the cathode when  $\text{CuSO}_4$  is in excess (cf. preceding abstract) and towards the anode when crystals of  $\text{CuSO}_4$  are placed in  $\text{K}_4\text{Fe}(\text{CN})_6$  solution. Electro-osmotic effects are

excluded, and the phenomenon is traced to the changes of ion concn. under the influence of the current.

E. S. H.

**Behaviour of Traube's cells under the influence of the electric current.** FE. SCHEMINZKY and FR. SCHEMINZKY (Z. Biol., 1933, 94, 90—91).—The results obtained by Wagner (cf. preceding abstract) are explicable only on the assumption that the walls of the membrane are rendered porous by structural alterations.

E. S. H.

**Distribution of molecules in liquids.** E. AMALDI (Nuovo Cim., 1932, 9, 141—151; Chem. Zentr., 1932, ii, 3833).—Theoretical.

A. A. E.

**Electrostriction produced by salts in aliphatic alcohols.** W. C. VOSBURGH, (MISS) L. C. CONNELL, and J. A. V. BUTLER (J.C.S., 1933, 933—942).—The apparent mol. vols. of NaCl, KCl, NaI, and KI in MeOH, and of LiCl in MeOH, EtOH, Pr<sup>n</sup>OH, Bu<sup>n</sup>OH, and Bu<sup>t</sup>OH have been determined. Except for concn. solutions of LiCl in the higher alcohols,  $\phi = \phi_0 + a\sqrt{c}$  in all cases. The val. of  $a$  for the different salts in MeOH varies slightly, but approximates to the limiting val. for uni-univalent salts as calc. by Redlich and Rosenfeld's equation (A., 1931, 905, 1122), being six times the val. in H<sub>2</sub>O. The electrostriction in the alcoholic solutions is much > in H<sub>2</sub>O. The apparent mol. vols. at infinite dilution agree approx. with Webb's theory (A., 1926, 1208).

D. R. D.

**Hydrotrophy amongst inorganic salts.** J. V. TAMCHYNA (Biochem. Z., 1933, 264, 24—27).—Concn. aq. solutions of readily sol. inorg. salts exhibit hydrotropic properties (I) much less frequently than salts with org. anions. As regards (I) Li halides form the series I > Br > Cl. Saturated aq. LiI dissolves uric acid (II) very readily and also insol. inorg. salts, e.g., MgCO<sub>3</sub>. Triethanolamine borate has very pronounced (I), especially towards (II).

W. McC.

**Action of electrolytes on kaolin suspensions.** PICHOR (Compt. rend., 1933, 197, 451—453).—Observations on the opacity in relation to the depth below the surface and the period of settling are described.

C. A. S.

**Preparation and properties of zirconium sulphosalicylic acid jellies.** S. PRAKASH (J. Indian Chem. Soc., 1933, 10, 281—285).—Sols are produced by mixing aq. solutions of ZrOCl<sub>2</sub> and sulphosalicylic acid. These set to hard, transparent jellies, but jellies cannot be obtained in neutral or alkaline systems. The particles are positively charged.

E. S. H.

**Diamagnetism of bismuth and antimony in the colloidal state.** M. R. VERMA and R. N. MATHUR (J. Indian Chem. Soc., 1933, 10, 321—328).—The diamagnetic susceptibility is practically independent of particle size of the metal. Contrary results are ascribed to the presence of oxide films.

E. S. H.

**Ionic interchange in sulphur sols. II. Influence of acids.** T. R. BOLAM and J. J. MUIR (J.C.S., 1933, 1022—1028; cf. this vol., 24).—The replacement of H<sup>+</sup> by metallic cations has been studied with undialysed S sols containing a higher concn. of acid. Total coagulation occurs before all the H<sup>+</sup> has been replaced. The degree of dis-

placement at the coagulation point is the same for all the cations examined (Na, K, Rb, Ca, Ba, Al) for the same concn. of HCl in the sol, but decreases with increasing acidity. The more acid is the sol, the greater is the concn. of salt necessary to secure this amount of replacement.

D. R. D.

**Effect of genotypism on properties of colloidal dispersions of fatty acid salts.** P. A. THIESSEN and E. EHRLICH (Z. physikal. Chem., 1933, 165, 464—471; cf. this vol., 116).—The vol.-temp. curve of a hydrogel of Na palmitate and the viscosity-temp. curve of a hydrosol each undergo an abrupt change in slope at a temp. near the m.p. of the acid. Hydrosols of Na soaps on cooling become turbid at a temp. near the m.p. of the acid,  $T$ , and opaque gels with a framework of cryst. fatty acid salts melt, whether they have been formed from fibrils or granules, at a temp. near  $T$ .

R. C.

**Phase-rule equilibria of acid soaps. II. Anhydrous acid sodium palmitates.** J. W. MCBAIN and M. C. FIELD. **III. Anhydrous acid potassium oleate.** J. W. MCBAIN and A. STEWART (J.C.S., 1933, 920—924, 924—928).—II. NaPl, HPl and 2NaPl, HPl exist as solid phases which decompose at 74.2° and 91.1°, respectively. No solid solutions are formed, but there is an extensive liquid crystal area.

**III.** The system KOl-HOl is similar, but there is only one acid soap, KOl, HOl, which decomposes at 47°. A preliminary investigation indicates the probable existence of NaStr, 2HStr and 2NaStr, HStr.

D. R. D.

**Conductivity in the three-component system oleic acid-potassium oleate-water.** J. W. MCBAIN and A. STEWART (J.C.S., 1933, 928—932).—At 25°, aq. K oleate (I) dissolves oleic acid (II) until a composition 2KOl, HOl is reached. With concn. solutions a liquid crystal phase is formed with the same ratio of (I) to (II) but with a smaller proportion of H<sub>2</sub>O. With more dil. solutions the second phase is isotropic and consists mainly of (II), with dissolved (I) and H<sub>2</sub>O. Conductivity, cryoscopic, and  $p_H$  data indicate that the acid soap is mostly in a colloidal undissociated state.

D. R. D.

**Kinetics of coagulation of colloids. V. Variation of viscosity during coagulation.** S. S. JOSHI and K. S. VISWANATH (J. Indian Chem. Soc., 1933, 10, 329—340).—The change of viscosity has been followed during coagulation of As<sub>2</sub>S<sub>3</sub> sols (4.5 g. per litre) at 35°. Viscosity cannot be used as a quant. indicator of coagulation.

A. S. C. L.

**Protective action of colloids. III. Influence of sucrose and sodium oleate on stability of colloid manganese dioxide.** S. S. JOSHI and A. N. LAL (J. Indian Chem. Soc., 1933, 10, 367—371).—Coagulation of MnO<sub>2</sub> sols (0.75 g. per litre) has been observed when solutions of sucrose and Na oleate are added as protectors.

A. S. C. L.

**Influence of lyophile colloids on precipitation from solution. Gelatin and silver chromate. III.** T. R. BOLAM and W. J. DONALDSON (Trans. Faraday Soc., 1933, 29, 864—877; cf. A., 1930, 414).—Measurements of potential in aq. mixtures

of  $\text{AgNO}_3$  and  $\text{K}_2\text{CrO}_4$  in which pptn. of  $\text{Ag}_2\text{CrO}_4$  is hindered by the presence of gelatin show that (1) part of the  $\text{Ag}_2\text{CrO}_4$  is in the form of a highly supersaturated solution, (2) the remainder is accounted for by  $\text{Ag}^+$  and  $\text{CrO}_4^{2-}$  combined with gelatin. The inhibitive action of gelatin is greatest at about  $p_H$  5. The degree of supersaturation at a given  $p_H$  is independent of the concn. of gelatin, above some undetermined low val. F. L. U.

**Lyotropic series in swelling and its extension to organic and non-ionising substances. X. Influence of benzene derivatives with two or more hydrophile groups on the swelling of potato starch.** J. R. KATZ, A. WEIDINGER, and F. J. F. MUSCHTER, jun. **XI. Influence of substances with two or more hydrophile groups on the swelling of collagen.** J. R. KATZ and A. WEIDINGER (Biochem. Z., 1933, 263, 323—331, 421—427).—X. With one hydrophile group, the increased swelling is in the order  $\text{PhOH} > \text{NH}_2\text{Ph} > \text{PhOBz} > \text{PhSO}_3\text{Na}$ . A second group impairs this activity in the same order, the impairment being slight with two phenolic groups. Similar results are given for substances with one phenolic and one non-phenolic hydrophile group ( $\text{CO}_2\text{Na}$ ,  $\text{SO}_3\text{Na}$ ,  $\text{NH}_2$ ) and with two non-phenolic hydrophile groups.

**XI. Curves show the effect of a variety of aliphatic substances having  $\leq 2$   $\text{CO}_2\text{H}$  and  $\text{OH}$  groups and aromatic substances with  $\leq 2$   $\text{CO}_2\text{H}$ ,  $\text{SO}_3\text{H}$ , and  $\text{OH}$  groups. In all cases, introduction of a second hydrophile group impairs the effect of the first.** P. W. C.

**Determination of the swelling of casein.** W. MOHR and J. MOOS (Milch. Forsch., 1933, 15, 384—389).—The swelling has been examined microscopically at  $p_H$  1—4.5 in different acids. At  $p_H$  4.5 there is slight contraction. E. B. H.

**Graphic representation of chemical equilibria.** P. JOLIBOIS (Compt. rend., 1933, 197, 451; cf. this vol., 904).—A claim to priority regarding the method described (cf. this vol., 464). C. A. S.

**Multiple equilibria.** F. SCHUSTER (Brennstoff-Chem., 1933, 14, 310—311).—The general problem of multiple equilibria is briefly discussed and various types are classified. A. B. M.

**Nomenclature of dissociating compounds. (Acid-base problem.)** F. KLAGES (Z. Elektrochem., 1933, 39, 663—668). E. S. H.

**Equilibrium in the system cyclohexane-benzene-hydrogen.** R. B. PURDUM and R. N. PEASE (J. Amer. Chem. Soc., 1933, 55, 3109—3111).—The equilibrium const. of the reaction  $\text{C}_6\text{H}_6(g) + 3\text{H} \rightleftharpoons \text{C}_6\text{H}_{12}(g)$  has been determined dynamically between  $250^\circ$  and  $275^\circ$  using a Cu catalyst. The free energy of the reaction in this range is given by  $\Delta F = -43,800 + 18.2T \log T - 0.008T^2 - 31.0T$ . J. G. A. G.

**Dissociation constant of hypochlorous acid.** J. M. GALLART (Anal. Fis. Quim., 1933, 31, 422—426).—The decomp. of  $\text{NaOCl}$  in dil. solution (approx. 0.02N) at  $25^\circ$  is termol. With increase of  $p_H$  of the solution the velocity coeff. rises from 7 at  $p_H$  5.75 to a max. (32.8) at  $p_H$  6.7, and falls to 7.2 at  $p_H$  7.87. The ionisation const. of  $\text{HOCl}$  at  $25^\circ$  is  $1.05 \times 10^{-7}$ .

H. F. G.

**Dissociation constants of bile acids.** B. A. JOSEPHSON (Biochem. Z., 1933, 263, 428—443).—Vals. for cholic, deoxy-, glyco-, glycodeoxy-, tauro-, and taurodeoxy-cholic acids are given. The results agree fairly closely with those of Hammarsten (A., 1924, i, 1139) but are very different from those of Henriques (A., 1931, 1369). P. W. C.

**Peptides of trivalent amino-acids. III. Apparent dissociation constants, free energy changes, and heats of ionisation of peptides involving arginine, histidine, lysine, tyrosine, and aspartic and glutamic acids, and the behaviour of lysine peptides towards nitrous acid.** J. P. GREENSTEIN (J. Biol. Chem., 1933, 101, 603—621).—The heats of ionisation of the free groups of peptides are independent of the constitution of the mol. and afford a means of identification of the ionising group. The change in free energy due to the ionisation of  $\text{CO}_2\text{H}$  in peptides (I) is  $>$  in  $\text{NH}_2$ -acids (II) and has an appreciable temp. coeff.; on the other hand, the energy change in (I) is  $<$  in (II) for  $\text{NH}_2$  and is independent of temp. In the transition of (II) to (I)  $\text{NH}_2$  and  $\text{CO}_2\text{H}$  are considerably weakened and may be modified by the presence of other groups. Whereas lysine requires 15 min. for complete deamination, lysyl-peptides require about half this time. H. G. R.

**[Electrolytic] dissociation of zinc sulphate.** C. W. DAVIES (Trans. Faraday Soc., 1933, 29, 834—835).—Attention is directed to errors in a paper by Cowperthwaite (this vol., 569). F. L. U.

**Study of saline solutions.** V. P. SCHISCHOKIN (Ann. Inst. Anal. Phys. Chem., 1933, 6, 21—24).—Theoretical. R. T.

**Relations between kinetics and chemical equilibria. III. Synthesis and decomposition of potassium pyrogallol carbonate.** A. BERTHOUD and D. PORRET (J. Chim. phys., 1933, 30, 453—466; cf. this vol., 903).—The synthesis of K pyrogallol carbonate from  $\text{KHCO}_3$  and pyrogallol, and its decomp. in aq. solution, takes place through the formation of an intermediate compound, probably  $\text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{O} \cdot \text{CO}_2\text{K}$ . The equilibrium const. increases with the temp. The results differ from those obtained by Widmer (A., 1929, 517). E. S. H.

**Vapour pressure of the systems sodium sulphate-water and sodium carbonate-water.** E. J. RODE (Ann. Inst. Anal. Phys. Chem., 1933, 6, 97—134).—V.p.-temp. and v.p.-composition curves are recorded. R. T.

**F.-p. curves of binary mixtures:  $\text{TiCl}_4$ - $\text{SiCl}_4$ ,  $\text{TiCl}_4$ - $\text{CCl}_4$ ,  $\text{TiCl}_4$ - $\text{SnCl}_4$ , and  $\text{TiCl}_4$ - $\text{SbCl}_5$ .** N. NASU (Bull. Chem. Soc. Japan, 1933, 8, 195—207).— $\text{TiCl}_4$  and  $\text{SnCl}_4$  form a continuous series of mixed crystals. The remaining systems give simple eutectics. F. L. U.

**System chlorine-phosphoryl chloride.** A. P. ROLLET and W. GRAFF (Compt. rend., 1933, 197, 555—557).—The thermal diagram shows the existence of  $2\text{POCl}_3 \cdot \text{Cl}_2$ . This has been isolated as yellow prisms, dissociating above  $-55^\circ$ .  $\text{POCl}_3$  has m.p.  $1.15 \pm 0.05^\circ$ . C. A. S.

**Ceramic refractory materials. VI. System  $ZrO_2$ -MgO.** F. EBERT and E. COHN. **VII. Binary systems MgO-CaO, MgO-BeO, CaO-BeO.** O. RUFF, F. EBERT, and U. KRAWCZYNSKI (Z. anorg. Chem., 1933, 213, 321—332, 333—335; cf. B., 1929, 474).—VI. The system is characterised by a eutectic at  $2150^\circ$  (50% MgO) and by a series of mixed crystals. The compound  $MgZrO_3$  reported by Wartenburg was not observed (cf. A., 1930, 847). X-Ray photographs were used in elucidating the nature of the solid phases.

VII. The authors' vals. for the eutectic temp. in the systems CaO-MgO and MgO-BeO are respectively  $80^\circ$  and  $280^\circ >$  those previously recorded (this vol., 27). The discrepancy is discussed. H. J. E.

**Sodium hydroxide-sodium cyanide melts.** R. HÖLTJE (Z. anorg. Chem., 1933, 214, 65—72; cf. A., 1932, 587).—Fused NaOH and NaCN react above  $500^\circ$  in absence of  $H_2O$  and  $O_2$ , forming  $Na_2CO_3$ ,  $Na_2CN_2$ ,  $Na_2O$ , and  $H_2$ . In presence of  $H_2O$  reaction starts at  $300^\circ$ , forming  $NH_3$  and  $HCO_2Na$ , which reacts with NaOH to form  $Na_2CO_3$  and  $H_2$ . In presence of  $O_2$ , excess of NaCN is partly oxidised to  $N_2$ , and partly forms  $NH_3$ ,  $H_2$ , and  $Na_2CO_3$  due to the resulting  $H_2O$ . Excess of  $O_2$  forms  $Na_2CO_3$ ,  $N_2$ ,  $NaNO_3$ , and  $H_2O$ . The ready reaction of NaOH-NaCN melts with  $SnO_2$  probably depends on the removal of  $H_2O$ , produced when stannate is formed, by reaction with NaCN. Addition of Na also removes  $H_2O$ , facilitating the attack of  $SnO_2$  by NaOH. NaCN is better than Na because it does not attack the Ni crucible. H. J. E.

**Thermal analysis of the system lithium fluoride-lithium metaborate.** I. I. KITAIGORODSKI, T. A. POPOVA, and O. K. BOTVINKIN (Ann. Inst. Anal. Phys. Chem., 1933, 6, 135—139).—LiF undergoes a change of form at  $812^\circ$ , and  $LiBO_2$  at  $785^\circ$ . The fusion diagram of the system indicates formation of the compound,  $2LiF \cdot 3LiBO_2$ , m.p.  $755^\circ$ , which shows transition points at  $545^\circ$  and  $585^\circ$ . R. T.

**Acid salts of monobasic organic acids. I. [*r*-Mandelic acid.]** J. D. M. ROSS and T. J. MORRISON (J.C.S., 1933, 1016—1022).—Isotherms at  $25^\circ$  indicate the existence of  $KM, HM, KM, 2HM, NaM, HM, NaM, 2HM, BaM_2, 2HM, H_2O$ ; and the salts  $KM, 3HM; NaM, 3HM; LiM, HM; SrM_2, 2HM$ , and  $CaM_2, 2HM$  ( $M = OH \cdot CHPh \cdot CO_2$ ). The structural formulæ and relative stabilities of these compounds are discussed. D. R. D.

**Phase-rule study of mixed derivatives of alcohols.** W. S. CALDWELL and K. R. MACLEAN (J. Amer. Chem. Soc., 1933, 55, 3458—3460).—Mixed crystals are formed by Me and Et *p*-nitrobenzoates (min. m.p.  $52^\circ$  with 20% of Me ester) and 3:5-dinitrobenzoates (min. m.p.  $73^\circ$  with equimol. mixtures), but not by Et and Bu 3:5-dinitrobenzoates (eutectic m.p.  $51^\circ$ , with 64% of Bu ester). R. S. C.

**Fusion curves of solid solutions with compound formation.** A. B. MŁODZIEJOWSKI (Ann. Inst. Anal. Phys. Chem., 1933, 6, 13—20).—Mathematical. R. T.

**Singular points of fusion curves.** A. B. MŁODZIEJOWSKI (Ann. Inst. Anal. Phys. Chem., 1933, 6, 5—12; cf. A., 1931, 1127).—Mathematical.

R. T.

**Systems of sulphur dioxide and hydrogen derivatives of benzene.** W. F. SEYER and E. G. KING (J. Amer. Chem. Soc., 1933, 55, 3140—3149).— $SO_2$ , in the presence of  $O_2$ , forms the white substance  $(C_6H_{10}, SO_2)_x$  with  $C_6H_{10}$ , whilst even in the absence of  $O_2$ ,  $C_6H_8$  yields the white polymeride  $(C_6H_8, SO_2)_x$ . No compound is formed in the  $O_2$ -free system  $C_6H_{10}-SO_2$ , but the f.-p. curve has a eutectic at  $-110^\circ$  with 89.5 mol.-% of  $C_6H_{10}$ . Physical properties do not provide a basis for predicting the behaviour of  $SO_2$  with  $C_6H_6$  and its hydrogenation products (cf. A., 1930, 405). A ring structure for  $SO_2$  is proposed. J. G. A. G.

**X-Ray study of the system nickel-oxygen-water.** M. LE BLANC and E. MÖBIUS (Z. Elektrochem., 1933, 39, 753—754).—The existence of new lines reported by Cairns and Ott (this vol., 352) is confirmed. Dissociation pressure measurements do not confirm the existence of  $Ni_2O_3 \cdot H_2O$ ,  $Ni_2O_3 \cdot 2H_2O$ , and hydrates of  $Ni_3O_4$  and  $Ni_6O_7$ . H. J. E.

**Ternary system ammonia-nitric anhydride-water.** N. S. KURNAKOV and M. N. RAVITSCH (Ann. Inst. Anal. Phys. Chem., 1933, 6, 169—184).—The equilibrium relations have been studied at  $-10^\circ$ ,  $0^\circ$ ,  $25^\circ$ ,  $35^\circ$ ,  $55^\circ$ ,  $80^\circ$ ,  $86^\circ$ ,  $100^\circ$ , and  $130^\circ$ . At  $-10^\circ$  and  $0^\circ$  the solid phases consist of  $NH_4NO_3$  and  $NH_4NO_3 \cdot 2HNO_3$  (alone or together), whilst at higher temp.  $NH_4NO_3$  is the only solid phase. The transition point of  $\alpha$ - into  $\beta$ - $NH_4NO_3$  is at  $32^\circ$ . R. T.

**Separation in the system KOH-NH<sub>3</sub>-H<sub>2</sub>O and ternary systems of the type ether-water-X.** E. JÄNECKE (Z. Elektrochem., 1933, 39, 682—686).—Equilibrium data are given for the portion of the KOH-NH<sub>3</sub>-H<sub>2</sub>O system in which the formation of two liquid phases is possible. The results are discussed in relation to other ternary systems.

E. S. H.

**System strontium nitrate-nitric acid-water.** A. SIEVERTS and W. PETZOLD (Z. anorg. Chem., 1933, 214, 27—32; cf. this vol., 782).—Solubilities have been measured between  $-25^\circ$  and  $50^\circ$ . In 60%  $HNO_3$ ,  $Sr(NO_3)_2$  is almost insol. Only the tetrahydrate was observed. H. J. E.

**Equilibria in the systems  $(NH_4)_2SO_4$ -NiSO<sub>4</sub>·H<sub>2</sub>O,  $(NH_4)_2SO_4$ -CoSO<sub>4</sub>·H<sub>2</sub>O,  $(NH_4)_2SO_4$ -ZnSO<sub>4</sub>·H<sub>2</sub>O,  $Na_2SO_4$ -NiSO<sub>4</sub>·H<sub>2</sub>O, and  $Na_2SO_4$ -CoSO<sub>4</sub>·H<sub>2</sub>O, at  $25^\circ$ .** R. M. CAVEN and W. K. GARDNER (J.C.S., 1933, 943—946).—Isotherms at  $25^\circ$  afford evidence of two series of double salts corresponding with  $(NH_4)_2SO_4 \cdot MSO_4 \cdot 6H_2O$ , and  $Na_2SO_4 \cdot MSO_4 \cdot 4H_2O$ . D. R. D.

**System ferrous sulphate-manganous sulphate-water at  $0^\circ$  and  $25^\circ$ .** A. McL. WHITE (J. Amer. Chem. Soc., 1933, 55, 3182—3185).—The data refer to the entire concn. range. At  $0^\circ$  a heptahydrate solid solution is produced, whilst at  $25^\circ$  two series of solid solutions, hepta- and penta-hydrate, are formed. J. G. A. G.

**Equilibrium in the oxidation of liquid iron by steam and the free energy of ferrous oxide**

in liquid steel. J. CHIPMAN (J. Amer. Chem. Soc., 1933, 55, 3131—3139).—From determinations of the O content of cold Fe previously molten and in equilibrium with a stream of H<sub>2</sub>-steam mixture, the O concn. in molten Fe is found to be almost directly proportional to the mol. ratio of steam to H<sub>2</sub>; from this it is inferred that the solute is an oxide of Fe containing 1 atom of O per mol. The activity of the FeO has been evaluated and the data for the range 1550—1770° are expressed by  $\log K = 6200/T - 3.28$  and  $\Delta F^\circ = -28,400 + 15.0T$ , where  $K = p_{\text{H}_2\text{O}} / (p_{\text{H}_2} \times a_{\text{FeO}})$ . The free energy of formation of FeO from its elements in molten Fe is  $\Delta F^\circ = -31,200 - 1.0T$ , which does not accord with previous results (this vol., 466).

J. G. A. G.

Causticisation of sodium carbonate by ferric oxide. XVI. Dissociation of sodium carbonate in presence of ferric oxide. III. M. MATSUI, K. BITO, and M. KADONO (J. Soc. Chem. Ind., Japan, 1933, 36, 468—471B).—The pressure-temp. curve for  $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$  is given from 310° to 850°.

A. G.

Action of strong acids on the equilibrium  $\text{H}_3\text{PO}_4 + \text{HF} \rightleftharpoons \text{H}_2\text{PO}_3\text{F} + \text{H}_2\text{O}$ . W. LANGE (Z. anorg. Chem., 1933, 214, 44—54; cf. A., 1932, 132).—The abnormal effect of H<sub>2</sub>O on the equilibrium does not depend on ionisation of H<sub>3</sub>PO<sub>4</sub>. HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, and PhSO<sub>3</sub>H lessen the abnormal effect, and HClO<sub>4</sub> causes increased formation of H<sub>2</sub>PO<sub>3</sub>F. The action of these acids is attributed to removal of H<sub>2</sub>O from the equilibrium mixture, due to hydrate formation.

H. J. E.

Activity coefficient of potassium chloride in aqueous solutions at 0° from e.m.f. and f.p. data. R. P. SMITH (J. Amer. Chem. Soc., 1933, 55, 3279—3282).—Vals. derived from the e.m.f. of the cell  $\text{Ag}|\text{AgCl}|\text{KCl}(c)|\text{K}_2\text{Hg}|0.1M\text{-KCl}|\text{AgCl}|\text{Ag}$  for  $c = 0.1-3.5$  agree with those from f.p. data (this vol., 126). The concordance confirms the trustworthiness of the flowing amalgam electrode.

J. G. A. G.

V.p., [density], and activity coefficients of aqueous solutions of perchloric acid at 25°. J. N. PEARCE and A. F. NELSON (J. Amer. Chem. Soc., 1933, 55, 3075—3081).—The data refer to 0.1—11.9M-HClO<sub>4</sub>. The activity of H<sub>2</sub>O in corresponding solutions of HCl and HClO<sub>4</sub> is identical up to 2M, but at higher concns. decreases more rapidly in HClO<sub>4</sub>. The ion activity coeffs.,  $\gamma$ , of these acids have min. in 0.4M solutions, but  $\gamma$  for HClO<sub>4</sub> rises more rapidly to very high vals. at high concn., as anticipated from the relative hydrating powers of the ions. Free energies of transfer and partial mol. vols. have been calc.

J. G. A. G.

Activity coefficients of salts in anhydrous acetic acid solutions from solubility measurements [at 25°]. A. W. SCHOLL, A. W. HUTCHISON, and G. C. CHANDLEE (J. Amer. Chem. Soc., 1933, 55, 3081—3088).—The solubility of KClO<sub>4</sub> in anhyd. AcOH containing LiCl, NaBr, and MgCl<sub>2</sub>, and that of BaCl<sub>2</sub> in the presence of NaBr, have been determined. The data accord with the predictions of the interionic attraction theory as extended by Gronwall, La Mer, and others.

J. G. A. G.

Thermal effects produced by the exposure of massive gold to saturated water vapour. F. BARRY and E. P. BARRETT (J. Amer. Chem. Soc., 1933, 55, 3088—3098; cf. A., 1922, ii, 473).—The rate of deposition of H<sub>2</sub>O, from its saturated vapour, on massive Au at 22—23° decreases exponentially with time. The heat,  $H$  (millical. per sq. cm.), evolved in time  $t$  is given by  $\log_{10} H = 1.5990 - 0.3486/t^{0.409}$ , leading to the total heat 0.0397 g.-cal. per sq. cm. when  $t = \infty$ . Initially, 7570 g.-cal. are evolved per g. of H<sub>2</sub>O deposited, and the val. falls to 560, affording a total heat of 1601. Capillary inhibition may account for the phenomena.

J. G. A. G.

Affinity of metals for sulphur. III. Heats of combustion and formation of the arsenic sulphides, As<sub>2</sub>O<sub>3</sub>, As<sub>2</sub>O<sub>5</sub>, and of As<sub>2</sub>O<sub>3</sub>, SO<sub>3</sub>. E. V. BRITZKE, A. F. KAPUSTINSKI, and L. G. TSCHENZOVA (Z. anorg. Chem., 1933, 213, 58—64; cf. A., 1932, 573).—Heats of combustion of As<sub>2</sub>S<sub>2</sub> and As<sub>2</sub>S<sub>3</sub>, and heats of dissolution of As<sub>2</sub>O<sub>3</sub>, As<sub>2</sub>O<sub>3</sub>.As<sub>2</sub>O<sub>5</sub>, and As<sub>2</sub>O<sub>3</sub>.SO<sub>3</sub> were measured directly. The heats of formation of As<sub>2</sub>S<sub>2</sub> and As<sub>2</sub>S<sub>3</sub> from solid As and rhombic S are 28.93 and 34.75 kg.-cal., respectively.

H. J. E.

Thermal data on organic compounds. XII. Heats of combustion of nine hydrocarbons. H. BANSE and G. S. PARKS (J. Amer. Chem. Soc., 1933, 55, 3223—3226).—The standardised heats of combustion per g. in vac. at 19° are: diisobutylene (*l*) 11,273, *n*-C<sub>8</sub>H<sub>18</sub> (*l*) 11,434, durene (*s*) 10,337, isodurene (*l*) 10,348, prehnitene (*l*) 10,370, C<sub>6</sub>HMe<sub>5</sub> (*s*) 10,432, C<sub>6</sub>Me<sub>6</sub> (*s*) 10,500, *n*-C<sub>12</sub>H<sub>26</sub> (*l*) 11,335, and dibenzyl (*s*) 9,914 g.-cal. The increment per CH<sub>2</sub> is 156,350 g.-cal.

J. G. A. G.

Entropy and free energy relations among hydrocarbons. G. S. PARKS (Ind. Eng. Chem., 1933, 25, 887—891).—The molal entropy at 25° ( $S$ ) for paraffins =  $25.0 + 7.7n - 4.5r$ , where  $n$  = no. of C atoms and  $r$  = no. of side branches in the main chain. An olefinic linking generally decreases the entropy by 2.7, but the effect is influenced by the neighbouring groups. For benzenoid hydrocarbons  $S = 25.0 + 7.7N - 4.5R + 19.5p_1$ , where  $N$  = no. of C atoms outside the C<sub>6</sub>H<sub>6</sub> ring,  $R$  = no. of hydrocarbon groups in excess of two attached to any C atom in the aliphatic chain, and  $p_1$  = no. of Ph groups. For 5- or 6-membered polymethylene ring compounds 26.5 $p_2$  is substituted for 19.5 $p_1$ . The free energy of formation at 25° ( $F$ ) for paraffins =  $-11,700 + 1080n + 800r$  g.-cal.; for olefines it is 23,000—17,000 g.-cal. > that of the corresponding paraffin. Passing from C<sub>6</sub>H<sub>6</sub> through the Me derivatives  $F$  decreases from 29,000 to a min. 20,000 for C<sub>6</sub>H<sub>2</sub>Me<sub>4</sub> and then increases to 27,000 for C<sub>6</sub>Me<sub>6</sub>. In the series CH<sub>4</sub> to CPh<sub>4</sub>  $F$  increases by 36,000 g.-cal. for each additional Ph group. The free energy of a no. of typical hydrocarbons is a linear function of the temp. The application of free energy data to (1) the conversion of cyclohexane into methylcyclopentane, (2) the polymerisation of *n*-hexene, and (3) the production of higher alcohols is considered.

D. K. M.

Simultaneous conduction by electrolytes during the measurement of resistance of palladium wires containing hydrogen. D. P. SMITH (Z.

Elektrochem., 1933, 39, 743—744; cf. Knorr and Schwartz, this vol., 676).—The effect due to simultaneous conduction by the electrolyte is shown theoretically to lie almost within the error of measurement. The lowering of resistance of the wire is attributed to ionised H in the Pd (cf. A., 1921, ii, 423).

H. J. E.

**Mobility of ions in  $H^2H^2O$ .** G. N. LEWIS and T. C. DOODY (J. Amer. Chem. Soc., 1933, 55, 3504—3506).—Conductivities of HCl and KCl in 97%  $H^2H^2O$  between 5° and 35° have been determined. The mobilities at 18° of  $H^2+$ ,  $K^+$ , and  $Cl^-$  in pure  $H^2H^2O$  are 213.7, 54.5, and 55.3, respectively.

J. G. A. G.

**Conductivity [and density] of sodium iodide solutions at 25° and the limiting conductance of the iodide ion.** P. A. LASSELLE and J. G. ASTON (J. Amer. Chem. Soc., 1933, 55, 3067—3071).—The data refer to 0.0007—0.17*M* solutions. The limiting equiv. conductivity of NaI is 126.85 reciprocal ohms and that of  $I^-$  is 76.75. Shedlovsky's modification of the Onsager equation is obeyed at concn. < 0.04*N*.

J. G. A. G.

**Conductivity of some weak electrolytes and glycerol solutions with 75-cm. waves.** B. G. WHITMORE (Physikal. Z., 1933, 34, 649—659).—The following solutions were used: LiBr,  $Co(NO_3)_2$ ,  $CdI_2$ ,  $CdBr_2$ ,  $ZnCl_2$ ,  $ZnI_2$ , in  $COMe_2$ ;  $HgCl_2$  in  $COMe_2-H_2O$ ; tartaric and propionic acids in  $H_2O$ . The increase of conductivity at high frequency observed in most cases agrees with the Debye-Falkenhagen theory, if only the ions present are considered.  $HgCl_2$  showed smaller effects than the theoretical, whilst  $ZnCl_2$  and  $ZnI_2$  in  $COMe_2$  gave unexpectedly large effects, although in  $H_2O$  these behave quite normally. The solutions of  $ZnCl_2$  and  $ZnI_2$  in  $COMe_2$  must contain large complex ions, or the absorption may be an "anomalous dipole absorption" of the undissociated mol. The anomalous absorption of glycerol was lowered by addition of  $Ca_2Fe(CN)_6$ ; the extent of lowering is dependent on the valency of the added salt. The explanation of this effect as a consequence of "ionic saturation" is discussed.

A. J. M.

**Electrical conductivities of liquid mixtures of phenol-aniline, phenol-*p*-toluidine, and phenol-*m*-cresol.** O. R. HOWELL and H. G. B. ROBINSON (J.C.S., 1933, 1032—1037).—The conductivity-composition curves (at 50°) afford no evidence of the compounds which separate out on freezing.

D. R. D.

**Conductivity and dielectric constant of liquids in high-frequency fields.** M. WIEN (Physikal. Z., 1933, 34, 625—627).—According to the Debye-Falkenhagen theory the dielectric const. and equiv. conductivity should be related to the square root of concn. This is complicated by (1) potential effect, (2) potential dissociation effect with weak electrolytes, (3) time effect, (4) dipole effect.

A. J. M.

**Dependence of dispersion of conductivity on temperature.** H. GEEST (Physikal. Z., 1933, 34, 660—671).—The dependence of dispersion of conductivity on temp. has been studied with waves of 8 m. length, using a resonance method. Solutions of  $MgSO_4$ ,  $La_2(SO_4)_3$ , and  $Ca_2Fe(CN)_6$ , were examined at

0—50°. The results for the last substance do not agree with the Debye-Falkenhagen theory.

A. J. M.

**Calculation of the e.m.f. of an element from osmotic data.** A. VALENTINI (Boll. Chim. farm., 1933, 72, 565—566).—A method of calculation is given.

H. F. G.

**Junction potentials between glass and salts in fusion.** H. B. ELKINS and G. S. FORBES (J. Amer. Chem. Soc., 1933, 55, 3250—3260).—From the e.m.f. at 490° of the cell  $Ag|0.952 \text{ mol.-% } AgCl + NaCl|glass|KNO_3 + NaNO_3|glass|AgCl + XCl(c)|Ag$ , where X is an alkali metal, the "transference consts.," depending on the case with which X enters the glass, are  $K_{Li} > K_{Na} \gg K_K > K_{Rb} \gg K_{Cs} > K_{Ag}$ . High mobility is attributed to smallness of ion and the low val. of  $K_{Ag}$  to the great stability of AgCl. An equation derived on the assumption of a concn. cell with transference by cation alone accounts for the e.m.f. of cells of the type  $Ag|AgCl + LiCl(+KCl \dots)|glass|KNO_3 + NaNO_3|glass|AgCl + LiCl(+KCl \dots)|Ag$  at 490°. Reproducible results are also obtained with bromides in place of chlorides, except in the case of KBr. Vals. of the activity coeff. agree with data (A., 1931, 309, 800) for AgBr in LiBr and NaBr. AgCl in LiCl and KCl yields less ideal solutions than the bromides. The results of Günther-Schulze (A., 1913, ii, 192) and new data are consistent with the view that the rate of diffusion of Ag into glass from fused AgCl is controlled by the rate of exit of  $Na^+$  rather than by weak dissociation of AgCl.

J. G. A. G.

**Acetic acid-acetate buffers in potassium chloride and sodium chloride solutions using the quinhydrone electrode.** E. F. CHASE (J. Amer. Chem. Soc., 1933, 55, 3072—3075).—The classical dissociation const. of AcOH in 0.1*M*-NaOAc and either 0.9*M*-KCl or -NaCl increases almost linearly with concn. of mol. AcOH from 0.001 to 5*M*.

J. G. A. G.

**Acid-base titrations in alcohol-water mixtures. I. Relative  $p_H$  values for some buffer solutions in alcohol-water mixtures.** H. BAGGESGAARD-RASMUSSEN and F. REIMERS (Dansk Tidsskr. Farm., 1933, 7, 164—178).—Buffers of  $CH_2Cl-CO_2H$ ,  $HCO_2H$ , and AcOH with their Na salts have been studied electrometrically in 20—85% EtOH. Relative dissociation consts. of the acids are calc. and found to increase with increasing salt concn.

R. P. B.

**Electrometric titration of *dl*-2-thiohistidine.** G. M. RICHARDSON (Biochem. J., 1933, 27, 1036—1039).—The titration curve of 0.03*M*-*dl*-2-thiohistidine (I) against 0.10*N*-NaOH and -HCl leads to  $p_{K_1}$  1.84,  $p_{K_2}$  8.47, and  $p_{K_3}$  11.4 for the  $CO_2H$ ,  $NH_2$ , and SH groups, respectively. Basic dissociation of a cyclic N atom is not evident. (I) does not readily form a reversible oxidation-reduction system.

F. O. H.

**Potentials of ascorbic acid.** D. E. GREEN (Biochem. J., 1933, 27, 1044—1048).—The potentials of ascorbic acid (I), which are of a drifting and readily polarisable nature, are for given  $p_H$  vals. a function only of the reductant and not of the oxidant. The

mol. strength of the reductant is also not a determining factor. Potential measurements confirm the presence of (I) in lemon juice. The presence of the reduced form of (I) in natural sources is discussed.

F. O. H.

**Chemical behaviour of polonium.** O. ERBACHER and H. KÄDING (Z. physikal. Chem., 1933, 165, 427—432).—The bivalent cation present in solutions of Po in mineral acids is not  $\text{PoO}^{++}$ ; it is probably  $\text{Po}^{++}$ . Assuming it to be  $\text{Po}^{++}$ , the normal electrode potential of Po calc. from the discharge voltage is more positive than the potential of Ag, which is consistent with the electrochemical separation of Po on Ag.

R. C.

**Size of electrolytically generated gas bubbles.** B. KABANOV and A. FRUMKIN (Z. physikal. Chem., 1933, 165, 433—452).—Cohn and Neumann's theory of the dependence of bubble diameter,  $d$ , on the conditions of electrolysis (Z. Physik, 1923, 20, 54) is untenable. For Hg, Ag, and Pt electrodes in 0.001—1*N* solutions of  $\text{Na}_2\text{SO}_4$ , NaOH, and  $\text{H}_2\text{SO}_4$  the variation of  $d$  with the angle of contact  $\theta$  is represented by the same curve. Since  $\theta$  depends on the electrode potential,  $E$ , the latter determines  $d$ . For a Hg electrode the  $d$ - $E$  curve is similar in form to the electrocapillary curve and the max. have approx. the same position. The above theory agrees with Cohn's experimental data. The equilibrium state of the bubble prior to detachment is determined solely by the surface tension, the hydrostatic pressure, and the gas pressure.

R. C.

**Hydrogen overvoltage of lead and lead-antimony alloys.** I, II. Y. KATO (J. Electrochem. Soc., Japan, 1932, 120—124, 161—167).—I. The H overvoltage of a Pb-Sb (1—10%) alloy varies from the beginning of the passage of the current; it is unaffected by the rate of cooling of the alloy. Antimonised Sb gives very low vals.

II. The H overvoltage at the same c.d. varies at first with the time, and then approaches a definite val. The H overvoltage on Pb is high for a smooth, and low for a rough, surface. Single-crystal Pb gives high vals., even when the surface is etched.

CH. ABS.

**Anodic behaviour of iron.** K. GEORGI (Z. Elektrochem., 1933, 39, 745—749; cf. this vol., 468).—C.d.-potential curves for the dissolution of Fe anodes in  $N\text{-H}_3\text{PO}_4$ ,  $\text{-H}_2\text{SO}_4$ ,  $\text{-HCl}$ ,  $\text{-HClO}_4$ ,  $\text{-CCl}_3\text{-CO}_2\text{H}$ ,  $\text{-NaBr}$ ,  $\text{-NaCl}$ ,  $\text{-NaClO}_4$ ,  $\text{-Na}_2\text{SO}_4$ ,  $\text{-CCl}_3\text{-CO}_2\text{Na}$ , and in 0.5*M*-Na phosphate show that  $\text{Fe}^{++}$  is formed without appreciable polarisation in solutions of the free acids, NaCl, and NaBr. For  $\text{NaClO}_4$  the c.d. rises rapidly at +1.4 volts, hydroxide being formed and no  $\text{O}_2$  evolved. For the other salts the rise occurs at >1.7 volts, with evolution of  $\text{O}_2$ . The change of potential with time at different  $p_{\text{H}}$  has been investigated. The mechanism of dissolution suggested is  $\text{Fe} + 2\text{H}^+ \rightarrow \text{FeH}_2^{++}$ ,  $\text{FeH}_2^{++} - 2\text{e}^- \rightarrow \text{Fe}^{++} + 2\text{H}^+$ . The abnormal behaviour of  $\text{ClO}_4^-$  is due to its small tendency to form complex ions. The behaviour of Fe in general resembles that of Co and Ni. H. J. E.

**Passivity of tantalum in non-aqueous solvents.** B. Formamide, acetone, methyl ethyl ketone, pyridine, acetic acid, and sulphuric acid. P. O.

SCHUPP (Z. Elektrochem., 1933, 39, 731—735; cf. A., 1932, 1209).—The thickness of the oxide layer on a Ta anode, rendered passive by electrolysis of  $\text{Ca}(\text{NO}_3)_2$  in the above solvents, is proportional to the voltage and independent of the solvent. At a given voltage the val. is the same as in  $\text{H}_2\text{O}$ , when aq.  $\text{CaCl}_2$  is used to measure the capacity and thickness of the oxide layer. Using 10%  $\text{H}_2\text{SO}_4$  for the capacity measurements the layer thickness in non-aq. solvents is approx. 10% < for Ta rendered passive in  $\text{H}_2\text{O}$ .

H. J. E.

**Reaction kinetics of coupled oscillators.** H. PELZER (Z. Elektrochem., 1933, 39, 608—611).—Theoretical. The rate of the homogeneous unimol. decomp. of a chain-like mol. is independent of the chain length. The rate of breaking of a particular linking is determined only by the strength of binding and the neighbouring mols.

H. J. E.

**Influences of electrical and magnetic fields on "spin" in gaseous detonations.** W. A. BONE (Nature, 1933, 132, 348).—A preliminary announcement of results.

L. S. T.

**Method of investigating gas reactions in absence of wall effects.** A. REIS and E. GLÜCKAUF (Z. Elektrochem., 1933, 39, 607—608).—A stream of the reacting gas is mixed with a heated inert gas, and the mixture passed through a heated porous tube. The latter is surrounded by inert gas under pressure, inward penetration of which prevents contact of the reacting gas with the tube wall. The decomp. of  $\text{HCO}_2\text{H}$ , using  $\text{H}_2$  as the inert gas, is described.

H. J. E.

**Kinetics of the hydrogen-oxygen low-pressure explosion.** A. A. FROST and H. N. ALYEA (J. Amer. Chem. Soc., 1933, 55, 3227—3233).—Upper and lower limits of the thermal explosion of  $\text{H}_2$  (0.04—0.9 mol. fraction)- $\text{O}_2$  mixtures were determined at 480—540° in a KCl-coated Pyrex vessel and the effect of  $\text{N}_2$  was investigated. The results for both limits are expressed by a kinetic equation including terms for (a) branching of reaction chains by collisions between a carrier and  $\text{O}_2$ ,  $E=24,200$ , (b) breaking of chains at the wall governed by diffusion, apparent  $E=13,500$ , and (c) breaking of chains in gas phase by triple collisions,  $E < 4000$  g.-cal.

J. G. A. G.

**Influence of pressure on the spontaneous ignition of inflammable gas-air mixtures.** I. Butane-air mixtures. D. T. A. TOWNEND and M. R. MANDLEBAR (Proc. Roy. Soc., 1933, A, 141, 484—493).—The influence of pressure on the spontaneous ignition of various  $\text{C}_4\text{H}_{10}$ -air mixtures at pressures up to 15 atm. has been studied. At 1 atm. the ignition points fell from >600° to about 550° with increase in the  $\text{C}_4\text{H}_{10}$  content of the mixtures, and at 1.5 atm. from 560° to 480°; at 1.75 atm., however, a fall of 130—140° took place for mixtures of  $\text{C}_4\text{H}_{10}$  content > 3.5%. A similar sharp fall was observed with all other mixtures, the crit. transition pressure depending on the composition of the mixture. The ignition points lie in two groups, the one, for determinations below 3 atm., at >450°, and the other, for determinations above 3 atm., at <370°. The effect of

PbEt<sub>4</sub> in raising ignition temp is much greater at the crit. transition pressure than at atm. pressure.

L. L. B.

**Kinetics of dissociation of typical hydrocarbon vapours.** R. N. PEASE and J. M. MORTON (J. Amer. Chem. Soc., 1933, 55, 3190—3200).—At 550—630°, the order of stability is *o*-C<sub>6</sub>H<sub>4</sub>Me<sub>2</sub> > PhMe > C<sub>6</sub>H<sub>6</sub> > *m*-C<sub>6</sub>H<sub>4</sub>Me<sub>2</sub> > PhEt > cyclohexane > Δ<sup>β</sup>-pentene > ethylcyclohexane > *n*-C<sub>7</sub>H<sub>16</sub>. The dissociations at 525—605° of *n*-C<sub>7</sub>H<sub>16</sub>, PhEt, Δ<sup>β</sup>-pentene, and cyclohexane are pseudo-unimol. homogeneous gas reactions, the first step in the last being the formation of methylcyclopentane, whilst PhEt affords H<sub>2</sub> and styrene. Velocity coeffs. and energies of activation are calc., and the stability of the C<sub>6</sub>H<sub>6</sub> ring as compared with the cycloparaffins is emphasised.

J. G. A. G.

**Thermal decomposition of methyl azide. A homogeneous unimolecular reaction.** J. A. LEERMAKERS (J. Amer. Chem. Soc., 1933, 55, 3098—3105; cf. A., 1929, 1018).—MeN<sub>3</sub>, at 200—240° and pressures between 0.07 and 46.6 cm., decomposes into N<sub>2</sub>, HN<sub>3</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, NH<sub>3</sub>, and (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub> in a homogeneous unimol. reaction. With initial pressures < 10 cm., the velocity coeff. falls below  $k=3.02 \times 10^{15} e^{43,500/RT}$ . The theoretical expression relating *k* and pressure accords with the data when a mol. diameter  $5 \times 10^{-8}$  cm. and 13 classical oscillators are assumed.

J. G. A. G.

**Thermal decomposition of 2:4:6-trinitro-1:3:5-triazobenzene.** S. Z. ROGINSKI and C. C. ANDRÉEV (J. Chim. phys., 1933, 30, 487—492).—Analysis of the kinetics of decomp. of 2:4:6-trinitro-1:3:5-triazobenzene at low temp. (35—50°) shows that the velocity of reaction is proportional to the 2/3 power of the mass of the substance. The calc. heat of activation is 32,300 g.-cal., which is the lowest val. recorded for an explosive.

E. S. H.

**Kinetic study of action of chlorine water on silver nitrate.** (MLLE.) M. L. JOSSEN (Compt. rend., 1933, 197, 449—450).—The interaction of AgNO<sub>3</sub> and aq. Cl<sub>2</sub> proceeds in two stages: (1), instantaneous, Cl<sub>2</sub> + H<sub>2</sub>O = HCl + HOCl, with pptn. of AgCl, and (2), more slowly, 3HOCl = HClO<sub>3</sub> + 2HCl, also with pptn. of AgCl. In absence of excess of AgNO<sub>3</sub>, HOCl is relatively stable. Dilution retards, whilst a higher temp. accelerates, disappearance of HOCl (cf. A., 1899, ii, 736).

C. A. S.

**Autoxidation. IX. Kinetics of sulphite autoxidation according to theory of radical chains.** P. GOLDFINGER and H. D. GRAF VON SCHWEINITZ (Z. physikal. Chem., 1933, B, 22, 241—256; cf. this vol., 911).—The kinetics of the autoxidation of sulphite by Cu<sup>II</sup> worked out by the radical chain theory, utilising the radicals OH and HSO<sub>3</sub>, and according to the method of stationary concns., agree with the observed velocity and heat effect data. A chain-breaking reaction, of the first order in respect of one radical, is postulated, and the reconversion of Cu<sup>I</sup> into Cu<sup>II</sup> is assumed to depend on the action of O<sub>2</sub> on CuSO<sub>3</sub>'. These assumptions lead to a linear relation between the rate of disappearance of O<sub>2</sub> and (SO<sub>3</sub>''), (O<sub>2</sub>), and the total Cu concn. The absence of proportionality to (O<sub>2</sub>) when an inhibitor is present is also explained.

R. C.

**Neutral salt action in the reaction between formic acid and iodine.** A. VON KISS and A. URMÁNCZY (Z. anorg. Chem., 1933, 213, 353—364).—The reaction velocity was measured at 25° in the dark in presence of various neutral salts. The primary and secondary salt action and the action of the medium were separated (cf. Brønsted, A., 1925, ii, 681). For the effect of the medium the log of the velocity coeff. was proportional to the salt concn.

H. J. E.

**Oxidation of cystine in non-aqueous media. II. Hydration of acetonitrile and acetic anhydride by a non-aqueous titration method.** T. F. LAVINE and G. TOENNIES (J. Biol. Chem., 1933, 101, 727—734; cf. this vol., 598).—The two colour changes of thymol-blue distinguish between strong and weak acids in non-aq. titrations with NaOMe as base and CHCl<sub>3</sub> as solvent. The titration is used to study the hydrolysis of MeCN and the rate of dehydration by Ac<sub>2</sub>O as applied to the prep. of cystine perchlorate in MeCN.

A. L.

**Combustion of graphite in Osram filaments in a stream of gas.** V. SIHVONEN (Ann. Acad. Sci. Fennicæ, 1933, A, 38, No. 2, 3—34).—The action of streaming H<sub>2</sub>O vapour, CO<sub>2</sub>, and O<sub>2</sub> at low pressures (10<sup>-4</sup> to 10<sup>-1</sup> mm.) on C filaments at various temp. has been studied. In H<sub>2</sub>O vapour CO is formed; part of this is then oxidised by the H<sub>2</sub>O. Diminished production of CO as the temp. is raised is due to desorption of H<sub>2</sub>O. In CO<sub>2</sub>, CO is formed only above 1400°. At 800—1400° O<sub>2</sub> forms CO<sub>2</sub> + 2CO at an unpoisoned surface, whereas if the filament is poisoned by CO, this gas is the sole product above 900°. Velocities and thermal effects of certain of the processes have been determined.

F. L. U.

**Atmospheric corrosion of magnesium. L.** WHITBY (Trans. Faraday Soc., 1933, 29, 844—853).—Wt.-increment-time curves are given for Mg exposed to outdoor and indoor atm. during 200 and 400 days, respectively. The rate of corrosion increases with R.H. Outdoors a loss of wt. always follows rain, owing to removal of MgSO<sub>4</sub>, which is formed to a considerable extent. Both indoors and outdoors MgCO<sub>3</sub> predominates in the corrosion product. No indication of protective film formation was observed.

F. L. U.

**Dissolution of magnesium in aqueous salt solutions. II.** L. WHITBY (Trans. Faraday Soc., 1933, 29, 853—861; cf. this vol., 233).—Dissolution-time curves for different specimens of Mg in aq. NaCl and Na<sub>2</sub>SO<sub>4</sub> are given. There is no evidence that inclusions of Mg<sub>3</sub>N<sub>2</sub> or MgO act either as cathodes or as nuclei for anodic attack in NaCl solution. The influence of variations in metallic impurities on the rate of dissolution is marked in 0.1*N*-NaCl, but small in 0.002*N*-NaCl or in 0.1*N*-Na<sub>2</sub>SO<sub>4</sub>. The mechanism of attack is discussed.

F. L. U.

**Rusting of iron with excess of oxygen.** G. SCHIKORR.—See B., 1933, 750.

**Kinetics of the transformation of austenite.** H. LANGE and F. WEVER.—See B., 1933, 708.

**Corrosion passivity. III. Changes in the natural oxide film on iron during corrosion.** W. MACHU.—See B., 1933, 709.

**Kinetics of the reaction of the hydrogen peroxide decomposing property of soil.** K. SCHARRE (Z. Pflanz. Düng., 1933, 31, A, 27—36).—Decomp. of  $H_2O_2$  by soils of varied origin and composition in no case corresponded with a unimol. reaction throughout its course, although certain sections of the reaction curves approximated closely with that of a reaction of this type. Deviations from the course of a unimol. reaction were greater in acid than in alkaline soils, and may be ascribed in part to the presence or absence of catalysts and to differences in the effective reactive surfaces in soils of different structure. A. G. P.

**Catalysis of Eder's reaction by cobalt compounds.** G. H. CARTLEDGE and T. G. DJANG (J. Amer. Chem. Soc., 1933, 55, 3214—3221).—At room temp., the reduction of  $HgCl_2$  to  $Hg_2Cl_2$  by oxalates is strongly catalysed in the light and in the dark by  $Co(C_2O_4)_3$ ;  $CoSO_4$  at concn.  $> 0.0002M$  accelerates the dark catalysis, whilst  $O_2$  retards all of these reactions. However,  $CoSO_4$  alone, in presence of  $O_2$ , produces only traces of  $Hg_2Cl_2$ , whilst oxidation by  $H_2O_2$  of  $Fe^{2+}$  instead of  $Co^{2+}$  is much more effective in inducing Eder's reaction. At  $100^\circ$  in  $H_2C_2O_4$  solution, the yield of  $Hg_2Cl_2$  is parallel with the stability of the catalyst:  $Co(C_2O_4)_3 > MnO_4 > Mn(C_2O_4)_3$ , and the life of the catalyst is decreased by rise of temp. and increase of acidity.  $Fe(C_2O_4)_3$  and  $Co(C_2O_4)_3$  accelerate the oxidation of  $H_2C_2O_4$  by dil.  $KMnO_4$ .  $Co(C_2O_4)_3$  and  $Mn(C_2O_4)_3$  are therefore significant in the enhanced oxidising activity of  $HgCl_2$ . J. G. A. G.

**Effect of hydrogen-ion concentration on the rate of oxidation of solutions of ferrous citrate.** J. M. BRYAN (Trans. Faraday Soc., 1933, 29, 830—833; cf. A., 1931, 1133).—Oxidation (by air) is rapid at  $p_H$  5.35 and 5.71 and relatively slow at  $p_H$  3.31. Secondary oxidation of the citric acid is a factor of considerable importance at the less acid end of the  $p_H$  range. The experiments were performed at  $25^\circ$ . F. L. U.

**Oxidation of thiol compounds by hydrogen peroxide. II. Catalysis of oxidation of cysteine by thiocarbamides and thiolglyoxalines.** N. W. PIRIE (Biochem. J., 1933, 27, 1181—1188).— $CS(NH_2)_2$  (I) catalyses the oxidation of cysteine (II) to cystine (III) by  $H_2O_2$  in acid solution; the kinetics of the reaction resemble those using Cu as catalyst (A., 1932, 27). Dithioformamidine has no action on (III), but oxidises (II) (under suitable conditions) to (probably)  $OH \cdot S \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$ , which is then reduced by (II) to (III). *N*-Allyl- and -phenyl-thiocarbamides, ergothioneine (IV), *dl*-2-thiolhistidine, and 2-thiolglyoxaline are almost as active as (I); the effects of other thiocarbamides are investigated. The catalytic effect of a mixture of Cu and (I) is the sum of their independent effects for slow rates of oxidation only; with larger amounts of the catalysts, one does not increase the rate due to the other. Similar results are found for  $Fe + (I)$  and metal + (IV). A reaction mechanism is given. Glutathione behaves similarly to (II). (I) appears to have no effect on the aerobic oxidation of (II) or methylene-blue at  $p_H$  7.6. H. B.

**Theory of heterogeneous catalysis.** L. V. PISARSHEVSKI (Bull. Acad. Sci. U.R.S.S., 1933, 7, 571—588).—The action of metallic catalysts is ascribed to the facility with which their free electrons react with those of the substrate; thus, Pt is assumed to catalyse hydrogenation by causing dissociation of H into proton and electron. R. T.

**Catalyst activity.** E. ROSENKRANZ (Chim. et Ind., 1933, Spec. no., 755—756).—A catalyst prepared by a reaction of the type solid I  $\rightarrow$  solid II + gas at a temp.  $>$  that at which it is to be used is to be considered as having undergone both decomp. and stabilisation (from the nascent state). It is deduced that for every catalyst there is a time of treatment necessary for max. activity, stabilisation being detrimental. Examples are ZnO prepared by the ignition of  $ZnC_2O_4$  for the decomp. of MeOH and  $Fe_2O_3$  prepared by the heating of  $Fe(OH)_3$  for the decomp. of  $H_2O_2$ . C. I.

**Conversion of ortho- into para-hydrogen over promoted iron synthetic ammonia catalysts at  $-190^\circ$ .** R. W. HARKNESS and P. H. EMMETT (J. Amer. Chem. Soc., 1933, 55, 3496—3497).—The efficiency of the catalyst, outgassed at  $450^\circ$ , is greatly diminished by cooling in  $H_2$  instead of He, and it appears that the activated adsorption of  $H_2$  at  $100$ — $450^\circ$  is primarily surface adsorption and not dissolution in the Fe. Exposure of the catalyst to  $O_2$  between room temp. and  $450^\circ$  eliminates the high-temp. activity towards ortho-para conversion, but only slightly impairs the activity at  $-190^\circ$ . J. G. A. G.

**Present position of the theory of ammonia catalysis.** C. KRÖGER (Z. Elektrochem., 1933, 39, 670—671).—A criticism (cf. this vol., 681).

E. S. H.

**Thermodynamic measure of activity of catalysts.** P. DOLCH (Z. Elektrochem., 1933, 39, 602—607).—The application of the reaction isochore in representing experimental data for the reactions  $CO + H_2O = CO_2 + H_2$  and  $2SO_2 + O_2 = 2SO_3$  is discussed. H. J. E.

**Catalytic reduction of carbon dioxide by hydrogen.** H. KOCH and H. KÜSTER.—See B., 1933, 737.

**Chemical inertia and heterogeneous catalysis.** M. LEMARCHANDS (Chim. et Ind., 1933, Spec. no., 747—754).—Many metals are attacked only very slowly by  $Cl_2$  or Br at low temp. Pure CaO at low temp. is only very slowly acted on by  $H_2O$  vapour or  $Cl_2$  and Na, Mg, and Zn by  $SO_2$  or  $CO_2$ . These phenomena, which are unexpected from the thermal balances, are described as instances of chemical inertia. The effect is due to adsorption which, in consequence of the surface reaction, produces a temp. at which further adsorption is impossible if the film is impermeable. In the case of  $Cl_2$  reactions the elements capable of giving volatile chlorides, Hg, Al, Sn, S, P, As, Sb, are attacked at low temp. Those with less volatile chlorides are not. (It is assumed that the solids tested have been deprived of the normally present film of adsorbed air.) Deductions from this theory enable the properties necessary for a catalyst of a gaseous reaction to be predicted. It must be capable of effective adsorption,

and it should not itself have an exothermic reaction with one of the gaseous components. Thus catalysts for  $\text{NH}_3$  syntheses are metals which do not readily form nitrides. In the Deacon  $\text{Cl}_2$  process the val. of  $\text{CuCl}_2$  lies in the fact that it has no action on  $\text{HCl}$ . The oxychloride is ineffective. "Chemical" explanations of this catalysis are unsound. C. I.

**Formation of hydrogen peroxide in catalytic dehydrogenation.** T. F. MACRAE (Biochem. J., 1933, 27, 1248—1252).—With Pd-black as catalyst, the combination of  $\text{H}_2$  and  $\text{O}_2$  and the aerobic dehydrogenation of  $\text{MeOH}$  and  $\text{EtOH}$  yield, as an intermediate product,  $\text{H}_2\text{O}_2$ , which is detectable by  $\text{Ce}(\text{OH})_3$  (A., 1931, 390). Support is thus afforded to Wieland's theory of dehydrogenation. F. O. H.

**Topochemical replacements. VII. Compact disperse materials.** H. W. KOHLSCHÜTTER and H. SIECKE (Z. Elektrochem., 1933, 39, 617—623; cf. this vol., 919).—Pseudomorphic  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  was prepared from  $\text{Fe}_2(\text{SO}_4)_3$  and aq.  $\text{NH}_3$ . Its catalytic activity in the decomp. of  $\text{H}_2\text{O}_2$  decreases with increasing  $\text{H}_2\text{O}$  content, depending also on the prep. and heat- and mechanical treatment of the specimen. The resemblance to  $3\text{Cu}(\text{OH})_2 \cdot \text{Cu}(\text{NO}_3)_2$  is discussed.

**Kjeldahl reaction and carbon disulphide.** J. MILBAUER and J. DOŠKAŘ (Chim. et Ind., 1933, Spec. no., 782—783).— $\text{CS}_2$  vapour commences to be oxidised by  $\text{H}_2\text{SO}_4$  at  $180^\circ$  or in presence of finely-divided Pd at  $105^\circ$ . Positive catalysts, in order of decreasing efficacy, are Pd, Se, Pt,  $\text{CuSO}_4$ ,  $\text{HgSO}_4$ .

**Catalytic properties and structure of metal films. I. Sputtered platinum.** G. I. FINCH, C. A. MURISON, N. STUART, and G. P. THOMSON (Proc. Roy. Soc., 1933, A, 141, 414—434).—The method of prep. of sputtered Pt films and their catalytic properties have been correlated with the structure as determined by electron diffraction.

**Distribution of arsenic in contact systems.** S. BYCHOVSKI.—See B., 1933, 746.

**Influence of admixtures of sodium sulphate to magnesium sulphate carriers on the activity of platinum catalyst in the reaction  $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$ .** N. S. ARTAMONOV.—See B., 1933, 746.

**Determination of the activity of catalysts which accelerate the synthesis of benzene from carbon monoxide and hydrogen at ordinary pressure.** S. WATANABE and K. MORIKAWA.—See B., 1933, 738.

**Catalytic oxidation of organic compounds in the vapour state. I. Toluene, its derivatives and homologues. II. Various compounds.** G. CHARLOT (Bull. Soc. chim., 1933, [iv], 53, 572—577, 577—581).—See this vol., 680. Data relating to  $\text{PhMe}$ , xylenes, *p*-cymene, cumene, chloro- and nitrotoluenes,  $\text{CH}_2\text{Ph}_2$ ,  $\text{C}_6\text{H}_6$ ,  $\text{C}_{10}\text{H}_8$ ,  $\text{EtOH}$ ,  $\text{BzOH}$ ,  $\text{C}_7\text{H}_{16}$ , and benzoic acid are given.

**Spongy zinc deposits obtained by electrolysis of aqueous solutions of zinc sulphate.** W. S. SEBBORN (Trans. Faraday Soc., 1933, 29, 825—829).—

The relations between concn. of solution, c.d., and character of deposit have been determined. Spongy Zn contains 15—25% of  $\text{ZnO}$  and  $\text{Zn}(\text{OH})_2$ . Coherent deposits are formed on the lower surface of a horizontal electrode under conditions which would yield a spongy deposit with a vertical electrode.

F. L. U.  
**Electrolysis of zinc sulphate solutions.** P. GUARESCHI.—See B., 1933, 751.

**Electrolytic refining of copper using complex salt of cuprous chloride. XI. Behaviour of bismuth.** N. KAMEYAMA and S. MAKISHIMA.—See B., 1933, 750.

**Theory of chromium plating.** E. LIEBREICH (Z. Elektrochem., 1933, 39, 628—629).—The effect of added acids on the current-potential curve for the electrolysis of pure  $\text{H}_2\text{CrO}_4$  is to cause two new breaks. At very high concn.  $\text{HClO}_4$  and  $\text{H}_3\text{PO}_4$  cause reduction;  $\text{H}_3\text{BO}_3$  does not. The formation of films on the electrodes is discussed.

H. J. E.  
**Electrodeposition of palladium.** R. H. ATKINSON and A. R. RAPER.—See B., 1933, 710.

**Oxidation of graphite by electric discharges.** V. SHIVONEN (Ann. Acad. Sci. Fennicæ, 1933, A, 38, No. 3, 3—22; cf. this vol., 1020).—With a d.c. discharge at high potential between plates of graphite and Pt in  $\text{CO}_2$  the reactions  $\text{CO}_2 + \text{Pt}_x \rightleftharpoons \text{CO} + \text{Pt}_x\text{O}$  and  $\text{CO}_2 + \text{C}_x \rightleftharpoons 2\text{CO} + \text{C}_{x-1}$  occur. With a.c. discharge in  $\text{O}_2$  the cathodic component is alone effective in promoting oxidation of C. Both  $\text{CO}_2$  and  $\text{CO}$  are formed, the proportion of the latter increasing with decreasing pressure of  $\text{O}_2$ . A very small a.c. at high potential between widely separated electrodes gives rise to more  $\text{CO}_2$  and  $\text{CO}$  than corresponds with the current, in consequence of the intense ionisation of the gas.

F. L. U.  
**Behaviour of dichlorodifluoromethane and of chlorotrifluoromethane in the electric discharge.** N. V. THORNTON and A. B. BURG [with H. I. SCHLESINGER] (J. Amer. Chem. Soc., 1933, 55, 3177—3182).— $\text{CCl}_2\text{F}_2$  attacks metals slowly at high temp. and at the same time reacts with the glass or  $\text{SiO}_2$  containers giving  $\text{SiF}_4$ ,  $\text{CO}_2$ , and  $\text{CO}$ ; in the absence of the metal no reaction occurs. In the high-tension electric discharge,  $\text{CCl}_2\text{F}_2$  decomposes partly into  $\text{Cl}_2$ ,  $\text{CClF}_3$ , and smaller quantities of  $\text{CF}_4$ ,  $\text{C}_2\text{Cl}_2\text{F}_4$ ,  $\text{C}_2\text{F}_4$ , and less volatile substances.  $\text{CClF}_3$  under similar conditions yields  $\text{CF}_4$ ,  $\text{Cl}_2$ ,  $\text{CCl}_2\text{F}_2$ , and small quantities of solid. The v.p. of  $\text{CCl}_2\text{F}_2$  is given by  $\log_{10} p = 7.385 - 1105/T$ , from which the b.p. is  $-27.8^\circ$ ; for  $\text{C}_2\text{Cl}_2\text{F}_4$ ,  $\log p = 7.568 - 1300/T$  and b.p.  $4.1^\circ$ , and for  $\text{CClF}_3$ ,  $\log p = 7.347 - 857.3/T$  and b.p.  $-81.1^\circ$ . Latent heats and Trouton's consts. are calc.

J. G. A. G.  
**Formation of silver in the photographic layer under the influence of X-rays.** P. GÜNTHER and H. TITTEL (Z. Elektrochem., 1933, 39, 646—655).—At wave-lengths 0.245, 0.63, 1.09, and 1.54 Å., 920, 363, 210, 148 atoms of Ag were liberated per absorbed quantum, agreeing approx. with Eggert and Noddack's vals. (A., 1927, 1154). The Ag was determined potentiometrically. The secondary electron energy

was calc., and at each wave-length approx. 1000 kg.-cal. was shown to be necessary to form 1 mol. Ag.

H. J. E.

**Oxidation of graphite by means of X-rays.** V. SIHVONEN (Ann. Acad. Sci. Fennicæ, 1933, A, 38, No. 4, 3—13).—In  $\text{CO}_2$  at low pressure X-rays promote the same reactions as does a high-potential d.c. discharge (cf. this vol., 1019), whether the graphite plate is directly exposed to the radiation or not. No  $\text{O}_2$  is formed. In  $\text{O}_2$  the product is at first  $\text{CO}_2 + 2\text{CO}$ , the proportion of the latter increasing later to  $\text{CO}_2 + \text{CO}$ . At extremely low pressures oxidation occurs only when the C plate is directly irradiated. F. L. U.

**Chemical reactions brought about by X-rays and their determination.** N. WATERMAN and H. LIMBURG (Biochem. Z., 1933, 263, 400—409).—An electrometric method for quant. observation of the changes in a reaction mixture on irradiation has been used in the reduction of benzoquinone, methylene-blue, and cysteine. P. W. C.

**Action of  $\alpha$ -rays from polonium, X-rays, and ultra-violet rays on nitrogen iodide and other explosives.** H. MURAOUR (Bull. Soc. chim., 1933, [iv], 53, 612—613).—None of the radiations has any effect. A. S. C. L.

**Simple type of isotopic reaction.** G. N. LEWIS (J. Amer. Chem. Soc., 1933, 55, 3502—3503).—The isotopic composition of  $\text{H}_2\text{O}$  is determined by means of the rapid reactions  $\text{H}^1\text{H}^2\text{O} + \text{NH}^1\text{H}^1\text{H}^1 = \text{H}^1\text{H}^1\text{O} + \text{NH}^1\text{H}^1\text{H}^2$  and  $\text{H}_2\text{O}^{18} + \text{SO}^{16}\text{O}^{16} = \text{H}_2\text{O}^{16} + \text{SO}^{16}\text{O}^{18}$  and determination of  $d$  after the removal of the more volatile products. J. G. A. G.

**Reaction between atomic hydrogen and carbon tetrachloride.** H. F. SMYSER and H. M. SMALLWOOD (J. Amer. Chem. Soc., 1933, 55, 3498—3499).—A greenish-blue luminescence accompanies the interaction of Wood's at. H with  $\text{CCl}_4$ . The products are a solid containing 55% Cl, HCl, and small quantities of an explosive volatile substance. J. G. A. G.

**Formation of metallic hydrides by atomic hydrogen.** E. PIETSCH [with F. SEUFERLING, W. ROMAN, and H. LEHL] (Z. Elektrochem., 1933, 39, 577—586; cf. A., 1931, 1019, 1020, 1379, 1380).—Hydrides of Ag, Cu, Au, Be, Ga, In, and Ta were formed by the action of at. H on the solid element. Products were contaminated with unattacked element. Reaction between In vapour and H gave a blue luminescence. The In line 4511 Å. ( $2p_1-2s$ ) was prominent, particularly on the glass walls, the excitation energy coming from the recombination of H atoms. This vapour reaction also yielded In hydride. H. J. E.

**Solubility of silver thiocyanate in potassium thiocyanate.** K. SCHERINGA (Chem. Weekblad, 1933, 30, 598).— $\text{AgCNS} \cdot 3\text{KCNS}$  is obtained by dissolving  $\text{AgCNS}$  in a saturated solution of  $\text{KCNS}$ . S. C.

**Absorption of silver by glasses.** I. WESTERMANN (Z. tech. Physik, 1932, 13, 617; Chem. Zentr., 1933, i, 1263).—Ca—Na glass in contact with  $\text{AgNO}_3$  (but not  $\text{AgBr}$ ) at  $380^\circ$  absorbs Ag as  $\text{Ag}_2\text{O}$  arising from decomp. of the  $\text{AgNO}_3$ . A. A. E.

**Preparation of colloidal gold solution.** T. L. RAMSEY and H. J. EILMANN (J. Lab. Clin. Med., 1932, 18, 298—300). CH. ABS.

**Action of alkali carbonates on lime-water and solutions of calcium salts, and the so-called Loiseau's lime.** I. O. SPENGLER and G. DORFMÜLLER (Z. Ver. deut. Zucker-Ind., 1933, 83, 562—581).—A microscopical study has been made of successive stages in the pptn. of aq.  $\text{CaO}$  and  $\text{Ca}(\text{OAc})_2$  by  $\text{Na}_2\text{CO}_3$  at various concns. and temp. The primary product is highly hydrated  $\text{CaCO}_3$  which is usually pptd. in a gelatinous form and is transformed into spherules and crystals of  $\text{CaCO}_3$  or its hydrates or double compound with  $\text{Na}_2\text{CO}_3$  (cf. Adler, B., 1897, 767; Hume and Topley, A., 1927, 12, 526; Krauss and Schriever, A., 1930, 718). J. H. L.

**Synthesis of calcium silicates.** VII. S. NAGAI and K. MURAKAMI (J. Soc. Chem. Ind. Japan, 1933, 36, 458—460B).—Mixtures of  $3\text{CaO} \cdot \text{SiO}_2$  and  $2\text{CaO} \cdot \text{SiO}_2$  were prepared by heating  $\text{CaCO}_3$  and  $\text{SiO}_2$  together in various proportions, and the compressive strength was tested after mixing with  $\text{H}_2\text{O}$ , storing for 1 day, and immersing in  $\text{H}_2\text{O}$  for several days. Pure  $2\text{CaO} \cdot \text{SiO}_2$  collapsed when immersed in  $\text{H}_2\text{O}$ , and pure  $3\text{CaO} \cdot \text{SiO}_2$  was much weaker than the mixed di- and tri-silicates. A. G.

**Chemical constitution of hydrated calcium aluminates.** P. ERCULISSE and S. SAGGIR (Chim. et Ind., 1933, Spec. no., 806—819).—The composition of hydrated Ca aluminates is best studied by phase-rule methods, as chemical analysis alone cannot differentiate between compounds and solid solutions or mechanical mixtures. Known quantities of the solid constituents are placed in contact with  $\text{H}_2\text{O}$ ; when equilibrium is attained, a portion of the liquid phase is removed for analysis and replaced by pure  $\text{H}_2\text{O}$ , and the process repeated. The systems  $\text{CaO}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$  and  $\text{CaO}-\text{Fe}_2\text{O}_3-\text{H}_2\text{O}$  were studied in this manner. In the first it appears probable that solid solutions are formed. In the second a solid phase,  $\text{Fe}_2\text{O}_3 \cdot \text{CaO} \cdot \text{aq.}$ , is believed to exist during the gradual removal of solid  $\text{CaO}$  by successive additions of  $\text{H}_2\text{O}$ . The only compounds of which there is evidence in the first system are  $\text{CaO} \cdot 4\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  and  $\text{Al}_2\text{O}_3 \cdot 3(\text{or } 4)\text{CaO} \cdot x\text{H}_2\text{O}$ , the first forming solid solutions with  $\text{Al}_2\text{O}_3$  or with the second. This conclusion is derived from the method of separate tests, not successive as above. The tetra-aluminate is analogous to borax. C. I.

**Substitution of O'' by F' in aluminates and silicates.** E. KORDS (Fortschr. Min. Kryst. Petr., 1932, 17, 432—433; Chem. Zentr., 1933, i, 1264).—Fusion of  $\text{SiO}_2$  with  $\text{NaF}$  and  $\text{LiF}$  does not lead to compound formation.  $\text{NaF}$  and  $\text{Al}_2\text{O}_3$  afford needles of undetermined composition. Substitution of  $\text{MgO}$  in  $\text{MgO} \cdot \text{Al}_2\text{O}_3$  by  $\text{LiF}$  affords crystals of the spinel type, m.p.  $> 1400^\circ$ ,  $d$  3.6.  $\text{CaF}_2$  and  $\text{Al}_2\text{O}_3$  afford at least one cryst. compound. A. A. E.

**Thermal decomposition of aluminium and ferric hydroxides. Reactions in the solid.** H. SCHWIERSCH (Chem. Erde, 1933, 8, 252—315).—Isobaric and isothermal dehydration curves were determined for  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$  [diaspore (I) and böhmite (II)] and  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  [goethite (III) and lepidocrocite (IV)]

and also for gibbsite and limonite, and the changes were followed by optical and X-ray examinations. There is no intermediate stage with the formation of a hemihydrate. The aggregate of crystals of the resulting oxide has a definite orientation with respect to the original crystal. (I) and (II) give similar results, but (III) and (IV) show marked differences in their behaviour.

L. J. S.

**Preparation of thallos hydroxide.** R. PHILLIPS and W. W. HARTMAN (J. Amer. Chem. Soc., 1933, 55, 3065—3066).—TiOH is prepared by passing a mixture of steam and air through a tube containing "mossy" Ti.

J. G. A. G.

**Combustion of graphite.** V. SIHVONEN (Acta Chem. Fennica, 1932, B, 5, No. 6/7, 1—6; cf. A., 1930, 1379).—A summary of work previously published.

F. L. U.

**Calcium cyanamide. II. Ammonolysis of dicyanodiamide.** Y. KATO, K. SUGINO, K. KOIDZUMI, and E. MITSUSHIMA.—See B., 1933, 748.

**Combination between zirconyl bromide and alkali bromides.** E. CHAUVENET and (MLLE.) J. BOULANGER (Compt. rend., 1933, 197, 410—411; cf. A., 1920, ii, 757).—By thermochemical analysis of mixed solutions of the constituents the existence of the following is indicated: NaBr, ZrOBr<sub>2</sub>; NH<sub>4</sub>Br, ZrOBr<sub>2</sub>; KBr, 2ZrOBr<sub>2</sub>; 2RbBr, 3ZrOBr<sub>2</sub>; 2CsBr, 3ZrOBr<sub>2</sub>, but no compound with LiBr. Of these only 2CsBr, 3ZrOBr<sub>2</sub>, 27H<sub>2</sub>O was isolated; it passed into 2CsBr, 3ZrOBr<sub>2</sub>, 21H<sub>2</sub>O in dry air at room temp.

C. A. S.

**Preparation of acid ammonium fluoride.** N. I. SPITZIN, G. V. SOKOLOVA, T. M. POPOVA, and I. I. ZORIN.—See B., 1933, 747.

**Behaviour of hydronitrogens and their derivatives in liquid ammonia. VIII. Influence of pressure on yields of hydrazine obtained by pyrolysis of liquid ammonia.** D. H. HOWARD, jun., and A. W. BROWNE (J. Amer. Chem. Soc., 1933, 55, 3211—3214; cf. this vol., 683).—With a W filament at 3000°, the yield of N<sub>2</sub>H<sub>4</sub> varies inversely with pressure between 80 and 1870 mm. Inorg. and org. solutes did not increase the yield of N<sub>2</sub>H<sub>4</sub>.

J. G. A. G.

**Direct combination of hydrogen with phosphorus.** R. DOLIQUE (Bull. Soc. chim., 1933, [iv], 53, 603—611).—Red P heated at 400° in a stream of H<sub>2</sub> vaporises and condenses in cooler parts of tube as yellow P. No liquid or solid PH<sub>3</sub> is formed; small traces of the gas are formed, but it decomposes at the temp. employed. The rate of change of red to yellow P increases with rise of temp.

A. S. C. L.

**Reversibility of the transformation of dimetaphosphates into Graham's salts.** P. PASCAL and BONNEMAN (Compt. rend., 1933, 197, 381—384).—If Ag hypophosphate is heated at 145° for 15 days, treated with aq. NaCl at 0°, and the resultant Na salt pptd. by EtOH the dimetaphosphate, Na<sub>2</sub>(PO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (cf. this vol., 475) is obtained: Ag<sub>4</sub>P<sub>2</sub>O<sub>6</sub> = Ag<sub>2</sub>(PO<sub>3</sub>)<sub>2</sub> + 2Ag. If heated for a shorter time the product is gummy, due to incomplete transformation; if for longer, complex polymetaphosphates

(Graham's salts), pptd. as oils, are produced. Ag<sub>2</sub>H<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, heated at 320° and similarly treated gives an uncrystallisable oily hydrated Na polymetaphosphate; the viscosity of a 1% solution of this is 25 times that of H<sub>2</sub>O, but becomes equal to it after 3 weeks, when the mol. wt. and conductivity become those of the dimetaphosphate, the ready change of which to acid pyrophosphate explains the slightly acid character of solutions of Graham's salts.

C. A. S.

**Decomposition of phosphates. I. Treatment of calcium phosphate with chlorine and carbon.** Y. KATO and S. FUJINO.—See B., 1933, 747.

**Decomposition of the arsenic acids.** B. ENGLUND.—See this vol., 1061.

**Constitution of potassium antimonyl tartrate and related antimony compounds.** K. BODENDORF (Pharm. Presse, 1933, 38, Wiss.-prakt. Heft 8—9; Chem. Zentr., 1933, i, 1930).—Reihlen's formula is supported by therapeutic properties and analogies. Formulæ are given for NH<sub>4</sub> Sb dipyrocatecholoxide and K (K Sb bispyrocatecholdisulphonate).

A. A. E.

**Method of preparation of radium-E.** M. HAISINSKY (Nature, 1933, 132, 317).—Ra-E is pptd. from a slightly acid solution of radio-Pb nitrate by pyrogallol in presence of Sb. Under suitable conditions, Ra-E and Po are practically completely pptd. with the Sb, which is then eliminated from the ppt. by electrolysis, as nitrate, in presence of tartaric acid and NH<sub>4</sub> tartrate: yield 47—80%.

L. S. T.

**Production of gaseous oxygen by chemical methods.** A. HLOCH.—See B., 1933, 702.

**Sulphur monoxide.** H. CORDES and P. W. SCHENK (Z. Elektrochem., 1933, 39, 594—596; cf. this vol., 475).—SO was prepared by the method previously described. Its absorption spectrum was observed even after keeping 2 days at room temp. At 100° the decomp. was rapid. SO is very sensitive to H<sub>2</sub>O, and reacts with Hg, Fe, and Cu. It is inert towards dry O<sub>2</sub>. Absorption spectrum observations prove that it is formed in the reaction of SOCl<sub>2</sub> and Ag at 180—350° and in the combustion of excess S in O<sub>2</sub> at low pressure.

H. J. E.

**Molybdenum compounds.** R. MONTEQUI and M. GALLEGRO (Anal. Fis. Quim., 1933, 31, 434—448).—Principally a reply to Malowan's criticism (A., 1931, 927) of Montequi's paper (A., 1930, 1028). Further experiments confirm that there exists an amphoteric molybdenyl hydroxide Mo<sub>2</sub>O<sub>3</sub>(OH)<sub>4</sub>, which in acid solution yields an insol. xanthate and in alkaline solution decomposes into Mo(OH)<sub>3</sub> and Mo(OH)<sub>6</sub>. Titration with KMnO<sub>4</sub> shows that Mavrov and Nikolov's formula for the alkali salts derived from Mo<sub>2</sub>O<sub>5</sub>, viz., RMo<sub>2</sub>O<sub>5</sub>·3H<sub>2</sub>O, cannot be correct; these compounds are more probably of the type RH<sub>3</sub>Mo<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O.

H. F. G.

**Atomic chlorine.** G. M. SCHWAB and H. FRIESS (Z. Elektrochem., 1933, 39, 586—594; cf. this vol., 580).—At. Cl was produced by an a.c. discharge through streaming Cl<sub>2</sub>. The discharge spectrum is recorded. The life of the Cl atoms, determined by measuring the heating effect accompanying recombina-

ation at different distances from the discharge, was  $3 \times 10^{-3}$  sec. Addition of  $\text{CH}_4$  poisons wall recombination. A concn. of 40% at. Cl was attained. The catalytic recombination on various materials was examined. It requires no appreciable activation energy. The reactions with  $\text{H}$ ,  $\text{CH}_4$ ,  $\text{CHCl}_3$ ,  $\text{CO}$ ,  $\text{N}_2\text{O}$ , and  $\text{O}_2$  were examined and the mechanisms are discussed. H. J. E.

**Thermal decomposition of manganous carbonate and its products.** J. CHLOUPEK (Chem. Listy, 1933, 27, 315—319).— $\text{MnCO}_3$  when heated at 200—300° in presence of  $\text{O}_2$  yields  $\text{Mn}_3\text{O}_4$ ,  $\text{Mn}_2\text{O}_3$ , and  $\text{MnO}_2$ . A product with an oxidising power equal to that of  $\text{Mn}_2\text{O}_3$  is obtained by heating anhyd.  $\text{MnCO}_3$  at 220° during 9 hr., with frequent stirring. R. T.

**Investigation of corrosion of iron by electron diffraction.** J. CATES (Trans. Faraday Soc., 1933, 29, 817—824).—Rusts formed on different specimens of Fe and steel give electron diffraction patterns identical with that given by  $\gamma\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ . The same pattern was observed with chemically prepared  $\text{Fe}_3\text{O}_4$ . The diffraction pattern of heated rust was that of  $\gamma\text{-Fe}_2\text{O}_3$ . F. L. U.

**Formation of  $\alpha\text{-Fe}_2\text{O}_3$  from  $\gamma\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  by friction.** O. BAUDISCH and L. A. WELO (Naturwiss., 1933, 21, 593).—If orange-yellow  $\gamma\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  is shaken with porcelain balls for 3 weeks, it becomes red, but remains paramagnetic. By removal of  $\text{H}_2\text{O}$  from  $\gamma\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  at 180—200°, red ferromagnetic  $\gamma\text{-Fe}_2\text{O}_3$  is produced, but the red form, produced by grinding, remains non-magnetic on similar treatment.  $\gamma\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  probably passes directly to  $\alpha\text{-Fe}_2\text{O}_3$  when heated, without the intermediate formation of  $\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ . A. J. M.

**Iron borates.** N. S. KURNAKOV, D. S. BELIANKIN, and F. A. KOTOMIN-BUDARIN (Ann. Inst. Anal. Phys. Chem., 1933, 6, 141—158).— $\text{FeO}$  and  $\text{B}_2\text{O}_3$  on fusion with subsequent cooling in a reducing atm. yield  $2\text{FeO} \cdot \text{B}_2\text{O}_3$ ,  $\text{FeO} \cdot 2\text{B}_2\text{O}_3$ , and  $5\text{FeO} \cdot \text{B}_2\text{O}_3$ . These salts absorb  $\text{O}_2$  at higher temp. with production of solid solutions of the general formulæ  $(\text{Fe}^{II}_{2-n} \cdot \text{Fe}^{III}_n) \text{O}_2 \cdot \text{B}_2\text{O}_3 \cdot \text{O}_{0.5n}$  and  $(\text{Fe}^{II}_{5-n} \cdot \text{Fe}^{III}_n) \text{O}_5 \cdot \text{B}_2\text{O}_3 \cdot \text{O}_{0.5n}$ ; at the same time the colour of the salts deepens from green to black. The black enamel of Etruscan pottery is a compound of this type. R. T.

**Spectroanalytical determination of traces.** W. GERLACH (Angew. Chem., 1933, 46, 557—562).—A review of the methods of quant. spectral analysis. E. S. H.

**Completion of combustion in gas analysis.** R. S. JAKOVLEV.—See B., 1933, 690.

**Alkaline pyrogallol solution in gas analysis.** J. S. HALDANE and R. H. MAKGILL.—See B., 1933, 737.

**Modes of expression of results of hydrochemical analyses.** B. N. FORSCH (Bull. Acad. Sci. U.R.S.S., 1933, 7, 589—595).—A discussion. R. T.

**Apparatus for detection of elements by the sodium fusion test (copper ignition tube and pellet press).** C. L. TSENG (J. Chinese Chem. Soc.,

1933, 1, 37—45).—Cu is a more suitable material for the tube than glass or Fe. The construction and use of such a tube are described. The tube is heated to redness and Na dropped in, followed by pellets of a mixture of  $\text{C}_{10}\text{H}_8$  and  $\text{EtOH}$  or  $\text{Et}_2\text{O}$ . The product is afterwards washed out with  $\text{EtOH}$  and then  $\text{H}_2\text{O}$ , and tested by the ordinary procedure. D. R. D.

**Electrometric titrations with oxygen electrodes.** J. A. V. BUTLER and G. ARMSTRONG (Trans. Faraday Soc., 1933, 29, 862—863; cf. A., 1932, 1092).—If a bright Pt electrode is polarised anodically for a short time and then given a very short cathodic polarisation, reproducible potentials depending on the  $p_{\text{H}}$  of the solution can be obtained. F. L. U.

**Use of antimony electrode in the electrometric determination of  $p_{\text{H}}$ .** T. GYSINCK (Archief Suikerind. Nederl.-Indië, 1932, [iii], Med. 10, 711—749).—Cast Sb rods gave the best results, but if the metal was not sufficiently pure the reproducibility suffered. Electrodes obtained by electrolytically coating a Pt rod with Sb gave gradually declining e.m.f. readings, owing to the oxidation of the layer of Sb. In general, the most const. results were obtained when the liquid was gently stirred, but if the rate of stirring was such that air was entrained in the buffer solution there was a strong drift of the potential towards the acid side. Better reproducibility was attained when the buffer solution under examination was covered with a layer of mineral oil to protect it from the air. J. P. O.

**Application of the antimony electrode to the measurement of  $p_{\text{H}}$  in acidimetric titration in aqueous and organic solutions.** E. VELLINGER (Chim. et Ind., 1933, Spec. no., 218—230).—The technique of using the Sb electrode is described in detail. The errors of the method and their elimination are discussed, and industrial applications suggested. J. W. S.

**Colorimetric determination of  $p_{\text{H}}$  at higher temperatures.** I. Water. W. NEUMANN (Z. anal. Chem., 1933, 94, 89—96).— $\text{H}_2\text{O}$  with various indicators showed on heating to its b.p. a colour change corresponding with a  $p_{\text{H}}$  change of about 1 unit, as anticipated from the dissociation const., the original val. being regained at room temp. Dissolution of alkali from the glass can produce a permanent  $p_{\text{H}}$  change which with Fiolax is < with  $\text{SiO}_2$  or  $\text{Na}_2\text{O}$  glass. J. S. A.

**Determination of hydrogen peroxide.** A. K. BALLS and W. S. HALE (J. Assoc. Off. Agric. Chem., 1933, 16, 395—397).—The presence of pyrogallol hinders the slow continued liberation of excess I in the iodometric determination of  $\text{H}_2\text{O}_2$ . Addition of 0.5 g. of pyrogallol per titration permits the accurate determination of small amounts of  $\text{H}_2\text{O}_2$  in presence of reducing substances interfering with the usual procedure. J. S. A.

**Electrode potential of chlorine, and its applications in analysis.** A. RIUS and V. ARNAL (Anal. Fis. Quím., 1933, 31, 325—347).—When a solution of  $\text{Cl}_2$  is titrated potentiometrically with  $\text{NaOH}$ , inflexions occur at 0.95—1.15 volts and 0.6—0.7 volt; the variations, and the smaller quantity of  $\text{NaOCl}$  formed as compared with the quantity of  $\text{NaOH}$  added, are due to volatilisation, decomp.,

and the action of  $\text{CO}_2$ . Potentiometric titration with HCl of NaOCl solution containing free NaOH yields three points of inflexion, corresponding with neutralisation of the NaOH, liberation of free HOCl, and decomp. of the HOCl; the method may be used for the determination, to within about 1%, of NaOCl, provided that recently-ignited Pt electrodes are used and that  $\text{CO}_2$ , if present, is first removed by means of  $\text{BaCl}_2$ . Low results are obtained if much Cl' is present. H. F. G.

**Starch iodide colour reaction and its application to quantitative analysis.** P. P. T. SAH (Sci. Rep. Nat. Tsing Hua Univ., 1933, A, 2, 105—128).—For micro- or colorimetric determinations the intensity of the blue colour is directly proportional to the I (optimum concn. 0.004—0.012 mg. per c.c.) only if the reducing substances in the starch solution are first removed by saturating with I. Inorg. ions, especially KI, affect the colour produced; hence acidity and KI concn. must be kept at a (const.) min. (1 c.c. each of  $N\text{-H}_2\text{SO}_4$ , 1% KI, and 1% starch with 25 c.c. of I solution giving a colour stable for 4 hr.). For determination of KI oxidation is best effected with 0.01*N*- $\text{KMnO}_4$ , excess of which is removed by exact titration with 0.01*N*- $\text{H}_2\text{C}_2\text{O}_4$ , and by this method 0.0167—0.05 mg. I may be determined in the presence of 5 mg. of ovalbumin. The new colorimetric method is successfully applied (details given) to the determination of I in defibrinated blood (proteins removed by  $\text{Na}_2\text{WO}_4$  method), iodo-ovalbumin and the ppt. produced by the latter on its anti-serum. J. W. B.

**Rapid determination of sodium hydrosulphide in sodium sulphide etc.** E. BENESCH.—See B., 1933, 701.

**Determination of sulphur in steel and ferroalloys.** I. KASSLER.—See B., 1933, 750.

**Micro-determination of phosphorus.** N. PROSKURLAKOV and S. TEMERN (Biochem. Z., 1933, 263, 387—394).—Using a modification of Roche's method for the micro-determination of P by pptn. as strychnine phosphomolybdate (A., 1928, 1392), the influence of various factors (concn. of reagents,  $p_{\text{H}}$ , influence of salts) on the completeness of pptn. has been investigated. An improved method which permits the determination of 0.05—0.15 mg. P with considerable accuracy is described. P. W. C.

**Detection and differentiation of phosphites and hypophosphites.** D. RAQUET and P. PINTE (J. Pharm. Chim., 1933, [viii], 18, 89—93).— $\text{PO}_3'''$  is detected by the decolorisation of a few drops of 0.1*N*-I in presence of NaOAc, whilst  $\text{H}_2\text{PO}_2'$  is detected by the decolorisation of the same reagent in presence of  $\text{H}_2\text{SO}_4$ . H. D.

**Volumetric determination of arsenic. Potentiometric titrations of reduced arsenic solutions with potassium iodate in sulphuric and hydrochloric acid solutions.** I. C. SCHOONOVER and N. H. FURMAN (J. Amer. Chem. Soc., 1933, 55, 3123—3130).—The first end-point corresponds with the completion of the reaction  $5\text{H}_3\text{AsO}_3 + 2\text{KIO}_3 + 2\text{HCl} = \text{I}_2 + 5\text{H}_3\text{AsO}_4 + 2\text{KCl} + \text{H}_2\text{O}$  (i) in 0.10—2*N*-HCl. The second end-point is achieved in 4—

6*N*-HCl and corresponds with  $2\text{I}_2 + \text{KIO}_3 + 6\text{HCl} \rightarrow 5\text{ICl} + \text{KCl} + 3\text{H}_2\text{O}$ . The non-appearance of I at the beginning of titration (i) is attributed to the slowness of  $\text{IO}_3' + 5\text{I}' + 6\text{H}' = 3\text{I}_2 + 3\text{H}_2\text{O}$ . In the presence of  $\text{Hg}_2\text{SO}_4$  and 0.5—2.0*N*-HCl, the first end-point is reached when  $\text{IO}_3'$  is reduced to I', which forms a complex with the  $\text{Hg}''$ ; the second, ICl, end-point is attained by increasing the HCl to 4—6*N*. The accurate potentiometric titration  $5\text{H}_3\text{AsO}_3 + 2\text{KIO}_3 + \text{H}_2\text{SO}_4 = \text{I}_2 + 5\text{H}_3\text{AsO}_4 + \text{K}_2\text{SO}_4 + \text{H}_2\text{O}$  proceeds in 0.5—8*N*- $\text{H}_2\text{SO}_4$ , but requires 0.0002*N*-HCl as catalyst with < *N*- $\text{H}_2\text{SO}_4$ . J. G. A. G.

**Sources of error in the Gutzeit method for the determination of arsenic.** C. R. GROSS (J. Assoc. Off. Agric. Chem., 1933, 16, 398—403).—(1)  $\text{C}_5\text{H}_5\text{N}$  compounds (when present) must be separated completely by pptg. the As as  $\text{MgNH}_4\text{AsO}_4$  together with  $\text{PO}_4'''$ . (2) Complete reduction of  $\text{AsO}_4'''$  by KI and  $\text{SnCl}_2$  requires at least 30 min. at 25°. The use of stick-in place of 30-mesh Zn increases the % recovery of As. J. S. A.

**Gravimetric determination of arsenic as  $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ .** J. DICK (Z. anal. Chem., 1933, 93, 429—433).—For the quant. pptn. of  $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$  the ppt. should be filtered and washed after approx. 2 hr. at 0—5°, washed with EtOH and Et<sub>2</sub>O, and dried in vac. at room temp. If the solution is not cooled, it must be kept for at least 12 hr. The process is suitable for semi-micro-determinations. D. R. D.

**Determination of silica in tissues.** E. KAHANE and M. KAHANE (Bull. Soc. Chim. biol., 1933, 15, 805—813).—The material is treated with  $\text{HNO}_3$  and  $\text{HClO}_4$  in presence of  $\text{H}_3\text{BO}_3$ . A. L.

**Interference with the volumetric determination of carbon dioxide by the silicic acid content of the barium hydroxide solution.** J. LINDNER (Z. anal. Chem., 1933, 94, 1—7).—The amount of silicate derived from glass vessels when aq.  $\text{Ba}(\text{OH})_2$  (0.05—0.1*N*) is stored therein for a few months renders the reagent useless for determining  $\text{CO}_2$ . E. S. H.

**Mercurimetric determination of cyanide and thiocyanate.** A. IONESCO-MATIU and (MME.) A. POPESCO (Chim. et Ind., 1933, Spec. no., 1011—1013; cf. A., 1928, 1230).—The solution of KCN is treated with  $\text{Hg}_2(\text{NO}_3)_2$  [ $2\text{KCN} + \text{Hg}_2(\text{NO}_3)_2 = 2\text{KNO}_3 + \text{Hg}(\text{CN})_2 + \text{Hg}$ ] and after 5 min. the mixture is centrifuged. The ppt. is washed and dissolved in  $\text{H}_2\text{SO}_4\text{-HNO}_3$ . The solution is diluted, boiled to remove HCN, treated with  $\text{KMnO}_4$  until a pink colour persists, and subsequently with  $\text{Na}_2(\text{NO})\text{C}_5\text{N}_5$ . The mixture is titrated with NaCl until the ppt. just disappears.  $\text{KCNS}$  ( $\text{NH}_4\text{CNS}$ ) is determined similarly:  $3\text{KCNS} + \text{Hg}_2(\text{NO}_3)_2 = 2\text{KNO}_3 + \text{KHg}(\text{CNS})_3 + \text{Hg}$  and  $\text{KHg}(\text{CNS})_3 + \text{Hg}_2(\text{NO}_3)_2 \rightarrow \text{KNO}_3 + \text{Hg}(\text{NO}_3)_2 + \text{Hg}(\text{CNS})_2$ . The practical factors are 1 c.c. 0.1*N*-NaCl = 0.00657 g. KCN, 0.00778 g. KCNS, or 0.00655 g.  $\text{NH}_4\text{CNS}$ . In mixtures of KCN and KCNS,  $\text{CN}' + \text{CNS}'$  is determined as above and  $\text{CNS}'$  as  $\text{BaSO}_4$  after oxidation with fuming  $\text{HNO}_3$ . H. W.

**Sodium cobaltinitrite as a reagent for potassium.** K. SCHERINGA (Chem. Weekblad, 1933, 30,

598).—This method of detecting K is much more sensitive if solid reagent is added to the solution.

S. C.

**Sodium hydrogen tartrate as a reagent for potassium.** K. SCHERINGA (Chem. Weekblad, 1933, 30, 598).—Solid  $\text{NaC}_4\text{H}_5\text{O}_6$  reacts much more readily with K salt solutions than either tartaric acid or the latter buffered with  $\text{NaOAc}$ .

S. C.

**Potassium perchlorate.** E. KAHANE (Bull. Soc. chim., 1933, [iv], 53, 547—555).—The solubility of  $\text{KClO}_4$  in  $\text{H}_2\text{O}$  is 1.67% at  $20^\circ$ , but addition of  $\text{HClO}_4$  reduces it until in 66% solution it is 0.07% of K. The reagent recommended for the determination of K as  $\text{KClO}_4$  is  $\text{HClO}_4$  75,  $\text{KClO}_4$  1, and  $\text{NH}_4\text{ClO}_4$  67.5 g. in 1 litre of  $\text{H}_2\text{O}$ . Cs and Rb are pptd. with K, and  $\text{NH}_3$  must be removed.

A. S. C. L.

**Uranyl magnesium sodium acetate.** E. KAHANE (Bull. Soc. chim., 1933, [iv], 53, 555—563).—From EtOH solution the triple salt separates at  $\text{Na} \prec 10^{-6}$  g. per litre. For general use, the reagent suggested is:  $\text{UO}_2(\text{OAc})_2$  25 g.,  $\text{Mg}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  150 g.,  $\text{AcOH}$  780 g., diluted to 1 litre with  $\text{H}_2\text{O}$ . Na, but not K or Li, is pptd. A list is given of metals pptd. and of anions which must be absent.

A. S. C. L.

**Colorimetric determination of sodium.** F. ALTEN and H. WEILAND (Z. Pflanz. Düng., 1933, 31, A, 252—255).—Na is pptd. as the complex  $\text{NaMgU}$  acetate and the ppt. treated with  $\text{AcOH}$  and  $\text{K}_4\text{Fe}(\text{CN})_6$ . The colour intensity is determined after 3 hr. Test solutions should contain 0.1—1.0 mg. Na per 100 c.c.

A. G. P.

**Determination of sodium fluoride by Penfield's method.** C. G. SCHWALBE and G. JUST (Z. anal. Chem., 1933, 94, 86—89).—Aeration of the  $\text{SiO}_2$ — $\text{H}_2\text{SO}_4$ —fluoride mixture on a glass filter-plate avoids risk of clogging and improves the accuracy of the method.

J. S. A.

**Rapid determination of soda in glasses.** S. R. SCHOLES.—See B., 1933, 704.

**Application of the polarographic method to the rapid determination of small quantities of alkalis, especially in silicates with high aluminium content.** V. MAJER (Chim. et Ind., 1933, Spec. no., 211—214).—5—20 mg. of the substance are dissolved in 0.3 c.c. of  $\text{H}_2\text{SO}_4$  and 0.5 c.c. of HF (40%). After evaporating to dryness, a drop of  $\text{H}_2\text{SO}_4$  is added, and the solution made alkaline with  $\text{NMe}_4\text{OH}$ . It is then analysed polarographically. The method has been applied particularly to refractory clays. The determination requires only about 40 min. and for 2% alkali content the accuracy is about 0.1%.

J. W. S.

**Influence of foreign metals on the potentiometric silver titration.** H. MOSER, E. RAUB, and W. STEIN (Z. Elektrochem., 1933, 39, 623—628).—Fe, Pt, and Pd in solution interfere with the potentiometric determination of Ag with  $\text{Cl}'$ ,  $\text{Br}'$ , or  $\text{CNS}'$ , using a pure Ag electrode. Cu interferes only when  $\text{CNS}$  is used. A Au electrode behaves similarly to Ag.

H. J. E.

**Must ammonium chloride be added in calcium determinations?** K. SCHERINGA (Chem. Week-

blad, 1933, 30, 598).— $\text{NH}_4\text{Cl}$  is unnecessary in presence of Al; the latter can be separated by neutralising the solution to phenolphthalein and filtering with a filter aid. In presence of Mg it delays pptn. of  $\text{MgC}_2\text{O}_4$  (I), but this can be achieved by using excess of  $\text{C}_2\text{O}_4^{2-}$ . The solubility of (I) is 1 in 1800 in  $\text{H}_2\text{O}$ , 1 in 700 in saturated  $\text{NH}_4\text{Cl}$ , and 1 in 500 in saturated  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ . When Mg is to be determined with soap, all  $\text{NH}_4$  salts must be avoided and  $\text{K}_2\text{C}_2\text{O}_4$  employed.

S. C.

**Gravimetric determination of calcium and its separation from magnesium.** O. BRUNCK (Z. anal. Chem., 1933, 94, 81—86).—Ca, pptd. as  $\text{CaC}_2\text{O}_4$ , is best weighed as  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ . The ppt. should be dried first at  $60$ — $70^\circ$  or by EtOH and  $\text{Et}_2\text{O}$ , and then at  $110^\circ$ . Separation from Mg is quant. even with ten-fold amount of Mg provided  $[\text{Mg}]$  is  $\succ 0.08$  g. per 100 c.c.

J. S. A.

**Characteristic reaction of magnesium and iodine.** S. AUGUSTI (Annali Chim. Appl., 1933, 23, 348—350).—With I or  $\text{NaOI}$ , Mg salts give a cryst. brownish-red ppt. the composition of which varies with the conditions and with washing. The filtrate from the group V ppt. is evaporated and calcined to expel  $\text{NH}_4$  salts, the residue being taken up in  $\text{H}_2\text{O}$  and the solution treated with I in KI and then dropwise with  $\text{NaOH}$ . Free I in a solution is detected by adding  $\text{NaOH}$  to almost complete decolorisation and then  $\text{MgSO}_4$  or  $\text{MgCl}_2$  solution. The reaction is not disturbed by  $\text{Cl}'$  or  $\text{Br}'$ .

T. H. P.

**Precipitation and titration of magnesium "oxyquinolate" in presence of calcium oxalate, and its application in the analysis of Portland cement and similar silicates.** J. C. REDMOND.—See B., 1933, 749.

**Volumetric determination of magnesium in salt-lake saline, using 2-hydroxyquinoline.** N. V. KOMAR and R. E. KIRILLOVA.—See B., 1933, 747.

**Detection of the elements belonging to the analytical group IV.** A. FOSCHINI (Annali Chim. Appl., 1933, 23, 294—296).—The ppt. of Zn, Mn, Co, and Ni sulphides is converted into a conc. solution of the chlorides. To this  $\text{NaOH}$  is added dropwise until the solution is slightly alkaline. Co, Ni, and Mn hydroxides are filtered off, and Zn is detected in the filtrate with  $\text{H}_2\text{S}$ . The pptd. hydroxides are dissolved in  $\text{HCl}$ , and Mn is separated by adding a large excess of  $(\text{NH}_4)_2\text{CO}_3$ . Ni and Co are detected separately in the filtrate.

O. J. W.

**Electrolytic zinc: determination of small amounts of germanium.** H. LUNDIN.—See B., 1933, 751.

**Utility of the mercury cathode.** W. BÖTTGER, N. BLOCK, and M. MICHOFF (Z. anal. Chem., 1933, 93, 401—422).—Paweck's Hg cathode (A., 1924, ii, 562) is suitable for the determination of Zn in acid solution,  $\text{H}_2\text{SO}_4$  being the best acid to use. It is less suitable for Cd, but gives good results with Bi and with Pb in alkaline solution, certain modifications being introduced into Paweck's procedure in this case. The liquid Hg cathode is more suitable for the determination of Fe and Ni.

D. R. D.

Separation of metals of the ammonium sulphide and alkaline-earth groups. A. KRÜGER (Z. anal. Chem., 1933, 93, 422—429).—The pptn. of ZnS by H<sub>2</sub>S in slightly acid solution at 70° is rendered quant. by addition of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. Fe<sup>++</sup>, Ni<sup>++</sup>, Co<sup>++</sup>, and Mn<sup>++</sup> do not interfere, but HNO<sub>3</sub> must be absent and NH<sub>4</sub><sup>+</sup> and alkali metals must not be present in high concn. S is pptd. with the ZnS, but is removed on roasting to convert into ZnO. If NH<sub>4</sub>Cl and excess of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> are added to the filtrate and H<sub>2</sub>S is passed under pressure, FeS, NiS, CoS, and MnS are pptd. quantitatively. Under similar conditions, Al and Cr are pptd. quantitatively as hydroxides. All these ppts. are granular. There is no danger of co-pptn. of Ca, Sr, Ba, or Mg. D. R. D.

1:2-Diaminoanthraquinone-3-sulphonic acid as a reagent for the detection of copper, cobalt, and nickel. J. V. DUBSKÝ and V. BENCKO (Z. anal. Chem., 1933, 94, 19—20).—The colorations produced are due to adsorption compounds. No stoichiometric compounds are formed. E. S. H.

Rapid determination of the copper content of sea-water. W. R. G. ATKINS (J. Marine Biol. Assoc., 1933, 19, 63—76).—Cu can be determined colorimetrically by means of Na diethyldithiocarbamate, extracting with CHCl<sub>3</sub>. C. W. G.

Ceric sulphate as a volumetric oxidising agent. XIV. Indicator methods for the standardisation and use of ceric sulphate. H. H. WILLARD and P. YOUNG (J. Amer. Chem. Soc., 1933, 55, 3260—3269; cf. this vol., 924).—The *o*-phenanthroline ferrous complex (I) indicates accurately the end-points of the oxalate-0.01—0.1*N*-Ce(SO<sub>4</sub>)<sub>2</sub> and arsenite-Ce(SO<sub>4</sub>)<sub>2</sub> titrations at 50° in presence of appropriate concn. of HCl or H<sub>2</sub>SO<sub>4</sub> with ICl as catalyst. Consistent with previous results, the potentiometric arsenite-Ce(SO<sub>4</sub>)<sub>2</sub> titration in the presence of ICl is stoichiometric in HCl at concn. < 3*N*. The titration with Ce(SO<sub>4</sub>)<sub>2</sub> in presence of (I), of Fe(CN)<sub>6</sub><sup>4-</sup>, Ti<sup>++</sup>, and H<sub>2</sub>O<sub>2</sub> is rapid at room temp., and of U<sup>4+</sup> at 50°, whilst the end-point for Sb<sup>3+</sup> is obscured by high acidity. (I) is added just before the end-point in the titration of Ce(SO<sub>4</sub>)<sub>2</sub> with H<sub>2</sub>O<sub>2</sub> and NaNO<sub>2</sub>. J. G. A. G.

Analytical chemistry of rhenium. IX. Determination of hydrochlororhenic acid in presence of perrhenic acid. W. GEILMANN and L. C. HURD (Z. anorg. Chem., 1933, 213, 336—342).—H<sub>2</sub>ReCl<sub>6</sub> is pptd. from slightly acid solution at 40—50° by a HCl or H<sub>2</sub>SO<sub>4</sub> solution of NN'-tetramethyl-*o*-tolidine. The cryst. ppt. is (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Me<sub>6</sub>N<sub>2</sub>·H<sub>2</sub>ReCl<sub>6</sub>. It is dried at 110—130° and weighed. HReO<sub>4</sub> is determined in the filtrate with nitron, or, better, by first treating with H<sub>2</sub>S, and converting the sulphide into nitron perrhenate (cf. Geilmann and Weibke, A., 1931, 328). H. J. E.

Colorimetric determination of iron. L. SZEGOE and B. CASSONI (Giorn. Chim. Ind. Appl., 1933, 15, 281—283).—Fe can be determined colorimetrically as Fe(CNS)<sub>3</sub> if the Fe is kept in the ferric state by means of an oxidising agent (e.g., HNO<sub>3</sub>) and if the concn. of KCNS is kept const. and < 8 g. per 100 c.c. O. J. W.

Interference by ferric ion in the colorimetric determination of copper and lead in potable water. P. KARSTEN.—See B., 1933, 734.

Detection and determination of cobalt by 1-nitro-β-naphthol. A. HERFELD and O. GERNGROSS (Z. anal. Chem., 1933, 94, 7—12).—A solution of 1-nitro-β-naphthol (I) in 50% AcOH is added to the hot CoCl<sub>2</sub> solution containing dil. H<sub>2</sub>SO<sub>4</sub>. [C<sub>10</sub>H<sub>6</sub>(NO<sub>2</sub>)<sub>2</sub>O]<sub>2</sub>Co is pptd., but salts of Ni or Fe are not pptd. Co is determined as CoSO<sub>4</sub>. The red coloration produced enables Co<sup>++</sup> to be detected at a dilution of 1 in 400,000 in warm solutions, but the sensitivity is increased to 1 in 2×10<sup>7</sup> by using the Na salt of (I). E. S. H.

Macro-electroanalysis of cobalt, zinc, cadmium, silver, and mercury. J. GUZMÁN and A. RANCAÑO (Anal. Fis. Quím., 1933, 31, 348—355; cf. A., 1932, 923).—A passive Fe anode is used for all the metals except Hg, for which a Pt anode is necessary. For Ag and Hg the Cu cathode should be silvered, and for Cd Cd-plated. For Co, Cd, and Ag an ammoniacal solution is used, for Zn an ammoniacal cyanide solution, and for Hg a HNO<sub>3</sub> solution. Full details are given for the procedure in each case. The determinations take < 1 hr. H. F. G.

Volumetric determination of chromium in chromates. L. IRRERA (Annali Chim. Appl., 1933, 23, 346—348).—The disadvantages attending the use of SnCl<sub>2</sub> for this determination are removed by using K<sub>2</sub>SnCl<sub>4</sub>·2H<sub>2</sub>O (cf. A., 1932, 712), which is stable in air. The excess of the salt is titrated with KMnO<sub>4</sub>. T. H. P.

Acidimetry of orthotungstates, using methyl-red. A. DEL CAMPO and F. SIERRA (Anal. Fis. Quím., 1933, 31, 356—360).—A nearly saturated solution of benzidine acetate is added to the neutral alkali orthotungstate solution (0.5—1.0% WO<sub>3</sub>) containing Me-red. The colour change occurs sharply at the end-point, owing to hydrolysis of the excess of reagent adsorbed on the ppt. In absence of the ppt. a considerable quantity of reagent is needed to produce the colour change. Satisfactory results are not obtained with other indicators. The reagent is standardised against Na<sub>2</sub>WO<sub>4</sub>. H. F. G.

Volumetric determination of bismuth. C. MAHR (Z. anal. Chem., 1933, 93, 433—437).—To an acid solution of the Bi salt in aq. KBr, aq. NaOH is added so long as the ppt. formed redissolves. Saturated aq. [Cr(NH<sub>3</sub>)<sub>6</sub>](NO<sub>3</sub>)<sub>3</sub> is then added. The compound [Cr(NH<sub>3</sub>)<sub>6</sub>][BiBr<sub>6</sub>] is pptd. and is decomposed by distillation with aq. NaOH, giving NH<sub>3</sub>, which is titrated. Alkali and alkaline-earth metals, Fe, Mn, Cr, Co, Ni, Al, Cu, and small quantities of Zn do not interfere. In presence of Hg, Cd, or much Zn, the ppt. must be decomposed to BiOBr by boiling with H<sub>2</sub>O, redissolved in aq. KBr, and re-pptd. as before. Addition of tartaric acid prevents pptn. of Sn with the Bi. D. R. D.

Electrolytic analysis of bismuth, tin, lead, and antimony without mechanical agitation of the electrolyte. T. GROSSET.—See B., 1933, 751.

Electric furnaces with interchangeable elements. M. BILLY and F. TROMBE (Bull. Soc.

chim., 1933, [iv], 53, 536—541).—Details of the construction of open-tube and muffle electric furnaces with standard interchangeable heating elements, and of regulating resistances, are given. Curves are given for relation between current input and temp. attained, and for temp. distribution along the tube.

A. S. C. L.

**Molybdenum resistance furnace.** G. BURROWS and F. L. CLARK (J. Sci. Instr., 1933, 10, 248—250).—A durable furnace for continuous use up to 1850°, having Mo resistance strips instead of wires, is described.

N. M. B.

**Freezing gases at low temperatures.** P. SAKMIN (Khimstroi, 1933, 5, No. 1, 1985—1990).—Technique applicable to small quantities of gas is described.

CH. ABS.

**Automatic refrigeration chamber.** J. WIRFEL (Chim. et Ind., 1933, Spec. no., 264—265).—The laboratory plant described permits the automatic maintenance of any desired low temp. down to -60°. Adequate space is provided and reactions carried out in the refrigerator can be followed, regulated, and modified from without through a window in the wall. Refrigeration is produced by expansion of liquid CO<sub>2</sub>.

J. W. S.

**Extremely low temperatures.** W. J. DE HAAS (Nature, 1933, 132, 373).—The magnetic method by which extremely low temp. have been reached is described. With CeF<sub>3</sub>, Dy Et sulphate, and Ce Et sulphate the upper temp. limits reached are 0.27°, 0.17°, and 0.085° abs., respectively.

L. S. T.

**Determination of absolute thermal coefficients of expansion of liquids.** J. ZAHRAĐ-ŃIČEK (Physikal. Z., 1933, 34, 624).—Apparatus similar to that described by the author (this vol., 689) has already been used by Hiedemann (A., 1931, 592).

A. J. M.

**Temperature regulation by means of contact thermometers.** H. BRÜCKNER (Chem. Fabr., 1933, 6, 342—343).—The apparatus described enables an oven to be kept at 300 ± 1° for a period of months.

E. S. H.

[Duboscq colorimeter.] A. VAN RAALTE [with J. KOSTER] (Chem. Weekblad, 1933, 30, 555).—The use of cylindrical ebonite jackets around the glass vessels is recommended; difficulties arising from the varying thickness of the walls of the vessel are thus obviated.

H. F. G.

**Colorimeter.** H. SCHNEIDER (Boll. Chim. farm., 1933, 72, 529—530).—The apparatus (of Rojahn and Heinrici), which is of the comparator type with matching discs of white, black, and colours, is described and its application to normal and fluorescence colours discussed.

F. O. H.

**High-vacuum spectrograph for chemical analysis with X-rays.** E. ALEXANDER (Z. Physik, 1933, 83, 512—516).

A. B. D. C.

**X-Ray spectrometer for high vacuum with Johann concave crystal.** A. SANDSTRÖM (Z. Physik, 1933, 84, 541—556).

A. B. D. C.

**Integrating photometer for X-ray crystal analysis.** B. W. ROBINSON (J. Sci. Instr., 1933, 10,

233—242).—A simple photo-electric photometer for measuring integrated X-ray intensities in crystal-analysis photographs, but adaptable to almost any form of X-ray photometry, is described. N. M. B.

**Plane-polarised light in the microscopical investigation of ores and metals.** F. F. OSBORNE (Trans. Canad. Inst. Min. Met., 1933, 35, 1—13).—A review of recent work on, and a description of modern optical apparatus for, detecting anisotropism in ores and metals. Vertical illuminators are less satisfactory than the film type, since they produce depolarising effects.

A. R. P.

**High-temperature X-ray camera.** A. H. JAY (Z. Krist., 1933, 86, 106—111; cf. A., 1932, 1078).—The camera is a modification of the powder camera, and enables the substance to be examined at a uniform temp. > 800°, accurate to within 5°.

C. A. S.

**X-Ray microscope.** W. BRAGG (Anal. Fis. Quím., 1933, 31, 399—400).

H. F. G.

**Simple arrangement for photo-electric absorption measurement.** R. SEIFERT (Pharm. Zentr., 1933, 74, 501—503).—A modification of the method (this vol., 366), in which the photo-cell is used merely as a comparator and whereby the disturbances caused by the apparatus are avoided, and its satisfactory and simple application for colorimetric analysis are described.

E. H. S.

**Capillary mercury-vapour lamp.** A. HOLLAENDER and J. F. STAUFFER (Science, 1933, 78, 62).—Improvements in the Daniels-Heidt lamp (A., 1932, 827) are described.

L. S. T.

**Use of cuprous oxide and other rectifier photo-cells in submarine photometry.** W. R. G. ATKINS and H. H. POOLE (J. Marine Biol. Assoc., 1933, 19, 67—72).—The current-illumination ratio is not linear.

C. W. G.

**Determination of colour-sensitivity of photographic layers.** J. O. BRAND (Physikal. Z., 1933, 34, 677—682).—An arrangement for producing a spectrum of equal energy distribution is described. The spectral sensitivity curves of some modern photographic emulsions are obtained.

A. J. M.

**Application of immersion method.** T. CAPPANESE (Z. Krist., 1933, 86, 145—152).—The observations obtainable with any possible position of the crystal fragment are tabulated, and methods described for determining  $n_a$ ,  $n_\beta$ , and  $n_\gamma$  for biaxial fragments without knowledge of their optical or crystallographic orientation.

C. A. S.

**Direct-current grid as a source of alternating current for measuring purposes.** A. BÜCHNER and A. ETZRODT (Z. Elektrochem., 1933, 39, 668—670).—The circuit is described.

E. S. H.

**Insulation for the introduction of electrical connexions into high-pressure vessels.** H. J. WELBERGEN (J. Sci. Instr., 1933, 10, 247—248).—Pyrex glass insulation embedded in a plug of high-Cr steel gives a seal suitable for work at 3000 atm. up to 200° with liquids, and 800 atm. with gases.

N. M. B.

**Electric sieve.** A. SCHLOEMER (Chem.-Ztg., 1933, 57, 682—683).—An apparatus constructed on the electrofiltration principle, suitable for separating powdered material into fractions of different particle size, is described. E. S. H.

**Technique of glass-electrode measurements.** B. S. PLATT and S. DICKINSON (Biochem. J., 1933, 27, 1069—1076).—The design, construction, and manipulation of a glass-electrode system, employing a thermionic valve for the potential measurement, are described, emphasis being laid on the need for careful temp. regulation. W. O. K.

**Electrode pair for rapid potentiometric analysis.** W. HILTNER (Chem.-Ztg., 1933, 57, 704).—The electrodes are Pt and Pt covered with fused AgI. The potential of the latter depends on the concn. of Ag<sup>+</sup> and of all ions forming therewith insol. salts or complexes difficult of dissociation. In acidimetry Pt may be replaced by Sb. AgI serves as an indicator electrode for Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, CNS<sup>-</sup>, CrO<sub>4</sub><sup>2-</sup>, SO<sub>3</sub><sup>2-</sup>, S<sup>2-</sup>, etc., but not for S<sub>2</sub>O<sub>3</sub><sup>2-</sup> and CN<sup>-</sup>, which attack it. It is also suitable for many pptn. reactions. For S<sub>2</sub>O<sub>3</sub><sup>2-</sup> a Ag<sub>2</sub>S electrode is better and serves, e.g., for the determination of Cu with S<sub>2</sub>O<sub>3</sub><sup>2-</sup>. A salt to be used as electrode in this way must be both insol. and conductive to cations. C. I.

**Simple, portable Wilson chamber.** K. PHILIPP and F. DÖRFFEL (Physikal. Z., 1933, 34, 491—492).—An apparatus which is portable and can be used in any position is described. A. J. M.

**Gas-analysis apparatus.** R. MARGARIA (J. Sci. Instr., 1933, 10, 242—246).—An improved Haldane apparatus, giving more rapid absorption by forcing the gas to circulate in the pipette and to bubble in the absorbing solution, is described. Hydroxyquinol solution is used for O<sub>2</sub> absorption, giving increased stability and speed. N. M. B.

**Simple and serviceable membrane-manometer of glass or quartz.** J. FISCHER (Chem. Fabr., 1933, 6, 377—378).—A manometer with a flexible diaphragm of the "oil-can" type and with simple devices for increasing the accuracy of the readings is described. D. F. T.

**Procedure with hydrogen sulphide in qualitative analysis.** J. V. DUBSKÝ and V. DOSTÁL (Z. anal. Chem., 1933, 94, 21—22).—A modified Kipp apparatus is described. E. S. H.

**Collodion thimbles for ultra-filtration.** B. K. MAREJKOWSKY and C. O. GUILLAUMIN (Bull. Soc. Chim. biol., 1933, 15, 849—854).—Details of manufacture are given. A. L.

**Stainless steel high-pressure ultra-filter.** S. J. FOLLEY and A. T. R. MATTICK (Biochem. J., 1933, 27, 1113—1115).—A stainless steel apparatus suitable

for high-pressure ultra-filtration is described. The apparatus has proved useful for clarification of biological solutions, sterilisation of bacteriological media without heat, and fractionation of colloidal solutions by ultra-filtration. A. W.

**Apparatus for continuous extraction in a vacuum.** M. A. MACHEBŒUF and N. FETHKE (Bull. Soc. Chim. biol., 1933, 15, 796—800).—The apparatus consists of a cylindrical glass extraction vessel fitted with a siphon, the whole being suspended inside two overlapping glass tubes, the overlap being sealed with Hg. A. L.

**Apparatus for continuous extraction of an aqueous solution by ether.** A. LEMAN (Bull. Soc. chim., 1933, [iv], 53, 635—636). A. S. C. L.

**Apparatus for the removal of supernatant liquids in centrifuge tubes.** J. CHEYMOL (Bull. Soc. Chim. biol., 1933, 15, 847—848). A. L.

**Apparatus for sublimation of iodine.** R. JACQUEMAIN (Bull. Soc. chim., 1933, [iv], 53, 633—635). A. S. C. L.

**Evaporation of metals in vacuum.** H. W. EDWARDS (Rev. Sci. Instr., 1933, [ii], 4, 449).—Small pieces of the metal may be hung along a heated W wire. C. W. G.

**Electrically heated sand-bath.** E. P. CLARK (J. Assoc. Off. Agric. Chem., 1933, 16, 418—420). J. S. A.

**Production of strong cellulose acetate films.** L. HARRIS and E. A. JOHNSON (Rev. Sci. Instr., 1933, [ii], 4, 454—455).—Films 10<sup>-3</sup> cm. thick are best prepared by spreading the solution on glass plates previously coated with a 5% solution of paraffin in CCl<sub>4</sub>. C. W. G.

**Simple arrangement to demonstrate liquid crystals.** G. VAN ITERSUN, jun. (Trans. Faraday Soc., 1933, 29, 915—919).—Apparatus suitable for the observation of liquid crystals by laboratory classes is described. E. S. H.

**γ-Ray radiographic testing.** G. E. DOAN (J. Franklin Inst., 1933, 216, 183—216, 351—385).—A lecture.

**Microscopical and microchemical examination of Egyptian pigments.** M. WAGENAAR (Pharm. Weekblad, 1933, 70, 894—902).—An examination of ancient Egyptian pigments (circa B.C. 1000) showed them to consist of powdered shells (white and rose), Cu silicate (green), lapis lazuli (blue), ochres (reds and yellows), blood (?) C (black), and malachite (green). S. C.

**Combining power of krypton and of xenon.** G. ONDO (Gazzetta, 1933, 63, 380—395).—Two letters dated 1902 from Sir W. Ramsay are published. O. J. W.

## Geochemistry.

**Vertical distribution of ozone in the atmosphere.** F. W. P. GÖTZ, G. M. B. DOBSON, and A. R. MEETHAM (Nature, 1933, 132, 281).—A new method gives a revised val. of 20 km. for the average height of O<sub>3</sub> at Arosa. There is an appreciable amount

of O<sub>3</sub> in lower layers of the atm., but the main amount appears between 15 and 50 km. L. S. T.

**Composition of rain-water of Sylhet.** A. K. DAS, G. C. SEN, and C. K. PAL (Indian J. Agric. Sci.,

1932, 3, 353—359).—The ratio  $\text{NH}_3:\text{NO}_3$  is 1:0.82, a higher val. for  $\text{NO}_3$  than is obtained in non-tropical countries (cf. Rothamsted, 1:0.43). Biochemical decomp. in the swamps is the main factor concerned in the high  $\text{NH}_3$  content; it is lowest during the monsoon when the ground is under  $\text{H}_2\text{O}$ . P. G. M.

**Lake Elton.** N. S. KURNAKOV and B. L. RONKIN (Ann. Inst. Anal. Phys. Chem., 1933, 6, 185—203).—Lake Elton (lower Volga district)  $\text{H}_2\text{O}$  has a max.  $d$  1.3642 during summer, and contains  $\text{NaCl}$  1.57,  $\text{MgCl}_2$  26.97,  $\text{MgSO}_4$  6.45,  $\text{MgBr}_2$  0.343,  $\text{Mg}(\text{HCO}_3)_2$  0.36, and  $\text{KCl}$  0.68%. During spring and autumn the  $\text{MgSO}_4$  and  $\text{NaCl}$  contents rise at the expense of  $\text{MgCl}_2$ . The lake is estimated to contain  $10^7$  tons of  $\text{MgCl}_2$ . R. T.

**Composition of water of certain salt lakes of the Omsk district.** A. P. USPENSKI (Ann. Inst. Anal. Phys. Chem., 1933, 6, 205—213).—The  $\text{H}_2\text{O}$  of Lake Ebeity consists during summer of a saturated solution of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . 80% of the substances in solution in lakes Kizil-Kak, Selety-Dengiz, and Teke are  $\text{NaCl}$  and 12%  $\text{MgSO}_4$ . R. T.

**Lake Medveshje.** D. V. RISHIKOV (Ann. Inst. Anal. Phys. Chem., 1933, 6, 215—227).—Analytical data are given for the mud and  $\text{H}_2\text{O}$  of Lake Medveshje (Ural). The chief solutes are  $\text{NaCl}$  (68.37%),  $\text{MgCl}_2$  (13.56%), and  $\text{MgSO}_4$  (12.72%). R. T.

**Composition of ice from the Gulf of Finland in connexion with its mechanical strength.** V. I. ARNOLD-ALJABJEV (Ann. Inst. Anal. Phys. Chem., 1933, 6, 229—233).—The ice contains 0.23—0.75% of salts, the relative  $\text{SO}_4$  content of which is < in the case of Baltic sea-salt. No connexion exists between salt content and mechanical strength of ice. R. T.

**Batalpaschinsk lakes.** M. A. KLOTSCHKO (Ann. Inst. Anal. Phys. Chem., 1933, 6, 235—247).—Analytical data are given for two salt lakes, the larger of which is estimated to contain  $\text{Na}_2\text{SO}_4$  200,000,  $\text{NaCl}$  195,000, and  $\text{MgSO}_4$  91,000 tons. R. T.

**Soda lakes of Egypt.** B. L. RONKIN (Ann. Inst. Anal. Phys. Chem., 1933, 6, 311—322).—A theory of formation of  $\text{Na}_2\text{CO}_3$  in the lakes is given. R. T.

**Formation of ore-deposits in lakes.** F. W. FREISE (Chem. Erde, 1933, 8, 1—24).—Analyses are given of the  $\text{H}_2\text{O}$  and sediments from several lakes in Brazil. The black muds show appreciable amounts of Fe and Mn. L. J. S.

**Physico-chemical studies of the mine waters of Příbram.** SPLÍCHAL, ŠÁNA, and JIRKOVSKÝ (Chim. et Ind., 1933, Spec. no., 284—292).—Radioactivity and conductivity have been studied. Analyses are given. C. W. G.

**Vertical distribution of hydrogen-ion concentration in eutrophic lakes during the stagnation period.** D. MIYAJI (Chikyû, 1929, 404—412).—Many Japanese eutrophic lakes show neutral reaction in the bottom layers. Weathering is retarded by lack of acid. CH. ABS.

**Spectroscopic researches on the Portuguese mineral waters.** Germanium as indicator of

deep waters. A. P. FORJAZ (Chim. et Ind., 1933, Spec. no., 260—261).—Spectroscopic examination of the saline constituents of some Portuguese mineral waters shows that secondary mineralisation is always accompanied by the presence of Ge, this confirming the view that this element is a sure indicator of a deep  $\text{H}_2\text{O}$ . J. W. S.

**$p_{\text{H}}$  values in some sulphurous waters from the [Italian] Marche.** A. HEMMELER and N. SETTE (Annali Chim. Appl., 1933, 23, 297—306).—Composition and  $p_{\text{H}}$  data for various sulphurous waters are given. The influence of bacteriological factors on the  $p_{\text{H}}$  is emphasised. O. J. W.

**Composition and classification of Italian mineral waters. II.** D. MAROTTA and C. SICA (Annali Chim. Appl., 1933, 23, 245—290; cf. A., 1930, 448).—Tabulated analyses and schemes of classification of potable and spa-waters are given. O. J. W.

**Action of iodine on sea-water.** G. DENIGÈS (Bull. Trav. Soc. Pharm. Bordeaux, 1932, 70, 241—255; Chem. Zentr., 1933, i, 1923—1924).—I in I-rich sea- $\text{H}_2\text{O}$  is not present in org. combination; the reaction  $\text{I} + \text{Ag}^+ \rightarrow \text{AgI}$  in aq.  $\text{NH}_3$  is masked by pptn. of  $\text{CaCO}_3$  and  $\text{MgCO}_3$ , which should be removed before  $\text{Ag}^+$  is added. The  $\text{H}_2\text{O}$  also contains  $\text{IO}_3^-$ :  $6\text{I}^- + 6\text{Ca}(\text{HCO}_3)_2 = \text{Ca}(\text{IO}_3)_2 + 5\text{CaI}_2 + 6\text{H}_2\text{O} + 12\text{CO}_2$ . A. A. E.

**Chemical constituents of biological importance in the English Channel. III. June-December, 1932.** Phosphate, silicate, nitrite, hydrogen-ion concentration, with a comparison of wind records. L. H. N. COOPER (J. Marine Biol. Assoc., 1933, 19, 55—62).—An unusual distribution occurred in Aug., 1932. C. W. G.

**Interrelationships of sunlight, aquatic plant life, and fishes.** T. A. OLSON (Trans. Amer. Fish Soc., 1932, 62, 278—289).— $\approx 24$  p.p.m. of dissolved  $\text{O}_2$  is present in  $\text{H}_2\text{O}$  of Minnesota lakes during periods of active photosynthesis. Shallow lakes may show severe  $\text{O}_2$  depletion in the winter. CH. ABS.

**Meteorite (diogenite) of Tataouine, Tunis (June 27, 1931).** A. LACROIX (Bull. Soc. franç. Min., 1932, 55, 101—122; Chem. Zentr., 1933, i, 1425).—The meteorite contained  $\text{SiO}_2$  54.94,  $\text{TiO}_2$  0.19,  $\text{Al}_2\text{O}_3$  0.62,  $\text{Cr}_2\text{O}_3$  0.35,  $\text{FeO}$  15.30,  $\text{MnO}$  10.26,  $\text{MgO}$  27.42,  $\text{CaO}$  0.76,  $\text{S}$  0.13,  $\text{Fe}$  0.22,  $\text{H}_2\text{O} + 0.06$ ,  $\text{H}_2\text{O} - 0.08\%$ ;  $\text{Fe}_2\text{O}_3$ ,  $\text{NiO}$ , and  $\text{P}_2\text{O}_5$  were absent. A. A. E.

**Stony meteorite which fell in Morocco, on August 22, 1932.** A. LACROIX (Compt. rend., 1933, 197, 368—370).—Stones which fell at Dwar Maghila had a greyish and brecciated fracture, showing a few chondrules. The constituents are olivine and hypersthene with about 8% of Ni-Fe, some maskelynite, and a little pyrrhotite and plagioclase. C. A. S.

**Young's modulus and Poisson's ratio with reference to geophysical applications.** W. A. ZISMAN (Proc. Nat. Acad. Sci., 1933, 19, 653—665).—Vals. have been obtained for a large no. of rocks. C. W. G.

**Compressibility and anisotropy of rocks at and near the earth's surface.** W. A. ZISMAN

(Proc. Nat. Acad. Sci., 1933, 19, 666—679).—Measurements on a no. of rocks at 30° up to 840 kg. per sq. cm. show a rapid decrease in compressibility as pressure increases. C. W. G.

**Comparison of the statically and seismologically determined elastic constants of rocks.** W. A. ZISMAN (Proc. Nat. Acad. Sci., 1933, 19, 680—686).—Lack of agreement is due to the presence of cracks and cavities. C. W. G.

**Geochemical considerations.** V. M. GOLDSCHMIDT (Fortschr. Min. Krist. Petr., 1932, 17, 415—417; Chem. Zentr., 1933, i, 1267).—The average amount of weathering of eruptive rocks has been calc. In the formation of sedimentary rocks partial oxidation simultaneously took place; the amount of O<sub>2</sub> required has been calc. Calculations have also been made of the amounts of various heavy metals liberated by weathering of eruptive rocks. A. A. E.

**Composition of leucoxene in the Permian of Oklahoma.** F. COIL (Amer. Min., 1933, 18, 62—65).—Leucoxene, TiO<sub>2</sub>.nH<sub>2</sub>O, contained TiO<sub>2</sub> 72.12, SiO<sub>2</sub> 24.49, Fe<sub>2</sub>O<sub>3</sub> 0.50, FeO 1.35, H<sub>2</sub>O 1.66, total 100.12%; quartz, hematite, and ilmenite were present. CH. ABS.

**Triplite from La Rioja Province, Argentina.** E. P. HENDERSON (Amer. Min., 1933, 18, 104—105).—The mineral, n<sub>a</sub> 1.675, n<sub>β</sub> 1.683, n<sub>γ</sub> 1.692, contained MnO 34.84, FeO 23.54, CaO 3.48, Na<sub>2</sub>O 0.27, K<sub>2</sub>O 0.33, P<sub>2</sub>O<sub>5</sub> 31.50, F 6.41, H<sub>2</sub>O 1.58, Cl trace, insol. 0.28, total (corr.) 99.54%. CH. ABS.

**Origin and classification of pegmatites.** K. K. LANDES (Amer. Min., 1933, 18, 33—56, 95—103).—A discussion. Pegmatites are classified as (simple or complex) (a) acid, (b) intermediate, (c) basic. CH. ABS.

**Basalt of the Kammerbühl near Eger.** H. JUNG (Chem. Erde, 1933, 8, 48—57).—A petrographical description of the rock and a chemical analysis of the fragmentary material are given. L. J. S.

**Rocks from the volcano "Pacaya," Guatemala.** E. DÜGER (Chem. Erde, 1933, 8, 45—47).—Two analyses are given of basalts. The high summation is attributed to the presence of silicide. L. J. S.

**Hydrothermal alteration of Greenland basalts.** K. HOLLE (Chem. Erde, 1933, 8, 25—44).—In certain layers adjacent to layers of brecciated basalt cemented with zeolites the rock shows a gradual transition to a red laterite-like material containing free Al hydroxide. L. J. S.

**Radioactivity measurements. I. Radium content of the Keweenaw basalts and some accessory minerals. II. Occurrence of radium, uranium, and potassium in the earth.** W. D. URRY (Proc. Amer. Acad. Arts Sci., 1933, 68, 125—136, 137—144).—I. A felsitic pebble had the highest Ra content (7.00 × 10<sup>-13</sup> g. Ra per g.) and an algononite the lowest (0.08 × 10<sup>-13</sup>). The average Ra content of the plateau basalts, not including felsitic rocks, was 1.29 × 10<sup>-13</sup> g. Ra per g. Evidence was obtained of correlation between Ra content and both depth and stratigraphical arrangement, and of a regular order

in the Ra content of the accessory minerals in the Cu lodes according to the method of pptn. from the mineralising solutions.

II. Average vals. are calc. The results show a considerably lower mean U content than has usually been adopted for the three outer shells and excludes the possibility of a complete concn. into the upper two shells. CH. ABS.

**Borsov deposit of corundum.** V. KOPEV-DVORNIKOV and E. KUZNETZOV (Trans. Inst. Econ. Min., Moscow, 1931, No. 47, 1—304).—Dunite, peridotite, pyroxenite, and gabbro were during one stage recryst. into olivine and pyroxene schists and amphibolites. In another the sedimentary rocks were transformed into cordierite, micaceous garnet gneiss, micaceous quartzite, and marble. In another, diopside and hornblende rocks were formed by a pneumatolytic process. Pyroxene alters to amphibole at about 550°. Olivine-bronzite rocks south of Borsov are also described. CH. ABS.

**Structural and morphological relations between ores of the formula type ABC.** W. HOFMANN (Fortschr. Min. Krist. Petr., 1932, 17, 422—425; Chem. Zentr., 1933, i, 1268—1269).—Wolfsbergite, CuSbS<sub>2</sub>, has *a* 6.00<sub>8</sub> ± 0.01, *b* 3.78<sub>1</sub> ± 0.01, *c* 14.45<sub>8</sub> ± 0.03 Å., with 4 mols. in the unit cell; space-group V<sub>h</sub><sup>6</sup>. Empectite, CuBiS<sub>2</sub>, has *a* 6.12<sub>3</sub> ± 0.01, *b* 3.89<sub>0</sub> ± 0.01, *c* 14.51<sub>2</sub> ± 0.03 Å. Miargyrite, AgSbS<sub>2</sub>, has *a* 13.16<sub>3</sub>, *b* 4.39<sub>1</sub>, *c* 12.82 Å.; β 98° 37½'. The unit cell is (100)-centred and contains 8 mols.; space-group C<sub>2h</sub><sup>6</sup>. Lorandite, TlAsS<sub>2</sub>, has *a* 15.02<sub>3</sub>, *b* 11.31<sub>5</sub>, *c* 6.10<sub>2</sub> Å.; β 127° 45'; the unit cell contains 8 mols.; space-group C<sub>2h</sub><sup>4</sup> or C<sub>2h</sub><sup>5</sup>. A. A. E.

**Crystal structure of boracite.** M. MEHMEI (Fortschr. Min. Krist. Petr., 1932, 17, 436—437; Chem. Zentr., 1933, i, 1268).—The rhombic modification has *a* 12.07, *b* 17.07, *c* 17.07 Å., with 8 mols. in the unit cell. The cubic modification stable at > 265° has *a* 12.1 Å., with 4 mols. in the unit cell; space-group T<sub>h</sub><sup>6</sup>. The structure is best expressed by the formula [B<sub>7</sub>O<sub>13</sub>]Mg<sub>3</sub>Cl. A. A. E.

**Carbonate-weathering of the gabbro of Neurode, Silesia.** E. KJIAK (Chem. Erde, 1933, 8, 58—166).—Petrographical descriptions and chemical analyses of the fresh and altered rock in which clay and carbonate minerals are developed are given. L. J. S.

**Varieties of microlite from Donkerhuk, South-West Africa.** E. REUNING (Chem. Erde, 1933, 8, 186—217).—Microlite occurs in pegmatite veins with tantalite and large crystals of beryl, apatite, and tourmaline. The yellow octahedra are often surrounded by a fibrous zone, and this appears to grade into brown pitchy metamict material. Analyses (in which some of the constituents were determined by the X-ray method) show Ta<sub>2</sub>O<sub>5</sub> 74.78—74.2, Nb<sub>2</sub>O<sub>5</sub> 2.85—6.2, UO<sub>2</sub> 0.3—11.2, CaO 13.96—1.9, PbO 0.4—3.0, H<sub>2</sub>O 1.31—9.7%, etc., *d* 6.0—4.14, *H* 5½—4. No definite formula can be deduced, and the mineral perhaps consists of a mixture of meta- and pyrotantalates. X-Ray photographs (of the metamict variety after heating at 800°) give a unit cell of edge 10.381 Å. (mean); the patterns are compared with

those given by loparite and betafite. X-Ray quantitative analyses are given of the tantalite,  $d$  6-17. L. J. S.

**Geochemistry of strontium.** W. NOLL (Fortschr. Min. Krist. Petr., 1932, 17, 440—442; Chem. Zentr., 1933, i, 1267—1268).—For the determination of small quantities of Sr the usual EtOH-Et<sub>2</sub>O method is inaccurate; an X-ray spectroscopic method was employed. The distribution of Sr and the substitution of Ca by Sr are discussed.

A. A. E.

**Optically uniaxial titanite.** B. E. DIXON and W. Q. KENNEDY (Z. Krist., 1933, 86, 112—120).—The titanite occurs in a plagioclase-diopside-hornfels xenolith in norite near Schivas (Aberdeenshire) as small plum-coloured crystals,  $d^{18}$  3.43. It is monoclinic, pleochroic (plum-coloured and light yellow),  $n_a = n_\beta = 1.741$ ,  $n_\gamma - n_a = 0.021$  (Na light); analysis: SiO<sub>2</sub> 37.52, Al<sub>2</sub>O<sub>3</sub> 14.29, Fe<sub>2</sub>O<sub>3</sub> 4.43, Cr<sub>2</sub>O<sub>3</sub> 0.11, TiO<sub>2</sub> 5.72, FeO 7.12, MgO 6.72, MnO 0.14, CaO 24.06, Na<sub>2</sub>O 0.09, K<sub>2</sub>O trace, total 100.20%. The rôle of Ti in this and other pyroxenes is discussed and Machatschki's formula (cf. A., 1930, 732; 1932, 12) deemed most applicable, but with the probability of some direct replacement of Si by Ti.

C. A. S.

**Deposits of giobertite in Czecho-Slovakia and the present state of their exploitation.** F. ULRICH (Chim. et Ind., 1933, Spec. no., 298—304).—Geological, mineralogical, and chemical particulars are given.

C. W. G.

**Thermo-optic studies of lepidomelane from Ishikawa.** B. YOSHIKI (Proc. Imp. Acad. Tokyo, 1933, 9, 324—326).—The change of  $n$  on heating has been measured.

C. W. G.

**Thermal and chemical studies of lepidomelane from Ishikawa.** S. TSURUMI (Proc. Imp. Acad. Tokyo, 1933, 9, 320—323).—An analysis and the change in wt. on heating are recorded.

C. W. G.

**Thermal expansion of diopside.** S. KÔZU and J. UEDA (Proc. Imp. Acad. Tokyo, 1933, 9, 317—319).—Between 20° and 1000° expansion along the  $b$ -axis is about three times that along the other two, and is not much affected by changes in chemical composition.

C. W. G.

**Effusive rocks from South-West Sardinia.** A. DEBENEDETTI (Atti R. Accad. Lincei, 1933, [vi], 17, 659—664).—Chemical and mineralogical data are given for some rocks of the andesite type.

O. J. W.

**Microscopical and chemical examination of two clays.** F. K. SCHLÜNZ (Chem. Erde, 1933, 8, 167—185).—Mechanical and chemical analyses of a glacial clay and one of Tertiary age from north Germany are given.

L. J. S.

**Physico-chemical properties of Japanese acid clay. VII. Solubility in alkaline solutions and the essential constituents of acid clay. II.** K. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1933, 36, 460—466B).—When acid clays containing various mol. ratios SiO<sub>2</sub> : Al<sub>2</sub>O<sub>3</sub> are shaken with 5% aq. NaOH at 90° more SiO<sub>2</sub> is dissolved from clays with higher ratios and the ratio in the residue is usually 4—5.

It is concluded that the clays are mixtures of SiO<sub>2</sub> and silicate. When the concn. of NaOH is increased, a rapid increase in the SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> dissolved at 70° occurs at 6—7*N*, corresponding with dissolution of the cryst. silicate, and this effect is not shown by ordinary kaolinic clays.

A. G.

**Manganese mineral deposits in the Carpathians in the north-west of Czecho-Slovakia and their genesis.** F. ULRICH and R. MUNK (Chim. et Ind., 1933, Spec. no., 305—313).—Analyses and geological details are given.

C. W. G.

**New map of mineral deposits and useful minerals in Czecho-Slovakia.** SLAVÍK (Chim. et Ind., 1933, Spec. no., 314).—Nine categories of metaliferous, 6 of combustible, and 17 of non-metallic minerals are shown.

C. W. G.

**Accumulation of copper in sedimentary rocks.** A. D. ARKHANGELSKI and E. V. ROZHKOVA (Bull. Soc. Nat. Moscow, 1932, [ii], 40, Geol. 10, No. 2, 295—307).—In 26 samples Cu was found combined with org. matter; none of the other samples contained Cu. The ratio Cu : C was: Recent, 0.0016—0.0022; Tertiary 0.0017—0.0041; Cretaceous, 0.0005; Jurassic, 0.0012—0.0036; Permian, 0.020—0.090; Devonian, 0.0012—0.0018; Cambrian, 0.0019.

CH. ABS.

**Mednorudyansk and Mount Vuisokaya (Ural) copper mines.** V. P. YARKOV (Tzvet. Met., 1932, 238—246).—The deposits of cupriferous magnetites (Fe 40—65, Cu 1—3%) are described and their utilisation is discussed.

CH. ABS.

**Copper deposit at Devdorak.** V. BOULYGO (Trans. Geol. Prospect. Serv. U.S.S.R., 1930, No. 15, 1—31).—The Cu content is 1.49—16%.

CH. ABS.

**Copper deposits of Laiskaja Datscha, Ural.** V. DOMAREV (Bull. Geol. Prospect. Serv. U.S.S.R., 1930, No. 49, 645—667).—The ore contains 1—2% Cu.

CH. ABS.

**Magnetite-bearing quartzites of Man and neighbourhood (Ivory Coast).** M. BOLGARSKY (Compt. rend., 1933, 197, 559—561).—The magnetite-bearing quartzites of the Nimba Mts. consist almost wholly of quartz and magnetite, with a little pyroxene or amphibole, and small quantities of Mn, Al, Ti, and Ni. They are probably of eruptive origin, apparently passing into basic eruptive rocks. Similar quartzites containing hæmatite in place of magnetite also occur.

C. A. S.

**Magnetic susceptibility of magnetites from basic eruptive rocks.** G. JOURAVSKY, P. CHARCZENKO, and G. CHOUBERT (Compt. rend., 1933, 197, 522—525).—Magnetite is distinguishable from ilmenite by its being more readily attacked by conc. HCl or HI (e.g., in 0.5—10 min.). The polished and attacked surface is examined in a metallurgical microscope provided with a Shand stage. Thus determined the amount of magnetite in a gabbro agrees closely with that deduced from the magnetic susceptibility. The results with this and titanomagnetite, dolerite, and basalts show that the susceptibility of the rock is almost entirely due to magnetite, the susceptibility of which, however, is much smaller (48.7—86.1%) when so present than in the pure state.

C. A. S.

**Iron ores at Itabira, Brazil.** B. H. SANDERS (Bull. Inst. Min. Met., July, 1933, No. 346, 23 pp.).—An account is given of the geology of the Fe ore deposits with a description and analysis of the various types of Fe minerals. Au exists in certain parts of the deposits as scales and grains of an alloy with 8–10% Pd and < 3% Ag (cf. A., 1932, 402).

A. R. P.

**Genetic peculiarities of the Briey basin and their relation to the distribution, constitution, and metallurgical properties of the oolitic [iron] minerals.** J. P. AREND (Rev. Mét., 1933, 30, 43–53, 142–151, 188–199, 227–237).—The genesis of the Fe ore deposits in the Briey basin has been investigated by experiments with the H<sub>2</sub>O which now circulates through the fissures in the faults; these indicate that the deposits constitute a perfect equilibrium between two gels,  $\alpha$  formed by (a) the colloidal compounds of the ter- and multi-valent elements and (b) the polymerisable compounds of the intermicellar liquid, and  $\beta$  the colloidal ppt. of alkaline earths enclosing (b). Both gels hold in physical suspension the marls which occur on the borders of the Toarcian lake. According to the conditions of oxidation or reduction in the solid system  $\alpha$  gives rise to oolites or to definite chemical compounds according to the scheme: oolite  $\leftarrow$  [(Fe<sub>2</sub>O<sub>3</sub>)<sub>n</sub>.xFe(OH)<sub>3</sub>]  $\leftarrow$  [(Fe<sub>2</sub>O<sub>3</sub>)<sub>n</sub>.v (groups of protective colloids consisting of hydroxides, hydrogen sulphides, carbonates, or org. compounds)]  $\rightleftharpoons$  [FeCO<sub>3</sub>, FeS<sub>2</sub>, etc.]  $\leftarrow$  [(FeO.OH)<sub>n</sub>.xFe(HCO<sub>3</sub>)<sub>2</sub>]. The course, alternation, and composition of the carbonates, the intermediate products, and the various more or less pure minerals are determined by the changing effects of the marl and by variation in the oxidising or reducing powers of the lake waters caused by changes in the fauna and flora through the geologic ages. The speed of reduction of minerals is influenced by the degree of polymerisation of the  $\alpha$  granules. The formation of oolites occurs in an absolutely homogeneous solid system which allows the establishment of centres of osmotic depression which can produce their effect in an identical manner in all directions and cause the larger ions to be displaced symmetrically to produce oolites the curvature of which varies with the degree of attraction between the colloidal matter being pectised on the surface and the sol from which it is derived.

A. R. P.

**Iron ore for the central [Russian] metallurgical industry.** N. N. CHINKIN (Gorno-Obogat. Delo, 1932, No. 9, 27–37).—The ore is chiefly of the brown type, containing Fe 23.25–40.79, SiO<sub>2</sub> 10.74–53.62, Al<sub>2</sub>O<sub>3</sub> 0.32–6.17, MnO 0.10–0.74, CaO 0–1.44, MgO trace–0.51, P<sub>2</sub>O<sub>5</sub> 0.39–1.38, and S 0.05–0.25%. Methods of concn. were studied.

CH. ABS.

**Iron deposits of the Nikolaevski works, Irkutsk.** S. DOKTOROVICH-GREBNITSKI (Trans. Geol. Prospect. Serv. U.S.S.R., 1931, No. 33, 1–14).—The FeO is 12.44–16.20%, and Fe<sub>2</sub>O<sub>3</sub> 57.90–68.23%.

CH. ABS.

**Alapaevsk iron ore deposits.** B. KROTOV (Trans. Geol. Prospect. Serv. U.S.S.R., 1931, No. 70, 1–52).

CH. ABS.

**Non-ferrous metals in Central Asia. Deposits of Kara-Mazara.** V. A. GLAZKOVSKI and I. SHCHUKIN (Gorno-Obogat. Delo, 1932, No. 1, 1–10).—The deposits (near Khodjent) contain 1.2–8.27% Cu. Other elements present are Pb 5–18, Zn 5–21, and As 1.5–3.5%, together with U, V, W, Sn, Mo, and Bi.

CH. ABS.

**Nickel sulphide at Grebni, Urals.** A. TALVINSKI (Bull. Geol. Prospect. Serv. U.S.S.R., 1930, No. 49, 120–123).—The Ni content is 0.92–1.60%.

CH. ABS.

**Alteration of black uranium mineral from Portugal [by weathering].** A. P. LEITE (Chim. et Ind. 1933, Spec. no., 805).—H<sub>2</sub>O in contact with this mineral becomes yellow and the mineral crumbles and becomes covered with a white deposit. The solution is found to contain U in proportion to the SO<sub>4</sub> present. P<sub>2</sub>O<sub>5</sub> is present when the SO<sub>4</sub> content of the solution exceeds a certain val. Dissolution of U in ordinary H<sub>2</sub>O is > in distilled H<sub>2</sub>O, but dissolved CO<sub>2</sub> is without influence.

C. I.

**Gem stones.** W. T. GORDON (Nature, 1933, 132, 267–269).—A lecture.

L. S. T.

**“Peat-dolomites” [“coal-balls”].** G. LINCK and E. KÖHLER (Chem. Erde, 1933, 8, 213–223).—The calcareous nodules containing plant remains found in coal seams are analysed and their origin is discussed.

L. J. S.

**Soil processes in volcanic ash beds. Beds of the northern King-country and their secondary alumina minerals. II.** N. H. TAYLOR (New Zealand J. Sci. Tech., 1933, 14, 338–352).—The nature and composition of the mineral matter in these soils have been examined and the probable process of their formation is discussed.

A. G. P.

**Processes of salinisation and desalinisation and the salt-profile of soils.** B. B. POLYNOV (Trans. Irrigation Commission, Acad. Sci., U.S.S.R., 1933, 1, 107–131).—A study of the formation and evolution of saline soils based on an examination of the salt-profile.

A. M.

**Rendzina soils of Polessie.** S. NIDA (Abh. Inst. Bodenk. Pulawy, 1932, 2, 124–156).—The parent material of these soils is cretaceous marl with more or less morainic material and varies widely in CaCO<sub>3</sub> content. No traces of podsolisation were found in pure rendzinas, but on mixed rendzinas (with loess) distinct podsolisation was observed.

A. M.

**Dissolution phenomena in the granite soils of Brittany.** M. VINCENT (Ann. Agron., 1933, 3, 323–332).—The decomp. of ground granitic rock by treatment with salt solutions, with consequent leaching of Na, K, and Mg, is examined and discussed in relation to the nutrient condition of granitic soils and the composition of the drainage H<sub>2</sub>O.

A. G. P.

**Chemical equivalents of clay acid and humic acids.** S. OHSUGI and S. MORITA (J. Agric. Chem. Soc. Japan, 1933, 9, 274–284).—The equivs., determined by Hissink's method, are 890–2513 and 149–181, respectively. When the acids were neutralised with Ba(OH)<sub>2</sub> the p<sub>H</sub> was approx. 10–11.

CH. ABS.

**Iodine content of Dutch soils in relation to geological and agricultural problems.** J. F. REITH (Z. Pflanz. Düng., 1933, 31, A, 215—224).—Summarised data from soils of different areas are given. The high I content of marine soils is attributed to deposition of I-rich plankton. Losses of free I by volatilisation from soils are unrelated to their Fe or Mn contents. Use of artificial instead of natural manures does not result in I impoverishment in soils. A. G. P.

**Micropedological examination of crystal formation in the pore spaces of soil.** W. KUBIENA (Z. Pflanz. Düng., 1933, 31, A, 255—278).—The formation of crystals of  $\text{CaCO}_3$  and  $\text{CaSO}_4$  in natural soils has been examined by a special microscopical technique. Crystal forms produced in air-filled pore spaces differ from those appearing in spaces filled with soil solution. Conditions of crystallisation are examined and the effects of the presence of org. and inorg. colloids described. A. G. P.

**Classification of soils on the basis of the composition of their colloidal fractions.** A. REIFENBERG (Z. Pflanz. Düng., 1933, 31, A, 287—

303).—Characteristic vals. of silica : sesquioxide ratios for soils of various types are recorded. A. G. P.

**Systematic examination of soils and soil mapping in Bavaria.** R. PÜRCKHAUER (Z. Pflanz. Düng., 1933, 31, A, 340—346).—The val. and uses of soil maps are discussed. A. G. P.

**Principles of soil mapping.** W. WOLFF (Z. Pflanz. Düng., 1933, 31, A, 1—13).—The val. of systematic classification of soils is discussed. A. G. P.

**Soil profiles from Cyprus. II. Profiles over diabase, gabbro-norite, and pillow lava.** A. REIFENBERG and E. K. EWBANK (Empire J. Exp. Agric., 1933, 1, 156—164; cf. this vol., 803).—Chemical changes involved in the weathering of, and soil formation from, these rocks are examined. A. G. P.

**Mineralogical composition and oil yield from sands.** V. P. BATURIN (Azerbaid. Neft. Choz., 1933, No. 1, 73—75).—Oil present in heavy-spar formations is retained more tenaciously by the mineral than that present in quartz sands. The nature of sand present in various Russian oilfields is discussed. CH. ABS.

## Organic Chemistry.

**Possible mechanism of racemisation and of the Walden inversion.** G. B. BONINO (Gazzetta, 1933, 63, 448—452).—Theoretical. The groups X, X', X'' of a compound CHXX'X'' are considered as forming a barrier of potential opposing oscillation of the H atom from one equilibrium position to another (representing the optical antipodes); in racemisation the CXX'X'' pyramid is turned inside out, with ease depending on the weakness of the potential barrier, the oscillation level of the C and H atoms, and on steric factors. The Walden inversion may be similarly regarded, taking into account the oscillation of the N atom. E. W. W.

**Effect of the decisive factors on the oxidation of paraffin to fatty acids under atmospheric pressure and the reaction mechanism of this oxidation.** H. PFLUGK (Braunkohlenarch., 1932, No. 37, 1—36; Chem. Zentr., 1932, ii, 3959—3960).—The optimum temp. for the oxidation of paraffin (I) to fatty acids (II) with air is 160°. An increase in the velocity of the air increases the yield of (II) to a defined limit. A low moisture content (1.2%) favours the yield.  $\text{H}_2\text{O}_2$ , peracids, and peroxides were detected in the reaction product. Two H of the paraffin are oxidised forming  $\text{H}_2\text{O}_2$  and unsaturated hydrocarbons which are further oxidised to (II) by fission of the chain. Acid anhydrides result from removal of  $\text{H}_2\text{O}$ , whilst oxidation by  $\text{H}_2\text{O}_2$  gives the peracids from the acid anhydride peroxide. Oxidation of the terminal Me groups gives alcohols which then form esters. Cracking of (I) does not occur at this temp. L. S. T.

**Syntheses in the olefine series. IV. Heptenes.** F. J. SODAY and C. E. BOORD (J. Amer. Chem. Soc., 1933, 55, 3293—3302; cf. A., 1932, 361).—The

following are prepared by extensions of the  $\beta$ -Br-ether synthesis:  $\alpha$ -bromo- $\beta$ -ethoxy-heptane, b.p. 89.9—90°/8 mm., - $\epsilon$ -, b.p. 164.6°/250 mm., - $\delta$ -, b.p. 88.5—89.5°/10 mm., - $\beta$ -, b.p. 103—104°/22 mm., and - $\gamma$ -methylhexane, b.p. 75—76°/1.5 mm., - $\beta\gamma$ -, b.p. 75.5—76.5°/4 mm., - $\gamma\delta$ -dimethyl-, b.p. 72—73°/3 mm., and - $\beta$ -ethyl-pentane, b.p. 73—75°/6 mm., and - $\gamma$ -methyl- $\beta$ -ethyl-butane, b.p. 66—68°/? mm.;  $\beta$ -bromo- $\gamma$ -ethoxy-heptane, b.p. 90—91°/3 mm., - $\epsilon$ -, b.p. 91—92°/19 mm., - $\delta$ -, b.p. 89—90°/15 mm., and - $\gamma$ -methylhexane, b.p. 69—70°/3 mm., - $\gamma\delta$ -dimethyl-, b.p. 71—72°/3 mm., and - $\gamma$ -ethyl-pentane, b.p. 69—70°/3 mm.;  $\gamma$ -bromo- $\delta$ -ethoxy-heptane, b.p. 88—89°/13.5 mm., and - $\epsilon$ -methylhexane, b.p. 88—90°/15 mm.;  $\alpha\beta$ -dibromo-heptane, b.p. 106.2°/13 mm., - $\epsilon$ -, b.p. 142.6—143.6°/101 mm., - $\delta$ -, b.p. 94.7—95.7°/11 mm., - $\gamma$ -, b.p. 84.0—84.2°/6 mm., and - $\beta$ -methylhexane, b.p. 100.5—101.5°/23 mm., - $\beta\gamma$ -, b.p. 72.5—73°/3 mm., and - $\gamma\delta$ -dimethyl-, b.p. 65.5—66°/4 mm., and - $\beta$ -ethyl-pentane, b.p. 77—78°/4 mm., and - $\beta$ -ethyl- $\gamma$ -methylbutane, b.p. 72.5—73.5°/3 mm.;  $\beta\gamma$ -dibromo-heptane, b.p. 96.2°/12 mm., - $\epsilon$ -, b.p. 89—90°/11 mm., - $\delta$ -, b.p. 91—92°/11 mm., - $\beta$ -, b.p. 73.0—73.1°/8 mm., and - $\gamma$ -methylhexane, b.p. 65.0—65.1°/2 mm., and - $\gamma\delta$ -dimethyl-, b.p. 65.5—66°/3 mm., and - $\gamma$ -ethyl-pentane, b.p. 76.0—76.4°/3 mm.;  $\gamma\delta$ -dibromo-heptane, b.p. 105.5—106.5°/23 mm., and - $\beta$ -methylhexane, b.p. 96°/19 mm.;  $\Delta^a$ -, b.p. 94.9°,  $\Delta^b$ -, b.p. 98.1—98.4°, and  $\Delta^c$ -heptene, b.p. 95.8—96.1°;  $\beta$ -methyl- $\Delta^a$ -, b.p. 91.1—91.5°, - $\Delta^b$ -, b.p. 94.4—94.6°, and - $\Delta^c$ -hexene, b.p. 86.4—86.9°;  $\gamma$ -methyl- $\Delta^a$ -, b.p. 83.4—84°, and - $\Delta^b$ -hexene, b.p. 93.1—93.3°;  $\delta$ -methyl- $\Delta^a$ -, b.p. 87.2—87.5°, and - $\Delta^b$ -hexene, two forms, b.p. 87.1—87.6° and 85.1—85.6°, respectively;  $\epsilon$ -methyl- $\Delta^a$ -, b.p. 84.7°, and - $\Delta^b$ -hexene, two forms, b.p. 91.1—91.6° and 85.6—86.1°, respectively;  $\beta\gamma$ -, b.p. 84.1—84.3°, and  $\beta\delta$ -dimethyl-

b.p. 80.9—81.3°, and  $\beta$ -ethyl- $\Delta^{\alpha}$ -pentene, b.p. 93.9—94.3°;  $\gamma\delta$ -dimethyl-, b.p. 86.2—86.4°, and  $\gamma$ -ethyl- $\Delta^{\beta}$ -pentene, b.p. 94.8—94.9°; and  $\beta$ -ethyl- $\gamma$ -methyl- $\Delta^{\alpha}$ -butene, b.p. 88.7—89.1°. Physical consts. are recorded for these compounds.

R. S. C.

**Reaction of  $\alpha$ -iodoacetylenes; mercury acetylides.** T. H. VAUGHN (J. Amer. Chem. Soc., 1933, 55, 3453—3458).—Diamylacetylene and  $\text{NaNH}_2$  in mineral oil at 210° give a 28% yield of  $\Delta^{\alpha}$ -dodecinene, b.p. 95—98°/12 mm.;  $\Delta^{\alpha}$ -decinene (I) was obtained similarly from  $\text{CBu:CBu}$ .  $\text{C}_2\text{H}_2$  derivatives and  $\text{Hg}(\text{CN})_2\text{-KOH}$  in  $\text{EtOH}$  give  $\text{Hg}$  diacetylides, also obtained similarly from substituted  $\alpha$ -iodoacetylenes, which may be identified in this way. The following new  $\text{Hg}$  diacetylides,  $\text{Hg}(\text{C:CR})_2$ , are described, the radical named being R: *Pr*, m.p. 118.4—118.8°; *Bu<sup>\alpha</sup>* (II), m.p. 96.2—96.4°; *hexyl*, m.p. 80.4—80.7°; *heptyl*, m.p. 67.8—68.5°; *octyl*, m.p. 79.5—80° (lit. 83—84°); *nonyl*, m.p. 79—79.3°; *decyl*, m.p. 84.3—85.1°; *vinyl*, unstable, m.p. 142—142.5°; *m-xyllyl*, m.p. 140.3—140.5°; *mesityl*, m.p. 238—239°. (I),  $\text{MgEtBr}$ , and I in  $\text{Et}_2\text{O}$  give  $\alpha$ -iodo- $\Delta^{\alpha}$ -decinene (70%), b.p. 84°/0.7 mm.;  $\alpha$ -iodo- $\Delta^{\alpha}$ -octinene (88%), b.p. 95—97°/7.5 mm., and  $\Delta^{\alpha}$ -dodecinene (94.5%), b.p. 99—102°/0.3 mm., were similarly prepared. (II), KI, and I at room temp. give  $\alpha$ -iodo- $\Delta^{\alpha}$ -hexinene (III) (22%), b.p. 58—59°/8 mm., and (probably)  $\alpha\beta$ -tri-iodo- $\Delta^{\alpha}$ -hexene, decomp. when distilled. (II) and I in liquid  $\text{NH}_3$  give a 54% yield of pure (III).  $\text{H}_2\text{S}$  ppts.  $\text{HgS}$  from the  $\text{Hg}$  compounds.

R. S. C.

**Preparation of isobutyl bromide.** V. LONGINOV and K. LERMAN (Khim. Farm. Prom., 1933, 14—18).—Purified  $\text{HBr}$  is passed through  $\text{Bu}^{\beta}\text{OH}$  at 88° rising to 135°. The product is washed with conc.  $\text{H}_2\text{SO}_4$ , 5%  $\text{NaHCO}_3$ , 2%  $\text{KMnO}_4$ , and  $\text{H}_2\text{O}$ .

CH. ABS.

**1-Nitroanthraquinone-2-carboxylic acid as a reagent for alcohols.** P. P. T. SAH and T. S. MA (J. Chinese Chem. Soc., 1933, 1, 51—58).—The following esters of 1-nitroanthraquinone-2-carboxylic acid are prepared by interaction of the chloride with the appropriate alcohol at 120—140° during 15 min.: *Me*, m.p. 249—251°; *Pr<sup>\alpha</sup>*, m.p. 182—183°; *Pr<sup>\beta</sup>*, m.p. 204—206°; *Bu<sup>\alpha</sup>*, m.p. 174—175°; *Bu<sup>\beta</sup>*, m.p. 159—160°; *sec.-Bu*, m.p. 155—156°; *tert.-Bu*, m.p. 220—221°; *n-amyl*, m.p. 166—168°; *isoamyl*, m.p. 165—167°; *sec.-amyl*, m.p. 136—137°; *tert.-amyl*, m.p. 221—223°; *n-hexyl*, m.p. 153—154°; *n-heptyl*, m.p. 140—141°; *n-octyl*, m.p. 131—132°; *sec.-octyl*, m.p. 114—115°; *n-nonyl*, m.p. 125—126°; *n-decyl*, m.p. 123—124°; *cetyl*, m.p. 105—106°; *allyl*, m.p. 184—185°; *benzyl*, m.p. 211—212°;  $\beta$ -chloroethyl, m.p. 192—193°; *menthyl*, m.p. 189—190°.

J. L. D.

**Tautomeric forms of substituted allyl alcohols.** H. W. J. HILLS, J. KENYON, and H. PHILLIPS (Chem. and Ind., 1933, 660—661).—Hydrolysis of (+) $\alpha\gamma$ -dimethylallyl H phthalate (I) with dil.  $\text{H}_2\text{SO}_4$  yields the *dl*-alcohol, but with dil. alkalis the (+)alcohol (II) is formed, which has a marked temp.-rotation coeff., is levorotatory in  $\text{Et}_2\text{O}$ , and exhibits anomalous rotatory dispersion and sometimes mutarotation. The parachors of  $\alpha$ - and some  $\gamma$ -substituted allyl

alcohols are not in accordance with the usually accepted formulæ; the vals. for  $\alpha\gamma$ -dimethyl- and  $\alpha$ -ethyl-allyl and cinnamyl alcohols suggest that ( $< 60^\circ$  in the first two cases) these exist mainly in cyclic forms, and the properties of (II) may therefore be due to the additional position of asymmetry. The H phthalate group of (I) is mobile and by replacement a (—) $\text{Bu}^{\alpha}$  ether is formed opposite in rotational sign to that from (II) and  $\text{Bu}^{\alpha}\text{Br}$ , indicating the occurrence of a Walden inversion during replacement.

H. A. P.

**Dehydration of capryl alcohol [octan- $\beta$ -ol].** F. C. WHITMORE and J. M. HERNDON (J. Amer. Chem. Soc., 1933, 55, 3428—3430).—Dehydration of octan- $\beta$ -ol by  $\text{H}_3\text{PO}_4$  gives a mixture of  $\Delta^{\alpha}$ - and  $\Delta^{\beta}$ -octene (cf. A., 1932, 830) in the ratio 2 : 1.

R. S. C.

**Grignard reagents from dialkyl sulphates.** C. M. SUTER and H. L. GERHART (J. Amer. Chem. Soc., 1933, 55, 3496).— $\text{Bu}^{\alpha}_2\text{SO}_4$  and  $\text{MgBu}^{\alpha}\text{Br}$  give  $\text{Bu}^{\alpha}\text{Br}$  and the compound,  $\text{Bu}^{\alpha}(\text{MgBu}^{\alpha})\text{SO}_4$ .  $\text{Et}_2\text{SO}_4$  and  $\text{Mg}$  in dry  $\text{Et}_2\text{O}$  give the slightly sol. Grignard reagent,  $\text{Et}(\text{MgEt})\text{SO}_4$ , which with  $\text{PhCHO}$  gives a good yield of  $\text{CHPhEt}\cdot\text{OH}$ .  $\text{Bu}^{\alpha}_2\text{SO}_4$  gives a similar reagent, readily hydrolysed to *n*- $\text{C}_{10}\text{H}_{20}$ .

R. S. C.

**Preparation of pure sulphuric acid esters of hydroxystearic acid and octadecanediol.** W. SECK and F. DITTMAR (Fettechem. Umschau, 1933, 40, 146—149; cf. this vol., 47).—Pure preps. of  $\text{Na}_2$ -*s*-sulphostearate from *s*-hydroxystearic acid, and of  $\text{Na}_2$  octadecyl disulphate (I) from octadecane- $\alpha\omega$ -diol, have been obtained. Sulphation of oleyl alcohol affords only a very small yield of (I) (impure).

E. L.

**Preparation of esters of chlorosulphonic and sulphurous acids.** R. LEVALLANT (Compt. rend., 1933, 197, 335—337).—The following chlorosulphonates, lachrymatory, are prepared from  $\text{SO}_2\text{Cl}_2$ : *Bu<sup>\alpha</sup>*, b.p. 76—77°/13 mm., *n-amyl*, b.p. 75—76°/4 mm.,  $\gamma$ -chloropropyl, b.p. 85°/4 mm., and  $\beta\gamma$ -dichloropropyl, b.p. 122—123°/15 mm. The stability of this series is a min. with the *Pr<sup>\alpha</sup>* compound, but is increased by substitution by *Cl*. *n*-Amyl alcohol, prepared from  $\text{MgBu}$  and  $(\text{CH}_2\text{O})_3$ , is accompanied by *di*-(*n*-amyl-oxym) methane, b.p. 99—101°/14 mm.  $\text{SOCl}_2$  gives the following *s*-sulphites,  $\text{SO}_2\text{R}_2$ : *di-n-amyl*, b.p. 124°/13 mm., *di-n-heptyl*, b.p. 181°/13 mm., *di- $\beta$ -bromoethyl*, b.p. 158—159°/13—14 mm., *di- $\gamma$ -chloropropyl*, b.p. 161—162°/13 mm., and *di- $\beta\gamma$ -dichloropropyl*, b.p. 175°/4 mm. Physical consts. are recorded.

R. S. C.

**New method of fluorination of organic compounds.** P. C. RAY (Nature, 1933, 132, 173).—*Me*, b.p. 40°, and *Et*, b.p. 57°, fluoroformate are prepared by the action of  $\text{TlF}$  on the corresponding cold chloroformate and subsequent distillation.

L. S. T.

**Reaction of some imino-ether hydrochlorides with alcohols.** P. P. T. SAH (J. Chinese Chem. Soc., 1933, 1, 100—105; cf. A., 1928, 394).—Prolonged interaction of acetimino-methyl (or -ethyl) ether hydrochloride with cold abs.  $\text{Bu}^{\beta}$  or *isoamyl* alcohol and  $\text{K}_2\text{CO}_3$  affords, respectively, *Me*, b.p. 205—206°, and *Et diisobutyl*-, b.p. 208—210°; *Me*, b.p. 219—223°, and *Et diisomyl-orthoacetate*, b.p. 236—238°.

$\text{CH}_2\text{Ph}\cdot\text{CH}_2\text{CN}$  and abs. EtOH in  $\text{Et}_2\text{O}$  containing HCl afford  $\beta$ -phenylpropioniminoethyl ether hydrochloride (I), which gives with excess of EtOH,  $\text{Et}_3\beta$ -phenylorthopropionate, b.p.  $242^\circ$ . Me and Et ethers [analogous to (I)] from PhCN do not afford esters with many alcohols. J. L. D.

**Insect wax. VI. Synthesis of triglycerides of palmitic and myristic acids.** F. N. SCHULZ and M. BECKER.—See this vol., 1066.

**Branched-chain aliphatic acids. isoMyristic, isopalmitic, and isostearic acids.** C. R. FORDYCE and J. R. JOHNSON (J. Amer. Chem. Soc., 1933, 55, 3368—3372).—Sebacyl chloride (I), b.p.  $155\text{--}156^\circ/8$  mm. (prepared by  $\text{SOCl}_2$ ), and  $n\text{-C}_8\text{H}_{17}\text{MgBr}$  in  $\text{Et}_2\text{O}$  at  $25\text{--}26^\circ$  give  $\iota$ -ketopalmitic acid (28%), m.p.  $75\text{--}75.8^\circ$  (semicarbazone, m.p.  $65\text{--}66^\circ$ ) [giving, when reduced (Clemmensen), palmitic acid], and a substance, m.p.  $85.8\text{--}87^\circ$ . The following were similarly prepared: from  $n\text{-C}_8\text{H}_{17}\text{MgBr}$ ,  $\iota$ -ketostearic acid (12%); from Mg isohexyl bromide,  $\iota$ -keto- $\nu$ -methylpentadecic ( $\iota$ -ketoisopalmitic) acid (24%), m.p.  $68\text{--}69^\circ$ , reduced to  $\nu$ -methylpentadecic (isopalmitic) acid, m.p.  $61.8\text{--}62.4^\circ$ ; from Mg iso-octyl bromide,  $\iota$ -keto- $\sigma$ -methylheptadecic ( $\iota$ -ketoisostearic) acid (11%), m.p.  $71.2\text{--}72^\circ$ , reduced to  $\sigma$ -methylheptadecic (isostearic) acid, m.p.  $67.6\text{--}68.2^\circ$ .  $\text{MgBu}^{\beta}\text{Br}$  and (better)  $o$ -carbethoxynonyl chloride, b.p.  $158\text{--}160^\circ/7$  mm. [from (I) and EtOH], give a small amount of a substance, m.p.  $43\text{--}44^\circ$ , probably  $\delta\nu$ -diketo- $\beta\sigma$ -dimethylhexadecane (semicarbazone, m.p.  $193\text{--}194^\circ$ ), and  $\iota$ -keto- $\lambda$ -methyltridecic acid (43—47%), m.p.  $52\text{--}53^\circ$ , which is reduced to  $\lambda$ -methyltridecic (isomyristic) acid (II), m.p.  $50.5\text{--}51^\circ$ .  $\text{MgPr}^{\beta}\text{Br}$  and  $(\text{CH}_3)_2\text{O}$  give isoamyl bromide, the Grignard reagent from which with Me  $\eta$ -aldehydo-octoate gives Me  $o$ -hydroxyisomyristate (30%), b.p.  $146\text{--}153^\circ/1$  mm., oxidised by  $\text{CrO}_3$  to  $o$ -ketoisomyristic acid, m.p.  $58.2\text{--}59.5^\circ$ , and converted by dehydration, reduction, and hydrolysis into (II). The Et ester, b.p.  $140\text{--}142^\circ/5$  mm., of (II) with Na and EtOH gives isomyristyl alcohol (75—80%), b.p.  $145\text{--}150^\circ/6$  mm. (bromide, b.p.  $120\text{--}123^\circ/3$  mm.).  $\text{MgBu}^{\beta}\text{Br}$  and  $(\text{CH}_3)_2\text{O}$  give isohexyl alcohol (40%), whence by  $\text{HBr}\text{--H}_2\text{SO}_4$  the bromide was obtained in 90—92% yield, and thence similarly iso-octyl bromide, b.p.  $65\text{--}68^\circ/10$  mm. R. S. C.

**Lycopodiumoleic acid.** J. L. RIEBSOMER and J. R. JOHNSON (J. Amer. Chem. Soc., 1933, 55, 3352—3357).—The acids of lycopodium oil are shown, mainly by fractionation of the Pb salts and esters and subsequent ozonolysis, to be chiefly oleic (55—60%) and  $\Delta^6$ -palmitoleic acid (30—35%), with a little linoleic, palmitic,  $0\iota$ -dihydroxystearic, and other acids. "Lycopodiumoleic acid" appears to be a mixture of these acids. R. S. C.

**Reaction between pyruvic acid and hydrogen peroxide in presence of hydrogen sulphide.** A. WASSERMANN (Biochem. Z., 1933, 263, 1—8; cf. this vol., 789).—A method for determining, in the same solution, the velocity of the reactions  $\text{H}_2\text{O}_2 + \text{H}_2\text{S}$  and  $\text{H}_2\text{O}_2 + \text{AcCO}_2\text{H}$  (I) in the presence of  $\text{Fe}^{+++}$  is described. The reactions do not interfere with each other. In (I) no  $\text{H}_2\text{C}_2\text{O}_4$  or succinic acid can be detected. W. McC.

**Lævulic acid. V. 2:4-Dinitrophenylhydrazones of its alkyl esters.** M. A. COWLEY and H. A. SCHUETTE (J. Amer. Chem. Soc., 1933, 55, 3463—3466; cf. this vol., 258).—Lævulic acid (I) in dil. HCl gives the 2:4-dinitrophenylhydrazone, m.p.  $206.5^\circ$  (lit.  $92^\circ$  and  $203^\circ$ ); in EtOH the derivative of the Et ester may be formed. 2:4-Dinitrophenylhydrazones of the following esters of (I) are prepared: Me, m.p.  $141.2^\circ$ ; Et, m.p.  $101^\circ$ ; Pr<sup>a</sup>, m.p.  $63^\circ$ ; Bu<sup>a</sup>, m.p.  $65.8^\circ$ ; n-amyl, m.p.  $84.2^\circ$ ; n-hexyl, m.p.  $56.6^\circ$ ; n-heptyl, m.p.  $79^\circ$ . R. S. C.

**Alkyl esters of lævulic acid.** G. J. COX and (Miss) M. L. DODDS (J. Amer. Chem. Soc., 1933, 55, 3391—3394).—Bw, b.p.  $225.8^\circ$ , dl-amyl, b.p.  $248.8^\circ$ , CHMePr, b.p.  $239.6^\circ$ , and CHEt, lævulic, b.p.  $239^\circ$ , are prepared, best from the crude acid. Physical consts. of these and other lævulates are recorded. The Bu<sup>a</sup> ester was obtained in 11% yield from hot Bu<sup>a</sup>OH, sucrose, and HCl. Bu<sup>a</sup>OH extracts lævulic acid from solutions of the crude product. R. S. C.

**Japanese beeswax. III. Composition of the "hydroxy-fatty acid."** H. IKUTA (J. Soc. Chem. Ind. Japan., 1933, 36, 444—447B; cf. B., 1933, 797).—A hydroxypalmitic acid, m.p.  $73.8\text{--}74.2^\circ$ , has been isolated from the fatty acids of Japanese beeswax, of which it constitutes about 20%, occurring partly in the free state. The "hydroxy-" and "isohydroxy-margaric" acids of Lipp and Kovacs (A., 1920, i, 140) probably consisted of mixtures of hydroxypalmitic and higher fatty (? hydroxylated) acids. E. L.

**Ethyl oxalosorbate and oxalic ester condensations.** W. BORSCHÉ and R. MANTEUFFEL (Annalen, 1933, 505, 177—194; cf. A., 1932, 721).—The K derivative of  $\text{Et}_2$  oxalosorbate (I) is converted by prolonged action of cold 10% KOH into oxalosorbic acid ( $\Delta^{\nu}$ -hexadiene- $\alpha$ -one- $\alpha\zeta$ -dicarboxylic acid, m.p.  $220\text{--}221^\circ$  (decomp.) ( $\text{Me}_2$  ester, m.p.  $132\text{--}133^\circ$ ), and by  $\text{Me}_2\text{SO}_4$  in boiling  $\text{C}_6\text{H}_6$  into  $\text{Et}_2$   $\alpha$ -methoxy- $\Delta^{\nu}$ -hexatriene- $\alpha\zeta$ -dicarboxylate (II), b.p.  $180\text{--}185^\circ/15$  mm. (I) is readily reduced ( $\text{PtO}_2\text{--EtOH}$ ) to  $\text{Et}_2$   $\alpha$ -hydroxysebacate, b.p.  $167\text{--}170^\circ/12$  mm. (Bz derivative, b.p.  $184\text{--}185^\circ/2$  mm., obtained by reduction of  $\text{Et}_2$  benzoyloxyhexatrienedicarboxylate). Complete reduction of (II) ( $\text{PtO}_2\text{--EtOH}$ ) leads to  $\text{Et}_2$   $\alpha$ -methoxysebacate, b.p.  $162\text{--}165^\circ/12$  mm., whereas partial reduction ( $\text{Pd--EtOH}$ ) affords  $\text{Et}_2$   $\alpha$ -methoxy- $\Delta^{\alpha}$ -hexene- $\alpha\zeta$ -dicarboxylate, b.p.  $172\text{--}174^\circ/12$  mm., transformed by boiling EtOH-HCl into  $\text{Et}_2$   $\alpha$ -ketosuberate (III), b.p.  $174\text{--}175^\circ/16$  mm. (III) and  $\text{NHPh}\cdot\text{NH}_2$  afford 2-carboxy-3- $\delta$ -indolylvaleric acid, m.p.  $193\text{--}195^\circ$ . In presence of  $\text{MeOH--HCl}$ , (I) and  $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$  yield  $\text{Et}_2$   $\alpha\beta$ -diketo- $\Delta^{\nu}$ -hexadiene- $\alpha\zeta$ -dicarboxylate  $\beta$ -p-anisylhydrazone,  $\text{CO}_2\text{Et}\cdot\text{C}(\text{OH})\cdot\text{C}(\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OMe})\cdot[\text{CH}\cdot\text{CH}]_2\cdot\text{CO}_2\text{Et}$  (IV), m.p.  $104\text{--}105^\circ$  (or  $+1\text{MeOH}$ , m.p.  $92\text{--}93^\circ$ ), and a small amount of 4:5-diketo-1-p-anisyl-3- $\delta$ -carbethoxy- $\Delta^{\nu}$ -butadienylpyrazoline,  $\text{CO}\text{---}\text{CO}\text{---}\text{C}(\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OMe})\cdot\text{N}\text{---}\text{C}[\text{CH}\cdot\text{CH}]_2\cdot\text{CO}_2\text{Et}$  (V), m.p.  $164\text{--}165^\circ$  (or  $+1\text{MeOH}$ , m.p.  $156\text{--}157^\circ$ ). The 2:4-dinitrophenylhydrazone of (V) has m.p.  $258\text{--}259^\circ$ . Treatment of (IV) or (V) with  $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$  in

presence of MeOH-NH<sub>3</sub> gives *Et* δ-(*pp'*-dimethoxyformazyl)butadienecarboxylate,

OMe·C<sub>6</sub>H<sub>4</sub>·NH·N·C(N:N·C<sub>6</sub>H<sub>4</sub>·OMe)·[CH:CH]<sub>2</sub>·CO<sub>2</sub>Et, m.p. 136—137°. (I) and *p*-C<sub>6</sub>H<sub>4</sub>Br·N<sub>2</sub>Cl yield *Et*<sub>2</sub> αβ-diketo-Δ<sup>γ</sup>-hexadiene-αζ-dicarboxylate *p*-bromophenylhydrazone, m.p. 126—127°, and 4:5-diketo-1-*p*-bromophenyl-3-δ-carbethoxy-Δ<sup>γ</sup>-butadienylpyrazoline, m.p. 158—159°, or, +1EtOH, m.p. 117—118° (2:4-dinitrophenylhydrazone, m.p. 264°). (I) and *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NMe<sub>2</sub> in boiling EtOH afford the anil NMe<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·N·CH·[CH:CH]<sub>2</sub>·CO<sub>2</sub>Et, m.p. 187—188°.

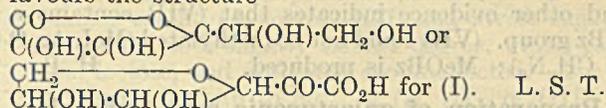
*Et*<sub>2</sub> oxalocrotonate (VI), m.p. 78° (2:4-dinitrophenylhydrazone, m.p. 117—118°), is converted into the K derivative and thence by Me<sub>2</sub>SO<sub>4</sub> into *Et*<sub>2</sub> α-methoxymuconate (VII), b.p. 118—120°/2 mm. Hydrogenation of (VI) (PtO<sub>2</sub>-EtOH) leads to *Et*<sub>2</sub> α-hydroxyadipate, b.p. 160—161°/17 mm. Complete reduction of (VII) (colloidal Pd-EtOH) yields *Et*<sub>2</sub> α-methoxyadipate, b.p. 142—144°/12 mm., whereas partial hydrogenation affords *Et*<sub>2</sub> α-methoxy-Δ<sup>γ</sup>-dihydromuconate, b.p. 153—156°/15 mm., transformed by HCl-EtOH into *Et*<sub>2</sub> α-ketoadipate, b.p. 155—157°/16 mm. (semicarbazone, m.p. 118°). *Et*<sub>2</sub> α-benzoyloxyadipate, b.p. 160—162°/2 mm., is derived from the corresponding muconate. 4:5-Diketo-1-*p*-bromophenyl-3-β-carbethoxyvinylpyrazoline (+1EtOH), m.p. 91° after softening and darkening at 82° (2:4-dinitrophenylhydrazone, m.p. 237°), is formed in addition to *Et*<sub>2</sub> *p*-bromobenzeneazo-oxalocrotonate, m.p. 125°, from (VI) and *p*-C<sub>6</sub>H<sub>4</sub>Br·N<sub>2</sub>Cl. The *p*-dimethylaminoanil, m.p. 151.5—152.5°, and the 2:4-dinitrophenylhydrazone, m.p. 290—292°, of *Et* β-formylacrylate are described.

HCO<sub>2</sub>Et under the influence of KOEt condenses with *Et* crotonate (VIII) to *Et* γ-aldehydocrotonate [2:4-dinitrophenylhydrazone, m.p. 147—148° (decomp.)] and with *Et* sorbate (IX) to *Et* ε-aldehydosorbate (2:4-dinitrophenylhydrazone, m.p. 148—150°). The primary stage of the condensation of (VIII) and (IX) is considered to consist in the production of the compounds CH<sub>2</sub>:CH·CH:C(OK)·OEt and CH<sub>2</sub>:CH·CH:CH·C(OK)·OEt, which undergo αδ and αζ addition with CO<sub>2</sub>Et·C(ONa)(OEt)<sub>2</sub>. H. W.

Conjugated compounds. XIX. Michael reaction applied to a triene ester. E. H. FARMER and S. R. W. MARTIN (J.C.S., 1933, 960—962).—Addition of CH<sub>2</sub>(CO<sub>2</sub>Me)<sub>2</sub> to Me Δ<sup>γ</sup>-heptatriene-α-carboxylate gives about 67% of the αβ and at least 10% of the αζ additive products; αδ addition could not be detected. The resultant mixture, b.p. 154—159°/1—2 mm., of *Me* β-methylheptadiene-ααη-tricarboxylate and *Me* Δ<sup>γ</sup>-heptadiene-α-carboxylate-β-malonate is reduced catalytically to a mixture, b.p. (mainly) 142—150°/1—2 mm., of *Me* β-methylheptane-ααη-tricarboxylate and *Me* heptane-α-carboxylate-β-malonate, which on hydrolysis (aq. MeOH-NaOH), decarboxylation of the resulting acids at 170°, and subsequent dehydration (Ac<sub>2</sub>O) gives β-*n*-amylglutaric anhydride, b.p. 138°/2 mm., and polymeric β-methylazelaic anhydride. *n*-Hexaldehyde and CN·CH<sub>2</sub>·CO·NH<sub>2</sub> give αα'-dicyano-β-*n*-amylglutaramide, which is hydrolysed (15% HCl) to β-*n*-amylglutaric acid, b.p. 208°/2 mm. β-*n*-Amylglutaranilic acid has m.p. 81°. H. B.

Vitamin-C. F. MICHEEL (Angew. Chem., 1933, 46, 533—536).—A lecture. H. W.

Structure of ascorbic acid (vitamin-C). P. A. LEVENE and A. L. RAYMOND (Science, 1933, 78, 64).—Ascorbic acid (I) absorbs 2 H on hydrogenation, giving an acid which forms a stable lactone. This favours the structure



Synthesis of *d*- and *l*-ascorbic acid (vitamin-C). T. REICHSTEIN, A. GRÜSSNER, and R. OPPENAUER (Nature, 1933, 132, 280).—An improved method (this vol., 594) is described for the conversion of *d*- and *l*-xylosone, respectively, into *d*- and *l*- (I) ascorbic acid, m.p. 186—189° (corr., decomp.) [α]<sub>D</sub><sup>20</sup> ±48° in MeOH. Equal amounts of the *d*- and *l*- forms give crystals, m.p. 168—169° (corr.) [α]<sub>D</sub><sup>20</sup> 0°. (I) is identical with natural ascorbic acid. L. S. T.

Biochemistry and physiology of glycuronic acid. I. Structure of glycuronic acid of animal origin. II. Methylation of glycurone of animal origin. III. Structure of benzoylglycuronic acid. J. PRYDE and R. T. WILLIAMS (Biochem. J., 1933, 27, 1197—1204, 1205—1209, 1210—1215).—I. β-Bornyl-*d*-glycuronide (borneolglycuronic acid) (I), C<sub>16</sub>H<sub>26</sub>O<sub>7</sub>·1.5H<sub>2</sub>O, m.p. 174—175°, isolated as its Zn salt (cf. Quick, A., 1927, 990) from the urine of dogs and human beings fed with borneol, is methylated (MeI, Ag<sub>2</sub>O) to 2:3:4-trimethyl-β-bornyl-*d*-glycuronide Me ester, m.p. 92—93°, [α]<sub>D</sub><sup>20</sup> -30.7° in EtOH, which is hydrolysed (MeOH-0.2*N*-H<sub>2</sub>SO<sub>4</sub> at 100°) to a mixture (II), b.p. 131°/4 mm., [α]<sub>D</sub><sup>20</sup> +98.9° in H<sub>2</sub>O, of α- and β-2:3:4-trimethylmethyl-*d*-glycuronide Me ester. Oxidation (HNO<sub>3</sub>, *d* 1.42) of (II) at 65—90° and subsequent esterification (MeOH-HCl) gives Me *d*-dimethoxysuccinate (small amount), Me *i*-xylotrimethoxyglutarate (III), and 2:3:4-trimethyl-δ-saccharolactone Me ester (IV). The isolation of (III) and (IV) establishes the pyranoid structure of the glycuronic acid residue of (I).

II. Hydrolysis of (I) (above) with boiling 0.2*N*-H<sub>2</sub>SO<sub>4</sub>, quant. removal of H<sub>2</sub>SO<sub>4</sub> from the filtrate with Ba(OH)<sub>2</sub>, evaporation of the resulting solution at 40°/vac. to a syrup, dissolution of this in the min. amount of H<sub>2</sub>O, and subsequent addition of EtOH gives *d*-glycurone, m.p. 177—178°, [α]<sub>D</sub><sup>20</sup> +21.3° in H<sub>2</sub>O. This is methylated (MeI, Ag<sub>2</sub>O) (cf. A., 1931, 1036; this vol., 259) to trimethylglycurone (V), m.p. 131—132°, [α]<sub>D</sub><sup>20</sup> +197.5° in H<sub>2</sub>O, the unsaturated trimethylglycuralone (VI), m.p. 88°, [α]<sub>D</sub><sup>20</sup> +110.8° in H<sub>2</sub>O, and (mainly) a syrup [which is methylated further to (probably) 2:3:4-trimethyl-β-methyl-*d*-glycuronide Me ester]. Possible structures are suggested for (V) and (VI). The formation of a double linking [in (VI)] is ascribed to the mild oxidising action of Ag<sub>2</sub>O.

III. Conjugated glycuronic acids are divided into three types: (a) glycoside-ether [as (I) (above)]; (b) glycoside-ester [as (VII) (below)]; (c) those containing two glycuronic acid residues, one being attached to a non-sugar group as in (a), the other attached by an ester linking as in (b). Benzoylglycuronide (benzoyl-

glycuronic acid) (VII) (improved method of prep. given; cf. Quick, A., 1926, 1056), m.p. 183° (lit. 170—172°),  $[\alpha]_{D}^{25} -29.9^\circ$  in  $H_2O$ , reduces sugar reagents owing to the ease of hydrolysis of the Bz group. Treatment of (VII) with aq. KCN causes hydrolysis and subsequent formation of glycuronic acid cyanohydrin (cf. Quick, *loc. cit.*). The above and other evidence indicates that (VII) contains a 1-Bz group. (VII) could not be methylated (MeI,  $Ag_2O$  or  $CH_2N_2$ ); MeOBz is produced. H. B.

**Preparation of galacturonic acid from plant materials and its derivatives.** H. R. NANJI (Biochem. J., 1933, 27, 1163—1165).—Lemon peel is a more satisfactory source of *d*-galacturonic acid [cinchonine salt, m.p. 173° (decomp.); phenylhydrazine salt phenylhydrazone, m.p. 131° (decomp.)] than apple pomace or sugar-beet residues. H. B.

**Composition of lemon albedo pectin.** (Miss) C. M. BRIDGHAM and C. G. KING (J. Amer. Chem. Soc., 1933, 55, 3319—3322).—Purified lemon albedo (white peel) pectin gives by hydrolysis *d*-galacturonic acid (4 mols.) (mostly present as the Me ester), galactose (1 mol.), and arabinose (1 mol.). R. S. C.

**Bromometric determination of sulphido-acids.** N. HELLSTRÖM (Svensk Chem. Tidskr., 1933, 45, 158—169).—Sulphido-acids are oxidised by a slight known excess of Br (in the form of  $KBr+KBrO_3$ ) and back-titrated with  $Na_2S_2O_3$  after adding KI. Alternatively, potentiometric titrations may be carried out directly with aq. Br. Titrations must be rapid to avoid further oxidation. Typical reactions are:  $\cdot CH_2 \cdot S \cdot CH_2 \cdot + 2Br + H_2O = \cdot CH_2 \cdot SO \cdot CH_2 \cdot + 2HBr$ ,  $\cdot CH_2 \cdot S \cdot S \cdot CH_2 \cdot + 10Br + 6H_2O = 2 \cdot CH_2 \cdot SO_2 \cdot OH + 10HBr$ ,  $\cdot CH_2 \cdot SH + 6Br + 3H_2O = \cdot CH_2 \cdot SO_2 \cdot OH + 6HBr$ ,  $\cdot CH(S \cdot CH_2)_2 + 12Br + 7H_2O = \cdot CHO + 2 \cdot CH_2 \cdot SO_2 \cdot OH + 12HBr$ ,  $\cdot CH_2 \cdot S(CH_2)_n \cdot S \cdot CH_2 \cdot + 4Br + 2H_2O = \cdot CH_2 \cdot SO(CH_2)_n \cdot SO \cdot CH_2 \cdot + 4HBr$ . Satisfactory results were obtained with the following acids:  $S(CH_2 \cdot CO_2H)_2$  (I),  $NH_2 \cdot CO \cdot CH_2 \cdot S \cdot CH_2 \cdot CO_2H$ ,  $SMe \cdot CH_2 \cdot CO_2H$ ,  $CHMe(S \cdot CH_2 \cdot CO_2H)_2$ ,  $CO_2H \cdot CH(S \cdot CH_2 \cdot CO_2H)_2$ ,  $(\cdot CH_2 \cdot S \cdot CH_2 \cdot CO_2H)_2$ ,  $CH_2(CH_2 \cdot S \cdot CH_2 \cdot CO_2H)_2$ ,  $(\cdot S \cdot CH_2 \cdot CO_2H)_2$  (II), and with  $(\cdot S \cdot CH_2 \cdot CO \cdot NH_2)_2$ .  $CH_2(S \cdot CH_2 \cdot CO_2H)_2$  gave unsatisfactory results. The method was used to analyse a mixture of (I) and (II). R. P. B.

**Stereochemistry of sulphur. I. Stereoisomeric  $\alpha\alpha'$ -dicarboxydipropyl disulphides.** R. AHLBERG (J. pr. Chem., 1933, [ii], 138, 128—144).— $\alpha$ -Thiodibutyric acid is prepared by interaction of aq.  $CH_2EtBr \cdot CO_2Na$  and  $OEt \cdot CS \cdot SK$ , hydrolysis with aq.  $H_2SO_4$ , and air-oxidation of the resulting  $\alpha$ -thiolbutyric acid in presence of  $MnSO_4$  or  $Fe^{II}$  salts and  $FeCl_3$ .  $H_2O_2$  may also be used as oxidising agent. With a slight deficit of  $NaOEt$  (?  $NaOH$ ) in  $EtOH$  the *Na* salt (+ $2H_2O$ ) of the racemic acid (I) separates; with excess of  $NaOEt$  more *Na* salt slowly forms, apparently by rearrangement of other racemic acids, as the *meso*-acid, separated as *cinchonine* salt, m.p. 67—68.5°, is unaffected by  $NaOEt$ . By optical resolution of (I) *cinchonidine* (+ $4H_2O$ ) and *brucine* salts of the (+)-acid ( $[\alpha]_D^{25} +427^\circ$  in  $H_2O$ ) and the *strychnine* salt (+ $5H_2O$ ) of the (—)-acid are obtained. H. A. P.

**Semi-acetal and hydrate formation of carbonyl and carboxyl derivatives.** W. HEROLD (Z. Elektrochem., 1933, 39, 566—571; cf. A., 1932, 982, 1188).—The change in absorption spectrum of aldehydes and ketones and their derivatives in alcoholic solvents is used to measure the extent of semi-acetal and hydrate formation. Data for many compounds containing the  $C=O$  group are discussed with reference to their stability and the influence of substituted groups.  $CCl_3 \cdot CHO$  has a strong tendency to semi-acetal formation. The kinetics of its reaction with  $EtOH$  in eight solvents were studied, and the influence of the solvent is discussed. H. J. E.

**Colour reaction of aldehydes.** P. RUMPF (Compt. rend., 1933, 197, 337—339).—A cold, freshly-prepared solution of 2—3 mg. of rosaniline hydrochloride in 98—100%  $HCO_2H$  gives the following colours: (a) with  $CH_2O$  and  $CCl_3 \cdot CHO$  fuchsin-red (max. 5480 Å. for  $CH_2O$ ); (b) with aromatic aldehydes and those having a *tert.* C atom, as (a), but brighter, and with  $\alpha\beta$ -unsaturated aldehydes [except acraldehyde (I)] as (a) with an orange shade (max. 4500 Å., possibly with a second max. at 4800 Å.); (c) with aldehydes having an  $\alpha$ - $CH_2$  group, the colour changes more or less rapidly to green (max. 6270 Å.), and two substances, violet (max. 5600 Å.) and pure blue (max. about 5980 Å.), respectively, can be isolated by  $H_2O$ ; (d) acraldehydes having no  $\beta$ -substituent and aldehydes having an  $\alpha$ - $CH<$  group, as (c) but more rapidly. Polymerides (*e.g.*, trioxymethylene), H sulphite and other compounds [*e.g.*,  $(CH_2)_6N_4$ , or acetal] which give the free aldehyde, even in traces, in anhyd. acid solution give the reaction. Certain terpenes give blue colours, thus preventing application of the reaction in this series. R. S. C.

**Action of hydrogen peroxide on aldehydes.** S. BEZZI (Gazzetta, 1933, 63, 345—355).—The gaseous product from  $MeCHO$  and  $H_2O_2$  in presence of  $H_2SO_4$  at 95° is largely  $CH_4$  and  $H_2$ ;  $AcOH$ ,  $HCO_2H$ , and  $CO_2$  are also formed. Similarly  $EtCHO$  yields  $C_2H_6$ ,  $H_2$ ,  $EtCO_2H$ , etc. Mechanisms for such reactions proposed by Wieland (A., 1921, i, 889) and Fry and Payne (A., 1931, 819) are rejected. The mechanism  $[CHR(OH) \cdot O]_2 \rightarrow H_2 + 2RCO_2H$  and  $\rightarrow RH + HCO_2H + RCO_2H$  is suggested. E. W. W.

**Thermal reaction between chlorine and form-aldehyde.** R. SPENCE and W. WILD (Nature, 1933, 132, 170).—At 150°, in the dark, the rapid reaction  $CH_2O + Cl_2 = CO + 2HCl$  occurs after a short induction period. A complex chain process is probably involved. No measurable reaction occurs at 100°. L. S. T.

**$\alpha\beta$ -Trihalogenobutaldehydes.** F. D. CHATTAWAY, H. IRVING, and G. H. OUTHWAITE (J.C.S., 1933, 993—995).— $\alpha$ -Chlorocrotonaldehyde (from  $CHMeCl \cdot CHCl \cdot CHO$  and aq.  $NaOAc$ ) and Br (1 mol.) at < 0° give  $\alpha$ -chloro- $\alpha\beta$ -dibromobutaldehyde (*monohydrate*, m.p. 45—50°), and  $\alpha$ -bromocrotonaldehyde (I) similarly affords  $\alpha\beta$ -tribromobutaldehyde (butyl bromal) [*monohydrate* (II), m.p. 42—45°].  $\alpha\beta$ -Dichloro- $\alpha$ -bromobutaldehyde (*monohydrate*, m.p. 70°) is similarly prepared from (I) and Cl. Cautious fusion of (II) with  $HCO \cdot NH_2$ ,  $NH_2Ac$ , and  $NH_2Bz$  gives

*form-*, m.p. 133° (decomp.), *acet-*, m.p. 140° (decomp.), and *benz-*, m.p. 142° (decomp.),  $\beta\beta\gamma$ -tribromo- $\alpha$ -hydroxybutylamide, respectively; with  $\text{CO}(\text{NH}_2)_2$ ,  $\beta\beta\gamma$ -tribromo- $\alpha$ -hydroxybutylcarbamide, m.p. 104° (decomp.), results. The following are similarly prepared: *form-*, m.p. 136° (decomp.), *acet-*, m.p. 142° (decomp.), and *benz-*, m.p. 144° (decomp.),  $\beta$ -chloro- $\beta\gamma$ -dibromo- $\alpha$ -hydroxybutylamide; *form-*, m.p. 140° (decomp.), *acet-*, m.p. 165° (decomp.), and *benz-*, m.p. 157° (decomp.),  $\beta\gamma$ -dichloro- $\beta$ -bromo- $\alpha$ -hydroxybutylamide;  $\beta$ -chloro- $\beta\gamma$ -dibromo-, m.p. 112° (decomp.), and  $\beta\gamma$ -dichloro- $\beta$ -bromo-, m.p. 153° (decomp.),  $\alpha$ -hydroxybutylcarbamide. The trihalogenobutaldehydes resemble butyl chloral in appearance and properties, give liquid alcoholates, and are oxidised (fuming  $\text{HNO}_3$ ) to the trihalogenobutyric acids. H. B.

**New ether-acetals and ether-aldehydes.** M. ROTBART (Compt. rend., 1933, 196, 2013—2015).—Na alkoxides are condensed with bromodiethylacetal by heating under pressure at  $>190^\circ$  to give ether-acetals,  $\text{OR}\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$  (75% yield), hydrolysed by 25%  $\text{H}_2\text{SO}_4$  in aq. AcOH to ether-aldehydes,  $\text{OR}\cdot\text{CH}_2\cdot\text{CHO}$ , the yield reaching 90% when R is *n*-alkyl. The following are described: *sec.-octyloxy-diethylacetal*, b.p. 131—132°/14 mm., *-acetaldehyde*, b.p. 98—99.5°/15 mm. (*semicarbazone*, m.p. 78.5—79.5°), *n-decyloxy-diethylacetal*, b.p. 159—160°/14 mm., *-acetaldehyde*, b.p. 133—135°/15 mm., m.p. 19.5—20° (*semicarbazone*, m.p. 103—104°), *n-dodecyloxy-diethylacetal*, b.p. 150—151°/3 mm., *-acetaldehyde*, m.p. 18°, b.p. 118—119°/3 mm. (*semicarbazone*, m.p. 108°), *n-tetradecyloxy-diethylacetal*, m.p. 25°, b.p. 161—162°/2 mm., *-acetaldehyde*, m.p. 36°, b.p. 138—140°/4 mm. (*semicarbazone*, m.p. 97°), *n-hexadecyloxy-diethylacetal*, m.p. 37°, b.p. 192—194°/1 mm., and *-acetaldehyde*, m.p. 47° (*semicarbazone*, m.p. 102°). A. C.

**Condensation of aldehydes with ketones and some of the products derived from the ketols.** L. P. KYRIDES (J. Amer. Chem. Soc., 1933, 55, 3431—3435).—Gradual addition of a  $\text{MeCHO}\cdot\text{COMeEt}$  (1 : 2) mixture to  $\text{COMeEt}$  at 8—9° in presence of a little NaOH gives a little crotonaldehyde and an 85% yield of  $\gamma$ -methylpentan- $\delta$ -ol- $\beta$ -one, b.p. 95—96°/35 mm., dehydrated by distillation with a little HBr to  $\gamma$ -methyl- $\Delta^7$ -penten- $\beta$ -one, b.p. 139.5—141°, and reduced electrolytically in presence of  $\text{NaHCO}_3$  to  $\gamma$ -methylpentane- $\beta\delta$ -diol (66% yield), whence by HBr a 64% yield of  $\gamma$ -methyl- $\Delta^{7,8}$ -pentadiene, b.p. 75—80°, was obtained.  $\text{PrCHO}$  and  $\text{COMeEt}$  give similarly  $\gamma$ -methylheptan- $\delta$ -ol- $\beta$ -one (78%), b.p. 105—120°/30 mm., dehydrated by distillation in partial vac. to  $\gamma$ -methyl- $\Delta^7$ -hepten- $\beta$ -one (95%), b.p. 174—176°. R. S. C.

**Acyloins.** V. Photochemical formation of acetoin, butyrolin, and acetylphenylcarbinol. W. DIRSCHERL (Z. physiol. Chem., 1933, 219, 177—190; cf. A., 1931, 1457).—The yield of acetoin formed by ultra-violet light from  $\text{AcCO}_2\text{H}$  (I) in  $\text{H}_2\text{O}$  decreases from 100% at 0.2—3*M* to 12% at 11.4*M* [pure (I)]. In presence of  $\text{PhCHO}$  the formation of  $\text{CHAcPh}\cdot\text{OH}$  was detected.  $\text{PhCHO}$ ,  $\text{C}_6\text{H}_6$ , salts, and other dehydrating agents hinder acyloin formation. Irradiation of  $\alpha$ -ketovaleric acid (0.5—2*M*) gives butyrolin in 30—40% yield. In all cases where the acyloin

yield is not quant. aldehyde is not detected in the products. J. H. B.

**Removal of sugars from dilute solutions.** J. L. BAKER and H. F. E. HULTON (Biochem. J., 1933, 27, 1040—1043).—Glucose (I) or maltose (II) in 0.2% aq. solution is completely fermented in 30 min. by 100 times its wt. of pressed brewer's yeast. Under similar conditions sucrose (III) and invert sugar are fermented to a slightly smaller degree, whilst galactose, lactose, and arabinose are unaffected. The rate of removal of up to 50% of (I), (II), or (III) from 0.2% aq. solution is dependent on the time of fermentation and on the relative amount of yeast present. The rate of  $\text{CO}_2$  evolution indicates that such rapid disappearance of sugar is due to fermentation and not to adsorption (cf. A., 1928, 912). The presence of  $\text{PhMe}$  or 12%  $\text{EtOH}$  only partly inhibits fermentation. F. O. H.

**Influence of hydrogen peroxide on determination of glucose by Bertrand's method.** A. MALKOV (J. Appl. Chem. Russ., 1933, 6, 567).— $\text{H}_2\text{O}_2$  alone or together with  $\text{Fe}^{++}$  does not interfere with determination of glucose by Bertrand's method. R. T.

**Biological reagents in sugar analysis.** V. J. HARDING and T. F. NICHOLSON (Biochem. J., 1933, 27, 1082—1094).—A strain of *Proteus vulgaris* (I) has been found which removes glucose (II) from solution but leaves fructose (III), mannose (IV), and sucrose (V) intact; it may be employed in the determination of (II) in presence of (III), (IV), and (V). Mixtures of (II), (III), and (V) may be analysed by the removal of (II) by (I) and subsequent treatment with *Monilia krusei* (VI), which removes (III) but leaves (V). The presence of (IV) and maltose (VII) leads to erroneous results. (VII) may be removed by treatment with *M. penoyi* (VIII) previous to hydrolysis of (V). Application of (I) shows the presence of (II) in normal fasting urine. The method applied to the Folin-Wu blood filtrates gives results of the expected val. (I), (VI), *S. marxiannus*, and *M. macedoninensis* do not act on (VII), whilst (VIII) and *M. tropicalis* remove (VII) completely. The removal of (VII) by brewer's or baker's yeast is somewhat variable. (VI) has no action on galactose (IX) and is therefore of use in the determination of this sugar in presence of (II), (III), and (IV). A scheme is given for the analysis of mixtures of (II), (III) or (IV), (IX), (V), (VII), and lactose. W. O. K.

**Walden inversion in the glucose series. Derivatives of altrose.** D. S. MATHERS and G. J. ROBERTSON (J.C.S., 1933, 1076—1081).—4 : 6-Benzylidene- $\alpha$ -methylglucoside 2 : 3-dibenzoate is hydrolysed (0.25%  $\text{HCl}$  in  $\text{COMe}_2$ ) to  $\alpha$ -methylglucoside 2 : 3-dibenzoate,  $[\alpha]_D +154.4^\circ$  in  $\text{EtOH}$ , which is methylated ( $\text{MeI}$ ,  $\text{Ag}_2\text{O}$ ) to an impure 4 : 6-Me<sub>2</sub> derivative. This is hydrolysed (aq.  $\text{EtOH}\cdot\text{KOH}$ ) to a product, b.p. 155° (bath)/0.03 mm.,  $[\alpha]_D +165.7^\circ$  in  $\text{CHCl}_3$ , containing  $< 54\%$  of 4 : 6-dimethyl- $\alpha$ -methylglucoside (isolated as the 2 : 3-di-*p*-toluenesulphonate); the remainder of the product probably consists of isomerides formed by the catalytic rearrangement of Bz groups during the methylation. 4 : 6-Benzylidene- $\alpha$ -methylglucoside 2 : 3-di-*p*-nitrobenzoate, m.p. 169—170°,  $[\alpha]_D +127.7^\circ$

in  $\text{CHCl}_3$ , is hydrolysed (as above) to  $\alpha$ -methylglucoside 2:3-di-*p*-nitrobenzoate, m.p. 143—155°; methylation of this is complicated also.  $\alpha$ -Methylglucoside 2:3-di-*p*-toluenesulphonate,  $[\alpha]_D^{25} +58.5^\circ$  in  $\text{CHCl}_3$ , prepared by hydrolysis of its 4:6-benzylidene derivative, is methylated (MeI,  $\text{Ag}_2\text{O}$ ) to 4:6-dimethyl- $\alpha$ -methylglucoside 2:3-di-*p*-toluenesulphonate (I), m.p. 116—117°,  $[\alpha]_D^{25} +54.7^\circ$  in  $\text{CHCl}_3$ , which is hydrolysed (aq. EtOH-KOH) to 66% of a dimethylanhydromethylhexoside (II), m.p. 63—64°,  $[\alpha]_D^{25} +188.9^\circ$  in  $\text{CHCl}_3$ , and 26% of a syrup (III), b.p. 150—155° (bath)/0.8 mm.,  $[\alpha]_D^{25} +138.9^\circ$  in  $\text{H}_2\text{O}$ . *p*-Toluenesulphonylation of (III) does not regenerate (I) but gives (probably) 4:6-dimethyl- $\alpha$ -methylaltroside 2:3-di-*p*-toluenesulphonate, m.p. 132—134°,  $[\alpha]_D^{25} +103.3^\circ$  in  $\text{CHCl}_3$ ; methylation (MeI,  $\text{Ag}_2\text{O}$ ) of (III) and subsequent hydrolysis of the glucosidic Me group affords (probably) 2:3:4:6-tetramethylaltrose, m.p. 76—78°,  $[\alpha]_D^{25} +97.4^\circ$  in EtOH. It is suggested that hydrolysis of (I) is accompanied by complete inversion of H and OH on  $\text{C}_2$  (or  $\text{C}_3$ ), simultaneously with a partial inversion on  $\text{C}_3$  (or  $\text{C}_2$ ), giving a mixture of mannose (or allose) and altrose derivatives; the former is then dehydrated. (II) is 4:6-dimethyl-2:3-anhydro- $\alpha$ -methyl-mannoside or -alloside. H. B.

**Acetylation of galactoseoxime.** V. DEULOFEU, M. L. WOLFROM, P. CATTANEO, C. C. CHRISTMAN, and L. W. GEORGES (J. Amer. Chem. Soc., 1933, 55, 3488—3493).—The substance (A., 1932, 1237) called  $\alpha$ -galactoseoxime hexa-acetate is a mixture. Galactoseoxime (I),  $\text{C}_5\text{H}_5\text{N}$ , and  $\text{Ac}_2\text{O}$  at 23—25° give *al*-galactoseoxime hexa-acetate (II),  $[\alpha]_D^{25} +23.6^\circ$  in  $\text{CHCl}_3$ , an isomeride (III), m.p. 106°,  $[\alpha]_D^{25} -27.5^\circ$  in  $\text{CHCl}_3$ , and galactonitrile penta-acetate (IV). Chiefly (IV) is obtained by acetylation at 100°. (I) with  $\text{NaOAc}$  and boiling  $\text{Ac}_2\text{O}$  forms (III) and (IV). (II), when melted or heated with  $\text{NaOAc}$  and  $\text{Ac}_2\text{O}$ , gives  $\text{AcOH}$  and (IV). (III) does not give (IV) when melted. *al*-*l*-Arabinoseoxime tetra-acetate gives the oxime, m.p. 137—139°,  $[\alpha]_D^{25} -5.2^\circ$  in  $\text{CHCl}_3$ , which with  $\text{Ac}_2\text{O}$  and  $\text{C}_5\text{H}_5\text{N}$  at 0° gives *l*-arabonitrile tetra-acetate. R. S. C.

**Alleged production of polysaccharides in alkaline solutions of hexoses.** H. A. SPOEHR and H. H. STRAIN (Biochem. Z., 1933, 264, 1—5).—Since aq. solutions of *d*-glucose, *d*-fructose, and *d*-galactose yield no polysaccharides after 2 months' contact with  $\text{Na}_2\text{CO}_3$  or  $\text{Ca}$ ,  $\text{Pb}$ , or uranyl acetate at 15.5—38.0° in the dark, Nef's conclusions (A., 1914, i, 490) must be rejected. W. McC.

**Trianhydroperiplogenin.** W. A. JACOBS and N. M. BIGELOW (J. Biol. Chem., 1933, 101, 697—700).—Periplogenin when heated with  $\text{MeOH-HCl}$  gives trianhydroperiplogenin,  $\text{C}_{23}\text{H}_{28}\text{O}_2$ , m.p. 191—193°,  $[\alpha]_D^{25} -130^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ , reduced in  $\text{AcOH}$  (Pt- $\text{H}_2$ ) to the  $\text{H}_8$ -derivative, m.p. 176—177°,  $[\alpha]_D^{25} +16.4^\circ$  in  $\text{CHCl}_3$ . F. R. S.

**Starch. Cinnamoyl esters.** W. S. REICH and A. F. DAMANSKY (Compt. rend., 1933, 197, 275—277).—In anhyd. solvents natural starch (I) or amylopectin gives a *dicinnamoyl* ester, whereas amylose (II) gives a *tricinnamoyl* ester,  $[\alpha]_D^{25} -187^\circ$  in  $\text{CHCl}_3$ . Both esters give the original material when hydrolysed. In  $\text{H}_2\text{O}$  at 90° (II) gradually gives (I), as

judged by the composition of the cinnamoylation products. R. S. C.

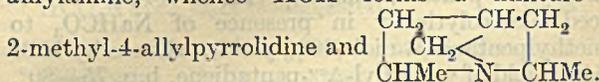
**Additive compounds of cellulose.** G. CHAMPETIER (Ann. Chim., 1933, [x], 20, 5—96).—Cellulose immersed in aq. solutions yields the compounds  $2\text{C}_6\text{H}_{10}\text{O}_5, \text{NaOH}$ ,  $\text{C}_6\text{H}_{10}\text{O}_5, \text{NaOH}$ ,  $3\text{C}_6\text{H}_{10}\text{O}_5, 2\text{NaOH}$ ,  $4\text{C}_6\text{H}_{10}\text{O}_5, 3\text{NaOH}$ ,  $3\text{C}_6\text{H}_{10}\text{O}_5, \text{H}_3\text{PO}_4$ . No compounds are formed with  $\text{AcOH}$  or  $\text{HCO}_2\text{H}$  and in solutions of  $\text{Na}_2\text{S}_2\text{O}_3$  and of  $\text{C}_5\text{H}_5\text{N}$  the hydrates  $2\text{C}_6\text{H}_{10}\text{O}_5, \text{H}_2\text{O}$  and  $\text{C}_6\text{H}_{10}\text{O}_5, \text{H}_2\text{O}$  are formed. The indications of X-ray diagrams require confirmation by experimental methods, and compounds with  $\text{H}_2\text{O}$  and with  $\text{H}_3\text{PO}_4$  can be formed without change in the cellulose lattice. Cotton cellulose forms hydrates much more rapidly than does dried animal cellulose. A. G.

**Nitration of cellulose.** A. BOUCHONNET, (MME.) TROMBE, and (MLE.) PETITPAS (Compt. rend., 1933, 197, 332—334).—The solubilities of  $\text{KNO}_3$ ,  $\text{NaNO}_3$ , and  $\text{NH}_4\text{NO}_3$  in 97%  $\text{HNO}_3$  are 50, 10, and 55%, respectively. These salts and 99.9%  $\text{HNO}_3$  give pliable cellulose nitrates containing up to 13.87% N. R. S. C.

**Nitration of cellulose fibres.** I. SAKURADA and M. SHÖJINO (J. Soc. Chem. Ind., Japan, 1933, 36, 306b).—The views expressed previously (this vol., 788) fit the nitration of cellulose. A. G.

**Introduction of amino-groups into cotton cellulose.** E. RIESZ (Bull. Soc. Ind. Mulhouse, 1933, 99, 349—356).—Anilinetrisulphonyl chloride combines with cotton cellulose (1 mol. to about 24  $\text{C}_6\text{H}_{10}\text{O}_5$ ). The compound can be diazotised and coupled, but has no affinity for acid dyes. A. G.

**Pentenylamine.** H. COTTIN (Compt. rend., 1933, 197, 254—256).— $\Delta^2$ -Pentenoic acid,  $\text{NH}_3$ , and  $\text{SiO}_2$  at 500° give pentenenitrile, b.p. 142—143°/749 mm., 60—61°/40 mm. (also obtained from cyanopentenoic acid), reduced (Na-EtOH) to  $\Delta^2$ -pentenylamine, b.p. 105—106° (hydrate, b.p. 93°; chloroplatinate, decomp.; *p*- $\text{C}_6\text{H}_4\text{MeSO}_2$  derivative, an oil) (cf. lit.). Allyl halides and Et sodiocyanoacetate give Et diallylcycanoacetate (70% yield), b.p. 85°/25 mm., reduced to  $\beta$ -allyl- $\Delta^2$ -pentenylamine, b.p. 57—58°/14 mm., which with  $\text{HBr}$  gives  $\epsilon$ -bromo- $\beta$ -( $\gamma$ -bromopropyl)-amylamine, whence  $\text{KOH}$  forms a mixture of



R. S. C.

**Complexes of ethylenediamine with ferrous halides.** R. E. BREUIL (Compt. rend., 1933, 196, 2009—2010).—The compounds  $\text{Fe en}_2\text{X}_2$  ( $\text{X}=\text{Cl}$ ,  $\text{Br}$ , or  $\text{I}$ ) are obtained when the ferrous halide is treated with  $(\cdot\text{CH}_2\text{-NH}_2)_2$  (I) in anhyd.  $\text{MeOH}$  in a stream of  $\text{H}_2$ . They lose (I) when heated or exposed to air. A. C.

**Red coloration of glycine with ferric chloride.** J. V. DUBSKÝ, M. VITU, and A. LANGER (Metallbörse, 1932, 22, 1533—1534; Chem. Zentr., 1933, i, 1280).—The following compounds have been prepared ( $\text{X}=\text{glycine}$ ):  $\text{FeCl}_3, \text{FeCl}_2, \text{OH}, 2\text{X}, 3\text{H}_2\text{O}$ , decomp. 110°;  $\text{FeBr}_3, \text{FeBr}_2, \text{OH}, \text{X}, \text{H}_2\text{O}$ , decomp. 183°;  $\text{FeCl}_3, \text{FeCl}_2, \text{OH}, 3\text{X}, 2\text{H}_2\text{O}$ , decomp. 175°;  $\text{FeBr}_3, \text{FeBr}_2, \text{OH}, 3\text{X}, \text{H}_2\text{O}$ , decomp. 181°;

$\text{FeCl}_3, \text{FeCl}_2 \cdot \text{OH}, 4\text{X}, 4\text{H}_2\text{O}$ , decomp.  $123^\circ$ ;  
 $\text{FeBr}_3, \text{FeBr}_2 \cdot \text{OH}, 4\text{X}, 4\text{H}_2\text{O}$ , decomp.  $112^\circ$ ;  
 $\text{Fe}(\text{NO}_3)_2 \cdot \text{OH}, 2\text{X}, 2\text{H}_2\text{O}$ , decomp.  $183^\circ$ . Similar compounds can be obtained with sarcosine and alanine.

A. A. E.

**Effect of  $p_{\text{H}}$  on the precipitation of arginine and histidine as the silver salts.** J. BUSSIR (Bull. Soc. Chim. biol., 1933, 15, 840—844).—A study of the influence of  $p_{\text{H}}$  on the pptn. of the Ag salts of arginine and histidine from their aq. solutions with aq.  $\text{Ba}(\text{OH})_2$  indicates that a complete separation by this method is impossible.

A. L.

**Preparation of ethyl  $l(+)$ -glutamate,  $l(-)$ -isoglutamine, and ethyl  $l(-)$ -*N*-carbobenzoyloxyglutamate.** E. ABDERHALDEN and H. NIENBURG (Z. physiol. Chem., 1933, 219, 155—157).—Treatment of Et  $l(+)$ -glutamate,  $\text{CO}_2\text{H} \cdot [\text{CH}_2]_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CO}_2\text{Et}$  (I), m.p.  $194^\circ$ ,  $[\alpha]_{\text{D}} +14.60^\circ$  in  $\text{H}_2\text{O}$ , with 25% aq.  $\text{NH}_3$  affords  $l(-)$ -isoglutamine, m.p.  $160^\circ$ ,  $[\alpha]_{\text{D}} -25.50^\circ$  in  $\text{H}_2\text{O}$  (cf. Bergmann and Zervas, A., 1932, 935). The carbobenzoyloxy-derivative of (I), m.p.  $88-89^\circ$ ,  $[\alpha]_{\text{D}} -9.31^\circ$  in EtOH, is described.

J. H. B.

**Complex of cobalt and cysteine, and its behaviour with hydrogen peroxide.** M. P. SCHUBERT (J. Amer. Chem. Soc., 1933, 55, 3336—3342).—Cysteine hydrochloride (I),  $\text{CoCl}_3$ , and KOH in complete absence of air give  $\text{K}_2$  cobaltodicysteinate,  $\text{K}_2(\text{CoR}_2) \cdot 2\text{H}_2\text{O}$  [ $\text{R} = \cdot\text{S} \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CO}_2$ ], the reddish-violet colour of which with  $\text{H}_2\text{O}_2$  fades but does not change to yellow (cf. A., 1931, 1403). More (I) and KOH lead to  $\text{K}_4$  cobaltotricysteinate,  $\text{K}_4(\text{CoR}_3) \cdot 4\text{H}_2\text{O}$ , violet (corresponding *Ba*<sub>2</sub> salt,  $+4\text{H}_2\text{O}$ ), which with air gives  $\text{K}_3$  cobaltitricysteinate (II),  $\text{K}_3(\text{CoR}_3) \cdot 3\text{H}_2\text{O}$ , green (corresponding *Ba* salt,  $+7\text{H}_2\text{O}$ ). (II) is very stable, but with  $\text{H}_2\text{O}_2$  (not other oxidising agents) gives a yellow solution, from which  $\text{K}_3$  cobaltitri-( $\alpha$ -amino- $\beta$ -sulphinopropionate) (III),  $\text{K}_3(\text{CoR}'_3) \cdot 3\text{H}_2\text{O}$  [ $\text{R}' = \cdot\text{SO}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CO}_2$ ] (corresponding *Ba* salt,  $+6\text{H}_2\text{O}$ , and acid, anhyd.), is obtained. With  $[\cdot\text{CH}_2 \cdot \text{NH}_2]_2$  at  $40^\circ$  (III) rapidly gives the complex,  $(\text{Co en})_3(\text{CoR}'_3) \cdot 7\text{H}_2\text{O}$ , and  $\alpha$ -amino- $\beta$ -sulphinopropionic acid (IV),  $\text{SO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CO}_2\text{H}$ ,  $+ \text{H}_2\text{O}$  (*Ba* salt,  $+ \text{H}_2\text{O}$ ). (IV) reduces  $\text{KMnO}_4$  (2.2 O) to form the sulphonic acid (not isolated) and with  $\text{CoCl}_3 \cdot 6\text{NH}_3$  (V) gives the complex,  $[\text{Co}(\text{NH}_3)_6][\text{CoR}'_3] \cdot 4\text{H}_2\text{O}$ , also obtained from (III) and (V).

R. S. C.

**Sources of error in the determination of cysteine and cystine in complex materials, using acid hydrolysis.** J. W. H. LUGG (Biochem. J., 1933, 27, 1022—1029).—When heated at  $100^\circ$  for 20 hr. in 5*N*-HCl alone or with  $\text{CO}(\text{NH}_2)_2$  and stable  $\text{NH}_2$ -acids, cystine (I) is fairly stable, whilst approx. 1% decomp. occurs with cysteine (II). At  $100^\circ$  (I) is reduced to (II) by  $\text{SnCl}_2$  in acid solution. In acid hydrolysates and in presence of carbohydrates and humin, considerable amounts of (I) and, more especially, of (II) are lost. Addition of  $\text{SnCl}_2$  during hydrolysis not only fails to prevent loss of (II), but causes loss of (I) by reduction to (II). The presence of  $\text{Fe}^{+++}$  and other heavy-metal salts also results in low vals. for (I) and (II).

F. O. H.

**Interaction of halogenoacetates and thiol compounds. Reaction of halogenoacetic acids**

with glutathione and cysteine. Mechanism of iodoacetate poisoning of glyoxalase. F. DICKENS (Biochem. J., 1933, 27, 1141—1151).—Largely a more detailed account of work previously reviewed (this vol., 314). The reaction between glutathione (I) and  $\text{CH}_2\text{I} \cdot \text{CO}_2\text{Na}$  (II) in dil. neutral solution is bimol.; a thio-ether,  $\text{C}_{12}\text{H}_{19}\text{O}_8\text{N}_3\text{S}_2 \cdot \text{H}_2\text{O}$ , is isolable. The respective velocity coeffs. for (I) and  $\text{CH}_2\text{Hal} \cdot \text{CO}_2\text{Na}$  at  $38^\circ$  are of the relative order, I : Br : Cl = 15 : 9 : 0.15. A similar reaction occurs with cysteine and (II);  $\alpha$ -amino- $\beta$ -(carboxymethylthiol)propionic acid, m.p.  $84^\circ$  (decomp.), is isolated. (II) inactivates the co-enzyme of glyoxalase; the enzyme is undamaged.

H. B.

**Aldehyde-imide condensation. I. Reactions between aldehydes and acetamide.** W. A. NOYES and D. B. FORMAN (J. Amer. Chem. Soc., 1933, 55, 3493—3494).— $\text{NH}_2\text{Ac}$ , MeCHO, and a little AcOH under reflux give ethylidenediacetamide,  $\text{CHMe}(\text{NHAc})_2$ , m.p.  $180^\circ$  (lit.  $169^\circ$ ). Butylidene-, m.p.  $189^\circ$ , isovalerylidene-, m.p.  $184^\circ$ , and heptylidenediacetamide, m.p.  $171-172^\circ$ , are described *inter al.* The compounds with mineral acids give  $\text{NH}_3$ , aldehyde, and AcOH.

R. S. C.

**Catalytic preparation of nitriles with Japanese acid clay.** J. ABE (Bull. Waseda Appl. Chem. Soc., 1933, 19, 8—14).—EtCO<sub>2</sub>H and  $\text{NH}_3$  passed over Japanese acid clay,  $\text{SiO}_2$  gel, or  $\text{Al}_2\text{O}_3$  at  $400^\circ$  afforded PrCN in 95.5, 80.16, or 85.9% yield, respectively.

CH. ABS.

**Brominated aliphatic nitriles and ketones.** P. TRUNEL (Compt. rend., 1933, 197, 453—456).— $\epsilon$ -Bromohexonitrile, b.p.  $120-130^\circ/11$  mm., and MgMeI give  $\eta$ -bromoheptan- $\beta$ -one (semicarbazone, m.p.  $136^\circ$ ). Bromination of undecic acid yields the  $\kappa$ -Br-derivative, m.p.  $51^\circ$ , converted successively into the acid chloride, amide, m.p.  $88^\circ$ , and nitrile, b.p.  $184^\circ/17$  mm., which with MgMeBr forms  $\mu$ -bromododecan- $\beta$ -one, m.p.  $22^\circ$ , b.p.  $153-154^\circ/5$  mm. (semicarbazone, m.p.  $118^\circ$ ).  $\lambda$ -Ketododecylphthalimide, m.p.  $69^\circ$  (semicarbazone, m.p.  $146^\circ$ ), yields  $\mu$ -aminododecan- $\beta$ -one, m.p.  $93^\circ$ . Undecenoic acid and HBr give  $\iota$ -bromoundecic acid, which is converted successively into the acid chloride, amide, m.p.  $93.5^\circ$ , and nitrile, b.p.  $174^\circ/15$  mm.

F. R. S.

**Formation of methyl radicals in the decomposition of azomethane.** J. A. LEERMAKERS (J. Amer. Chem. Soc., 1933, 55, 3499—3500).—Decomp. of NMe·NMe in  $\text{H}_2\text{O}$  vapour at  $475^\circ$  gives Me radicals, which remove a Pb mirror 10 cm. from the furnace.

R. S. C.

**Tertiary phosphines containing sec.-alkyl radicals.** W. C. DAVIES (J.C.S., 1933, 1043—1044).—Triisopropylphosphine, b.p.  $81^\circ/22$  mm. (1 : 1-compound, m.p.  $111^\circ$ , with  $\text{CS}_2$ ), and trisec-butylphosphine, b.p.  $108^\circ/11$  mm. (1 : 1-compound, m.p.  $66^\circ$ , with  $\text{CS}_2$ ), are prepared from  $\text{PCl}_3$  and MgRBr. A large excess of Mg and sec.-bromide must be used, since the yield of MgRBr is low and a reaction can occur between  $\text{PR}_3$  and, e.g.,  $\text{PCl}_3$ . *p*-Phenoxyphenyldiisopropylphosphine, b.p.  $209^\circ/13$  mm. (methiodide, m.p.  $203-204^\circ$ ; 1 : 1-compound, m.p.  $46^\circ$ , with  $\text{CS}_2$ ), is similarly prepared from *p*-OPh·C<sub>6</sub>H<sub>4</sub>· $\text{PCl}_2$  and MgPr <sup>$\beta$</sup> Br. Methyl-triisopropyl- and methyltrisec-butyl-phosphonium iod-

ides have m.p.  $> 360^\circ$  and  $149^\circ$ , respectively. All b.p. and m.p. are corr. H. B.

**Influence of poles and polar linkings on the course pursued by elimination reactions. XIX. Thermal decomposition of phosphonium chlorides.** G. W. FENTON, L. HEY, and C. K. INGOLD. **XX. Elimination of saturated primary alcohols by thermal decomposition of sulphonium hydroxides.** C. K. INGOLD and K. I. KURIYAN (J.C.S., 1933, 989—991, 991—993).—XIX. Contrary to Collic *et al.* (cf. *ibid.*, 1888, 53, 636, 714), thermal decomp. of  $\text{PR}_4\text{Cl}$  gives  $\text{RCl}$  and  $\text{PR}_3$ , which is in accordance with the theoretical considerations previously developed (A., 1929, 1431). Thus,  $\text{PEt}_4\text{Cl}$  gives  $\text{EtCl}$  and  $\text{PEt}_3$ ;  $\text{PMe}_4\text{Cl}$  affords  $\text{MeCl}$  and  $\text{PMe}_3$ ;  $\text{PMe}_3\text{EtCl}$  yields  $\text{MeCl}$  and  $\text{PMe}_2\text{Et}$ ; benzyltriethylphosphonium chloride furnishes  $\text{CH}_2\text{PhCl}$  and  $\text{PEt}_3$ .

XX (cf. this vol., 701).  $\text{SR}_3\cdot\text{OH}$  containing Me and Et (or  $\text{Pr}^a$ ) groups undergo decomp. in all three possible directions [formation of  $\text{MeOH}$ ,  $\text{EtOH}$  (or  $\text{Pr}^a\text{OH}$ ), and olefine]. The total alcohols (mols.-%) found are:  $\text{Me}_3$ , 100;  $\text{Me}_2\text{Et}$ , 73;  $\text{MeEt}_2$ , 45;  $\text{Et}_3$ , 14;  $\text{Me}_2\text{Pr}^a$ , 92;  $\text{MePr}^a_2$ , 82;  $\text{Pr}^a_3$ , 64.  $\text{SR}_3\cdot\text{OH}$  containing combinations of the groups Et and  $\text{Pr}^a$ ,  $\text{Pr}^a$  and  $\text{Bu}^a$ , and Et and  $\text{Bu}^b$  give both alcohols and olefines; the proportions of the lower homologue in the olefine mixtures are determined and show the absence of any considerable mutual influence between the different alkyl groups. The following are described: *triethyl-*, m.p.  $152\text{—}153^\circ$ , *tri-n-propyl-*, m.p.  $75\text{—}76^\circ$ , *methyl-diethyl-*, m.p. about  $170^\circ$ , *methyl-di-n-propyl-*, m.p.  $68^\circ$ , *diethyl-n-propyl-*, m.p.  $72\text{—}73^\circ$ , *ethyl-di-n-propyl-*, m.p.  $73\cdot5\text{—}74^\circ$ , *di-n-propyl-n-butyl-*, m.p.  $73^\circ$ , *n-propyl-di-n-butyl-*, m.p.  $67\text{—}68^\circ$ , and *ethyl-diisobutyl-*, m.p.  $75\text{—}76^\circ$ , *-sulphonium picrates*. H. B.

**Thermal decomposition of mercury dibutyl.** F. E. FREY and H. J. HEPP (J. Amer. Chem. Soc., 1933, 55, 3357—3361).—Quant. analysis of the decomp. products of  $\text{HgBu}_2$  in Pyrex at  $350\text{—}450^\circ/3$  mm. proves formation of  $\text{Bu}^a$  radicals, which give mostly  $\text{C}_2\text{H}_4$  and Et radicals and only a little  $\text{C}_5\text{H}_{10}$ ; the free radicals then form  $\text{C}_2\text{H}_6$ ,  $\text{C}_4\text{H}_{10}$ , and  $\text{C}_6\text{H}_{14}$ .  $\text{HgBu}_2$  similarly gives  $\text{Bu}^b$ , which also ruptures only at one point to give  $\text{C}_3\text{H}_6$  and  $\text{Me}^\cdot$ ; the products are thus  $\text{CH}_4$ ,  $\text{CH}_2\text{EtMe}_2$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_4\text{H}_8$ ,  $\text{C}_4\text{H}_{10}$ , and much  $\text{C}_8\text{H}_{18}$ . R. S. C.

**Stereochemistry of platinum.** H. D. K. DREW and F. S. H. HEAD (Nature, 1933, 132, 210).—*iso*Butylenediamine and the mixed  $\beta$ -diammine,  $\text{Pt}(\text{NH}_3)(\text{NH}_2\text{Et})\text{Cl}$ , give a mixture of two isomeric  $\beta$ -plato-tetrammines,  $[\text{Pt}(\text{NH}_3)(\text{NH}_2\text{Et})(\text{NH}_2\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{NH}_2)]_2\text{Cl}_2$ , which are both of  $\beta$ -structure, and do not become interchanged; they give rise to different plato-salts. A similar pair of isomeric  $\beta$ -plato-tetrammines,  $[\text{Pt}(\text{NH}_2\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{NH}_2)_2]\text{Cl}_2$ , have been obtained in admixture and give rise to a mixture of two different plato-salts which are separable. The pairs of isomerides appear to represent *cis*- and *trans*-forms in each case, giving the first chemical evidence of planar structure among the plato-tetrammines. L. S. T.

**Molecular structure of co-ordination compounds of platinum and palladium.** E. G. COX

and G. H. PRESTON (J.C.S., 1933, 1089—1093; cf. A., 1932, 797; this vol., 41).—X-Ray examination of bisethylenediaminoplatinous chloride  $[\text{Pt}(\text{en})_2]\text{Cl}_2$ , bisethylenediaminopalladous chloride, tetramminopalladous chloride  $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2\cdot\text{H}_2\text{O}$ , and  $\alpha$ - and  $\beta$ -diamminoplatinic tetrachlorides  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$ , and re-examination of tetramminoplatinous chloride and  $\text{NH}_4$  chloropalladite (I) give further evidence of the planar distribution of  $\text{Pt}^{++}$  and  $\text{Pd}^{++}$  valencies. It is also concluded from the results that the valencies of the metal atom are not all crystallographically equiv., but are differentiated into pairs. Only those valencies which are *trans* to each other are equiv.; this applies to all the above compounds except (I), *i.e.*, to those compounds in which the metal atom is the centre of a positive or neutral complex. This supports the suggestion of paired valencies made by Drew *et al.* (A., 1932, 562) and also affords a physical basis for Werner's hypothesis of *trans*-elimination. H. B.

**Complex compounds of iridium. II. Compounds of organic sulphides and pyridine.** P. C. RAY, N. ADHIKARI, and R. GHOSH (J. Indian Chem. Soc., 1933, 10, 275—279).— $\text{IrCl}_4$  and  $\text{Et}_2\text{S}$  in cold  $\text{EtOH}$  give (after 12 days) a brownish-red compound,  $\text{IrCl}_3\cdot 3\text{Et}_2\text{S}$  (I), m.p.  $171^\circ$ , in addition to the orange isomeride (II), m.p.  $131^\circ$  (A., 1932, 1017); (I) and (II) are probably the *trans*- and *cis*-compounds, respectively. (II) and  $\text{C}_5\text{H}_5\text{N}$  in boiling  $\text{C}_6\text{H}_6$  afford the compound,  $\text{IrCl}_3\cdot\text{C}_5\text{H}_5\text{N}\cdot 2\text{Et}_2\text{S}$ , m.p.  $171\text{—}172^\circ$ , whilst (II) and  $\text{C}_5\text{H}_5\text{N}$  at  $120\text{—}150^\circ$  give the compound,  $\text{IrCl}_3\cdot 2\text{C}_5\text{H}_5\text{N}\cdot\text{Et}_2\text{S}$ , m.p.  $260^\circ$ .  $\text{NH}_4$  chloroiridate and aq.  $\text{EtOH}\text{—Et}_2\text{S}$  yield some (II) and the compound,  $\text{Ir}_2\text{Cl}_5\cdot 4\text{Et}_2\text{S}$ , m.p.  $222^\circ$  (decomp.) (lit.  $207^\circ$ ). The compound,  $\text{IrCl}_3\cdot 3\text{S}(\text{CH}_2\text{Ph})_2$ , m.p.  $201^\circ$ , is described. H. B.

**Preparation of mono- and di-alkylcyclohexanes.** F. K. SIGNAIGO and P. L. CRAMER (J. Amer. Chem. Soc., 1933, 55, 3326—3332).—*cyclo*Hexanone or its Me derivatives yield by the Grignard reagent 1-*n*-butyl- (I), b.p.  $88\text{—}91^\circ/7$  mm., 1-*n*-amyl- (II), b.p.  $96\text{—}96\cdot5^\circ/5$  mm., 2-methyl-1-*n*-butyl- (III), b.p.  $76\text{—}80^\circ/2$  mm., 2-methyl-1-*n*-amyl- (IV), b.p.  $89\text{—}90^\circ/1\cdot5$  mm., 3-methyl-1-*n*-butyl- (V), b.p.  $85\text{—}86^\circ/2$  mm., and 4-methyl-1-*n*-butyl- (VI), b.p.  $74\text{—}76^\circ/2$  mm., -*cyclohexanol*, together with some *cyclohexanol* formed by simple reduction of the parent ketone. Thence distillation with  $\text{Al}_2(\text{SO}_4)_3$  or (in the last four cases) I in  $\text{EtOH}$  at  $100^\circ$  affords the corresponding substituted cyclohexenes, (I) b.p.  $180\cdot8\text{—}182\cdot9^\circ$ , (II) b.p.  $203\cdot4\text{—}205^\circ$ , (III) b.p.  $197\cdot8\text{—}199\cdot1^\circ$ , (IV) b.p.  $218\cdot9\text{—}219\cdot7^\circ$ , (V) b.p.  $195\cdot2\text{—}195\cdot7^\circ$ , (VI) b.p.  $196\cdot3\text{—}197\cdot1^\circ$ . By hydrogenation ( $\text{PtO}_2$ ; 45 lb.) in  $\text{AcOH}$  of these or similar cyclohexenes were prepared 1-methyl-2-*n*-propyl-, b.p.  $175\cdot2\text{—}177^\circ$ , -2-*n*-amyl-, b.p.  $215\cdot8\text{—}219\cdot1^\circ$ , -3-*n*-butyl-, b.p.  $194\cdot8\text{—}195\cdot2^\circ$ , -4-*n*-propyl-, b.p.  $174\cdot3\text{—}177\cdot1^\circ$ , and -4-*n*-butyl-, b.p.  $195\cdot9\text{—}196\cdot6^\circ$ , -*cyclohexane*. The physical consts. of these and 57 other compounds of these series (similarly prepared) are recorded. R. S. C.

**Constitution of  $\alpha$ -carotene.** P. KARRER, R. MORF, and O. WALKER (Nature, 1933, 132, 171).—Ozonisation of  $\alpha$ -carotene gives geronic and isogeronic acids and proves the correctness of the proposed formula (this vol., 733). L. S. T.

**Nitration of *o*-dichlorobenzene.** J. R. RUHOFF (J. Amer. Chem. Soc., 1933, 55, 3470—3471).—Much 3 : 4- and a little 2 : 3-dichloronitrobenzene are formed. R. S. C.

**Determination of aromatic nitro- and nitroso-compounds.** S. UENO and H. SEKIGUCHI (J. Soc. Chem. Ind. Japan, 1933, 36, 410—412B).—NO<sub>2</sub>- and NO-compounds containing SO<sub>3</sub>H, CO<sub>2</sub>H, or OH (as alkali salt if necessary) are reduced with Zn and cold HCl, and the amine is titrated with NaNO<sub>2</sub> (cf. A., 1920, ii, 331). Addition of KBr assists the titration. Other compounds are previously sulphonated, a method not applicable to *p*-C<sub>6</sub>H<sub>4</sub>Cl·NO<sub>2</sub>, *o*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·OH, and *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·OMe. A. A. L.

**Mercury as sulphonation catalyst.** K. LAUER (J. pr. Chem., 1933, [ii], 138, 81—91).—As in the case of anthraquinone, Hg acts as a directive catalyst in the sulphonation of C<sub>6</sub>H<sub>6</sub> derivatives. The mechanism involves formation of an organo-Hg compound and replacement of the Hg by SO<sub>3</sub>H. The action may be obscured, however, by the poor solubility of HgSO<sub>4</sub> in H<sub>2</sub>SO<sub>4</sub>, the slow formation of the organo-Hg compounds, and their ready hydrolysis. Thus marked *op*-sulphonation occurs with PhNO<sub>2</sub>, BzOH, and PhSO<sub>3</sub>H, and 10—20% oleum previously saturated with HgSO<sub>4</sub>, whereas in absence of Hg substitution is almost exclusively *m*-. That sulphonation occurs by replacement of Hg by SO<sub>3</sub>H is shown by the fact that *o*- and *p*-mercuriphenols and the *m*-mercuri-derivatives of PhNO<sub>2</sub> and BzOH give the direct replacement products almost exclusively with 3—20% oleum (according to the example chosen), but mainly the normal sulphonation product of the Hg-free compound with 92% H<sub>2</sub>SO<sub>4</sub>. *o*-Xylene, *o*-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>, *o*-C<sub>6</sub>H<sub>4</sub>Br<sub>2</sub>, and phthalic anhydride, which with oleum alone give the 4-SO<sub>3</sub>H, in presence of Hg give the 3-SO<sub>3</sub>H in addition, but in the case of the last-named the 3 : 5-(SO<sub>3</sub>H)<sub>2</sub> is formed by further sulphonation. 4-Sulphophthalic anhydride cannot be further sulphonated, and the use of stringent conditions results in destructive oxidation. *o*-Xylene-3-sulphonic acid [Na salt (+1H<sub>2</sub>O); chloride, m.p. 46°; amide, m.p. 165°], 1 : 2-dichlorobenzene-3-sulphonic acid [Na salt (+2H<sub>2</sub>O)], and 1 : 2-dibromobenzene-3-sulphonic acid [Na salt (+1H<sub>2</sub>O); chloride, m.p. 31—32°; amide, m.p. 165°] appear to be new. H. A. P.

**Catalytic oxidation of organic compounds in the vapour state.** I. Toluene, its derivatives and homologues. II. Various compounds. G. CHARLOT.—See this vol., 1019.

**Coupling action of the Grignard reagent.** V. Influence of the halogen atom of the reagent. E. ELLINGBOE and R. C. FUSON (J. Amer. Chem. Soc., 1933, 55, 2960—2966).—CHPhCl<sub>2</sub> and MgMeCl in Et<sub>2</sub>O give cumene (a little), βγ-diphenylbutane (I), two forms, m.p. 124—125° (also obtained from CHPhMeBr and Na or Mg in Et<sub>2</sub>O), and an oil, b.p. 150—151°/20 mm., respectively, and α-chloro-αγ-diphenylpropane (II). (I) and (II) form solid solutions, separable by change of (II) by KOH-EtOH into α-methylstilbene, m.p. 48°. This with O<sub>3</sub> gives BzOH and CPhMe, and with a drop of HBr in AcOH gives an isomeride, m.p. 82—83°. *p*-C<sub>6</sub>H<sub>4</sub>Cl·CHCl<sub>2</sub> and

MgMeCl in Et<sub>2</sub>O give α-chloro-αβ-di-*p*-chlorophenylpropane, m.p. 167°, βγ-di-*p*-chlorophenylbutane, m.p. 147—148°, αβ-di-*p*-chlorophenyl-Δ<sup>α</sup>-propene, m.p. 80°, and *p*-chlorocumene, b.p. 79—81°/15 mm., also prepared by hydrogenation of β-*p*-chlorophenylpropene, b.p. 89°/14 mm. (obtained from *p*-chloroacetophenone and MgMeI). Attention is directed to the marked difference in behaviour of benzyldene chlorides towards MgMeCl and MgMeI, respectively (cf. this vol., 385). R. S. C.

**Conjugated systems. XIII. Preparation and properties of α-bromo-δ-phenylbutadiene.** I. E. MUSKAT and L. B. GRIMSLEY (J. Amer. Chem. Soc. 1933, 55, 2860—2867; cf. A., 1929, 1170).—*cis*-α-Phenylbutadiene (I) reacts with Br more rapidly than the *trans*-form, giving, in both cases, only one γδ-dibromo-α-phenylbutene (II). This with more Br gives αβγδ-tetrabromo-α-phenylbutane, with Ag<sub>2</sub>O affords (I), and with NH<sub>2</sub>Ph (2 mols.) in C<sub>6</sub>H<sub>6</sub> δ-bromo-γ-anilino-α-phenyl-Δ<sup>α</sup>-butene, m.p. 110° (hydrobromide, m.p. 124°; excess of Br in CHCl<sub>3</sub> affords αβδ-tribromo-γ-tribromoanilino-α-phenylbutane hydrobromide, m.p. 215°), with NH<sub>2</sub>Ph (4 mols.) γδ-dianilino-α-phenyl-Δ<sup>α</sup>-butene (dihydrochloride, m.p. 113°), with NH<sub>3</sub>-EtOH γδ-diamino-α-phenyl-Δ<sup>α</sup>-butene (dihydrochloride, m.p. 124°), and with KOH (1 mol.) in Et<sub>2</sub>O-EtOH δ-bromo-α-phenylbutadiene (III), two forms, m.p. 52°, and an oil (formed also from the former, when kept) (giving a dimeride, m.p. 138°, when distilled at 137°/6 mm.), presumably *cis-trans* isomerides, isomerism being probably at the γδ-linking, since both forms give (II) with HBr. (III) liberates I from aq. KI, and with Br gives γδδ-tribromo-α-phenyl-Δ<sup>α</sup>-butene, m.p. 140—140·5°, which with O<sub>3</sub> affords BzOH. R. S. C.

**Stereochemistry of the free triarylmethyl radical. Total asymmetric synthesis.** G. KARAGUNIS and G. DRIKOS (Naturwiss., 1933, 21, 607).—By irradiating phenyl-*p*-tolyl-*p*-ethylphenylmethyl with circularly polarised light (4300 Å.) in presence of Cl<sub>2</sub> at 0°, an activity of 0·1° has been obtained and with phenyldiphenyl-α-naphthylmethyl 0·2° has been measured. These results indicate that the three C valencies are not in one plane. F. R. S.

**Photochemical production of triphenylmethyl.** J. O. HALFORD and L. C. ANDERSON (Proc. Nat. Acad. Sci., 1933, 19, 759—762).—CPh<sub>3</sub>Br in cyclohexane irradiated with sunlight is converted into a peroxide and unidentified products. The absorption spectrum suggests that CPh<sub>3</sub> is formed as an intermediary. E. S. H.

**Addition of free radicals to dienes, pyrrole, and maleic anhydride.** J. B. CONANT and B. F. CHOW (J. Amer. Chem. Soc., 1933, 55, 3475—3479).—Diphenyldixanthyl and isoprene, best at 100°, give αδ-di(phenylxanthyl)-β-methyl-Δ<sup>β</sup>-butene, m.p. 249—250°. Dibenzoyldixanthyl gives similarly αδ-di(benzylxanthyl)-β-methyl-Δ<sup>β</sup>-butene, m.p. 224°. CPh<sub>3</sub> (I) with butadiene in C<sub>6</sub>H<sub>6</sub>-PhMe at room temp. gives αααζζζ-hexaphenyl-Δ<sup>γ</sup>-hexene (II), m.p. 224° (oxidised by O<sub>3</sub>-Ag<sub>2</sub>O to βββ-triphenylpropionic acid), and with piperylene in C<sub>6</sub>H<sub>6</sub> αααζζζ-hexaphenyl-β-methyl-Δ<sup>γ</sup>-hexene, m.p. 174°. (I) and pyrrole in C<sub>6</sub>H<sub>6</sub> at room temp. give 2 : 5-di(triphenylmethyl)-Δ<sup>3</sup>-pyrroline, m.p.

250° (decomp.), the Bz derivative, m.p. 265—266°, of which with PBr<sub>5</sub> in C<sub>6</sub>H<sub>6</sub> gives PhCN and βγδε-tetrabromo-αααζζζ-hexaphenylhexane, m.p. 168°, hydrogenated (PtO<sub>2</sub>) to αααζζζ-hexaphenylhexane, m.p. 189°, also obtained by hydrogenation of (II). 2:3-Dimethylpyrrole and (I) (2 mols.) give the adduct, C<sub>43</sub>H<sub>37</sub>N, m.p. 227°. Maleic anhydride and (I) give *s-di(triphenylmethyl)succinic acid*, m.p. 148° (decomp.) (Me<sub>2</sub> ester, m.p. 212—213°), and its anhydride, m.p. 232°.

R. S. C.

**Preparation of diphenyl.** A. GARCÍA BANÚS and J. GUITERAS (Anal. Fis. Quím., 1933, 31, 255—259).—A yield of 2 g. of Ph<sub>2</sub> per hr. per 100 g. C<sub>6</sub>H<sub>6</sub> is obtained by the method of Lowe and James (A., 1924, i, 275), using nichrome wire of 0.25 mm. diam. at 1020—1030°. Deposition of graphite and accumulation of tarry products lower the rate of formation after 10—12 hr.

R. K. C.

**Diphenylindenes. II. Dehydration of benzylhydrobenzoin and formation of 1:2-diphenylindene.** A. GARCÍA BANÚS and E. DE SALAS (Anal. Fis. Quím., 1933, 31, 378—389; cf. A., 1929, 688).—Benzylhydrobenzoin, CH<sub>2</sub>Ph·CPh(OH)·CHPh·OH (I) (modified prep.), and AcCl, either cold or boiled for a short time, yield the Ac derivative (II), but (II) is slowly converted into 1:2-diphenylindene (III) in presence of the HCl formed. This mechanism accounts for the varying proportions of (II) and (III) isolated when (I) is treated with hot AcCl, either alone or with added SO<sub>2</sub>Cl<sub>2</sub> or SOCl<sub>2</sub>. Treatment of (I) with Ac<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub> yields (II) or (III) with low or high proportions of H<sub>2</sub>SO<sub>4</sub>, respectively. Conc. H<sub>2</sub>SO<sub>4</sub> and (I) yield CH<sub>2</sub>Ph·CO·CHPh<sub>2</sub> (IV), whilst with dil. H<sub>2</sub>SO<sub>4</sub> (III) and (IV) are formed. Treatment of (I) with AcOH and aq. HCl in a sealed tube at 140° yields 75% of (III). (II) is unchanged by P<sub>2</sub>O<sub>5</sub>, AcCl, or Ac<sub>2</sub>O, but in Ac<sub>2</sub>O with a little H<sub>2</sub>SO<sub>4</sub>, or in AcCl in presence of moisture, (III) is formed. Oxidation of (II) by CrO<sub>3</sub> in AcOH yields benzoin acetate.

R. K. C.

**1-Diphenylene-3-phenylindene.** C. F. KOELSCH (J. Amer. Chem. Soc., 1933, 55, 3394—3399).—The Grignard reagent from ββ-diphenylvinyl bromide and fluorenone give α-diphenylene-γγ-diphenylallyl alcohol, m.p. 98—99° (this vol., 66, m.p. 139—140°), which at 225—230° gives a substance, C<sub>27</sub>H<sub>18</sub>, m.p. 308—311°, and with a little H<sub>2</sub>SO<sub>4</sub> in hot AcOH affords 3-phenyl-1-diphenyleneindene (I), m.p. 140—141° (cf. loc. cit.). (I) with CrO<sub>3</sub>-AcOH yields 9-*benzoylphenylfluorene-9-carboxylic acid*, m.p. 160—163° (decomp.) [decarboxylated by heat or by hot aq. K<sub>2</sub>CO<sub>3</sub> to 9-*benzoylphenylfluorene* (II), m.p. 168—169°], *o*-benzoylbenzophenone-*o'*-carboxylic acid, and two substances, C<sub>27</sub>H<sub>18</sub>O<sub>2</sub> and C<sub>26</sub>H<sub>18</sub>O<sub>2</sub>, respectively. (I) is nitrated to the (?2-)NO<sub>2</sub>-derivative, m.p. 197—198°, and gives a (?2-)Br-derivative, m.p. 157—158°, which does not form a Grignard reagent, but with CuCN at 250—260° gives the (?2-)CN-derivative, m.p. 210—212° (resists hydrolysis). (I) with Na and hot amyl alcohol gives a hydrocarbon, C<sub>27</sub>H<sub>20</sub>, m.p. 125—127°, and with 40% Na-Hg yields an orange Na salt, giving with H<sub>2</sub>O a hydrocarbon, C<sub>27</sub>H<sub>18</sub>, m.p. 213—215°, and with CO<sub>2</sub> an acid, C<sub>28</sub>H<sub>18</sub>O<sub>2</sub>, double m.p. 187—190° (decomp.) and 203—

206° (m.p. of pure decarboxylated product, 213—215°). The Grignard reagent from *o*-ω-ethoxytolyl bromide and fluorenone give 9-*hydroxy-9-*o*-ω-ethoxytolyl fluorene* (III), m.p. 102—103°, which with SOCl<sub>2</sub> forms the 9-Cl-compound, m.p. 113—114°. (III) is oxidised (Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>-AcOH) to *diphenylene-phthalide*, m.p. 219—220°, which is reduced by 8% Na-Hg to *o*-9-*fluorenylbenzoic acid*, m.p. 237—238°; this with MgPhBr gives *triphenyl-*o*-9-fluorenylcarbinol* (IV), m.p. 214°, also obtained from (II) and MgPhBr. (IV) gives with SOCl<sub>2</sub> *triphenyl-*o*-9-fluorenylmethyl chloride*, m.p. 242—248° (decomp. commencing at 220°), with AcOH and Zn *triphenyl-*o*-9-fluorenylmethane*, m.p. 258—260°, and with a drop of H<sub>2</sub>SO<sub>4</sub> in hot AcOH a substance, C<sub>32</sub>H<sub>22</sub>, m.p. 215—220° (decomp.), probably 10:10-*diphenyl-1:9-diphenylene-9:10-dihydroanthracene*. The allene structure assigned (loc. cit.) to (I) is refuted by the above evidence.

R. S. C.

**Synthesis of compounds related to the sterols, bile acids, and oestrus-producing hormones. I. 1:2-cycloPentenophenanthrene.** J. W. COOK and C. L. HEWETT (J.C.S., 1933, 1098—1111).—The additive compound from cyclohexene and CH<sub>2</sub>Ph·COCl in presence of SnCl<sub>4</sub> and CS<sub>2</sub> is converted by NPhMe<sub>2</sub> at 180° into 1-*phenylacetyl-Δ<sup>1</sup>-cyclohexene* (I), m.p. 46—48° (*semicarbazone*, m.p. 168—169°), which could not be transformed (AlCl<sub>3</sub> or conc. H<sub>2</sub>SO<sub>4</sub>) into the corresponding keto-octahydrophenanthrene. Clemmensen reduction of (I) gives an oil, b.p. 153—159°/12—15 mm., which is dehydrogenated (Se at 340°) to phenanthrene (II), showing that cyclisation occurs at some stage. 9-Methylphenanthrene is not formed by dehydrogenation of the product from (I) and MgMeI. The additive compound from 1-naphthylacetyl chloride (III) and 1-methyl-Δ<sup>1</sup>-cyclopentene is converted (NPhMe<sub>2</sub>) into 1-*α-naphthylacetyl-2-methyl-Δ<sup>1</sup>-cyclopentene*, m.p. 32—33° (*picrate*, m.p. 130.5—131.5°). A pure product could not be obtained from (III) and cyclopentene. *cycloHexanone* and CH<sub>2</sub>Ph·CH<sub>2</sub>·MgCl give 1-β-*phenylethylcyclohexanol* (IV), m.p. 55—56°, dehydrated by KHSO<sub>4</sub> at 160° or short treatment with SnCl<sub>4</sub> in cold CS<sub>2</sub> to 1-β-*phenylethyl-Δ<sup>1</sup>-cyclohexene* (V), b.p. 145°/10 mm. (V) is converted by AlCl<sub>3</sub> in CS<sub>2</sub> or boiling AcOH-conc. H<sub>2</sub>SO<sub>4</sub> into 1:2:3:4:9:10:11:12-octahydrophenanthrene, b.p. 159°/15 mm., also formed from (IV) and conc. H<sub>2</sub>SO<sub>4</sub> at -5° to 0° or SnCl<sub>4</sub>-CS<sub>2</sub> (prolonged treatment), which is dehydrogenated to (II). The Grignard reagent from β-1-*naphthylethyl chloride*, b.p. 167—168°/17 mm. (*picrate*, m.p. 67—68°) [the alcohol is prepared from α-C<sub>10</sub>H<sub>7</sub>·MgBr and (CH<sub>2</sub>)<sub>2</sub>O], and *cyclopentanone* give 1-(β-1'-*naphthylethyl*)*cyclopentanol* (VI), m.p. 59.5—60°, dehydrated by KHSO<sub>4</sub> at 160—170° to 1-(β-1'-*naphthylethyl*)-Δ<sup>1</sup>-*cyclopentene* (VII), b.p. 164°/4—5 mm. (*picrate*, m.p. 78—79°). (VII) is isomerised by AlCl<sub>3</sub> in CS<sub>2</sub> to *trans-1:2-cyclopentano-1:2:3:4-tetrahydrophenanthrene* (VIII), b.p. 160—161°/3—4 mm. (*picrate*, m.p. 128—129°), whilst (VI) or (VII) and AcOH-conc. H<sub>2</sub>SO<sub>4</sub> at 100° give 1:2-cyclopentenophenanthrene (IX), m.p. 134.5—135° (not 152—153° as stated in this vol., 710) (*picrate*, m.p. 134.5—135°). (VIII) is dehydrogenated (Se at 335—340°) to 1:2-cyclo-Δ<sup>1:4</sup> or -Δ<sup>1:3</sup>-*pentadienophenanthrene*, m.p. 142.5—143.5° (*picrate*, m.p. 192—

193°), and a little of an isomeride (?), m.p. 68—70° (picrate, m.p. 208—209°). Dehydrogenation (Se at 305—325°) of the mixture of hydrocarbons obtained from (VI) and SnCl<sub>4</sub> or of the saturated, non-picrate-forming constituents of the crude mixture containing (VIII) gives a mixture of hydrocarbons containing (IX) (which probably arises from *cis*-cyclopentano-tetrahydrophenanthrene). (IX) could not be dehydrogenated. These results suggest that the course pursued by the dehydrogenation reaction is determined by the stereochemical configuration of the reduced ring system.

Cyclisation of 1-benzyl- $\Delta^1$ -cyclohexene could not be effected with AlCl<sub>3</sub>, SnCl<sub>4</sub>, or AcOH-conc. H<sub>2</sub>SO<sub>4</sub>; with P<sub>2</sub>O<sub>5</sub> at 140—150°, 1 : 2 : 3 : 4 : 10 : 11-hexahydrofluorene, b.p. 137°/15 mm., results.  $\beta$ -2-Naphthylpropionic acid (Mayer and Sieglitz, A., 1922, i, 740) [the intermediate  $\beta$ -naphthylmethylmalonic acid has m.p. 145° (lit. 94—95°)] and SnCl<sub>4</sub> at 120° give 4 : 5-benz-3-hydrindone, which could not be condensed (AlCl<sub>3</sub>) with succinic anhydride and which is reduced (Clemmensen) to 4 : 5-benzhydrindene, b.p. 170°/15 mm.

Comparison [spectrum; m.p.; m.p. of picrate and compound with s-C<sub>5</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>3</sub>] of the hydrocarbon C<sub>18</sub>H<sub>16</sub> (Diels *et al.*, A., 1928, 169; 1930, 470; Ruzicka and Thomann, this vol., 278), now prepared by dehydrogenation (Se at 320—340°) of cholesteryl chloride (X), with (IX) indicates that the former consists of (IX) contaminated with some persistent impurity. Dehydrogenation of (X) proceeds more rapidly at higher temp., but it is then difficult to isolate the C<sub>18</sub>H<sub>16</sub> in a state approaching purity. Thus at 330—350°, the hydrocarbon, m.p. 123—124°, and the hydrocarbon C<sub>25</sub>H<sub>24</sub> (now formulated as C<sub>25</sub>H<sub>22</sub>), m.p. 221—222.5° (1 : 1-compound, m.p. 239—240°, with 2 : 7-dinitroanthraquinone), of Diels *et al.* (A., 1928, 169) were isolated, whilst at 340—360°, impure chrysene probably results. The conclusions of Ruzicka *et al.* (this vol., 820) are criticised.

H. B.

**New route to chrysene and 1 : 2-benzanthracene.** R. D. HAWORTH and C. R. MAVIN (J.C.S., 1933, 1012—1016).—3-Phenanthryl CH<sub>2</sub>Br ketone (from the Me ketone and Br in CHCl<sub>3</sub>) and CHNa(CO<sub>2</sub>Et)<sub>2</sub> in C<sub>6</sub>H<sub>6</sub> give [after hydrolysis (10% MeOH-KOH) and decomp. of the resulting acid at 180—185°] 45% of  $\beta$ -3-phenanthrolylpropionic acid (I), m.p. 157—158° [oxime, m.p. 169—170° (decomp.)], also obtained in 60% yield from phenanthrene, succinic anhydride, and AlCl<sub>3</sub> in PhNO<sub>2</sub>. Clemmensen reduction of (I) affords  $\gamma$ -3-phenanthrylbutyric acid, m.p. 138—139°, converted by 85% H<sub>2</sub>SO<sub>4</sub> at 100° into 1-keto-1 : 2 : 3 : 4-tetrahydro-5 : 6-benzanthracene (II), m.p. 179—180°, and a little of a compound, C<sub>18</sub>H<sub>14</sub>O<sub>2</sub>, m.p. 246—248°. Clemmensen reduction of (II) and subsequent dehydrogenation (Se at 280—315°) gives 1 : 2-benzanthracene.  $\beta$ -2-Phenanthrolylpropionic acid, m.p. 205—206°, prepared as above [CHNa(CO<sub>2</sub>Et)<sub>2</sub> method] from 2-phenanthryl CH<sub>2</sub>Br ketone, m.p. 140—142°, is similarly reduced to  $\gamma$ -2-phenanthrylbutyric acid, m.p. 134°, which is cyclised to 7-keto-4 : 5 : 6 : 7-tetrahydrochrysene, m.p. 124—125°. Clemmensen reduction of this affords an amorphous product (which is considered to be composed largely of 4 : 5 : 6 : 7-

tetrahydrochrysene), readily dehydrogenated (Se at 290—310°) to chrysene (III).  $\beta$ -1-Naphthylethyl bromide, b.p. 145—148°/0.3 mm. [the alcohol is prepared from  $\alpha$ -C<sub>10</sub>H<sub>7</sub>MgBr and (CH<sub>2</sub>)<sub>2</sub>O], and Et potassiocyclohexanone-2-carboxylate in C<sub>6</sub>H<sub>6</sub> give *Et* 2-( $\beta$ -1-naphthylethyl)cyclohexanone-2-carboxylate, b.p. 210—215°/0.3 mm., which when heated with 85% H<sub>2</sub>SO<sub>4</sub> at 100° undergoes ketonic hydrolysis and ring closure; the resulting oil is dehydrogenated to (III). Clemmensen reduction of 2- and 3-phenanthryl Me ketones gives 2-, m.p. 64—65° (picrate, m.p. 92—93°), and 3-ethylphenanthrene, an oil (picrate, m.p. 117—118°; styphnate, m.p. 114—116°).

Attempts to condense 1-keto- or 1-keto-2-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene with CH<sub>2</sub>Br·CO<sub>2</sub>Et (IV) or CH<sub>2</sub>Br·CH<sub>2</sub>·CO<sub>2</sub>Et (V) were unsuccessful; 2 : 6-dimethylcyclohexanone (IV), and NaNH<sub>2</sub> in Et<sub>2</sub>O give, however, *Et* 2 : 6-dimethylcyclohexanone-2-acetate, b.p. 132—134°/15 mm. Et sodiocyclohexanone-2-carboxylate and (V) in C<sub>6</sub>H<sub>6</sub> afford *Et* 2-carbethoxycyclohexanone-2- $\beta$ -propionate, b.p. 199—202°/15 mm., hydrolysed (10% MeOH-KOH) to cyclohexanone-2- $\beta$ -propionic acid, b.p. 155—160°/0.2 mm., m.p. 65—66° [*Me* ester, b.p. 140—142°/15 mm., which with MgMeI gives a lactone, b.p. 155—160°/15 mm., and with (IV) and Zn affords an oil, b.p. 180—185°/15 mm.], and the anhydride, b.p. 250—260°/0.2 mm., m.p. 72—73°, of heptane- $\alpha\gamma\eta$ -tricarboxylic acid.

H. B.

**Action of  $\alpha\gamma$ -dichloropropylene on primary aromatic amines.** C. DORIER (Compt. rend., 1933, 196, 1677—1678).—The above reactants condense in C<sub>6</sub>H<sub>6</sub> solution affording a secondary amine, Ar·NH·CH<sub>2</sub>·CH·CH<sub>2</sub>Cl.  $\gamma$ -Chloroalkyl-aniline, b.p. 137°, -o-toluidine, b.p. 145°, and -m-toluidine, b.p. 148° (all at 13 mm.), are described.

A. C.

**Preparation of alkyanilines containing tert.-alkyl groups.** W. J. HICKINBOTTOM (J.C.S., 1933, 946—951).—The following are prepared by a modification of Nef's method (A., 1900, i, 4) : *tert*.-butyl-aniline, b.p. 214—216°/753 mm. (corr.) [hydrochloride; hydrobromide; sulphate; picrate, m.p. 191—192° (decomp.); *Ac*, m.p. 55—56°, b.p. 124—125°/22 mm., *p*-toluenesulphonyl, m.p. 82—83°, *m*-nitrobenzenesulphonyl, m.p. 100—101°, *NO*-, m.p. 61—62°, and *Me*, b.p. 81—82°/39 mm. [picrate, m.p. 162—163° (decomp.)], derivatives;  $\alpha\beta$ -diphenyl- $\beta$ -*tert*.-butylcarbamide, m.p. 81° (Ph·NCO)}; *tert*.-amyl-aniline, b.p. 227.5—229.5°/744 mm. (corr.) [hydrochloride; *NO*-, m.p. 47—48°, and *p*-toluenesulphonyl derivative, m.p. 73—74°]; and *tert*.-hexylaniline ( $\gamma$ -anilino- $\gamma$ -methylpentane), b.p. 253—254°/759 mm. (corr.) [hydrochloride; picrate, m.p. 133—135°; *p*-toluenesulphonyl, *m*-nitrobenzenesulphonyl, m.p. 85—86°, and *Me* (picrate, m.p. 127—128°) derivatives]. Separation from NH<sub>2</sub>Ph is achieved by virtue of their resistance to acetylation. The *N*-Me derivatives do not react with HNO<sub>2</sub>, and the nitrosoamines eliminate HNO<sub>2</sub> in the Fischer-Hepp reaction, no *p*-NO-derivative being formed.

H. A. P.

**Elimination of tert.-alkyl groups from alkyanilines by hydrolysis.** W. J. HICKINBOTTOM (J.C.S., 1933, 1070—1073).—*tert*.-Butyl- (I), -amyl-

and -hexyl-anilines give  $\text{NH}_2\text{Ph}$  when heated with mineral acids ( $15N\text{-H}_2\text{SO}_4$  at  $110\text{--}140^\circ$ , conc.  $\text{HBr}$ ,  $\text{HI}$ , or  $\text{H}_3\text{PO}_4$ ), but *n*-alkyl groups are unaffected, e.g.,  $\text{NHPbBu}^a$  is stable to  $19N\text{-H}_2\text{SO}_4$  at  $120\text{--}140^\circ$ , and  $\text{NPhMe}\cdot\text{CMe}_3$  gives only  $\text{NHPbMe}$ . The  $\text{CMe}_3$  group is also eliminated from the  $\text{ArSO}_2$  and  $\text{NO}$ -derivatives of (I) by aq.  $\text{H}_2\text{SO}_4$ , although in the case of the latter only a small amount of diazonium salt is formed, the main reaction being the elimination of  $\text{HNO}_2$ .

H. A. P.

***p*-Aminophenylurethanes as local anaesthetics.** W. H. HORNE, R. F. B. COX, and R. L. SHRINER (J. Amer. Chem. Soc., 1933, 55, 3435—3439).—*p*-Nitrophenylurethanes,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}_2\text{R}$ , were prepared in which R was (a)  $\beta$ -diethylaminoethyl, m.p.  $59\text{--}60^\circ$  [hydrochloride, m.p.  $212^\circ$  (block)]; nitrate, m.p.  $192\text{--}193^\circ$ ], (b)  $\beta$ -diisoamylaminoethyl, m.p.  $70\text{--}71^\circ$  (hydrochloride, m.p.  $129\text{--}130^\circ$ ), (c)  $\gamma$ -di-*n*-amylaminopropyl, an oil (hydrochloride, m.p.  $153\text{--}154^\circ$ ), and (d)  $\gamma$ -diisoamylaminopropyl, an oil (hydrochloride, m.p.  $150\text{--}151^\circ$ ; nitrate, m.p.  $111\text{--}112^\circ$ ), hydrogenated ( $\text{PtO}_2$ -Pt black) in  $\text{AcOH}$  to the corresponding *p*-aminophenylurethanes, (a) [hydrochloride, an oil; dihydrochloride, m.p.  $219\text{--}220^\circ$ ; (approx. tri-)borate, m.p.  $368^\circ$  (decomp.) (block)], (b) [hydrochloride, an oil; dihydrochloride, m.p.  $212\text{--}214^\circ$  (decomp.)], (c) (hydrochloride, m.p.  $126^\circ$ ), and (d) (hydrochloride, an oil). Similarly were prepared hydrochlorides of *p*-aminophenylurethanes in which R was *Me*, m.p.  $238^\circ$ , *Et*, m.p.  $238^\circ$ , *Pr*<sup>a</sup>, m.p.  $221^\circ$ , *Pr*<sup>b</sup>, m.p.  $228^\circ$ , *Bu*<sup>a</sup>, m.p.  $219^\circ$ , *sec*-*Bu*, m.p.  $241^\circ$ , *Bu*<sup>b</sup>, m.p.  $225^\circ$ , *amyl*, m.p.  $215^\circ$ , *isoamyl*, m.p.  $230^\circ$ , *hexyl*, m.p.  $210^\circ$ , and *sec*-*octyl*, m.p.  $195^\circ$ . All the above are photosensitive. The pharmacological action of the *p*-aminophenylurethanes is described. R. S. C.

**Reactivity of the chlorine atom in the benzene nucleus.** B. B. DEY and Y. G. DORAISWAMI (J. Indian Chem. Soc., 1933, 10, 309—320).—The activating influence of the *o*- $\text{NO}_2$ , *o*- $\text{CN}$ , and *o*- $\text{CO}_2\text{H}$  groups on the case of replacement of the Cl atom in 1-chloro-2:4-dinitrobenzene (I), 2-chloro-5-nitrobenzotrile (II), and 2-chloro-5-nitrobenzoic acid (III) during treatment with  $\text{NH}_2\text{Ph}$  and *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$  is in the order  $\text{NO}_2 > \text{CO}_2\text{H} > \text{CN}$ , whilst for  $\text{NHEt}_2$ ,  $\text{CO}(\text{NH}_2)_2$  (IV),  $\text{NaOMe}$ , and  $\text{NaOEt}$ , the order is  $\text{NO}_2 > \text{CN} > \text{CO}_2\text{H}$ . (I) reacts only with  $\text{CHNa}(\text{CO}_2\text{Et})_2$  and  $\text{CHNaAc}\cdot\text{CO}_2\text{Et}$ , whilst (I) and (II) react with  $\text{CN}\cdot\text{CHNa}\cdot\text{CO}\cdot\text{NH}_2$ ; reaction could not be effected with the Na derivatives of  $\text{MeNO}_2$  or  $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  even with Cu or  $\text{Cu}(\text{OAc})_2$  as catalysts. (II) reacts with *p*- but not with *o*- and *m*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$  or  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ . (III) does not react with  $\text{NaOMe}$ ,  $\text{NaOEt}$ , or (IV), whilst (I) and (IV) at  $160^\circ$  give 2:4-dinitroaniline. The following appear to be new: 4-chloro-3-cyanoaniline, m.p.  $133^\circ$  (*Ac* derivative, m.p.  $190^\circ$ ), prepared by reduction ( $\text{Sn}$ -conc.  $\text{HCl}$ ) of the  $\text{NO}_2$ -derivative, which could not be hydrolysed; 4-nitro-2-cyano-, m.p.  $171^\circ$ , 4-nitro-2-cyano-3'-, m.p.  $140^\circ$ , and -4'-, m.p.  $217^\circ$ , -methyl- and 4'-chloro-4-nitro-2-cyano-, m.p.  $282^\circ$ , -diphenylamines; 5-nitro-2-anilinobenzamide, m.p.  $190^\circ$ ; *Me* 5-nitro-2-anilino-benzoate, m.p.  $100^\circ$ ; 4-nitro-2-cyanodiethylaniline, m.p.  $88^\circ$ ; 5-nitro-2-carbamidobenzamide, m.p.  $198^\circ$ , from (II) and (IV) at  $165\text{--}170^\circ$ , which is hydrolysed by

$15\%$   $\text{KOH}$  to 5-nitroanthranilic acid and by  $20\%$   $\text{KOH}$  to 5-nitrosalicylic acid. H. B.

**Saponification of nitrosodiarylamines and attempts to prepare a salt of aquoammononitrous acid.** W. C. FERNELIUS and G. W. WATT (J. Amer. Chem. Soc., 1933, 55, 3482—3485).— $\text{NPh}_2\cdot\text{NO}$  (I) reacts quantitatively with  $\text{LiNH}_2$ ,  $\text{NaNH}_2$ ,  $\text{KNH}_2$ , and  $\text{Ca}(\text{NH}_2)_2$ , and (*p*- $\text{C}_6\text{H}_4\text{Me}$ ) $_2\text{N}\cdot\text{NO}$  with  $\text{NaNH}_2$  and  $\text{KNH}_2$  in liquid  $\text{NH}_3$ , to give the metallic salt of the diarylamine,  $\text{N}_2$ , and  $\text{NH}_3$ . Salts of the type  $\text{NHK}\cdot\text{NO}$  are possible intermediates.  $\text{N}(\text{CH}_2\text{Ph})_2\cdot\text{NO}$  (II) and  $\text{NPhMe}\cdot\text{NO}$  react otherwise, no  $\text{N}_2$  being evolved. (I) and (II) with  $\text{NaNH}_2$  in  $\text{PhMe}$  give low yields of  $\text{N}_2$  and tars. (I) is stable to  $\text{KOH}\text{-EtOH}$ .

R. S. C.

**Substitution reactions of 4-aminodiphenylmethane.** W. A. WATERS (J.C.S., 1933, 1060—1064).—Halogenation of  $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$  (*p*) and its *Ac* and *Bz* derivatives substitutes successively the 3, 5, and 4' positions; nitration occurs 3, 4'. Orientation is established by deamination followed by oxidation to the known  $\text{COPh}_2$  derivatives (cf. A., 1929, 1299), or by fission with  $\text{Br}$  to  $\text{PhCHO}$  or derivative and 2:4:6- $\text{NH}_2\cdot\text{C}_6\text{H}_2\text{Br}_3$ . The following are described: 4-benzamidodiphenylmethane, m.p.  $161^\circ$  (4'-*Br*-derivative, m.p.  $181^\circ$ ); 3:5-dibromo-, m.p.  $92^\circ$  (*Ac*, m.p.  $116^\circ$ , and *Bz*, m.p.  $222^\circ$ , derivatives); 3:5:4'-tribromo-, m.p.  $141^\circ$  (*Ac* derivative, m.p.  $209^\circ$ ); 3-bromo-, b.p.  $204\text{--}208^\circ/15$  mm. [hydrobromide, m.p.  $216^\circ$  (decomp.); *Ac*, m.p.  $91^\circ$ , *Ac*, m.p.  $112^\circ$ , and *Bz*, m.p.  $97^\circ$ , derivatives]; 3:4'-dibromo- (*Bz* derivative, m.p.  $135^\circ$ ); 3:5-di-iodo-, m.p.  $137^\circ$  (*Bz* derivative, m.p.  $257^\circ$ ); 3-bromo-5-iodo-, m.p.  $91^\circ$ , and 3:4'-dinitro-4-aminodiphenylmethane, m.p.  $122^\circ$  (*Ac* derivative, m.p.  $150^\circ$ ); 5-*Br* derivative, m.p.  $181^\circ$ : (?) 2-iodo-, m.p.  $201^\circ$ , and (?) 3-iodo-4-acetamidodiphenylmethane, m.p.  $113^\circ$ ; 3:5-dibromo-, m.p.  $61^\circ$ , b.p.  $201^\circ/15$  mm., and 3:5-di-iodo-diphenylmethane, m.p.  $73^\circ$ . In one case by bromination of 4- $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$  at  $100^\circ$  the (?) 2-*Br*-derivative, m.p.  $194^\circ$  (*Bz* derivative of base, m.p.  $166^\circ$ ), was obtained, but this prep. could not be repeated.

H. A. P.

**Mechanism of aromatic rearrangements. II. Benzidine change.** C. K. INGOLD and H. V. KIDD (J.C.S., 1933, 984—988).—The conversion of 2:2'-di-methoxy- and -ethoxy-hydrazobenzenes into the corresponding benzidines by  $\text{HCl}$  in  $\text{EtOH}$  occurs at substantially the same rate, and when a mixture of the two is used leads only to the symmetrical benzidines, no 2-methoxy-2'-ethoxybenzidine being formed. Consequently the rearrangement is regarded as strictly intramol. The reaction is accompanied by disproportionation of the hydrazo-compound to amine and azo-compound.

H. A. P.

**Alkylation of  $\alpha$ -naphthol-orange.** K. H. T. PFISTER (Ber., 1933, 66, [B], 1052).—In consequence of the final acidity of the solution and the sensitivity of the alkyl ethers of  $\alpha$ -naphthol-orange to acids, the product obtained by Slotta (this vol., 270) is essentially initial material.

H. W.

**Synthesis of chloromethyl derivatives of phenols.** M. SOMMELET (Compt. rend., 1933, 197, 256—257).— $\text{Ph Et}$  carbonate,  $\text{CH}_2\text{Cl}\cdot\text{OMe}$ , and  $\text{SbCl}_5$

in  $\text{CCl}_4$  at  $-15^\circ$  give *p*-chloromethylphenyl *Et* carbonate, m.p. 25—26°, b.p. 163—166°/15 mm., hydrolysed by  $(\text{CH}_2)_6\text{N}_4$  to *p*-OH-C<sub>6</sub>H<sub>4</sub>-CHO. Similarly were prepared the chloromethyl derivatives of *o*-, m.p. 35°, b.p. 162°/16 mm., *m*-, m.p. 29°, b.p. 165—167°/13 mm., and *p*-tolyl, b.p. 125—126°/2 mm., *thymyl*, b.p. 155—156°/3 mm., and *o*-chlorophenyl, b.p. about 162°/5 mm., *Et* carbonates. R. S. C.

**Direct dibromination of *m*-bromophenol and an example of group migration.** H. H. HODGSON, J. WALKER, and [in part] J. NIXON (J.C.S., 1933, 1053—1056).—The orientation of 2 : 3 : 4- and 2 : 4 : 5-tribromo-, 3 : 4 : 6-tribromo-2-nitro-, and 2 : 3 : 4-tribromo-6-nitro-phenols and their *Me* ethers is established. Attempted dibromination of *m*-C<sub>6</sub>H<sub>4</sub>Br·OH in glacial AcOH (cf. A., 1925, i, 1264) gives a mixture containing 2 : 3 : 4 : 6-tetra- and 2 : 3 : 4-, m.p. 95°, and 2 : 4 : 5-tri-bromophenol, m.p. 87°, but in  $\text{CCl}_4$  3 : 4-dibromo- and on long keeping (or better in  $\text{PhNO}_2$ ) 2 : 4 : 5-tribromo-phenols are formed. Nitration of 2 : 5-dibromophenol (I) gives the 4- and 6-NO<sub>2</sub>-derivatives, the latter of which with NaOBr gives 3 : 4 : 6-tribromo-2-nitrophenol (II), m.p. 127° [*Me* ether, m.p. 72° ( $\text{CH}_2\text{N}_2$ )], also obtained by bromination of 3-bromo-2-nitrophenol with NaOBr or in EtOH; Br in AcOH, however, gives 2 : 3 : 4-tribromo-6-nitrophenol (III), m.p. 123°, migration of the NO<sub>2</sub> having occurred. (III) is also obtained from 5-bromo-2-nitrophenol and NaOBr or by nitration of 2 : 3-C<sub>6</sub>H<sub>3</sub>Br<sub>2</sub>·OH in AcOH and bromination of the resulting 2 : 3-dibromo-6-nitrophenol, m.p. 105°, in EtOH. Its orientation is confirmed by conversion of its *Me* ether through the anisidine into 2 : 3 : 4-tribromoanisole, m.p. 106°, identified by demethylation; the same method is applied to (II), which with Br in AcOH gives an unidentified substance, m.p. 220—225°. H. A. P.

**Bromo-derivatives of thymoquinol.** S. R. CHECHIK (J. Amer. Pharm. Assoc., 1933, 22, 506—510).—Thymoquinol (2-methyl-5-isopropylquinol) treated with 3 or 4 mols. of Br yields a tribromide (not further characterised), m.p. 65°. 6-Bromothymoquinone, prepared by bromination of thymoquinone in  $\text{CHCl}_3$  at 5°, yields 6-bromothymoquinol, m.p. 63—64° (cf. A., 1887, 1036), on reduction with SO<sub>2</sub> or semicarbazide + HCl but not with Zn + HCl. Reduction by Zn + HCl or SO<sub>2</sub> of a mixture of di- and tribromothymoquinone affords 3 : 6-dibromothymoquinol, m.p. 59—60° [diacetate, m.p. 96—97° (cf. A., 1882, 838)], whilst reduction with H<sub>2</sub>S yields a substance, m.p. 118—119°. F. O. H.

**Preparation of cryptophenols.** L. H. FARINHOLT, W. C. HARDEN, and D. TWISS (J. Amer. Chem. Soc., 1933, 55, 3383—3387).— $\text{CH}_2\text{PhCl}$  and the appropriate phenoxide in hot PhMe give 2 : 4-dibenzylphenol, b.p. 238°/10 mm. (m.p. 111—112°), *o*-benzyl-, b.p. 147—148°/7 mm. (m.p. 144°), 3 : 5-dibenzyl-*p*-cresol, b.p. 205—207°/5 mm. (m.p. 129—130°), 2-benzyl-4-propylphenol, b.p. 186—187°/10 mm. (m.p. 92°), 2-benzyl-, m.p. 46—46.5°, b.p. 180—185°/8 mm. (m.p. 116°), and 2 : 6-dibenzyl-4-tert.-amylphenol, b.p. 225—230°/7 mm. (m.p. 146°), the m.p. in parentheses being those of the phenylcarbamates. Ph, *o*-, b.p. 245°, and *p*-propyl-, b.p. 254—256°, and 2 : 4-dipropyl-

phenyl propionate, b.p. 277—279°, afford by the Fries reaction *o*-, b.p. 115°/15 mm., and *p*-propionyl-, m.p. 148°, *p*-propionyl-*o*-propyl-, m.p. 77°, *o*-propionyl-*p*-propyl-, b.p. 270°, and 6-propionyl-2 : 4-dipropylphenol, b.p. 295—298°, respectively, which are reduced to *o*-, b.p. 223—225°, and *p*-propyl-, b.p. 230—232°, 2 : 4-dipropyl-, b.p. 263°, and 2 : 4 : 6-tripropylphenol, b.p. 288—289°. PhOH,  $\text{CH}_2\text{PhCl}$ , and Zn at 70° give tribenzylphenol, b.p. 272°/10 mm. (phenylcarbamate, m.p. 120°). *o*-Propionylphenol and AlCl<sub>3</sub> give *o*-propionylphenol and EtCO<sub>2</sub>H. R. S. C.

**Organic reactions with boron fluoride. V. Rearrangement of phenyl, *o*-*m*-, and *p*-tolyl isopropyl ethers.** F. J. SOWA, H. D. HINTON, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1933, 55, 3402—3407).—Rearrangement of PhOPr<sup>*β*</sup> without external cooling by BF<sub>3</sub> gives 2-isopropyl- (I), b.p. 212—214° (this and other b.p. at 745 mm.), 2 : 4-diisopropyl- (II), b.p. 228—230°, and 2 : 4 : 6-triisopropylphenol (III), b.p. 249°, and their *Pr*<sup>*β*</sup> ethers, b.p. 225—227°, 248°, and 263°, respectively, and PhOH. *p*-Tolyl *Pr*<sup>*β*</sup> ether, b.p. 197°, gives similarly *p*-cresol, 3-isopropyl-, b.p. 233—235°, and 3 : 5-diisopropyl-, b.p. 249—250°, *p*-cresol, and their *Pr*<sup>*β*</sup> ethers, b.p. 241—243° and 257—259°, respectively. *o*-Tolyl *Pr*<sup>*β*</sup> ether, b.p. 191°, affords 5-isopropyl-, b.p. 231—235°, and 3 : 5-diisopropyl-, b.p. 253—256°, *o*-cresol, and their *Pr*<sup>*β*</sup> ethers, b.p. 241—242° and 257—259°, respectively, and *o*-cresol. *m*-Tolyl *Pr*<sup>*β*</sup> ether, b.p. 197°, with slight cooling yields *m*-cresol, thymol, 6-isopropyl-*m*-cresol, thymol *Pr*<sup>*β*</sup> ether (IV), b.p. 233°, and 4 : 6-diisopropyl-*m*-cresol (V), b.p. 261°; without cooling, the *Pr*<sup>*β*</sup> ether, b.p. 262°, of (III) is also formed. (IV) and BF<sub>3</sub> give (V). Conductivity measurements of PhOH-BF<sub>3</sub> mixtures prove the existence of a compound, BF<sub>3</sub>·2PhOH. PhOMe (stable to BF<sub>3</sub>) gives with propylene and BF<sub>3</sub> 2-isopropylphenyl *Me* ether, b.p. 200°. The *Pr*<sup>*β*</sup> ether of (III) (also stable to BF<sub>3</sub>) with PhOH and BF<sub>3</sub> gives (I) and (II). Most of the above ethers were also prepared from PhOH or the cresol, propylene, and BF<sub>3</sub>. These results prove that the *Pr*<sup>*β*</sup> migrates both by inter- and intra-molecular reactions. R. S. C.

**Synthesis of fast-violet B base, its isomeride, and analogous compounds.** N. KISHNER and U. KRASOVA (Anilinokras. Prom., 1933, 3, 179—184).—Fast-violet B base has been identified as 6-benzamido-4-methoxy-*m*-toluidine (I) by analysis and subsequent synthesis. *o*-Nitro-*p*-tolyl *Me* ether was reduced with NaCl and gun-metal filings to the NH<sub>2</sub>-compound, m.p. 47°, the Ac compound, m.p. 95.5°, of which was nitrated with H<sub>2</sub>SO<sub>4</sub>-HNO<sub>3</sub> at < 3° to 5-nitro-4-methoxy-*o*-acetotoluidide, m.p. 139°, hydrolysed by aq. NaOH to the free base, m.p. 166°. The *Bz* compound of this, m.p. 197°, was reduced with Zn and 5% HCl to (I), m.p. 189° (*Ac* derivative, m.p. 240°). Similarly, 6-nitro-4-methoxy-*m*-toluidine was converted into the *Bz* derivative, m.p. 123°, which was reduced to 5-benzamido-4-methoxy-*o*-toluidine (II), m.p. 176°, giving slightly bluer shades than (I) in conjunction with Naphthol AS. 6-Nitro-4-ethoxy-*m*-toluidine, m.p. 93°, was converted into the *Bz* compound, m.p. 158°, and this reduced to 5-benzamido-4-ethoxy-*o*-toluidine, m.p. 126°, giving somewhat bluer

shades than (II) with Naphthol AS. 3-Chloro-4-nitro-6-methoxyaniline was converted into the Bz derivative, m.p. 142°, and this reduced to 2-chloro-4-benzamido-5-methoxyaniline, giving reddish-violet shades with Naphthol AS. 2:5-Dichloro-*p*-nitroaniline was converted into the Bz derivative, m.p. 151°, and this reduced to 2:5-dichloro-4-benzamidoaniline, m.p. 179.5°, which gives crimson shades with Naphthol AS (cf. B.P. 361,909; B., 1932, 337).

G. A. R. K.

**Condensation of formaldehyde, amines, and phenols.** J. DÉCOMBE (Compt. rend., 1933, 197, 258—260).—Contrary to patent lit., CH<sub>2</sub>O and NHMe<sub>2</sub> do not condense with β-C<sub>10</sub>H<sub>7</sub>·OH (I) at 0°. CH<sub>2</sub>O, piperidine, and (I) at 0° give N-2-hydroxy-naphthylmethylpiperidine, m.p. 94—95° [benzoate, m.p. 115°, unstable (hydrochloride)], insol. in NaOH. *o*-, *m*-, and *p*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>, and phloroglucinol (II) give resins with CH<sub>2</sub>O and NHMe<sub>2</sub> at 0°, but with NHMe<sub>2</sub>·HCl cryst. products are obtained, resinified by alkali. (II) gives single and double condensation products. Pyrocatechol Me ether with NHMe<sub>2</sub> and CH<sub>2</sub>O gives 2-hydroxy-3-methoxybenzylidimethylamine, b.p. 127—129°/5 mm., m.p. 46—47° (hydrochloride of Bz derivative, m.p. about 160°). Similarly is obtained 2-hydroxy-5-methoxybenzylidimethylamine, b.p. 115—117°/2 mm. (hydrochloride of Bz derivative, m.p. 155—156°). Resorcinol Me ether and phloroglucinol Me and Me<sub>2</sub> ethers give resins.

R. S. C.

**Molecular dissymmetry and physiological activity [urethanes of α-*m*-hydroxyphenylalkyldimethylamines].** L. H. EASSON and E. STEDMAN (J.C.S., 1933, 1094—1098).—Interaction of *m*-OMe·C<sub>6</sub>H<sub>4</sub>·CHO with MgEtI gives *m*-methoxyphenylethylcarbinol, b.p. 135—138°/11 mm., the bromide from which with NHMe<sub>2</sub> in C<sub>6</sub>H<sub>6</sub> gives α-*m*-methoxyphenyl-*n*-propyldimethylamine, b.p. 119°/11 mm. (hydrochloride, m.p. 149°; methiodide, m.p. 187°; picrate, m.p. 117°), hydrolysed by HBr to α-*m*-hydroxyphenyl-*n*-propyldimethylamine, m.p. 103°, b.p. 149—150°/8 mm. {hydrochloride, m.p. 163°; methiodide, m.p. 150°; picrate, m.p. 141°; methylurethane [hydrochloride, m.p. 153°; methiodide (+1H<sub>2</sub>O), m.p. 111° (decomp.)] (MeNCO)}. The following are prepared similarly: α-*m*-methoxyphenylisopropyldimethylamine (I), b.p. 125—127°/13 mm. (hydrochloride, m.p. 96°; methiodide, decomp. 180°; picrate, m.p. 138°); α-*m*-hydroxyphenylisopropyl-, m.p. 129° {methiodide, m.p. 151°; hydrochloride, m.p. 213°; methylurethane, m.p. 96° [hydrochloride, m.p. 234° (decomp.); methiodide, m.p. 160° (rapid heating)]}; α-*m*-methoxyphenyl-*n*-butyl-, b.p. 129—130°/11.5 mm. (methiodide, m.p. 119.5°; picrate, m.p. 99—100°); α-*m*-hydroxyphenyl-*n*-butyl-, m.p. 107°, b.p. 170°/12 mm. {hydrochloride, (+1H<sub>2</sub>O), m.p. 86°; methiodide, m.p. 191—192° (rapid heating); picrate, m.p. 154°; phenylurethane, m.p. 96° [hydrochloride, m.p. 201° (decomp.; rapid heating); methiodide, m.p. 146°]; methylurethane [hydrochloride, m.p. 143°; methiodide, m.p. 176° (decomp.)]; *m*-methoxyphenyl-*n*-butylcarbinol, b.p. 130—133°/3 mm.}; α-*m*-methoxyphenyl-*n*-amyl-, b.p. 146—148°/13 mm. (hydrochloride, m.p. 130.5°; picrate, m.p. 91°); α-*m*-hydroxyphenyl-*n*-amyl-, m.p. 91°, b.p. 173°/10 mm. [methiodide, m.p. 141°; picrate, m.p. 126°;

phenylurethane, m.p. 103° (hydrochloride, m.p. 166°)]; *m*-methoxydiphenylmethyl-, b.p. 179°/12 mm. (hydrochloride, m.p. 182°); and *m*-hydroxydiphenylmethyl-dimethylamine, m.p. 94°, b.p. 205—207°/10 mm. {hydrobromide (+1H<sub>2</sub>O); picrate, m.p. 129°; phenylurethane, m.p. 109° [methiodide, m.p. 186° (decomp.; rapid heating)]; methylurethane, m.p. 80° [hydrochloride, m.p. 204° (decomp.); methiodide, decomp. > 140°; picrate, m.p. 182°]}. Attempted prep. of *m*-OMe·C<sub>6</sub>H<sub>4</sub>·CMe<sub>2</sub>·OH from *m*-OMe·C<sub>6</sub>H<sub>4</sub>·COMe gave only *m*-methoxyisopropenylbenzene, from which (I) is obtainable in poor yield by successive action of HBr and NHMe<sub>2</sub>.

H. A. P.

**Preparation of *p*-hydroxyphenylaminoacetic acid.** A. TERENTIEV and S. CHERNIN (Khim. Farm. Prom., 1933, 18—19).—*p*-OH·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub> (300 mol.) in boiling H<sub>2</sub>O is treated with CH<sub>2</sub>Cl·CO<sub>2</sub>H (150 mol.), heated, stirred for 1 hr., and acidified with HCl; the centrifuged product is dissolved in aq. NH<sub>3</sub>, treated with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, and filtered through C. The ppt. obtained on addition of HCl is washed, and dried at 40—45°.

CH. ABS.

**Styphnic acid. II. Bromopicrin, the bromination product of sodium styphnate.** H. H. LEI and P. P. T. SAH (Sci. Rep. Nat. Tsing Hua Univ., 1933, A, 2, 129—131).—Addition of Br to styphnic acid in 11% aq. Na<sub>2</sub>CO<sub>3</sub> at 5° affords bromopicrin, b.p. 89—90°/20 mm., readily separated by steam distillation. When heated with NH<sub>3</sub>-EtOH at 100° it explodes.

J. W. B.

**Styphnamic acid.** P. P. T. SAH and C. T. HSLA (J. Chinese Chem. Soc., 1933, 1, 92—95).—Reduction of styphnic acid (cf. A., 1909, ii, 487) with Na<sub>2</sub>S<sub>2</sub> in boiling H<sub>2</sub>O affords styphnamic acid, m.p. 219° (lit., 190°), the diazonium compound of which is decomposed to 4:6-dinitropyrogallol (cf. A., 1904, i, 241).

J. L. D.

**Preparation, toxicity, and absorption of bis-muth compounds. V. Pyrocatechol, pyrogallol, and gallic acid.** W. M. LAUTER, A. E. JURIST, and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1933, 22, 531—534).—The prep. is described of Na Bi gallate, digallate (I), and methylgallate (II) and Bi pyrogalloside and pyrocatecholoxide. These compounds are unstable in aq. solution and, whilst (I) and (II) are relatively low in toxicity, their absorption, tested on rats, is slow and incomplete.

F. O. H.

**Dehydrogenation of phenols. III. Transition from the dibenzyl to the phenanthrene series by dehydrogenation.** H. ERDTMAN (Annalen, 1933, 505, 195—202).—Reduction of veratril with Zn-Hg and conc. HCl in AcOH or hydrogenation (PtO<sub>2</sub>) of 3:4:3':4'-tetramethoxystilbene gives 3:4:3':4'-tetramethoxydibenzyl (I), m.p. 109—110°, demethylated by 48% HBr to 3:4:3':4'-tetrahydroxydibenzyl (II), m.p. 153—155° (Ac<sub>1</sub> derivative, m.p. 147—149°). In alkaline solution (I) readily absorbs O<sub>2</sub> giving an intense green colour; acids ppt. a violet mass probably containing a quinone, since reductive acetylation leads to 2:3:6:7-tetra-acetoxy-9:10-dihydrophenanthrene (III), m.p. 173—175°. Similar dehydrogenation is effected by FeCl<sub>3</sub> in neutral or slightly acid solution. The yield is poor, the main

product being a humus. (II) is very smoothly oxidised by tetrabromo-*o*-benzoquinone in Et<sub>2</sub>O without production of a phenanthrene derivative. (I) is transformed by Br in AcOH into 6:6'-*dibromo*-3:4:3':4'-*tetramethoxydibenzyl*, m.p. 157—159°, and by I and HgOAc followed by KI into 6:6'-*di-iodo*-3:4:3':4'-*tetramethoxydibenzyl* (IV), m.p. 152—153° (transformed by AcOH-HNO<sub>3</sub> into 6:6'-*dinitro*-3:4:3':4'-*tetramethoxydibenzyl*, m.p. 205—206°). (IV) and Cu powder at 220° yield 2:3:6:7-*tetramethoxy*-9:10-*dihydrophenanthrene*, m.p. 174—175.5°, demethylated and acetylated to (III). H. W.

**Preparation of aminocycloheptanols and their resolution into [optically] active components.** M. GODCHOT and M. MOUSSERON (Compt. rend., 1933, 196, 1680—1682).—*cyclo*Heptene oxide and conc. aq. NH<sub>3</sub> at 120—130° give dl-*trans*-2-*aminocycloheptanol* (I), m.p. 72—73°, b.p. 129—130°/16 mm. (*hydrochloride*, m.p. 115—116°; *d-H camphorate*, m.p. 176—177°, [α]<sub>D</sub> +16.31°), converted by PCl<sub>5</sub> in CHCl<sub>3</sub> at 0° into 2-*chlorocycloheptylamine*, b.p. 97—98°/16 mm. (I) is accompanied by some 2:2'-*dihydroxydicycloheptylamine*, b.p. 210°/16 mm. [NO-derivative, m.p. 220° (decomp.)]. Fractional crystallisation of the *d-H tartrate* of (I), m.p. 179—180°, [α]<sub>D</sub> +14.20°, affords the *d-H tartrates* of *l*- and *d-trans*-2-*aminocycloheptanols*, m.p. 197—198° and 152—153°, [α]<sub>D</sub> +4.95° and +24.20°, respectively. The corresponding *l-H tartrates* have also been prepared. From these are obtained *d*- and *l-trans*-2-*aminocycloheptanol*, m.p. 89—90°, [α]<sub>D</sub> ±14.45° (*hydrochloride*, m.p. 124—125°).

Prolonged heating of *cycloheptene oxide* with EtOH-NH<sub>2</sub>Me at 130° affords dl-*trans*-2-*methylaminocycloheptanol*, b.p. 121—122°/16 mm. The *d-H tartrate*, m.p. 129—130°, [α]<sub>D</sub> +13.00°, is fractionated into the *d-H tartrates* of *l*- and *d*-base, m.p. 156—157° and 115—116°, [α]<sub>D</sub> +3.0° and +20.70°, respectively, which give *d*- and *l-trans*-2-*methylaminocycloheptanol*, b.p. 118—119°/16 mm., [α]<sub>D</sub> ±22.64°.

The low rotatory powers of the above bases compared with those of the corresponding 5- and 6-membered ring compounds may be due to the influence of the C<sub>7</sub> ring on the spatial relationship of the OH and NH<sub>2</sub>. A. C.

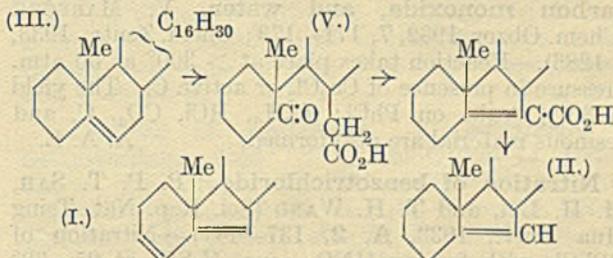
**Preparation and resolution of aminocyclooctanols.** M. GODCHOT, M. MOUSSERON, and R. GRANGER (Compt. rend., 1933, 196, 2011—2013).—Prolonged heating of *cyclooctene oxide* (I) with NH<sub>3</sub> in H<sub>2</sub>O-EtOH under pressure at 150—155° affords *r*-2-*aminocyclooctanol*, m.p. 77—78°, b.p. 132—133°/16 mm. (*hydrochloride*, m.p. 107—108°). The *d-H tartrate*, m.p. 195—196°, [α]<sub>D</sub> +13.9°, is resolved into *d*-, m.p. 159—160°, [α]<sub>D</sub> +22.85°, and *l*-2-*aminocyclooctanol d-H tartrates*, m.p. 205—206°, [α]<sub>D</sub> +5.55°. These yield *d*- and *l*-2-*aminocyclooctanols*, m.p. 93—94°, [α]<sub>D</sub> ±12.85°, respectively. *r*-2-*Methylaminocyclooctanol*, m.p. 25°, b.p. 123—124° [from (I) and NH<sub>2</sub>Me] (*hydrochloride*), affords *d*-, m.p. 119—120°, [α]<sub>D</sub> +27.6°, and *l*-2-*methylaminocyclooctanol d-H tartrates*, m.p. 160—161°, [α]<sub>D</sub> +3.65°, which yield *d*- and *l*-2-*methylaminocyclooctanols*, b.p. 121—122°/16 mm., [α]<sub>D</sub> ±19.9°, respectively. A. C.

**Dehydrogenation of cholesterol.** O. DIELS (Ber., 1933, 66, [B], 1122—1127).—The identity of the hydrocarbon obtained by dehydrogenation of cholesterol and cholic acid with chrysene is confirmed. Reply is made to Ruzicka *et al.* (this vol., 820) and Cook and Hewett (*ibid.*, 710). H. W.

**Conversion of sterols into aromatic compounds.** A. WINDAUS (Nachr. Ges. Wiss. Göttingen, Math.-Phys. Kl., 1932, 408—417; Chem. Zentr., 1933, i, 1296—1297).—The constitutions of Diels' hydrocarbons are discussed. A. A. E.

**Dehydrogenation of cholesterol.** E. BERGMANN (Chem. and Ind., 1933, 681).—The identity of Cook's hydrocarbon, C<sub>17</sub>H<sub>14</sub> (cf. this vol., 710), with that of Diels is questioned. F. R. S.

**Degradation products of cholesterol.** H. LETTRÉ (Z. physiol. Chem., 1933, 218, 67—73).—The dibromide of the doubly unsaturated hydrocarbon (I), m.p. 76°, of Windaus and Resau (A., 1915, i, 678) is C<sub>26</sub>H<sub>42</sub>Br<sub>2</sub>. (I) is therefore C<sub>26</sub>H<sub>42</sub> and the singly unsaturated hydrocarbon (II), m.p. 67° (A., 1914, i, 682), is C<sub>26</sub>H<sub>44</sub>. The non-cryst. acid oxidation products of cholestene (III) yield a cryst. *Me ester* (IV), C<sub>28</sub>H<sub>48</sub>O<sub>3</sub>, m.p. 102—103°, [α]<sub>D</sub><sup>20</sup> +103.8° in CHCl<sub>3</sub>, which gave no typical :CO derivative. Treatment of (IV) with AcOH and conc. HCl or distillation of the free acid (V) gives (II). Distillation in vac. of the acid products obtained by the action of CrO<sub>3</sub> on cholesteryl chloride affords (I). The reactions are formulated:



The ultra-violet spectrum shows that the double linkings in (I) are probably conjugated. J. H. B.

**Number of members in ring B of cholesterol.** O. STANGE (Z. physiol. Chem., 1933, 218, 74—76).—Thermal decomp. of the Ba salt of the acid C<sub>27</sub>H<sub>46</sub>O<sub>4</sub>, obtained from cholestan-6(or 7)-one, affords a *ketone*, C<sub>27</sub>H<sub>44</sub>O, m.p. 93°, [α]<sub>D</sub><sup>20</sup> +35.7° in CHCl<sub>3</sub> (*oxime*, m.p. 186°), thereby proving that ring B is six-membered. J. H. B.

**Cholestanols.** G. VAVON and (MLLE.) B. JAKUBOWICZ (Bull. Soc. chim., 1933, [iv], 53, 581—588).—The prep. of β-cholestanol (I) [*benzoate*, m.p. 135° (clears at 155°), [α]<sub>5780</sub> +19.3° (this and other [α] in CHCl<sub>3</sub>); *isovalerate*, m.p. 110—111°, [α]<sub>5780</sub> +14.7°] and β-cholestanone (II) is modified. Hydrogenation (very active Pt-black) of (II) in Bu<sub>2</sub>O-HCl gives mostly ε-cholestanol (III), [α]<sub>5780</sub> +25° (*benzoate*, m.p. 102—103°, [α]<sub>5780</sub> +24°; *isovalerate*, m.p. 79—80°, [α]<sub>5780</sub> +26°). Esterification and hydrolysis of its esters are more rapid, dehydration and oxidation by CrO<sub>3</sub> are slower, for (I) than for (III), whence it is concluded that the OH group and cyclopentane ring

are in *trans*- and *cis*-positions in (I) and (III), respectively.

R. S. C.

**Nomenclature of the cestrin group.** N. K. ADAM, J. F. DANELLI, E. C. DODDS, H. KING, G. F. MARRIAN, A. S. PARKES, and O. ROSENHEIM (*Nature*, 1933, **132**, 205—206).—It is suggested that the parent saturated hydrocarbon of the cestrin group,  $C_{18}H_{20}$ , containing the sterol skeleton with one Me but without the side-chain, be termed "cestrane." Systematic names for the principal compounds of this group are tabulated on this basis and with the same numbering as in Rosenheim and King's formula for the sterols.

L. S. T.

**Identification of  $\beta$ -phenylethyl alcohol as oxalate.** L. PALFRAY, S. SABETAY, and D. SONTAG (*Ann. Chim. Analyt.*, 1933, [ii], **15**, 338—339).—The oxalate, m.p. 51—51.5°, of  $CH_2Ph\cdot CH_2\cdot OH$  (I) is formed by boiling (I) for 1—2 min. with anhyd.  $H_2C_2O_4$  and crystallising from 60% EtOH. E. C. S.

**Law of periodicity. VIII. Theory of coloured inorganic and organic compounds.** P. PETRENKO-KRITSCHENKO (*Ber.*, 1933, **66**, [B], 1049—1051).—The dependence of intensity of colour of inorg. compounds on valency, accumulation of similar and dissimilar groups, mol. wt., and temp. can be represented by graphs which in some cases can be united to graphs with inflexions apparently representing a portion of the periodic curve. The formulation of aminotriphenylmethyl salts is discussed.

H. W.

**Synthesis of benzoic acid from chlorobenzene, carbon monoxide, and water.** V. MAREČEK (*Chem. Obzor*, 1932, **7**, 171—173; *Chem. Zentr.*, 1933, i, 1286).—Reaction takes place at  $> 300^\circ$  at 50 atm. pressure in presence of  $Cu_2Cl_2$  or active C. The yield is 3.9%, calc. on  $PhCl$ ;  $C_6H_6$ , HCl,  $CO_2$ , C, and resinous material are also formed.

A. A. E.

**Nitration of benzotrichloride.** P. P. T. SAH, H. H. LEI, and T. H. WANG (*Sci. Rep. Nat. Tsing Hua Univ.*, 1933, **A**, **2**, 137—141).—Nitration of  $CPhCl_2$  with fuming  $HNO_3$ -conc.  $H_2SO_4$  at 25—30° gives an 85% yield of  $m\text{-}NO_2\cdot C_6H_4\cdot CO_2H$ , 3 : 5-dinitrobenzoic acid being obtained with excess of  $HNO_3$  at 185°.

J. W. B.

**New class of "free" radicals.** A. SCHÖNBERG and E. RUPP (*Naturwiss.*, 1933, **21**, 561).—Solutions of  $(PhS\cdot)_2$  and  $(\alpha\text{-}C_{10}H_7\cdot CS\cdot S\cdot)_2$  in inert solvents do not obey Beer's law and are thermochromic. They contain "thiyl" radicals,  $R\cdot S\cdot$ , and react with heavy metals,  $CPh_3$ , and aliphatic diazo-compounds. Diphenylene disulphide solutions obey Beer's law, since dissociation entails no increase in no. of mols.

R. K. C.

**2 : 5-Dibromo-*p*-toluic acid.** A. MARZIN (*J. pr. Chem.*, 1933, [ii], **138**, 103—106).—The 5-Br atom in 2 : 5-dibromo-*p*-toluic acid (I) is readily replaced. With NaOH-MeOH in presence of Cu, 2-bromo-5-methoxy-*p*-toluic acid, m.p. 130—133°, is formed, demethylated by HI to 2-bromo-5-hydroxy-*p*-toluic acid, m.p. 205—208°, and oxidised by alkaline  $KMnO_4$  to 2-bromo-5-methoxyterephthalic acid, m.p. 265—268° [*5*-hydroxy-acid (HI)]. The Na salt of 2 : 5-dibromoterephthalic acid, prepared from (I), is converted by

hot aq. NaOAc in presence of Cu into 2 : 5-dihydroxyterephthalic acid, m.p.  $> 300^\circ$ .

H. A. P.

**Cleavage of carbonyl compounds by alkalis.**  
**X. Trihalogenomethylketonic acids.** B. A. BULL and R. C. FUSON (*J. Amer. Chem. Soc.*, 1933, **55**, 3424—3428; cf. this vol., 956).—4-Carbomethoxy-2 : 6-dimethylbenzoic acid and  $SOCl_2$  give the *acid chloride*, b.p. 147—150°/8 mm., which with ZnMeI gives 4-acetyl-3 : 5-dimethylbenzoic acid (I), m.p. 160—161°, yielding with cold 10% NaOCl and NaOBr solutions 4-trichloro-, m.p. 165—166°, and 4-tribromoacetyl-3 : 5-dimethylbenzoic acid, m.p. 161—162°, both fairly stable to 5% NaOH at 0°, but less stable at room temp. Solubility, therefore, plays little part in determining the stability of these compounds. 2 : 6-Dimethylterephthalic acid and  $PCl_5\text{-}POCl_3$  give the *di-acid chloride*, b.p. 124—138°/20 mm., giving with ZnMeI a poor yield of 2 : 5-diacetyl-*m*-xylene, m.p. 61.5—62° (4-phenylhydrazone, m.p. 154—156°), whence by NaOBr impure (I) was obtained.

R. S. C.

**Reactions of olefinic compounds. III. Orienting influence of Ph group.** E. H. FARMER and C. G. B. HOSE (*J.C.S.*, 1933, 962—968).—The direction of addition of HOCl to  $CHPh\text{:}CH\text{-}CO_2H$  (I),  $CHPh\text{:}CMe\text{-}CO_2H$  (II), and  $\delta$ -phenyl- $\Delta^\alpha$ -,  $-\Delta^\beta$ - (III), and  $-\Delta^\gamma$ - (IV) -pentenoic acids is studied. The influence of the Ph group, contrary to that of phenylalkyl, is overwhelmingly in favour of the orientation  $\cdots OH\cdot CPh\text{-}CCl\cdots$ , and is referred to its absorption of the negative charge normally expected in the  $\beta$ -position. The  $\Delta^\alpha$ -acids [(I) and (II)] react much less readily than do the  $\Delta^\beta$ - or  $\Delta^\gamma$ -acids. With HOCl (I) in  $Et_2O$  gives exclusively  $\alpha$ -chloro- $\beta$ -hydroxy- $\beta$ -phenylpropionic acid, the constitution of which is proved by its reduction with Na-Hg in neutral ( $H_2CO_3$ ) solution to  $\beta$ -hydroxy- $\beta$ -phenylpropionic acid [*Et* ester, b.p. 154—156°/13 mm. (synthesis by Andrievski's method improved)], and dehydration with  $Ac_2O$  at the b.p. to  $\alpha$ -chlorocinnamic acid. Condensation of  $PhCHO$  with  $CHMeBr\text{-}CO_2Et$  and Zn in  $C_6H_6$  gives *Et*  $\beta$ -hydroxy- $\beta$ -phenyl- $\alpha$ -methylpropionate, b.p. 157—158°/11 mm., dehydrated by  $SOCl_2$  and  $C_5H_5N$  to (II). This with HOCl gives  $\alpha$ -chloro- $\beta$ -hydroxy- $\beta$ -phenyl- $\alpha$ -methylpropionic acid, m.p. 156° (approx. 60%), and  $\beta$ -chloro- $\alpha$ -phenyl- $\Delta^\alpha$ -propylene, b.p. 118—123°/28 mm.; the former is reduced by Na-Hg to an oily acid which on oxidation gives  $BzOH$ .

$\delta$ -Phenyl- $\Delta^\alpha$ -pentenoic acid, m.p. 103°, prepared from  $CH_2Ph\text{-}CH_2\text{-}CHO$  (V) and  $CH_2(CO_2H)_2$  in  $C_5H_5N$  ( $\Delta^\alpha$  structure proved by oxidation to  $CH_2Ph\text{-}CH_2\text{-}CO_2H$  and  $H_2C_2O_4$ ), gives with HOCl  $\alpha$ -chloro- $\beta$ -hydroxy- $\delta$ -phenylvaleric acid, reduced by Na-Hg in acidified aq. EtOH at 0° to  $\beta$ -hydroxy- $\delta$ -phenylvaleric acid, m.p. 130° (*Et* ester, b.p. 178—182°/12 mm.), synthesised for comparison from (V) and  $CH_2Br\text{-}CO_2Et$  by the Reformatsky reaction. (III) was obtained together with some (IV) by reduction of  $CHPh\text{:}CH\text{-}CH_2\text{-}CO_2H$  (cf. A., 1931, 233) and in poor yield from (II) and  $CH_2(CO_2H)_2$  in presence of strong bases. With HOCl it gives  $\beta$ -chloro- $\gamma$ -hydroxy- $\delta$ -phenylvalerolactone, liquid, and a small amount of (?) isomeride, m.p. 113°; the former on distillation/vac. loses all its Cl as HCl to give a liquid lactone oxidised by  $KMnO_4$  to  $H_2C_2O_4$

and a neutral substance and converted by KOH in aq. EtOH into  $\gamma$ -hydroxy- $\delta$ -phenyl- $\Delta^{\alpha}$ -pentenoic acid, m.p. 57°. Addition of HOCl to (III) (prep. improved) gives a cryst. chlorohydroxy- $\delta$ -phenylvalerolactone and a liquid lactone, b.p. 180—190°/6 mm., probably an isomeride. Both readily lost HCl on heating and gave BzOH and  $(\text{CH}_2\text{-CO}_2\text{H})_2$ , but no  $\text{CHPhCl-CO}_2\text{H}$  on oxidation with  $\text{KMnO}_4$  or  $\text{CrO}_3$  under varied conditions, hence are regarded as stereoisomeric  $\gamma$ -chloro- $\delta$ -hydroxy- $\delta$ -phenylvalerolactones. H. A. P.

**Synthetic substances with oestrogenic activity**  
O. BLUM-BERGMANN (Naturwiss., 1933, 21, 578).—Definite but slight activity is shown by 1-hydroxy-1-allyl- and 2-methyl-1:2:3:4-tetrahydrophenanthrene, but 1:2-dihydrophenanthryl-4-acetic acid, m.p. 153—155°, and its  $\Delta^{\alpha}$ -isomeride, 1:2:3:4-tetrahydrophenanthryl-4-methylenecarboxylic acid, m.p. 215—217°, are inactive. H. A. P.

**Perceric salicylate.** A. FOUCHET (Bull. Soc. chim., 1933, [iv], 53, 570—571).—The compound described as perceric salicylate, obtained by addition of  $\text{H}_2\text{O}$  to a dry mixture of  $\text{Na}_2\text{CO}_3$ ,  $\text{Ce}(\text{NO}_3)_4$ , and Na salicylate, is shown to be a mixture of  $\text{Ce}_2(\text{CO}_3)_3$  and decomp. products of salicylic acid. A. S. C. L.

**Phenolic acids. IV. Benzyl salicylate and its derivatives.** T. S. MA, V. HOO, and P. P. T. SAH (Sci. Rep. Nat. Tsing Hua Univ., 1933, A, 2, 133—136).— $\text{CH}_2\text{Ph}$  salicylate, b.p. 211°/20 mm. (*p*-nitrobenzyl ether, charring at 260°), is best prepared by addition of  $\text{CH}_2\text{PhCl}$  to Na salicylate in boiling EtOH. With fuming  $\text{H}_2\text{SO}_4\text{-HNO}_3$  at 0° it gives a  $(\text{NO}_2)_4$ -derivative, m.p. 156—158°. J. W. B.

**Hydrolysis of 2-chloro-, -ethoxy-, and -methoxy-5-nitrobenzonnitriles.** B. B. DEY and Y. G. DORAISWAMI (J. Indian Chem. Soc., 1933, 10, 353—359).—2-Chloro-5-nitrobenzonnitrile is hydrolysed by hot slightly diluted  $\text{H}_2\text{SO}_4$  to the amide, which is further hydrolysed (conc. HCl) to 2-chloro-5-nitrobenzoic acid (*ethylamide*, m.p. 148°; *propylamide*, m.p. 142°; *diethylamide*, m.p. 72°; *ethylenediamide*, m.p. 310°). 5-Nitro-2-methoxy-, m.p. 212°, and -2-ethoxy-, m.p. 176°, -*benzamides* are obtained similarly from the nitriles and are hydrolysed further (conc. HCl) to the corresponding acids. All the above nitriles, amides, and acids are converted by aq. or EtOH-KOH into 5-nitrosalicylic acid. 2-Chloro-5-nitrobenzoylcarbamide has m.p. 216°. H. B.

**Structure of  $\alpha$ -benzoyl- $\alpha$ -bromo-esters.** B. W. HOWK and S. M. McELVAIN (J. Amer. Chem. Soc., 1933, 55, 3372—3380).—Et  $\alpha$ -bromo- $\alpha$ -benzoylpropionate, b.p. 144—145°/1 mm., and  $\text{MgPhBr}$  give PhBr (81%) and  $\text{CHMeBz-CO}_2\text{Et}$  (85%). Et  $\alpha$ -bromo- $\alpha$ -benzoylacetate, however, gives  $\text{C}_6\text{H}_6$  (20%), PhBr (56%),  $\text{Ph}_2$  (11.3%),  $\text{CH}_2\text{Bz-CO}_2\text{Et}$  (56.5%), and  $(\text{-CHBz-CO}_2\text{Et})_2$  (10.8%), whilst 14.5% was unchanged. Study of the rate of reaction of these Br-esters with KI and  $\text{N}_2\text{H}_4$  indicates partial reaction which is of a complicated order. It is concluded that the esters exist partly in the  $\text{-C(OBr)C}$  form. R. S. C.

**Syntheses of cyclic compounds. X. Thermal decomposition of substituted glutaric acids. I.  $\beta\beta$ -Dimethylglutaric, cyclopentane- and cyclo-**

**hexane-1:1-diacetic acid; mechanism of reaction.** A. I. VOGEL (J.C.S., 1933, 1028—1031).—The principal products at 290—>370° are unsaturated ketone and hydrocarbon (I) according to the scheme (cf. A., 1929, 700)  $\text{>C:CH-COMe} + \text{CO}_2 \leftarrow \text{>C}(\text{CH}_2\text{-CO}_2\text{H})_2 \rightarrow \text{>C:CH}_2 + \text{AcOH} + \text{CO}_2$ , except in the case of  $\beta\beta$ -dimethylglutaric acid, which is unchanged. The yield of (I) from cyclohexane-1:1-diacetic acid (33%) is higher than from the cyclopentane acid in agreement with the smaller tendency to ring formation. In presence of Fe and a little  $\text{Ba(OH)}_2$  (*loc. cit.*) both products were formed in every case, although in very poor yield from the glutaric acid, which also gave some isophorone. H. A. P.

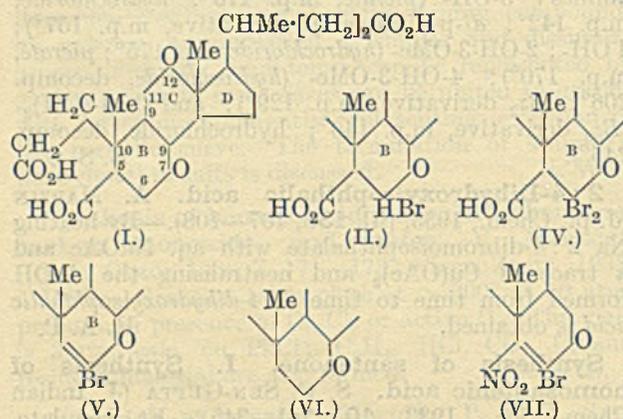
**Reduction of hydroxymandelonitriles. Synthesis of tyramine.** J. S. BUCK (J. Amer. Chem. Soc., 1933, 55, 3388—3390).—The following substituted mandelonitriles were prepared: 3-, m.p. 110°, and 4-OH-, m.p. 98°, 2-OH-3-OMe-, m.p. 85°, 4-OH-3-OMe-, m.p. 83°, and 3:4-(OH) $_2$ -, m.p. 95°. When hydrogenated ( $\text{PtO}_2$ ) these give 31—77% yields of the following substituted phenylethylamines: 3-OH- (*picrate*, m.p. 170°; *hydrochloride*, m.p. 142°; *di-p-nitrobenzoyl* derivative, m.p. 157°); 4-OH-; 2-OH-3-OMe- (*hydrochloride*, m.p. 175°; *picrate*, m.p. 170°); 4-OH-3-OMe- (*hydrochloride*, decomp. 206°; *Bz* $_2$  derivative, m.p. 129°); and 3:4-(OH) $_2$ - (*Bz* $_3$  derivative, m.p. 140°; *hydrochloride*, decomp. 245°). R. S. C.

**2:4-Dihydroxyisophthalic acid.** A. MARZIN (J. pr. Chem., 1933, [ii], 138, 107—108).—By heating Na 2:4-dibromoisophthalate with aq. NaOAc and a trace of  $\text{Cu(OAc)}_2$  and neutralising the AcOH formed from time to time 2:4-dihydroxyisophthalic acid is obtained. H. A. P.

**Synthesis of santenone. I. Synthesis of homosantenic acid.** S. C. SEN-GUPTA (J. Indian Chem. Soc., 1933, 10, 341—345).—Et laevulate,  $\text{CHBrMe-CO}_2\text{Et}$ , and Zn in  $\text{C}_6\text{H}_6$  give the lactone, b.p. 148—149°/8 mm., of  $\alpha$ -Et H  $\beta$ -hydroxy- $\alpha\beta$ -dimethyladipate, which when heated with KCN at 200—220°, then hydrolysed (conc. HCl), and subsequently esterified (EtOH vapour; conc.  $\text{H}_2\text{SO}_4$ ) affords Et  $\gamma$ -methylpentane- $\alpha\gamma\delta$ -tricarboxylate, b.p. 147—152°/5 mm. This is converted by Na in  $\text{C}_6\text{H}_6$  into Et 2:3-dimethylcyclopentanone-3:5-dicarboxylate, b.p. 145—150°/5 mm., hydrolysed (dil. HCl) to 2:3-dimethylcyclopentanone-3-carboxylic acid, b.p. 150—153°/5 mm. (*semicarbazone*, m.p. 208°), the Et ester, b.p. 105—106°/5 mm. (*semicarbazone*, m.p. 191°), of which with  $\text{CH}_2\text{Br-CO}_2\text{Et}$  and Zn in  $\text{C}_6\text{H}_6$  gives (after complete dehydration with  $\text{POCl}_3$  in  $\text{C}_6\text{H}_6$ ) Et dehydrohomosantenate (Et 3-carbethoxy-2:3-dimethylcyclopentylideneacetate), b.p. 125—130°/4 mm. This is reduced ( $\text{H}_2$ ,  $\text{PtO}_2$ ,  $\text{Et}_2\text{O}$ ) to Et homosantenate (Et 3-carbethoxy-2:3-dimethylcyclopentylacetate), b.p. 130—135°/5 mm. (*free acid*, m.p. 170°). H. B.

**Constitution of bile acids. LI. Bromination of bilianic acid and of some other keto-acids.** H. WIELAND and M. A. KENNELLY (Z. physiol. Chem., 1933, 219, 138—147; cf. this vol., 609).—Bromination of bilianic acid (I) in AcOH gives bromobilianic acid (II), m.p. 180—190° (decomp.) (+AcOH, froths at

125—127°), which, on oxidation with  $\text{HNO}_3$ , affords biloidanic acid (III). At 65° bromination of (I) yields *dibromobilianic acid* (IV), m.p. 208—209° (decomp.) (*Me* ester, m.p. 133°). When warmed with  $\text{C}_5\text{H}_5\text{N}$ , (IV) gives an unsaturated *Br-acid* (V),  $\text{C}_{23}\text{H}_{31}\text{O}_6\text{Br}$ , m.p. 213°, which is very resistant to hydrolysis. Catalytic hydrogenation eliminates Br from (V), affording a saturated *diketocarboxylic acid* (VI),  $\text{C}_{23}\text{H}_{34}\text{O}_6$ , m.p. 221—222° (*Me* ester, m.p. 109—110), readily oxidised to (III). Reduction of (V) with Zn dust and acid gives a *ketodicarboxylic acid*,  $\text{C}_{23}\text{H}_{36}\text{O}_5$ , m.p. 198—200°. Oxidation of (V) directly with fuming  $\text{HNO}_3$  yields the unsaturated *bromonitrodiketodicarboxylic acid* (VII),  $\text{C}_{23}\text{H}_{30}\text{O}_8\text{NBr}$ , m.p. 215°. Bromination of (I) sometimes yields a mol. compound (VIII), m.p. 180°, of a *mono-* (IX) and *di-bromobilianic acid*. Hydrolysis of (IX) with 0.1*N*-KOH gives a *hydroxyketodicarboxylic acid*,  $\text{C}_{23}\text{H}_{34}\text{O}_7$ , m.p. 222—223° (*Me* ester, m.p. 105°). The  $\text{C}_5\text{H}_5\text{N}$  reaction with (VIII) gives a resinous product, which, when heated with *N*-KOH, affords an unsaturated *acid*,  $\text{C}_{23}\text{H}_{30}\text{O}_6$ , m.p. 151—152°. The reactions are formulated:



Bromination of 3:6-diketocallocholic acid gave the *Br-*, m.p. 164—165°, *Br<sub>2</sub>-*, m.p. 194—195°, and *Br<sub>3</sub>-*, m.p. 219—220°, *-acids*. 3-Hydroxy-6-ketocholic acid (*Me* ester, m.p. 140—142°) gave the *Br-*, m.p. 193° (*Me* ester, m.p. 108—109°), and *Br<sub>2</sub>-*, m.p. 175°, *-acids*. 3-Hydroxy-6-ketocallocholic acid afforded the *Br-acid*, m.p. 162°. J. H. B.

**Lichen substances. XXVIII. Occurrence of stictic acid in various lichens.** Y. ASAHINA, M. YANAGITA, T. HIRAKATA, and M. IDA (Ber., 1933, 66, [B], 1080—1086).—Stictic acid (I) is converted by  $\text{Ac}_2\text{O}$  containing a drop of  $\text{H}_2\text{SO}_4$  into a *tetra-acetate*, m.p. 221—222°, in which 2 Ac are in the form of aldehyde diacetate. (I) and boiling  $\text{Ac}_2\text{O}$  afford the *diacetate* (II),  $\text{C}_{19}\text{H}_{12}\text{O}_9\text{Ac}_2$ , m.p. 235—236°, probably identical with Zopf's compound from *ψ*-psoromic acid. Since (II) gives an *oxime*, m.p. 213° (decomp.), the CHO group is intact. (I) is hydrolysed by conc. NaOH to MeOH and atranol. Catalytic reduction of (I) (Pd-C) leads to a *compound* (III),  $\text{C}_{19}\text{H}_{16}\text{O}_8$ , m.p. 265° (decomp.), transformed by  $\text{CH}_2\text{N}_2$  into the substance  $\text{C}_{18}\text{H}_{11}\text{O}_5(\text{OMe})_3$ , m.p. 165°, identical with the *Me<sub>3</sub> ether* of the first reduction product of salazic acid (III). Reduction of (III) with Zn dust and AcOH gives the *compound*  $\text{C}_{19}\text{H}_{16}\text{O}_7$ , m.p. 263°

(decomp.), transformed by  $\text{CH}_2\text{N}_2$  into a substance, m.p. 283°, identical with the *Me<sub>2</sub> ether* of the second reduction product of (IV). Extraction of *Stereocaulon nabewariense*, A. Zahbruckner, with  $\text{Et}_2\text{O}$  and  $\text{COMe}_2$  yields atronorin (V) and (I). (V), (I), and lobaric acid are obtained from *Stereocaulon japonicum*, Th. Fr.; *Parmelia pertusa* (Schrank), Schaier, yields (V) and (I). The probable identity of (I) with physodalic, scopuloric, and *ψ*-psoromic acids is indicated.

H. W.

**Action of phosphoryl chloride on aldehydes.** M. BACKÈS (Compt. rend., 1933, 196, 1674—1675; cf. this vol., 376).—Equimol. mixtures of PhCHO (I) and MeCHO afford cinnamaldehyde when treated with  $\text{POCl}_3$  at 30—35°. (I) and heptaldehyde give *α*-amylcinnamaldehyde. In the absence of H attached to the C adjacent to the CHO group, chlorination occurs. Thus, (I) alone gives BzCl and  $\text{CHPhCl}_2$ , and  $\text{CH}_2\text{O}$  gives  $(\text{CH}_2\text{Cl})_2\text{O}$ .  $\text{SO}_2\text{Cl}$  may be used instead of  $\text{POCl}_3$ . A. C.

**Isomerism of the oximes. XXXVIII. Constitution of the acetyl derivatives of *α*- and *β*-aldoximes.** O. L. BRADY and H. J. GRAYSON (J.C.S., 1933, 1037—1038).—Comparison of absorption spectra of the *α*- and *β*-Ac derivatives of anisaloxime and *p*-nitrobenzaloxime with those of the *α*- and *β*-O-Me ethers and of the *N*-Me ether of the oximes indicates that the two Ac derivatives are similarly constituted and have the Ac attached to O. F. R. S.

**Anishydroxamyl chloride.** C. R. KINNEY, E. W. SMITH, B. L. WOOLLEY, and A. R. WILLEY (J. Amer. Chem. Soc., 1933, 55, 3418—3424).—*α*- or *β*-Anisaloxime (I), best with  $\text{Cl}_2$  (1 mol.) in cold dry  $\text{Et}_2\text{O}$ , gives anishydroxamyl chloride (II), m.p. 88—89°, in 45% yield, which, when kept, gives dianisnylazoxime oxide, m.p. 179°, and anisoylanishydroxamic acid. With hot 6*N*-HCl or NaOH (II) gives anisic acid, with  $\text{AgNO}_3$  dianisylfurazan oxide (III), with  $\text{AgOBz}$  in  $\text{Et}_2\text{O}$  anishydroxamic acid benzoate and (III), and with  $\text{NH}_3\text{-Et}_2\text{O}$  anisohydroxamamide. With more  $\text{Cl}_2$  (I) gives 3-*chloro-*, m.p. 106.5°, and 3:5-*dichloro-*, *cryst.*, 4-*methoxybenzhydroxamyl chloride*, hydrolysed to the corresponding chloroanisic acids and affording the *di-3-Cl-* and *di-3:5-Cl<sub>2</sub>-* derivatives of (III), m.p. 165° and 146°, respectively. (I) and NOCl in  $\text{Et}_2\text{O}$  give an intermediate *compound*, m.p. about 50°, readily passing into (II). Rheinboldt's compound, m.p. 120° (A., 1927, 245), was not obtained; it was probably a mixture of (II) and anisic acid. R. S. C.

**Behaviour of vanillin substitution products: (a) Perkin reaction; (b) preparation of substituted vanillic acids.** L. C. RAIFORD, V. S. WEBSTER, and D. J. POTTER (Proc. Iowa Acad. Sci., 1931, 38, 171).—The Cl and Br substitution products of vanillin previously described (A., 1931, 90) have been converted by the Perkin reaction into the corresponding cinnamic acids. The latter with alkaline  $\text{KMnO}_4$  afford the original vanillin derivatives; the vanillic acids were obtained by hydrolysis of the nitriles prepared from the oximes. CH. ABS.

**Jute-lignin. II. Potassium hydroxide fusion of lignin.** P. B. SARKAR (J. Indian Chem. Soc., 1933,

10, 263—270).—Fusion of jute-lignin (I) with KOH at 220—230° in air gives lignic acid (II) [24.6% of (I) used],  $\text{PrCO}_2\text{H}$  (9.13%),  $\text{H}_2\text{C}_2\text{O}_4$  (18.72%), protocatechuic acid (III) (12.1%), and  $o\text{-C}_6\text{H}_4(\text{OH})_2$  (IV) (3.5%); at 280—300°,  $\text{H}_2\text{C}_2\text{O}_4$  (20.3%) is the sole product. (II) is the precursor of (III) and (IV). The production of  $\text{PrCO}_2\text{H}$  and (III) shows that Cross and Bevan's formula (J.C.S., 1882, 41, 90) for (I) is untenable. Delignified jute-fibre does not yield  $\text{PrCO}_2\text{H}$  or aromatic compounds; the latter must arise from aromatic groupings in the mol. of (I). Synthetic lignin, prepared from delignified jute by Hawley and Harris' method (B., 1932, 836), does not give any of the above products. H. B.

**Lignin. VIII. Oxidation of alkali-lignin.** M. PHILLIPS and M. J. Goss (J. Amer. Chem. Soc., 1933, 55, 3466—3470; cf. A., 1932, 1032).—Alkali-lignin (I) from corn cobs with  $\text{Me}_2\text{SO}_4\text{-NaOH}$  gives a product (OME, 27.2%) (II), which with hot 5*N*- $\text{HNO}_3$  gives an amorphous  $\text{NO}_2$ -compound [oxidised by  $\text{KMnO}_4$  to anisic acid (III)], (III), and  $\text{H}_2\text{C}_2\text{O}_4$ . The ethylation product (similarly prepared) gives  $p\text{-OEt}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ . (I) with  $\text{O}_3$  gives  $\text{H}_2\text{C}_2\text{O}_4$ , but (II) gives also (III). (I), therefore, contains  $p\text{-HO}\cdot\text{C}_6\text{H}_4\cdot\text{C}$  groups. R. S. C.

**Lignin and its derivatives. II.** L. LEMMEL (Anal. Fis. Quim., 1933, 31, 50—52; cf. A., 1932, 1296).—*Orcinol-lignin*, m.p. 250—257° after darkening at 180° and softening at 225°, is prepared by fusion of pine sawdust with orcinol. The *Ac* derivative is formulated:  $\{(\text{C}_6\text{H}_7)(\text{OMe})(\text{OAc})[\text{C}_6\text{H}_2\text{Me}(\text{OAc})_2]\}_x$ . R. K. C.

**Hydroaromatic compounds of the cyclooctane series.** M. GODCHOT and (Mlle.) CAUQUIL (Chim. et Ind., 1933, Spec. no., 1019—1023; cf. A., 1930, 596).—2-Methylcyclooctanone (I), b.p. 74—75°/7 mm. (oxime, b.p. 115°/7 mm., and its phenylurethane, m.p. 117—118°), is oxidised by dil.  $\text{KMnO}_4$  to  $\eta$ -keto-nonoic acid (semicarbazone, m.p. 116—117°). Treatment of (I) with  $\text{NaNH}_2$  and  $\text{MeI}$  leads to 2:2-dimethylcyclooctanone (II), b.p. 88—90°/12 mm. (which does not react with  $\text{NH}_2\text{OH}$  or  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ ), containing a little of the 2:8-isomeride (III). *Me* 1-hydroxycycloheptyl-1-carboxylate, b.p. 117—118°/11 mm., m.p. 24°, and  $\text{MgMeI}$  in  $\text{Et}_2\text{O}$  yield  $\alpha$ -cycloheptyl- $\beta$ -methylpropane- $\alpha\beta$ -diol, b.p. 128—130°/7 mm., m.p. 45°, dehydrated by aq.  $\text{H}_2\text{C}_2\text{O}_4$  at 135—140° or conc.  $\text{H}_2\text{SO}_4$  at 0° to the ethylenic hydrocarbon  $\text{C}_{10}\text{H}_{16}$ , b.p. 68°/7 mm., 188—190°/760 mm., containing small amounts of (II) and (III). Reduction of (I) ( $\text{Pt-black-AcOH}$ ) gives exclusively 2-methylcyclooctanol A, b.p. 100—101°/16 mm., 201—202°/760 mm. (*H* phthalate, m.p. 104°; phenylurethane, m.p. 137°), whereas treatment with  $\text{Na}$  and  $\text{EtOH}$  leads almost exclusively to 2-methylcyclooctanol B, b.p. 103—104°/16 mm. (*H* phthalate, m.p. 119—120°; phenylurethane, m.p. 154°). (II) with  $\text{Na}$  and  $\text{EtOH}$  affords 2:2-dimethylcyclooctanol, b.p. 91—92°/6 mm., 219—220° (corr.)/754 mm. (*H* phthalate, m.p. 110—113°; phenylurethane, m.p. 147°). cycloOctanol is readily transformed into cyclooctyl bromide and thence through the  $\text{Mg}$  derivative into cyclooctanecarboxylic acid, b.p. 150°/19 mm. (chloride, b.p. 110°/19 mm.; amide, m.p. 191°). H. W.

**Behaviour of keten in the Friedel-Crafts reaction.** K. PACKENDORFF, N. D. ZELINSKI, and L. LEDER-PACKENDORFF (Ber., 1933, 66, [B], 1069—1073).—Keten is passed into a mixture of  $\text{C}_6\text{H}_6$  and  $\text{AlCl}_3$ , whereby  $\text{HCl}$  is freely evolved. The crude ketones are hydrogenated ( $\text{Pt-C+Pd}$ ) giving  $\text{PhEt}$  and (?) 2-ketotetrahydronaphthalene [semicarbazone, m.p. 212°; oxime, m.p. 74° (lit. 77.5—78°)]. It appears probable that 1:3-diketotetrahydronaphthalene is present in the mixture of ketones. Its formation is not due to intermediate production of cyclobutanedione, which ultimately yields only  $\text{PhEt}$  when similarly treated with  $\text{C}_6\text{H}_6$  and  $\text{AlCl}_3$ .  $\text{PhMe}$  similarly affords *p*-ethyltoluene and a semicarbazone, m.p. 219°. H. W.

**Side-chain chlorination of *pp'*-dimethylbenzophenone.** I. 4:4'-Dichlorodimethylbenzophenone. E. CONNERADE (Bull. Soc. chim. Belg., 1933, 42, 311—329).—4:4'-Dimethylbenzophenone (improved separation from the 4:2'-compound described) with  $\text{Cl}_2$  (slightly > 2 mols.) at 130—135° affords the 4:4'-di(chloromethyl) compound (I), m.p. 110.5°, mixtures of  $\text{Cl}_2$ - and  $\text{Cl}_3$ -, and of  $\text{Cl}_2$ - and  $\text{Cl}_4$ -derivatives being removed by  $\text{C}_6\text{H}_6$ -ligand (5:20). With  $\text{KOH}$  in aq.  $\text{MeOH}$  at 65° (I) affords the 4:4'-di(hydroxymethyl) derivative (II), m.p. 51°, b.p. 197—203°/Hg vac. (oxime, not pure), readily polymerised by light to a resin which affords ( $p\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4$ )<sub>2</sub> $\text{CO}$  by oxidation with  $\text{CrO}_3$ , the corresponding  $\text{Ac}_2$  derivative, m.p. 42—48°,  $\text{Me}_2$  [contaminated with (II)] and *Et*<sub>2</sub>, b.p. 267—270°/high vac., ether being obtained from  $\text{AgOAc-AcOH}$ , and  $\text{NaOR-ROH}$ , respectively, and (I). Oxidation of (II) with 65%  $\text{HNO}_3$  in 60%  $\text{AcOH}$  gives benzophenone-4:4'-dialdehyde, partial fusion at 180° to a plastic which liquefies at 265° [*di*-phenylhydrazone, m.p. 234—235° (decomp.); dioxime, partial fusion at 150—152°, liquid at 190°]. With 3%  $\text{NH}_3$  in  $\text{EtOH}$  at 80—82° (I) gives a polymeride  $\text{NH}_2\cdot\text{CH}_2\cdot\text{R}\cdot\text{CH}_2\cdot[\text{NH}\cdot\text{CH}_2\cdot\text{R}\cdot\text{CH}_2]_n\cdot\text{NH}\cdot\text{CH}_2\cdot\text{R}\cdot\text{CH}_2\cdot\text{NH}_2$  [ $\text{R}=\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4$ ;  $n=10$ (?)], similar treatment with  $\text{NHEt}_2$  giving 4:4'-tetraethyldiaminodimethylbenzophenone. Reduction of (II) in 90%  $\text{EtOH}$  with  $\text{Na-Hg}$  gives a theoretical yield of *di- $\omega$ -hydroxy-*p*-tolylcarbinol* ( $\text{Ac}_3$  and  $\text{Cl}_3$ -derivatives not characterised). The reactions of these compounds are discussed on an electronic basis. J. W. B.

**2:4-Dinitrobenzophenone.** I. TANASESCU and (MME.) M. MACAROVICI (Bull. Soc. chim., 1933, [iv], 53, 597—599).—2:4-Dinitrobenzyl chloride,  $\text{AlCl}_3$ , and  $\text{C}_6\text{H}_6$  give a viscous mass (A), whence a substance (B), m.p. 190°, is obtained. (A), but not (B), with  $\text{CrO}_3\text{-AcOH}$  gives 2:4-dinitrobenzophenone, m.p. 167°. R. S. C.

**Substitution in compounds containing two or more phenyl groups. IV. Nitration of diphenyl derivatives containing *m*-directing substituents.** W. S. M. GRIEVE and D. H. HEY (J.C.S., 1933, 968—972).—Mononitration occurs when a negatively 2- or 4-substituted  $\text{Ph}_2$  derivative is added to well-stirred  $\text{HNO}_3$  (*d* 1.46) at -5° to 0°; under other conditions either dinitration or no reaction occurs. It is exclusively heteronuclear. The reaction is applied to the prep. of 4'-, m.p. 152—153°, and 2'-nitro-4-diphenyl *Me* ketone, m.p. 110°, 4'-, m.p.

127°, and 2'-nitrodiphenyl-4-aldehyde, m.p. 101°, and 4'- (Et ester, m.p. 112°) and 2'-nitrodiphenyl-4-carboxylic acid. Under the same conditions quant. mononitration of 2- and 4-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>Ph and dinitration of Ph<sub>2</sub> occur. The nitro-4-diphenyl Me ketones are also obtained (the 4'-compound in 55% yield) from the NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>Ph, AcCl, and AlCl<sub>3</sub>. 2 : 4'-Dinitro-4-diphenyl Me ketone has m.p. 155—146°.

H. A. P.

**Organic molecular compounds of titanium tetrachloride.** F. EVARD (Compt. rend., 1933, 196, 2007—2009).—Treatment of TiCl<sub>4</sub> with an excess of an aromatic ketone (I) in anhyd. C<sub>6</sub>H<sub>6</sub> affords halochromic compounds, the colour deepening as the no. of double linkings in (I) increases. The compounds TiCl<sub>4</sub>·COPh<sub>2</sub> and TiCl<sub>4</sub>·(COPh·CH·CHPh)<sub>2</sub> are described.

A. C.

**Isomerism of halochromic compounds.** I. P. PFEIFFER and H. KLEU (Ber., 1933, 66, [B], 1058—1063).—Dissolution of Ph *p*-dimethylaminostyryl ketone in 70% HClO<sub>4</sub> yields the colourless salt (I), HClO<sub>4</sub>·NMe<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CH·CH·COPh, m.p. 165° after becoming brown at 140° and softening at 155°, slowly hydrolysed by H<sub>2</sub>O. Dissolution of (I) in molten CH<sub>2</sub>Cl·CO<sub>2</sub>H (III) followed by rapid cooling and removal of (III) with anhyd. Et<sub>2</sub>O leads to the pinkish-violet salt (II), NMe·C<sub>6</sub>H<sub>4</sub>·CH·CH·CPh·O·HClO<sub>4</sub>, immediately hydrolysed by H<sub>2</sub>O. Similarly, *p*-dimethylaminostyryl Me ketone, m.p. 135·5°, gives a colourless perchlorate, slowly hydrolysed by cold H<sub>2</sub>O, and a blue perchlorate, rapidly hydrolysed. Ph styryl ketone affords a canary-yellow perchlorate. H. W.

**Preparation of azines by means of hydrazine hydrochloride.** N. SCHAPIRO (Ber., 1933, 66, [B], 1103—1107).—Fluorenone and N<sub>2</sub>H<sub>4</sub>·HCl (I) in hot EtOH afford fluorenoneketazine, m.p. 266°. *p*-Tolilketazine (II), m.p. 248—249° after softening at 247°, and 4 : 4'-diphenoxybenzilketazine, m.p. 228—229° after softening at 226°, are similarly prepared, whereas *p*-toluoin affords (II) and a small amount of (?) tetra-*p*-tolylpyrazine, m.p. > 250°. Di-2-tetrahydronaphthyl diketone, anthraquinone, carvone, camphor, and lævulic acid do not react with (I). Similarly are prepared aldazines of PhCHO, m.p. 92—93°, *o*-OH·C<sub>6</sub>H<sub>4</sub>·CHO, m.p. 214—215°, *o*-OMe·C<sub>6</sub>H<sub>4</sub>·CHO, m.p. 139·5—140°, *p*-OMe·C<sub>6</sub>H<sub>4</sub>·CHO, m.p. 179—179·5° after softening at 168°, *piperonal*, m.p. 202—203° (decomp.), vanillin, m.p. 231—232°, *ψ*-cumaldehyde, m.p. 168°, *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO, m.p. 307° (partial decomp.), *o*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO, m.p. 204·5° after softening at 203·5°, *m*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO, m.p. 193—194° after softening at 193°, and 2-methoxynaphthaldehyde, m.p. 265—266° (decomp.) after softening. Furfuraldehyde yields a dark brown powder, apparently neither ketazine nor hydrazone. Citral does not react. CCl<sub>3</sub>·CH(OH)<sub>2</sub> at 20° yields a brownish-red substance, m.p. > 300° after changing at 230°.

H. W.

**Phenanthrene series.** V. 9-Acetylphenanthrene. Reduction products of 2-, 3-, and 9-acetylphenanthrenes. VI. *ω*-Aminoacetylphenanthrenes and aminomethylphenanthrylcarbinols. E. MOSETTIG and J. VAN DE KAMP (J. Amer. Chem. Soc., 1933, 55, 3442—3448, 3448—3452; cf.

this vol., 951).—V. Me phenanthrene-9-carboxylate, much EtOAc, and Na at 170° give an ester, which, when hydrolysed, affords 9-acetylphenanthrene (I), m.p. 74—74·5° (semicarbazone, m.p. 199—201°; oxime, m.p. 154—154·5°; picrate, m.p. 107—108°), giving with CrO<sub>3</sub> phenanthraquinone and with NaOCl phenanthrene-9-carboxylic acid. 2-, 3-, and 9-Acetylphenanthrene with (NH<sub>4</sub>)<sub>2</sub>S gives 2- m.p. 181—183° (Me ester, m.p. 78—78·5°), 3-, m.p. 175—177° [Me ester, an oil (picrate, m.p. 103·5—104°), and 9-phenanthrylacetic acid, m.p. 219—221° (Me ester, m.p. 75—75·5°); they are hydrogenated very slowly in presence of PtO<sub>2</sub>, and much better in presence of Cu-Cr-BaO at 100° or 140°/1200—1900 lb., to *α*-2-, m.p. 135—135·5°, *α*-3-, m.p. 83—83·5° (picrate, m.p. 118—119°; also a by-product, m.p. 109—109·5°), and *α*-9-phenanthrylethyl alcohol, m.p. 135—136°, and at 150° to 2-, m.p. 67—68° (picrate, m.p. 95—96°), 3-, an oil (picrate, m.p. 121·5—122°), and 9-ethylphenanthrene, m.p. 62·5—63° (picrate, m.p. 123—124°), also obtained by Clemmensen reduction in 5—10% yield. The nature of Willgerodt's supposed (I) (A., 1911, i, 882) is not clear.

VI. The acetylphenanthrenes and Br-Et<sub>2</sub>O at 0° afford 2-, m.p. 142·5—143°, 3-, m.p. 87—88° (picrate, m.p. 104·5—105·5°), and 9-*ω*-bromoacetylphenanthrene, m.p. 93—93·5° (picrate, m.p. 122—122·5°) (oxidised to the corresponding halogen-free acids), whence by the appropriate base the following substituted acetylphenanthrenes were prepared, the m.p. in parentheses being those of the hydrochlorides and picrates, respectively: (a) 2-*ω*-dimethylamino-, an oil (227—228°; 198—199°), (b) 2-*ω*-diethylamino-, an oil (—; 176·5—178°; perchlorate, m.p. 182—182·5°), (c) 2-*ω*-piperidino-, m.p. 94—95° (276—277°; 192—193°), (d) 3-*ω*-dimethylamino-, an oil (228—230°; 189—189·5°), (e) 3-*ω*-diethylamino-, an oil (231—232°; 181—182°), (f) 3-*ω*-piperidino-, an oil (259·5—261°; 189—190°), (g) 9-*ω*-dimethylamino-, an oil (199—201°; 189—190°), (h) 9-*ω*-diethylamino-, an oil (158—159°; 138—139°), and (i) 9-*ω*-piperidino-, an oil (250—251°; 150—151°). These give by hydrogenation (PtO<sub>2</sub>) in EtOH the corresponding substituted *β*-amino-*α*-phenanthrylethyl alcohols, the m.p. in parentheses being those of the hydrochlorides and picrates, respectively: (a) m.p. 100—101° [222—223°; 235—236°; benzoate, m.p. 108·5—109° (hydrochloride, m.p. 244—245°)], (b) m.p. 75—76° (194—195°; 154—155°), (c) m.p. 126—127° (254·5—255·5°; 180·5—181·5°), (d) m.p. 76—76·5° (179·5—180·5°; 218—218·5°; hydrochloride of benzoate, m.p. 223—224°), (e) m.p. 59—60° (168—169°; 163—164°), (f) m.p. 108—109° (242—243°; 174—175°), (g) m.p. 93—94° (211—211·5°; 210—211°; hydrochloride of benzoate, m.p. 228—229°), (h) m.p. 87—88° (—; 178·5—179·5°), and (i) m.p. 111·5—112° (216—216·5°; 196—196·5°). Phenanthrene and CH<sub>2</sub>Cl·COCl give a mixture of 2- and 3-*ω*-chloroacetylphenanthrene, m.p. 139—139·5° and 93·5—94°, respectively, identified by condensation with piperidine. R. S. C.

**Alkylcyclopentanones.** III. Synthesis of 3'-methylcyclopentanespirocyclohexane-3 : 5-dione. R. D. DESAI (J. Indian Chem. Soc., 1933, 10, 257—261).—Et 3-methylcyclopentan-1-ol-1-acetate (A.,

1932, 740) is dehydrated ( $\text{POCl}_3\text{-C}_6\text{H}_6$  or  $\text{SOCl}_2\text{-C}_5\text{H}_5\text{N}$ ) to the *Et* ester, b.p. 94—95°/10 mm., of 3-methylcyclopentenylacetic acid, b.p. 127—128°/12 mm., the chloride of which with  $\text{ZnMeI}$  gives 3-methylcyclopentenylacetone, b.p. 93—94°/18 mm. [semicarbazone, m.p. 185° (decomp.)]. Condensation of this with  $\text{CHNa}(\text{CO}_2\text{Et})_2$  and hydrolysis ( $\text{KOH}$ ) of the resulting ester gives 3'-methylcyclopentanespirocyclohexane-3 : 5-dione (I), m.p. 127—128° [condensation product,  $\text{C}_{23}\text{H}_{32}\text{O}_4$ , m.p. 161—162°, with  $\text{CH}_2\text{O}$ ; anil, m.p. 156°]. The chloride from *Et* H 3-methylcyclopentane-1 : 1-diacetate and  $\text{ZnMeI}$  give *Et* 1-acetonyl-3-methylcyclopentane-1-acetate, b.p. 152—155°/14 mm. {145°/14 mm., when prepared from the free acid, b.p. 181—182°/12 mm. [semicarbazone, m.p. 182° (decomp.)]} (semicarbazone, m.p. 87—88°), converted by  $\text{EtOH-NaOEt}$  into (I). The latter method is recommended. H. B.

**Identification of carbonyl compounds by 2 : 4-dinitrophenylhydrazine.** J. FERRANTE and A. BLOOM (Amer. J. Pharm., 1933, 105, 381—384).—*EtOH* contains traces of aldehydes. 2 : 4-Dinitrophenylhydrazine is, therefore, best used in *MeOH* solution. 2 : 4-Dinitrophenylhydrazones of the following substances are described:  $\text{CO}(\text{CH}_2\text{Ph})_2$ , m.p. 238°; *o*-, *m*-, and *p*-methoxycyclohexanone, m.p. 135°, 135.5°, and 150°, respectively;  $\text{COPhEt}$ , m.p. 187.5°; *p*- $\text{OMe-C}_6\text{H}_4\text{-CHO}$ , m.p. 253.5°; *o*- $\text{C}_6\text{H}_4\text{Cl-CHO}$ , m.p. 213.6°; *p*- $\text{OMe-C}_6\text{H}_4\text{-COPh}$ , m.p. 180°; *p*- $\text{OH-C}_6\text{H}_4\text{-COPh}$ , m.p. 242.4°;  $\text{CO}(\text{C}_6\text{H}_4\text{Me-}p)_2$ , m.p. 229.4°;  $\text{COPhPr}$ , m.p. 188°; *o*- $\text{OH-C}_6\text{H}_4\text{-CHO}$ , m.p. 258.3° (lit. 237°); *p*- $\text{C}_6\text{H}_4\text{Me-COPh}$ , m.p. 202.4°; *p*- $\text{C}_6\text{H}_4\text{Me-COMe}$ , m.p. 260.4°; furfurylidene-, m.p. 241°, vanillylidene-, m.p. 229°, di-*p*-tolylidene-, m.p. 165.5°, dipiperonylidene-, m.p. 238.2°, dicinnamylidene-, m.p. 195.7°, and dianisylidene-acetone, m.p. 82—83°; furfurylidene-, m.p. 169°, *p*-methoxy-, m.p. 231.8°, *p*-hydroxy-, m.p. 261.5°, cinnamylidene-, m.p. 222°, 2-methyl-5-isopropyl-, double m.p. 140—142° (turbid) and 160° (clear), and *p*-bromo-acetophenone, m.p. 237°. M.p. above 195° are corr. Allen's method of analysis is best for these substances. R. S. C.

**Reaction of diazonium salts with open-chain hydroxymethyleneketones.** S. N. ROY and H. K. SEN (J. Indian Chem. Soc., 1933, 10, 347—351; cf. A., 1928, 185).—Hydroxymethylenedeoxybenzoin (*Ph*  $\beta$ -hydroxy- $\alpha$ -phenylvinyl ketone) and  $\text{PhN}_2\text{Cl}$  in cold aq. *EtOH-NaOAc* (excess) give the monophenylhydrazone of benzil (phenylhydrazone-*p*-nitrophenylhydrazone, m.p. 255°); the mono-*p*-nitrophenylhydrazone is similarly obtained using *p*- $\text{NO}_2\text{-C}_6\text{H}_4\text{-N}_2\text{Cl}$ . Reaction probably occurs thus:  $\text{OH}\cdot\text{CH}\cdot\text{CPh}\cdot\text{COPh} \rightleftharpoons \text{CHO}\cdot\text{CHPh}\cdot\text{COPh} \rightarrow \text{NPh}\cdot\text{N}\cdot\text{CPh}(\text{CHO})\cdot\text{COPh} \rightarrow \text{HCO}_2\text{H} + \text{NPh}\cdot\text{N}\cdot\text{CHPh}\cdot\text{COPh} \rightarrow \text{NPh}\cdot\text{N}\cdot\text{CPh}\cdot\text{COPh}$ . *Ph*  $\beta$ -hydroxy- $\alpha$ -methylvinyl ketone and  $\text{PhN}_2\text{Cl}$  afford the monophenylhydrazone, m.p. 146—147°, of *PhMe* diketone (phenylhydrazone-*p*-nitrophenylhydrazone, m.p. 230°). H. B.

**Cleavage of carbonyl compounds by alkalis.** XI. Action of hypobromite solutions on  $\beta$ -diketones. C. F. WOODWARD and R. C. FUSON (J. Amer. Chem. Soc., 1933, 55, 3472—3475; cf. this vol., 1048).—*p*-Bromobenzoylacetone and  $\text{NaOBr}$

give  $\text{C}_6\text{H}_4\text{Br-CO}_2\text{Na}$ ,  $\text{NaOAc}$ , and  $\text{CBr}$ . Acetomesitylene,  $\text{EtOAc}$ , and  $\text{NaOEt}$  give acetylacetomesitylene, m.p. 45—46° (gives with  $\text{NH}_2\text{-NHPh}$  the phenylhydrazone, m.p. 128.5—129.5°, and phenylpyrazolone derivative, m.p. 86—87°), which with  $\text{NaOBr}$  gives  $\text{NaOAc}$  and  $\omega\omega\omega$ -tribromoacetomesitylene. 2-Methoxy-1-naphthoylacetone, m.p. 71—72.5° (from 1-aceto-2-methoxynaphthalene), with  $\text{NaOBr}$  gives 1-tribromoacetyl-2-methoxynaphthalene.  $\text{NaOBr}$  is thus shown to cleave  $\text{CO}$  compounds by preliminary attack on the active  $\text{CH}_2$  group.

R. S. C.

**Synthesis of an isomeride of plumbagin.** J. S. DE BURUAGA (Anal. Fis. Quim., 1933, 31, 185—188).—Oxidation of 8-acetoxy-2-methylnaphthalene by  $\text{CrO}_3$  in *AcOH* and hydrolysis yields 8-hydroxy-2-methyl- $\alpha$ -naphthaquinone, m.p. 158°, which resembles plumbagin (A., 1928, 1376) except in m.p. Plumbagin is probably the 3-Me derivative.

R. K. C.

**Biochemistry of micro-organisms.** XXXII. Cynodontin (1 : 4 : 5 : 8-tetrahydroxy-2-methyl-anthraquinone), a metabolic product of *Helminthosporium cynodontis*, Marignoni, and *H. euchlaena*, Zimmermann. H. RAISTRICK, R. ROBINSON, and A. R. TODD.—See this vol., 1082.

**Conversion of phthaloylnaphthalenes and naphthoyl-2-benzoic acids into benzanthraquinones.** L. F. FIESER and (MRS.) M. FIESER (J. Amer. Chem. Soc., 1933, 55, 3342—3352).—Quinones are formed from naphthoylbenzoic acids more smoothly by  $\text{H}_2\text{SO}_4$  than by  $\text{AlCl}_3$ , migration of both acyl and alkyl groups sometimes occurring with the latter reagent. The following are obtained by means of phthalic anhydride and  $\text{AlCl}_3$  in  $\text{C}_6\text{H}_2\text{Cl}_4$  at 0°: from 2 : 6- $\text{C}_{10}\text{H}_6\text{Me}_2$ , 2' : 6' (I) (47%) and 3' : 7' (II) (20%) -dimethyl-1'-naphthoyl-2-benzoic acid, m.p. 225° (*Me* ester, m.p. 110°; *Na* salt); from 1 : 6- $\text{C}_{10}\text{H}_6\text{Me}_2$ , 4' : 7' (III), m.p. 189°; from 2 : 3- $\text{C}_{10}\text{H}_6\text{Me}_2$ , 2' : 3' (IV) (35%), m.p. 229°, and 6' : 7' (V) (17%), m.p. 234° (*Me* ester, m.p. 125°) -dimethyl-1', and 6' : 7' -dimethyl-2'-naphthoyl-2-benzoic acid (VI), m.p. 193° (*Me* ester, m.p. 145°) (7.3%); from 2 : 7- $\text{C}_{10}\text{H}_6\text{Me}_2$ , 2' : 6' -dimethyl-1' (75%) and 3' : 6' -dimethyl-1' or -2'-naphthoyl-2-benzoic acid, m.p. 193° (*Me* ester, m.p. 85°; *Na* salt) (1%); from 2- $\text{C}_{10}\text{H}_7\text{Me}$ , 2'-methyl-1', m.p. 197° (lit. 190—191°) (*Me* ester, m.p. 112°) (> 47%), and 7'-methyl-1' or -2'-naphthoyl-2-benzoic acid, m.p. 190° (*Me* ester, an oil) (> 3%) (gives 2'-methyl-1 : 2-benzanthraquinone with  $\text{H}_2\text{SO}_4$ ). The following 1 : 2-benzanthraquinones were obtained by ring-closure with hot  $\text{H}_2\text{SO}_4$ : from (II) 2' : 4- $\text{Me}_2$ , m.p. 173°, also obtained from 1 : 8-phthaloyl-2 : 6-dimethylnaphthalene (VII) by 82%  $\text{H}_2\text{SO}_4$ ; from (III) 2' : 3- $\text{Me}_2$  (VIII), m.p. 203° (previously considered to be 2' : 4), also obtained from 1 : 8-phthaloyl-2 : 5-dimethylnaphthalene (IX), m.p. 140°; from (V) 2' : 3'- $\text{Me}_2$  (X), m.p. 247°, also obtained from (VI) and 1 : 8-phthaloyl-2 : 3-dimethylnaphthalene. The substance, m.p. 195°, previously called 4 : 3'-dimethyl-1 : 2-benzanthraquinone, is of unknown orientation, the substance really having this structure having m.p. 175°. By  $\text{AlCl}_3\text{-NaCl}$  fusion were obtained: from (II), (VII) and (VIII);

from (I), (VIII); from (III), (VIII) and (IX); from (IV), (X); from (V), (X) and 1:8-*phthaloyl*-??-*dimethylnaphthalene*, m.p. 182° (*quinone*, m.p. 223°); from (VI), (X) and two ??-*dimethyl-2:3-benzanthraquinones*, m.p. 230° and 296°, respectively. 1:8-Phthaloyl-2-methylnaphthalene and H<sub>2</sub>SO<sub>4</sub> give 2'-methyl-1:2-benzanthraquinone. 1:8-Phthaloyl-β-naphthol gives similarly 2'-hydroxy-1:2-benzanthraquinone, m.p. 253° (*Ac* derivative, m.p. 255°), and 1:8-phthaloyl-2-chloronaphthalene gives 2'-chloro-1:2-benzanthraquinone, m.p. 233—234°, probably identical with the substance described by Heller (A., 1913, i, 631) as the 2:3-benzanthraquinone. Decarboxylation of (II) gives 1-benzoyl-2:6-dimethylnaphthalene.

R. S. C.

**Use of acenaphthene in the production of dyes of the anthanthrone series.** II. New synthesis of naphthastyryl. A. CORBELLINI and L. BARBARO (Giorn. Chim. Ind. Appl., 1933, 15, 335—337).—Naphthastyryl may be synthesised according to the scheme: acenaphthene → 8-hydroxymercuri-1-naphthoic anhydride → 8-bromo(or chloro)-1-naphthoic acid → naphthastyryl. 4:9-Dibromoanthanthrone, m.p. above 350°, has been prepared by diazotisation of 5-bromo-8-amino-1-naphthoic acid, reduction to 4:4-dibromo-1:1'-dinaphthyl-8:8'-dicarboxylic acid, and cyclisation of the latter. It has approx. the same properties as the isomeride already described (B., 1931, 623), but the Me<sub>2</sub> ester of the acid from which it is derived is not identical with the isomeric ester obtained by dibromination of Me<sub>2</sub> 1:1'-dinaphthyl-8:8'-dicarboxylate. Hence the dibromoanthanthrone derived from the latter, and also the corresponding diamino- and dinitroanthanthrones, cannot be 4:9-derivatives.

T. H. P

**Oxidation of theelin and some theelol derivatives.** D. W. MACCORQUODALE, L. LEVIN, S. A. THAYER, and E. A. DOISY (J. Biol. Chem., 1933, 101, 753—761).—Quant. oxidation (KMnO<sub>4</sub>) of theelin (I), its Me ether, and theelol (II) shows that, except with the Me ether, the reaction varies with the temp. and concn. of KMnO<sub>4</sub>. Methylation of the phenolic OH stabilises the aromatic nucleus, but reduction of the CO of (I) does not affect the oxidation val. Oxidation of the Me ether of (II) in COMe<sub>2</sub> affords a *OMe-lactone*, C<sub>18</sub>H<sub>22</sub>O<sub>3</sub>, m.p. 182°, and an *acid*, C<sub>19</sub>H<sub>24</sub>O<sub>5</sub>, m.p. 192°, identical with the Me ether of the acid obtained by fusion of (II) with KOH, and oxidised by KMnO<sub>4</sub> to a dibasic *acid*, C<sub>19</sub>H<sub>22</sub>O<sub>5</sub>, m.p. 234—235°, and by CrO<sub>3</sub> to a dilactonic *acid*, C<sub>18</sub>H<sub>18</sub>O<sub>5</sub>, m.p. 243—244°. Fusion of (I) (from either mare's or human urine) with KOH yields a phenolic monobasic *acid*, C<sub>17</sub>H<sub>22</sub>O<sub>3</sub>, m.p. 195°. The oxidation products have several times the oestrogenic potency of (I).

F. R. S.

**Aspergillin, the spore pigment of *Aspergillus niger*.** III. A. QUILICO (Gazzetta, 1933, 63, 400—410; cf. this vol., 536, 751).—The acid character of aspergillin (I) is due to CO<sub>2</sub>H groups, since at 150—250° CO<sub>2</sub> is evolved and the product is insol. in alkali. Oxidation by H<sub>2</sub>O<sub>2</sub> yields mellitic, without oxalic acid; both are formed by HNO<sub>3</sub> oxidation. The

presence of a hexagonal nucleus  $\left[ \text{C}(\text{OH}) \begin{array}{l} \leftarrow \text{CO}\cdot\text{CH}- \\ \text{CH}\cdot\text{CH}- \end{array} \right]_3$  is suggested; (I) is regarded as a humic acid in pure form.

E. W. W.

**isoPulegone.** Pyrolysis of *isoamylisopulegol*. J. DÆUVRE (Bull. Soc. chim., 1933, [iv], 53, 589—596).—*d*-Citronellal (I), [α]<sub>D</sub><sup>20</sup> +13.45° [containing 90% of the *isopropylidene* form], and MgPr<sup>β</sup>Br form βε-*trimethyl-Δ<sup>0</sup>-decen-γ-ol*, b.p. 126—127°/12 mm., [α]<sub>D</sub><sup>20</sup> +5.28°, giving with O<sub>3</sub> COMe<sub>2</sub> (96), CH<sub>2</sub>O (1), and HCO<sub>2</sub>H (7%). (I) and boiling Ac<sub>2</sub>O give a little diacetate of (I) and much *isopulegol* acetate, b.p. 105—108°/14 mm., hydrolysed to *isopulegol* (II), b.p. 93—94°/14 mm., [α]<sub>D</sub><sup>23</sup> +0.04°, [α]<sub>D</sub><sup>14360</sup> -0.02° [giving with O<sub>3</sub> CH<sub>2</sub>O (55), HCO<sub>2</sub>H (37), and COMe<sub>2</sub> (3%)]. This with CrO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> at < 40° gives *isopulegone* (III), [α]<sub>D</sub><sup>23</sup> -0.66°, [α]<sub>D</sub><sup>14360</sup> -2.06°. (II) and (probably) (III) are mixtures of stereoisomerides. The latter gives two *semicarbazones*, m.p. 172—173° (block) and 156° (lit. 155—157° form only), [α]<sub>D</sub><sup>23</sup> -29.96° and +4.50° in C<sub>6</sub>H<sub>6</sub>, respectively, both giving with O<sub>3</sub> only traces of COMe<sub>2</sub>. (III) and *iso*-C<sub>5</sub>H<sub>11</sub>·MgBr give < 35% of *isoamylisopulegol* (IV), b.p. 139—141°/15 mm., [α]<sub>D</sub><sup>16</sup> +14.01°, probably formed mostly from the *d*-isomeride of (III), the *l*-isomeride being supposed to enolise more rapidly and thus give very little (IV). (IV) at 540—550°/50 mm. gives βγλ-*trimethyl-Δ<sup>κ</sup>-dodecen-ε-one* (V), b.p. 148—150°/16 mm., [α]<sub>D</sub><sup>16</sup> +2.34°, giving with O<sub>3</sub> 93% of COMe<sub>2</sub>, and with O<sub>3</sub>-CrO<sub>3</sub> ε-*keto-γ-0-dimethyl-decoic acid* [*semicarbazone* (VI), m.p. 140—141° (block)]. (I) and *iso*-C<sub>5</sub>H<sub>11</sub>·MgBr give a 50% yield of βγλ-*trimethyl-Δ<sup>κ</sup>-dodecen-ε-ol*, b.p. 153—154°/15 mm., [α]<sub>D</sub><sup>16</sup> +1.80°, yielding with Cu at 250°/20 mm. (V) and thence (VI). Pyrolytic fission of (IV) is probably preceded by formation of an O-ring between C3 and C8.

R. S. C.

**Caoutchouc.** XV. Polymerisation of caoutchouc, isoprene, and styrene by light in presence of sensitising agents. R. PUMMERER and H. KEHLEN (Ber., 1933, 66, [B], 1107—1122).—Sol caoutchouc (I) in Et<sub>2</sub>O is converted by sufficiently prolonged exposure to sunlight into a material (II) completely insol. in Et<sub>2</sub>O; incidence of the reaction is somewhat uncertain. The I val. of (II) is 94—98% of that of (I). The conception that the action is polymerisation is strengthened by the analogous behaviour of isoprene (III) and styrene (IV). Gel formation of caoutchouc solutions is caused with certainty by CO compounds. Eosin renders good service, whereas methylene-blue and malachite-green present no advantages and bleach more easily. COPh<sub>2</sub> and benzanthrone are serviceable. PhCHO yields gels, but, as with MeCHO, the relationships appear less simple than with ketones. COPhMe and COEt<sub>2</sub> are active. Moderate action is shown by AlkOBz, whereas aliphatic esters and coloured hydrocarbons such as perylene and carotene are inactive. The use of sensitisers permits the utilisation of light of longer wave-length. Polymerisation of (III) as liquid or in soap emulsion is similarly accelerated by CO compounds, the synthetic isoprene-caoutchouc having an I val. of 94—99% (with evolution of halogen acid). Polymerisation of (IV) to styrene-resin is

readily effected by CO compounds in glass vessels at room or raised temp. The view that the action of sensitizers is due to traces of activated O (V) is supported by the observation that polymerisation is inhibited by antioxidants, e.g., quinol. The formation of (V) during irradiation of CO compounds is detected by benzidine solutions containing NaCl. Heavy metals, particularly Fe, appear without influence.

H. W.

**Synthesis of camphor.** J. J. RITTER (J. Amer. Chem. Soc., 1933, 55, 3322—3326).—In the reaction of bornyl chloride with  $\text{NH}_2\text{Ph}$ , excess of the latter increases the amount of isobornylamine (I) and decreases the amount of camphene formed, indicating an equilibrium between the two products. (I) with S at 215—220° (75% yield) or Ni (better with a little KOH) at 340° gives camphoranil, whence camphor is obtained by dil. HCl slowly at room temp. and in a few min. at 100°.

R. S. C.

**Azulene.** J. MELVILLE (J. Amer. Chem. Soc., 1933, 55, 3288—3292).—Azulene (I), b.p. 169°/12 mm. (from guaiacum wood oil and S), probably Ruzicka's "sulphur-guaiazulene," gives with  $\text{O}_3$  in  $\text{CCl}_4$   $\text{CH}_2\text{O}$ ,  $\text{HCO}_2\text{H}$ , and  $\text{COMe}_2$ . The rate of its hydrogenation (Pd) in EtOH decreases greatly after reduction of 3·5—3·7 ethylenic linkings (55% saturation); the mixture thus obtained gives with  $\text{O}_3$  no  $\text{CH}_2\text{O}$ ,  $\text{HCO}_2\text{H}$ , or  $\text{COMe}_2$ , but a ketone [semicarbazone, m.p. about 234° (decomp.)], a non-ketonic substance, b.p. 125—145°/3 mm.,  $\text{Pr}^n\text{CO}_2\text{H}$ , and an acid,  $\text{C}_{14}\text{H}_{21}\cdot\text{CO}_2\text{H}$ , b.p. about 180°/1·5 mm. (p-phenylphenacyl ester, m.p. 144·5°). (I) gives a Na-derivative, unstable, whence  $\text{CO}_2$  yields an acid,  $\text{C}_{30}\text{H}_{36}(\text{CO}_2\text{H})_2$ , m.p. about 100°, which with  $\text{O}_3$  gives  $\text{CH}_2\text{O}$  and  $\text{HCO}_2\text{H}$ , but no  $\text{COMe}_2$ .  $\text{O}_3$  attacks the  $\text{CH}_2$ ; Na the  $\text{CMe}_2$  group.

R. S. C.

**Terpenoid ring systems. I. Synthesis of a substance with blue antimony trichloride reaction.** H. VOGEL and M. STOHL (Ber., 1933, 66, [B], 1066—1069).— $\beta$ -Ionone is converted by moderately dil.  $\text{H}_2\text{SO}_4$  at room temp. into a substance  $\text{C}_{20}\text{H}_{28}\text{O}_2$ , m.p. 216—217° (corr.) after softening at 188° (corr.). Its colour reactions resemble those of the sterols; the very intense blue colour with  $\text{SbCl}_3$  in  $\text{CHCl}_3$  is particularly characteristic. Carotene yields a similar product.

H. W.

**Constitution of carlina oxide.** H. GILMAN, P. R. VAN ESS, and R. R. BURTNER (J. Amer. Chem. Soc., 1933, 55, 3461—3463).—Furfuryl chloride and  $\text{CPh}_2\text{C}\cdot\text{MgBr}$  give phenyl-2-furfurylacetylene (I), b.p. 160—161° [different from carlina oxide (II)], reduced by Na-EtOH to  $\alpha$ -phenyl- $\gamma$ -2-furylpropane [5-HgCl-derivative, m.p. 94—95°, also obtained by reduction and mercuration of (II)]. (II) with  $\text{O}_3$  in AcOH gives  $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$ . (I), but not (II), with maleic anhydride gives an adduct, m.p. 112°. (II) is, therefore, benzyl-2-furylacetylene.

R. S. C.

**New condensing agent for the preparation of benzo- $\gamma$ -pyrones and their derivatives. Mode of action of sulphoacetic acid during acetylation.** E. GOTTESMANN (Ber., 1933, 66, [B], 1168—1177).—The following condensations (yields in parentheses) are rapidly effected by AcCl containing 1/40th of its

weight of conc.  $\text{H}_2\text{SO}_4$  or  $\text{HClO}_4$ ;  $\text{Ac}_2\text{O}$ ,  $(\text{EtCO})_2\text{O}$ , or  $\text{BzCl}$  may replace AcCl, but are less volatile. Phenylsalicylic acid to xanthone (100%); o-methoxyphenylsalicylic acid to 4-methoxyxanthone (100%);  $\beta$ -naphthylsalicylic acid to 1:2-benzoxanthone (100%); 4:6-diphenoxyisophthalic acid to dixanthone (100%); dihydroxy-p-diphenoxyterephthalic acid to 9:10-dihydroxyxanthone (60%); cis- $\beta$ -phenoxyacrylic acid, m.p. 129° (from NaOPh and Et propiolate in  $\text{Et}_2\text{O}$ ) (K salt), to chromone (100%); phenoxyfumaric acid, m.p. 216° (from Me bromofumarate and NaOPh in  $\text{Et}_2\text{O}$ ), to chromone-2-carboxylic acid, m.p. 260° (100%);  $\beta$ -phenoxypropionic acid to chromanone (25%); quinol-O-propionic acid (I), m.p. 168—169° [from quinol, KOH, and  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CO}_2\text{K}$  (II)], to 6-hydroxychromanone, m.p. 134—135° (25%); quinol-OO'-dipropionic acid, m.p. 200° [from the K salt of (I) and (II)], to dichromanone, decomp. 200° (10%). o- $\text{C}_6\text{H}_4\text{Bz}\cdot\text{CO}_2\text{H}$  is not converted into anthraquinone by  $\text{AcCl}\text{--}\text{H}_2\text{SO}_4$ . AcCl without catalyst produces only traces of xanthenes from arylsalicylic acids. It is considered that the primary product of the xanthone synthesis is a mixed anhydride and that reaction between the anhydride group and the heteronuclear H atom is induced by sulphoacetic acid (III). The action of (III) does not differ widely from that of  $\text{AlCl}_3(\text{FeCl}_3)$  in the Friedel-Crafts reaction.

H. W.

**Pigment of birch buds.** K. H. BAUER and H. DIETRICH (Ber., 1933, 66, [B], 1053—1054).—Successive extraction of the buds with light petroleum and EtOH yields 1-hydroxy-3:4'-dimethoxyflavone, m.p. 174—174·5° (Ac derivative, m.p. 199°), demethylated to apigenin, m.p. 347°.

H. W.

**Chromone group. IX. Synthesis of 5:7:4'-trihydroxy-3':5'-dimethoxyflavone, believed to be identical with tricrin.** K. C. GULATI and K. VENKATARAMAN. VIII. Derivatives of o-hydroxy-, 2:5-dihydroxy-, and 2:4:5-trihydroxyacetophenone. T. C. CHADHA and K. VENKATARAMAN (J.C.S., 1933, 942—943, 1073—1076).—IX. Phloracetophenone, O-benzylsyngic anhydride, and Na O-benzylsyngate afford 5:7-dihydroxy-3':5'-dimethoxy-4'-benzyloxyflavone, m.p. 234°, which with  $\text{HCl}\text{--}\text{AcOH}$  forms 5:7:4'-trihydroxy-3':5'-dimethoxyflavone, probably identical with tricrin. 5:7:3':4':5'-Penta-acetoxyflavone has m.p. 241—242° (cf. Anderson, A., 1932, 1256).

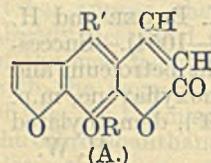
VIII. o-Hydroxyacetophenone with  $\text{Bz}_2\text{O}$  gives a small yield of flavone (cf. A., 1931, 963), and with trimethylgallic anhydride (I) affords 3':4':5'-trimethoxyflavone. 2:5-Dihydroxyacetophenone with anisic anhydride and Na anisate forms 6-hydroxy-4'-methoxy-, m.p. 249° (Ac derivative, m.p. 161°), and with (I) yields 6-hydroxy-3':4':5'-trimethoxy-, m.p. 232—233° (Ac derivative, m.p. 185°), demethylated to 6:3':4':5'-tetrahydroxyflavone, m.p. 347° (Ac derivative, m.p. 258—259°). 6:7-Dihydroxyflavone has m.p. 254° (lit. 135°, 250°).

F. R. S.

**Rotenone. XXVII. Hydrogenation of rotenone.** H. L. HALLER and P. S. SCHAFFER (J. Amer. Chem. Soc., 1933, 55, 3494—3495; cf. this vol., 955).—Hydrogenation of rotenone with a freshly-prepared  $\text{PtO}_2$  catalyst gives mostly rotenonic acid (I); use of the same catalyst a second time leads chiefly to

dihydrorotenone (II), in presence or absence of a little  $C_5H_5N$  (cf. *ibid.*, 512). With Pd-BaSO<sub>4</sub> in  $C_5H_5N$  only (I) is formed. Raney's catalyst (Ni-Al) in neutral solution at room temp. and atm. pressure gives 90% of (II), but with a special Ni catalyst in BuOAc at 90—105°/35—60 lb. dihydrorotenol is quantitatively obtained. R. S. C.

**Vegetable fish poisons. V. Constitution of imperatorin (from *Imperatoria Ostruthium*).** E. SPÄTH and H. HOLZEN. **VI. Constitution of isoimperatorin (from *I. Ostruthium*).** E. SPÄTH and L. KAHOVEC. **VII. Constitution of ostruthol (from *I. Ostruthum*).** E. SPÄTH and A. VON CHRISTIAN (Ber., 1933, 66, [B], 1137—1145, 1146—1150, 1150—1156).—V. *Imperatorin* (I),  $C_{16}H_{14}O_4$ , m.p. 102°,  $[\alpha]_D^{20} \pm 0^\circ$  in  $C_5H_5N$ , does not contain OH, OAlk, or CO. Its solubility in cold MeOH-KOH indicates the presence of a lactone group. Catalytic hydrogenation of (I) (Pd-C) leads to a substance,  $C_{11}H_{10}O_4$ , m.p. 128° [*Me ether*, b.p. 150° (bath)/0.004 mm.], and *hexahydroimperatorin*, m.p. 85°, oxidised by HNO<sub>3</sub> (*d* 1.4) to  $H_2C_2O_4$  and succinic acid, showing the adherence of the lactone ring to a coumarin system. Oxidation of (I) with  $H_2O_2$  in AcOH yields furan-2 : 3-dicarboxylic acid (II), showing the presence of the furan ring. Treatment of (I)



with AcOH containing a little conc.  $H_2SO_4$  at room temp. yields the substance (A) ( $R=R'=H$ ), m.p. 244° (*Ac derivative*, m.p. 174—175°), converted by  $CH_2N_2$  into xanthotoxin and by KOH-NaOH at 205—210° into 2 : 3 : 4-trihydroxybenzoic and 4 : 5 : 6-trihydroxyisophthalic acid. A volatile alcohol (and its acetate) obtained during hydrogenation is hydrolysed, hydrogenated, and the product is identified as  $\gamma$ -methylbutanol by conversion into the trinitrobenzoate, m.p. 125—126°. Since oxidation of (I) by  $KMnO_4$  and  $CrO_3$  yields  $\alpha$ -hydroxyisobutyric acid and  $COMe_2$ , respectively, (I) is (A) ( $R=CH_2\cdot CH\cdot CMe_2$ ;  $R'=H$ ). Small amounts of (I) can be distilled in high vac. Under rather higher pressure (0.5 mm.) (I) is isomerised to *alloimperatorin* (III), m.p. 233°, oxidised by  $H_2O_2$  to (II) and converted by  $CH_2N_2$  into the *Me ether*, m.p. 113.5°. Hydrogenation of (III) in AcOH (Pd-C) affords *hexahydroalloimperatorin*, m.p. 129°, oxidised by HNO<sub>3</sub> to  $C_2H_4(CO_2H)_2$  and  $\gamma$ -methyl-*n*-valeric acid, identified as the phenylhydrazide, m.p. 140°. (III) is oxidised by  $CrO_3$  to  $COMe_2$ . Hence (III) is (A) ( $R=H$ ;  $R'=CH_2\cdot CH\cdot CMe_2$ ).

**VI. isoImperatorin (II)**,  $C_{16}H_{14}O_4$ , m.p. 109°,  $[\alpha]_D^{20} \pm 0^\circ$ , does not contain OH, OMe, or CO. Catalytic hydrogenation leads to the absorption of 3  $H_2$  and the product is oxidised by HNO<sub>3</sub> (*d* 1.4) at room temp. to  $H_2C_2O_4$  and  $C_2H_4(CO_2H)_2$ . Treatment of (IV) with NaOMe and  $Me_2SO_4$  and subsequent hydrolysis leads to a *OMe-acid*,  $C_{17}H_{18}O_5$ , m.p. 117.5°, showing the presence of a lactone group. Oxidation of (IV) by  $H_2O_2$  in alkaline solution leads to (II). Treatment of (IV) with AcOH containing a little conc.  $H_2SO_4$  gives a *phenol*, m.p. 277° (decomp.), transformed by  $CH_2N_2$  into bergapten, m.p. 188—189°, and an unsaturated alcohol (or its acetate),

which is hydrogenated and hydrolysed, thus yielding *isoamyl alcohol*, identified as the trinitrobenzoate.  $COMe_2$  is produced when (IV) is oxidised by  $CrO_3$  in AcOH. (IV) is therefore (A) (H for OR;  $R'=O\cdot CH_2\cdot CH\cdot CMe_2$ ). Treatment of (IV) with  $BzO_2H$  in  $CHCl_3$  leads to oxypeucedanin.

**VII. Ostruthol (V)**,  $C_{21}H_{22}O_7$ , has m.p. 136—137°,  $[\alpha]_D^{20} + 8.36^\circ$  in  $COMe_2$ ,  $[\alpha]_D^{20} - 18.3^\circ$  in  $C_5H_5N$ . It does not contain OH or  $CO_2H$ , but behaves as a lactone. It is hydrolysed by KOH-MeOH to  $\alpha$ -methyl- $\Delta^2$ -butenoic acid, m.p. 43° (hydrogenated to  $\alpha$ -methyl-*n*-butyric acid, identified as the phenylhydrazide, m.p. 103—104°), and (+)-oxypeucedanin hydrate (VI), m.p. 131°,  $[\alpha]_D^{20} + 18.9^\circ$  in  $COMe_2$ . (V) is converted by  $H_2O_2$  in alkaline solution into (II) and with  $Ac_2O$  yields *acetylostruthol*, m.p. 125°. Catalytic hydrogenation of (V) in AcOH (Pd-C) yields *hexahydro-ostruthol*, m.p. 139—140°, oxidised by HNO<sub>3</sub> to  $C_2H_4(CO_2H)_2$ . Oxidation of (V) by  $KMnO_4$  in alkaline solution yields  $\alpha$ -hydroxyisobutyric acid. Bergapten is formed from (V) by treatment with boiling AcOH containing a little conc.  $H_2SO_4$ , and subsequently with  $CH_2N_2$ . (VI) is converted by  $P_2O_5$  in PhMe into *isooxypeucedanin*. (V) is therefore (A) with H for OR and  $R'=O\cdot CH_2\cdot CH(CMe_2\cdot OH)\cdot O\cdot CO\cdot CMe\cdot CHMe$ . H. W.

**Thionaphthen series. III. G. KOMPPA and S. WECKMAN (J. pr. Chem., 1933, [ii], 138, 109—127).**—The Mg compound of bromothionaphthen (I) (*picrate*, m.p. 114—114.5°) (A., 1929, 1077) gives with  $O_2$  in dry  $Et_2O$  the known 2-hydroxythionaphthen, m.p. 69—70°, and some thionaphthen (II); it is therefore the 2-Br-derivative. With  $CO_2$  the main products are thionaphthen-2-carboxylic acid (III), m.p. 174—175° [*Ag, Cu, and Ba salts; Me*, b.p. 165—166°/17 mm., 285—287°/750 mm., and *Et*, b.p. 172—173°/17 mm., 304—306°/750 mm., esters; *chloride* (IV), m.p. about 50°, b.p. 296—298°/758 mm.; *amide*, m.p. 197—198°; *anilide*, m.p. 172—173°] (cf. *loc. cit.*), and 2 : 2'-dithionaphthenyl ketone, m.p. 167—167.5°, which is better prepared from the Mg compound and (IV); this ketone does not give an oxime or semicarbazone. With  $CH(OEt)_3$  or, better, with  $OEt\cdot CH\cdot NPh$  the Mg compound of (I) gives *thionaphthen-2-aldehyde*, m.p. 58°, b.p. 149—150°/10 mm. (*semicarbazone*, m.p. 235—235.5°; *phenylhydrazone*, m.p. 115°; *p-nitrophenylhydrazone*, m.p. 232—233°), which is oxidised to (III) by  $KMnO_4$ . Action of KOH in MeOH at 200—220° on (I) gives (II), 2-hydroxythionaphthen (V), m.p. 46.5°, and *o-methylthiophenylacetic acid* (VI), m.p. 128° (*amide*, m.p. 164—165°), identified by synthesis by methylation of  $o-SH\cdot C_6H_4\cdot CH_2\cdot CO_2H$ ; in EtOH under the same conditions no product corresponding with (VI) is formed, but mainly (II) and some (V). At 200—220° KOH in MeOH has no action on (II) or (VI), but with (V) some *diphenyl disulphide-2 : 2'-diacetic acid* (VII), m.p. 147—148°, is formed. (VI) was not demethylated by HI (*d* 1.96) or by heating its chloride in xylene, but its chloride with  $AlCl_3$  in  $CS_2$  gives some (V), the cyclisation product of the SH-acid. The last-named readily cyclises with boiling dil. HCl, some (VII) being formed at the same time. The occurrence of the labile form of (V), m.p. 34—34.5° (cf. Marschalk,

A., 1913, i, 1088), in a single experiment is recorded; it could not be obtained under Marschalk's conditions, and rapidly changes into the stable form on keeping. No interaction was observed between the latter and PhNCO; it is therefore probably the keto-form. Benzamidothionaphthen has m.p. 152° (not 132°; cf. *loc. cit.*).

H. A. P.

**2-Methylpiperidinopropyl thiol- and thionbenzoates.** S. A. KARJALA and S. M. McELVAIN (*J. Amer. Chem. Soc.*, 1933, **55**, 2966—2973).— $\gamma$ -Thiolpropyl alcohol, b.p. 81—82°/10 mm., and 48% HBr or PBr<sub>3</sub> give  $\gamma$ -thiolpropyl bromide (A), b.p. 55—56°/12 mm., which with BzCl and aq. Na<sub>2</sub>CO<sub>3</sub> form  $\gamma$ -bromopropyl thiolbenzoate, b.p. 148—149°/1 mm., whence by 2-methylpiperidine (I) at 100°  $\gamma$ -2-methylpiperidinopropyl thionbenzoate hydrochloride, SBz·[CH<sub>2</sub>]<sub>3</sub>·NH·C<sub>5</sub>H<sub>10</sub>Cl, m.p. 137—138°, was obtained. PhCN and CH<sub>2</sub>Cl·CH<sub>2</sub>·CH<sub>2</sub>·OH give  $\gamma$ -chloropropylbenzimidino-ester hydrochloride, CPh·(NH<sub>2</sub>Cl)·O·[CH<sub>2</sub>]<sub>2</sub>·CH<sub>2</sub>Br, m.p. 122—123°. Similarly was prepared the  $\gamma$ -Br-compound, m.p. 115—116°, the free base from which with H<sub>2</sub>S in Et<sub>2</sub>O gives crude  $\gamma$ -bromopropyl thionbenzoate (III), CPhS·O·[CH<sub>2</sub>]<sub>2</sub>·CH<sub>2</sub>Br, b.p. 148—150°/1 mm., and 2-phenyl-4 : 5-dihydro-1 : 3-oxazine hydrobromide, m.p. 139—140°.  $\gamma$ -Chloropropyl thionbenzoate (IV), similarly prepared, has b.p. 145—146°/1 mm. (III) or (IV) with (I) gives mostly (II) and some  $\gamma$ -2-methylpiperidinopropyl thionbenzoate (V), which is, however, best prepared from PhCN and  $\gamma$ -2-methylpiperidinopropyl alcohol and then has m.p. 149—149.5°. (V) rapidly gives (II) at 175° or when distilled. (A), PhCN, and HCl give  $\gamma$ -bromopropyl thiolbenzimidino-ester hydrochloride, m.p. 157—158°, whence by evaporation in Et<sub>2</sub>O 2-phenyl-4 : 5-dihydro-1 : 3-thiazine hydrobromide, m.p. 171—172°, is obtained, and by H<sub>2</sub>S  $\gamma$ -bromopropyl dithiobenzoate, m.p. 112—114°, which with (I) in hot, dry C<sub>6</sub>H<sub>6</sub> gives a resin. (V) is active as a surface anaesthetic or when injected, (II) only when injected; the former is more efficient than the O-analogue. Thion S can be determined by AgNO<sub>3</sub> in the dark at room temp. Thiol S reacts only when heated.

R. S. C.

**Structure of amines of platinous chloride.** F. W. PINKARD, H. SAENGER, and W. WARDLAW.—See this vol., 1001.

**Additive reactions of the indole nucleus.** S. G. P. PLANT and (Miss) M. L. TOMLINSON (*J.C.S.*, 1933, 955—960).—Nitration of 2 : 3-dimethylindole (I) gives the 5-NO<sub>2</sub>-derivative, m.p. 188°, also obtained (Fischer reaction) from the *p*-nitrophenylhydrazone of COMeEt. 1-Acetyl-2 : 3-dimethylindole (II), m.p. 74°, is nitrated to the 4(or 6)-NO<sub>2</sub>-derivative, m.p. 170°, deacetylated to the 4(or 6)-NO<sub>2</sub>-derivative of (I), m.p. 142°, similarly obtained from the *m*-nitrophenylhydrazone of COMeEt. 1-Benzoyl-2 : 3-dimethylindole, m.p. 98°, and HNO<sub>3</sub> form an additive compound, 3-nitro-2-hydroxy-1-benzoyl-2 : 3-dimethyl-2 : 3-dihydroindole, m.p. 125° (decomp.), debenzoylated to the corresponding -dihydroindole, m.p. 103°. (I) and Br·AcOH give 2-methyl-3-hydroxymethylindole, m.p. 225°, the dibromide not being isolated. Similarly (II) yields 1-acetyl-3-methyl-2-hydroxymethylindole, m.p. 90—91°, deacetylated to the 2-hydroxymethyl com-

pound, m.p. 122°; with less AcOH, 1-acetyl-3-methyl-2-bromomethylindole, m.p. 92—94°, is obtained. 2 : 3-Diphenylindole and Br give after ethylation *Et* 4(or 6)-bromo-2 : 3-diphenylindole-1-carboxylate, m.p. 110°. 1-Acetyl-2 : 3-diphenylindole is brominated to the 4(or 6)-Br-compound, m.p. 141—142°, also obtained with the 6(or 4)-Br-derivative, m.p. 223—225°, from the *m*-bromophenylhydrazone of CPhBz. 4(or 6)-Bromo-1-benzoyl-, m.p. 174—176°, and -1-cinnamoyl-2 : 3-diphenylindole, m.p. 176°, are similarly obtained. The *p*-bromophenylhydrazone of CPh·CH<sub>2</sub>·Ph gives 5-bromo-2 : 3-diphenylindole, m.p. 148° (1-Ac derivative, m.p. 218°). Bromination of 2-phenyl-3-methylindole affords the 4(or 6)-Br-derivative, m.p. 147°; CPhPr, *p*-bromophenylhydrazine, and HCl·EtOH give the 5-Br-compound, m.p. 141°. F. R. S.

**Adamkiewicz reaction with *p*-dimethylamino-benzaldehyde (Rohde reaction).** E. GHIGI (*Gazzetta*, 1933, **63**, 411—419).—The coloured condensation product of tryptophan and *p*-NMe<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO in presence of HCl and H<sub>2</sub>O<sub>2</sub> (cf. A., 1920, ii, 786) is formulated C<sub>23</sub>H<sub>25</sub>O<sub>2</sub>N<sub>3</sub>·HCl, is insol. in alkali, and is probably a dialdehyde; that formed in presence of NaNO<sub>2</sub> (cf. Neri, *Biochim. Ter. Sper.*, 1932, **19**, 49) is formulated C<sub>31</sub>H<sub>29</sub>O<sub>6</sub>N<sub>3</sub>·HCl, and is probably a OH-acid; the product formed in presence of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is colourless.

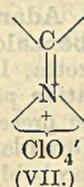
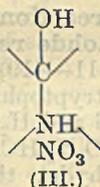
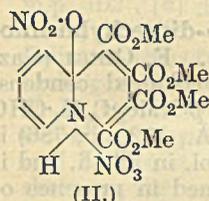
E. W. W.

**Heterocyclic acetylcholines.** E. MACOVSKI and E. RAMONTEANU (*J. pr. Chem.*, 1933, [ii], **138**, 92—98).—The following quaternary salts from heterocyclic bases and CH<sub>2</sub>Cl·CH<sub>2</sub>·OAc or CH<sub>2</sub>I·CH<sub>2</sub>·OAc are described:  $\beta$ -acetoxyethylpyridinium chloride ("pyridine acetylcholine chloride") [iodide; chloroplatinate, m.p. 183—186° (decomp.) (lit. 193—194°)];  $\beta$ -acetoxyethyl-2-methylpyridinium chloride [iodide, m.p. 117—118°; chloroplatinate, m.p. 196—199° (decomp.)];  $\beta$ -acetoxyquinolinium iodide, m.p. 122—123° [chloroplatinate, m.p. 202—203° (decomp.)]; and  $\beta$ -acetoxyethyl-2-methylquinolinium iodide, m.p. 137° (diffuse).

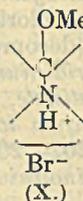
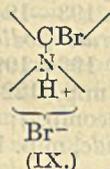
H. A. P.

**2-Anilino-epidine derivatives.** O. G. BACKEBERG (*J.C.S.*, 1933, 1031—1032).—The following are prepared from 2-chloro-epidine etc. (cf. A., 1932, 951): 2-anilino- (*picrate*, m.p. 228°), 2-*o*-, m.p. 140° (*picrate*, m.p. 223°), and 2-*p*-anisidino-, m.p. 129° (*picrate*, m.p. 190°), 2-*o*-, m.p. 127° (*picrate*, m.p. 226°), and 2-*p*-phenetidino-epidine, m.p. 165° (*picrate*, m.p. 215°); 2-anilino-, m.p. 139° (*picrate*, m.p. 213°), 2-*o*-, m.p. 151° (*picrate*, m.p. 228°), and 2-*p*-anisidino-, m.p. 137° (*picrate*, m.p. 216°), 2-*o*-, m.p. 119° (*picrate*, m.p. 237°), and 2-*p*-phenetidino-6-methoxyepidine, m.p. 149° (*picrate*, m.p. 183°); 2-anilino-, m.p. 127° (*picrate*, m.p. 236°), 2-*o*-, m.p. 158° (*picrate*, m.p. 241°), and 2-*p*-anisidino-, m.p. 172° (*picrate*, m.p. 203°), 2-*o*-, m.p. 141° (*picrate*, m.p. 224°), and 2-*p*-phenetidino-6-ethoxyepidine, m.p. 128° (*picrate*, m.p. 218°). The following are prepared by cyclisation of the corresponding acetoacetaryl amides with conc. H<sub>2</sub>SO<sub>4</sub> at 100°: 2-hydroxy-6-methoxy-, m.p. 272° (*picrate*, m.p. 204°) (cf. A., 1931, 1433), and 2-hydroxy-6-ethoxy-epidine, m.p. 232° (*picrate*, m.p. 179°); 2-chloro-6-ethoxyepidine, m.p. 123°. Acetoacet-*o*-anisidide and -*o*-phenetidide were not cyclised by H<sub>2</sub>SO<sub>4</sub>, HCl, H<sub>3</sub>PO<sub>4</sub>, P<sub>2</sub>O<sub>5</sub>, POCl<sub>3</sub>, or Ac<sub>2</sub>O. H. A. P.

Syntheses in the hydroaromatic series. XVIII. "Diene" syntheses with heterocyclic nitrogen compounds. VI. "Diene" syntheses of pyridine, quinolizine, indolizine, norlupinane, and  $\psi$ -lupinine. O. DIELS and K. ALDER [with FRIEDRICHSEN, KLARE, WINKLER, and SCHRUM] (Annalen, 1933, 505, 103—150; cf. A., 1932, 1144).—Further examination of the acid  $C_9H_7O_5N$  (*loc. cit.*) establishes the formula  $C_6H_5O_3N$  and its identity with 2-carboxypyridine 1-oxide prepared from pyridine-2-carboxylic acid and  $H_2O_2$  in AcOH at  $100^\circ$ . Me quinolizine-1 : 2 : 3 : 4-tetracarboxylate (I) is converted by conc.  $HNO_3$  under specified conditions into the ester nitrate (II), m.p. 110—111° (decomp.), described (*loc. cit.*) as  $C_{17}H_{17}O_8N, 2HNO_3$ , transformed by warm  $H_2O$  into the OH-nitrate (III), m.p.

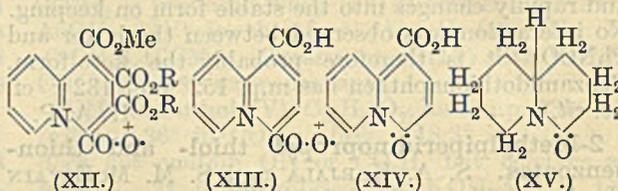


92—93° (decomp.). (III) is converted by boiling  $C_5H_5N$  into the compound  $C_{16}H_{13}O_3N$  (IV), by dil.  $HNO_3$  or  $H_2SO_4$  into Me indolizinetricarboxylate (V), by  $HBr$  in  $COMe_2$  into the dibromide (VI), m.p.  $102^\circ$ , and by dil.  $HClO_4$  into the perchlorate (VII), m.p.  $201^\circ$  (decomp.). (I) is transformed by an excess of  $Br$  in AcOH or MeOH into the perbromide (VIII), decomp.  $129—130^\circ$ , in which  $Br$  is entirely in ionic



union, since (VIII) is transformed by aq.  $HClO_4$  into (VII). Hydrolysis of (VIII) with  $KOAc$ ,  $Na_2CO_3$ , or  $H_2O$  leads very readily to (V). (VIII) is converted by  $COMe_2$  (owing to liberated  $HBr$ ) into the colourless bromide (IX), decomp.  $100—102^\circ$ , obtained also by the action of 1 mol. of  $Br$  on (I) in  $CHCl_3$ . (IX) is re-converted into (I) by reduction ( $Pd-CaCO_3$ ) in alkaline solution. Treatment of (IX) with cold MeOH yields the substance (X), decomp. about  $102—103^\circ$ , transformed by  $Ag_2CO_3$  into the free base (XI), m.p.  $160^\circ$ , from which (X) is regenerated by  $HBr$ . Warm  $C_5H_5N$  converts (IX) into (IV). Direct or indirect hydrogenation of (I) appears to lead invariably to (IV), which is best prepared as above, but is also obtained as by-product in the prep. of (I) and from (I) by means of  $PbO_2$  or Et azodicarboxylate. Oxidation of (IV) shows it to retain the substituted  $C_5H_5N$  nucleus. Hydrolysis occurs with difficulty under the influence of boiling  $HCl$ , leading to the dicarboxylic acid (XII;  $R=H$ ) [re-converted into (IV) by  $CH_2N_2$ ] and thence through the acid (XIII), m.p.  $272^\circ$  (decomp.) after darkening at  $250^\circ$ , into the monocarboxylic acid (XIV), m.p. about  $295^\circ$  (decomp.) after darkening at  $280^\circ$  [obtained directly

from (IV) and conc.  $H_2SO_4$  at  $90—130^\circ$ ]; the hydrochloride and Me ester, m.p.  $148—149^\circ$ , are described.



(XIV) does not react with the customary reagents for  $OH$  or  $CO$  and is not reduced by  $Zn-Hg$  and conc.  $HCl$  or by  $Zn$  dust. The presence of amide-like  $CO$  is therefore postulated and the structure (XIV) is supported by the prep. of an  $H_8$ -derivative, m.p.  $189^\circ$ , not affected by  $Ac_2O$  (Me ester, m.p.  $76—77^\circ$ , does not react with  $NH_2OH$  or  $NH_2-CO-NH-NH_2$ ). Distillation of (XIV) with  $CaO$  leads to the substance (XV), b.p.  $250—260^\circ$ . The production of octahydroindolizine instead of octahydroquinolizine (norlupinane) by treatment of (XV) with  $Na$  and amyl alcohol is unexplained. Confirmation of the structure of (IV) (XII,  $R=Me$ ) is found in its transformation by  $N_2H_4, H_2O$  into the hydrazinodihydrazide (XVI) ( $R=NH-NH_2$ ), m.p.  $>350^\circ$ , converted by boiling dil.  $HCl$  into the dihydrazide (XVI;  $R=OH$ ) and by hot conc.  $H_2SO_4$  into the substance  $C_{12}H_8O_4N_5$ , m.p.  $>350^\circ$ . Treatment of (IV) with  $NaOMe$  and subsequently with  $HClO_4$  leads to (VII).

Repetition of the alkaline hydrolysis and subsequent decarboxylation of (I) shows that the product, provisionally regarded as quinolizine (*loc. cit.*), consists mainly of indolizine. Hydrolysis of (I) with  $PhOH$  leads to the Me<sub>3</sub> ester, m.p.  $75^\circ$ , identical with that obtained by use of  $HCO_2H$  (*loc. cit.*), converted by acids into the Me  $H_2$  ester, m.p.  $235—236^\circ$  (decomp.), which when heated in phenanthrene affords the Me  $H$  ester of the dicarboxylic acid (XVII), m.p.  $201—202^\circ$ , and transformed by alkali into the dicarboxylic acid obtained directly from (I) and alkali. Since this product is obtained by devious routes, it is probable that isomerisation does not occur during hydrolysis and initial loss of  $CO_2$ , but during decarboxylation of (XVII). Hydrogenation of the products of decarboxylation and treatment with picric acid leads to octahydroindolizine picrate, and the picrate, m.p.  $193^\circ$ , of a base  $C_9H_{17}N$ , which, provided isomerisation has not occurred at any stage, must be identical with norlupinane. The picrates have identical m.p. and do not give depression when mixed, but the method of mixed m.p. has restricted val. with these substances and the chloroaurates do not appear identical. Hydrolysis of (I) with aq.  $HCl$  leads to the hydrochloride of a monocarboxylic acid (XVIII), hydrogenated to the acid  $C_{10}H_{17}O_2N$  [Me ester (XIX), b.p.  $135—136^\circ/20$  mm., its picrate, m.p.  $161—162^\circ$ , and methiodide, m.p.  $179—181^\circ$ ]. Oxidation of (XVIII) affords only pyridine-2-carboxylic acid. Reduction of (XIX) by  $Na$  and EtOH gives the primary alcohol  $C_{10}H_{19}ON$ , m.p.  $75—76^\circ$  (H phthalate, m.p.  $229^\circ$ ; phenylurethane, m.p.  $110—111^\circ$ ; methiodide, m.p.  $149—150^\circ$ ), not identical with lupinine

or *isolupinine*. If the acid belongs to the quinolizine group, the  $\text{CO}_2\text{H}$  is not in the  $\beta$ -position.

$\text{LiPh}$ , 2-methylpyridine, and  $\text{Pr}^{\beta}\text{Br}$  yield 2-*isobutylpyridine*, b.p. 180—185° (*chloroplatinate*, m.p. 193°), hydrogenated ( $\text{PtO}_2$  in  $\text{AcOH}$ ) to 2-*isobutylpiperidine*, b.p. 177—179° (hydrochloride, m.p. 203°; *picrolonate*, m.p. 208—209° after darkening at 198°). 2-Acetylpyridine is transformed by  $\text{MgEtI}$  into 2- $\alpha$ -hydroxy- $\alpha$ -methylpropylpyridine, b.p. 93°/10 mm. (*chloroplatinate*, m.p. 190°), transformed by successive treatment with  $\text{HI}$  (*d* 1.7) and red P and Zn dust into 2- $\alpha$ -methylpropylpyridine (2- $\psi$ -butylpyridine), b.p. 174—175° (*chloroplatinate*, m.p. 166°), whence ( $\text{PtO}_2$  in  $\text{AcOH}$ ) 2- $\alpha$ -methylpropylpiperidine, b.p. 179—181° (hydrochloride, m.p. 169°; *picrolonate*, m.p. 209°).

H. W.

Separation and purification of organic bases by means of metalammnes. I. *o*-Phenanthroline. II. Pyridine,  $\alpha$ -picoline, and *isoquinoline*. G. TARTARINI and T. SAMAJA (*Annali Chim. Appl.*, 1933, 23, 351—356, 356—362).—I. When *o*-phenanthroline is synthesised from  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$  and is extracted from the acidified products, either much tar is extracted as well or, if little acid is used, a large proportion of the product remains unrecovered in the viscous mass. This difficulty is removed by treating the product of the reaction with  $\text{FeSO}_4$ , precipitating the complex as *mercurichloride*,  $[\text{Fe}^{\text{II}}(\text{C}_{12}\text{H}_8\text{N}_2)_3]\text{Hg}_2\text{Cl}_6 \cdot 4\text{H}_2\text{O}$  (*perchlorate* also described), decomposing this with  $\text{NaOH}$ , evaporating, and extracting the free base with light petroleum.

II. Similarly,  $\text{C}_5\text{H}_5\text{N}$  may be separated from homologous bases by means of its  $\text{Cu}(\text{ClO}_4)_2$  compound;  $\alpha$ -picoline from crude picoline by means of the compound,  $\text{Ag}_2\text{S}_2\text{O}_8$ ,  $4\text{C}_6\text{H}_7\text{N}$ , and *isoquinoline* from quinoline by means of its insol. compound,  $\text{Ni}(\text{SCN})_2 \cdot 4\text{C}_9\text{H}_7\text{N}$ .

T. H. P.

*Acridol* [5-hydroxyacridine]. A. MARZIN (*J. pr. Chem.*, 1933, [ii], 138, 99—102).—5-Chloroacridine (I) in boiling  $\text{PhNO}_2$  gives a red substance, m.p. 250°, regarded as 5-hydroxyacridine. It does not depress the m.p. of acridone, being converted into it at 250°, and gives *N*-methylacridone, m.p. 203—204°, with  $\text{Me}_2\text{SO}_4$  and  $\text{KOH}$  and (I) with  $\text{POCl}_5 + \text{POCl}_3$ .

H. A. P.

Canavanine, an amino-acid. III. *Canaline*, a decomposition product of canavanine. M. KITAGAWA and H. YAMADA (*J. Agric. Chem. Soc. Japan*, 1932, 8, 1201—1208).—*Canaline*,  $\text{C}_4\text{H}_{10}\text{O}_3\text{N}_2$ , m.p. 214° (decomp.),  $\alpha_D - 8.31^\circ$  [*picrate*, m.p. 192—193° (decomp.); *flavianate*, m.p. 211° (decomp.); *Cu* salt; *hydrochloride*, m.p. 166°; *Bz* derivative, m.p. 99°], is formed in 75% yield on decomp. of canavanine by liver extract. It has one (probably  $\alpha$ -)  $\text{NH}_2\text{-N}$ , is pptd. by  $\text{HgNO}_3$  and Nessler's solution, and has no reducing power.

CH. ABS.

$p$ -Xylylmethylpyrazolones and [their] derivatives. R. C. HUSTON, H. M. SELL, and H. R. BRIGHAM (*J. Amer. Chem. Soc.*, 1933, 55, 3407—3408).— $p$ -Xylylhydrazine (modified prep.; 68% yield), b.p. 120°/4 mm., m.p. 76—77°, and its *Ac* derivative, m.p. 104—106° (lit. 196°), give, 1- $p$ -xylyl-3-methyl-, m.p. 164° (5-*Bz* derivative, m.p. 119°), and -2:3-dimethyl-5-pyrazolone, m.p. 97.5°

and 1- $p$ -xylyl-5-methyl-3-pyrazolone (3-*Bz* derivative, m.p. 74°).

R. S. C.

Naphthyl derivatives of barbituric acid. DE W. T. KEACH (*J. Amer. Chem. Soc.*, 1933, 55, 2975—2979).—1- $\text{C}_{10}\text{H}_7\text{-CH}_2\text{Br}$  and 5-alkylbarbituric acids give 5- $\alpha$ -naphthylmethyl-5-ethyl-, m.p. 247°, -*n*-butyl-, m.p. 214°, and -allyl-, m.p. 212°, -barbituric acids.  $\alpha$ -Naphthylethyl derivatives could not be so obtained. 1- $\text{C}_{10}\text{H}_7\text{-CH}_2\text{-CH}_2\text{Br}$  affords *Et*<sub>2</sub>  $\alpha$ -naphthylethylmalonate, b.p. 198—203°/4 mm., whence *Et*<sub>2</sub>  $\alpha$ -naphthylethyl-ethyl-, b.p. 188—193°/3—4 mm., -*n*-butyl-, b.p. 202—206°/3—4 mm., and -allyl-, b.p. 212—213°/5—6 mm., -malonate were prepared. With  $\text{CO}(\text{NH}_2)_2$  these led to 5- $\alpha$ -naphthylethyl-, m.p. 196—198°, 5:5- $\alpha$ -naphthylethyl-ethyl-, m.p. 178°, -*n*-butyl-, m.p. 187°, and -allyl-, m.p. 169°, -barbituric acid. These compounds have relatively weak hypnotic properties.

R. S. C.

Synthesis of 5- $\alpha$ -naphthyl-5-ethylbarbituric acid. DE W. T. KEACH (*J. Amer. Chem. Soc.*, 1933, 55, 3440—3442).— $\alpha\text{-C}_{10}\text{H}_7\text{-CH}_2\text{-CO}_2\text{Me}$ ,  $\text{Me}_2\text{C}_2\text{O}_4$ , and  $\text{NaOMe}$  give an oxalo-ester, which at 150°/5—6 mm. gives *CO* and *Me*<sub>2</sub>  $\alpha$ -naphthylmalonate, b.p. 160—173°/5—6 mm., m.p. 104°, whence by prolonged alkylation at 100° *Me*<sub>2</sub>  $\alpha$ -naphthylethylmalonate, m.p. 109—110°, b.p. 168—175°/5—6 mm., is obtained. This with  $\text{CO}(\text{NH}_2)_2$  and  $\text{NaOEt}$  gives 5- $\alpha$ -naphthyl-5-ethylbarbituric acid, m.p. 254—255°, the hypnotic val. of which for white rats is inferior to that of luminal.

R. S. C.

Pyrimidines. CXXXIV. Reaction of phenylacetaldehyde and acetophenone with carbamide. K. FOLKERS and T. B. JOHNSON (*J. Amer. Chem. Soc.*, 1933, 55, 3361—3368; cf. this vol., 957).— $\text{CH}_2\text{Ph-CHO}$ ,  $\text{CO}(\text{NH}_2)_2$ , and a little  $\text{HCl}$  in hot  $\text{EtOH}$  (with or without  $\text{CH}_2\text{Ac-CO}_2\text{Et}$ ) give 2-keto-5-phenyl-4-benzyl-1:2:3:4-tetrahydropyrimidine (I), m.p. 214—216°, hydrogenated ( $\text{PtO}_2$ ; 3 atm.) in  $\text{AcOH}$  to 2-keto-4-cyclohexylmethyl-5-cyclohexylhexahydropyrimidine, m.p. 267.5—269.5°. 2-Keto-4:6-diphenyl-4-methyl-1:2:3:4-tetrahydropyrimidine (II) (improved prep.), m.p. 179.5—180°, previously considered to be *s*-di-( $\alpha$ -methylbenzylidene)carbamide (A., 1915, i, 846), is hydrogenated to 2-keto-4:6-dicyclohexyl-4-methylhexahydropyrimidine, m.p. 262—263°, which is stable to hot  $\text{NaOH-EtOH}$  and phthalic anhydride at 250—300°. Similarly, the substance considered (*loc. cit.*) to be *s*-di-( $\alpha$ -ethylbenzylidene)carbamide is 2-keto-4:6-diphenyl-5-methyl-4-ethyl-1:2:3:4-tetrahydropyrimidine (III). The structures of (I), (II), and (III), based on the stability and hydrogenation of the compounds, are supported by the absorption spectra. *Et* acetoacetate,  $\text{CO}(\text{NH}_2)_2$ , and a little  $\text{HCl}$  in hot  $\text{EtOH}$  give a little *Et*  $\beta$ -aminocrotonate.

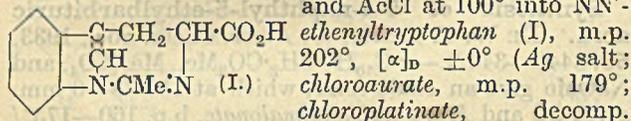
R. S. C.

New reaction of certain diazosulphonates derived from  $\beta$ -naphthol-1-sulphonic acid. XI. Constitution of the phthalazine derivatives. F. M. ROWE and A. T. PETERS (*J.C.S.*, 1933, 1067—1070).—Methylation ( $\text{Me}_2\text{SO}_4\text{-KOH}$ ) of 1-hydroxy-3-aryl-3:4-dihydrophthalazine-4-acetic acids, obtained by hydrolysis of *Na* 3-aryl-3:4-dihydrophthalazine-1-sulphonate-4-acetates (cf. A., 1926, 625), gives 1-keto-3-aryl-2-methyltetrahydrophthalazine-4-acetic acids,

which form Me esters: (aryl group) 4'-nitrophenyl, m.p. 207° (Me ester, m.p. 188°), 3'-nitrophenyl, m.p. 235° (Me ester, m.p. 180°), 4'-nitro-2'-methylphenyl, m.p. 211° (Me ester, m.p. 201°), 2'-chloro-4'-nitrophenyl, m.p. 218° (Me ester, m.p. 210—211°), 2':6'-dichloro-4'-nitrophenyl, m.p. 216° (Me ester, m.p. 186°), 2':6'-dibromo-4'-nitrophenyl, m.p. 240° (Me ester, m.p. 215°), benzeneazophenyl, m.p. 189°, and 4'-nitrobenzeneazophenyl, m.p. 246°. Reduction products (*loc. cit.*) are 1-hydroxy-3-(4'-aminophenyl)-, m.p. 239°, -(3'-aminophenyl)-, m.p. 252°, and -(4'-amino-2'-methylphenyl)-3:4-dihydrophthalazine-4-acetic acid, m.p. 217°. The constitution of "Soluble Yellow-I" and "-II" products (cf. Bucherer and Fröhlich, A., 1931, 1409) are discussed. F. R. S.

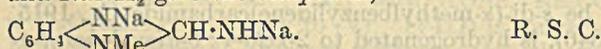
#### Reaction of tryptophan and acetyl chloride.

F. WREDE and G. FEUERRIGEL (Ber., 1933, 66, [B] 1073—1076).—l-Tryptophan is converted by AcOH and AcCl at 100° into NN'-

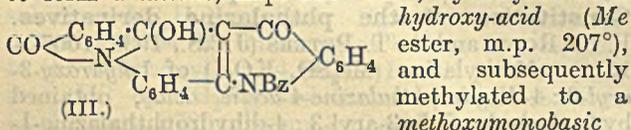


ethenyltryptophan (I), m.p. 202°, [ $\alpha$ ]<sub>D</sub> ± 0° (Ag salt; chloroaurate, m.p. 179°; chloroplatinate, decomp. about 240°; non-cryst. Me ester; corresponding amide, decomp. about 180°). H. W.

Attempts to prepare nitrogenous derivatives of bivalent carbon. D. WOOD, jun., and F. W. BERGSTROM (J. Amer. Chem. Soc., 1933, 55, 3314—3319).—Attempts to prepare Scheibler's C(OEt)<sub>2</sub>, Pinner's compound, (C<sub>10</sub>H<sub>21</sub>N<sub>3</sub>HCl)<sub>2</sub>PtCl<sub>4</sub> (A., 1884, 724), C(OK)<sub>2</sub>, and C(OK)·OEt failed. Diphenylmethylformamidine, b.p. 335—340°, 215.5—216.5°/24 mm. [*picrate*, m.p. 152—152.5° (decomp.)], with an excess of the appropriate metal amide in liquid NH<sub>3</sub> gives NPhMe, a substance [*picrate*, m.p. 146.5° (decomp.)], and salts, NPh·CHR·NM, in which R=NPhMe, and M=Ba, Ca, Na<sub>2</sub>, and Ag<sub>2</sub> (from KNH<sub>2</sub> and AgI), and NPhBa<sub>0.5</sub>·CHR·NBa. Glyoxaline affords similarly the Na, Li (+0.5, 1, and 2NH<sub>3</sub>), and Ba (+0 and 1NH<sub>3</sub>) salts; the K salt was prepared by using only 1 mol. of KNH<sub>2</sub>. N-Methylglyoxaline and NaNH<sub>2</sub> give the compound,



Benzoyl derivatives of indigotin. E. HOPE, R. W. R. KERSEY, and D. RICHTER (J.C.S., 1933, 1000—1003).—Höchst Yellow R and 15% KOH at 100° (autoclave) give BzOH, anthranilic acid, and a substance, C<sub>16</sub>H<sub>11</sub>O<sub>3</sub>N (I), m.p. 237°, whilst 10% KOH at atm. pressure gives the lactam, C<sub>16</sub>H<sub>9</sub>O<sub>2</sub>N (II), m.p. 232°. (I) forms Ac, m.p. 199°, and Bz derivatives, m.p. 236°, and is methylated to Me, m.p. 183—184°, and Me<sub>2</sub> derivatives, m.p. 98°. (II) is oxidised (KMnO<sub>4</sub>) to phthalic acid and an acid, C<sub>16</sub>H<sub>11</sub>O<sub>6</sub>N, m.p. 135—138° (efferv.) (Ag<sub>2</sub> salt; Me<sub>2</sub> ester), which, when heated, loses H<sub>2</sub>O and CO<sub>2</sub> to form a lactone, m.p. 216—217°, hydrolysed to a



hydroxy-acid (Me ester, m.p. 207°), and subsequently methylated to a methoxymonobasic acid, m.p. 172—173°. The formula (III) is suggested for Höchst Yellow R (all C<sub>6</sub>H<sub>4</sub> < are o). F. R. S.

Bilirubinoid pigments. V. Chromoproteins of red algæ. III. Phycobilins of red algæ. Transformation into mesobilirubin and dehydro-mesobilirubin. R. LEMBERG [with, in part, G. BADER] (Annalen, 1933, 505, 151—177; cf. A., 1930, 488; 1932, 1266).—Proof that the phycobilins are bile pigments is found in the transformation of phycoerythrin (I) by boiling KOH-MeOH into dehydro-mesobilirubin (glucobilin) (II), isolated as the Me<sub>2</sub> ester, m.p. 218—218°, and mesobilirubin (III); the total yield is 1.53%, whereas 1.69% is calc. for a mol. of wt. 34,500. c-Phycocyan from *Nori* yields (II) but not (III). The work of Levene *et al.* (A., 1931, 1436) is criticised. The behaviour of (I) towards MeOH-HCl is described and also the oxidation of phycoerythrobilin Me ester to phyco-cyanobilin Me ester. Mesobiliviolin is shown to be a mixture of a blue mesobilicyanin corresponding with the unsaturated bilicyanin and identical with phyco-cyanobilin and a red pigment spectroscopically similar to phycoerythrobilin and probably composing the pigment constituent of (I) for which the name mesobilerythrin is proposed. Reply is made to Siedel and Fischer (this vol., 405). H. W.

#### Magnetic behaviour of hæmoglobin derivatives.

F. HAUROWITZ and H. KITTEL (Ber., 1933, 66, [B] 1046—1049).—Mesoporphyrin Me<sub>2</sub> ester and protoporphyrin are diamagnetic; the two radical positions are therefore so arranged that their magnetic moments neutralise one another as indicated in the formula of Clar and Haurowitz (this vol., 404). Chlorohæmin I and II and oxyhæmin are strongly paramagnetic. It must be assumed that the Fe atom in them retains the high paramagnetism of Fe<sup>III</sup>; the apparent contradiction in the chemical properties of the hæmins is explained by assuming that in them Fe is attached by weak forces but is sterically sheltered from the dissociating action of H<sub>2</sub>O and the influence of acids and alkalis by the peculiar structure of the porphyrin skeleton. The diamagnetic susceptibility of Fe<sup>II</sup> in hæmoglobin is the same as that of Fe<sup>II</sup> in hæmin. H. W.

4:5'-Diisoxazoloyl ketone. II. M. FRERI (Gazzetta, 1933, 63, 419—425; cf. A., 1931, 968).—This substance (I) when isolated in EtOH or isoamyl alcohol is reduced to s-4:5':4'' : 5'''-tetraisoaxazolylpinacol, m.p. 195—196°, which with BzCl gives (I) and the carbinol. (I) forms a single oxime, m.p. 155° (Bz derivative, m.p. 121°), which when heated decomposes slowly to a product, m.p. 135—140°. E. W. W.

Quinoline derivatives. I. Furanquinolines. M. A. HAQ, M. L. KAPUR, and J. N. RAY (J.C.S., 1933, 1087—1089).— $\alpha$ -Piperonylidene-, m.p. 226° (lactone),  $\alpha$ -2-nitrobenzylidene-, m.p. 262° (lactone, m.p. 200°), reduced to the furanoquinoline, m.p. 172°, lactone of  $\alpha$ -6-nitro-3:4-methylenedioxybenzylidene-, m.p. 232° (reduced to the base, m.p. 262°), and the lactone of  $\alpha$ -6-nitroveratrylidene- $\beta$ -3:4-dimethoxybenzoylpropionic acid, m.p. 206° [reduced to the base, m.p. 245° (*picrate*, m.p. 241°)], are prepared by condensing  $\beta$ -3:4-dimethoxybenzoylpropionic acid with the appropriate aldehyde.  $\beta$ -6-Nitro-3:4-dimethoxybenzoylpropionic acid, m.p. 212° (Me ester, m.p. 118°), is

reduced to the  $NH_2$ -compound, m.p.  $118^\circ$  (*Bz*, m.p.  $225^\circ$ , and *Ac* derivative, m.p.  $187^\circ$ ; *Me* ester, m.p.  $127^\circ$ ), which gives 6:7-dimethoxy-3-acetyl-2-methylquinoline, m.p.  $245^\circ$  (decomp.) (with acetylacetone), -3-benzoyl-2-phenylquinoline-, m.p.  $229^\circ$  (decomp.) (with dibenzoylmethane), 6:7-dimethoxy-2-phenylquinoline-, m.p.  $231-232^\circ$  (with *COPhMe*), and 6:7-dimethoxyquinoline-4-propionic acid, m.p.  $120-121^\circ$  (with  $MeCHO$ ).  
F. R. S.

**Alkaloid cuprichlorides.** Specific precipitation by cupric chloride of cinchona alkaloids containing the vinyl group. A. COHEN (J.C.S., 1933, 996—1000).—The cuprichlorides of *quinine*, m.p.  $210^\circ$  (decomp.), *quinidine*, m.p.  $208-209^\circ$  (decomp.), *cinchonine* ( $+1.5H_2O$ ), m.p.  $130-132^\circ$  (decomp.), and *cinchonidine* ( $+2H_2O$ ), m.p.  $128-129^\circ$  (decomp.),  $Q_2HCl$ ,  $CuCl_2$ , have been obtained; they are recryst. from  $HCl$  and decomposed by  $H_2O$ . The corresponding dehydro-bases do not form complex salts and hence the salts may be used for purification of alkaloidal derivatives. The constitution of the salts is discussed. *Quinine*, decomp.  $125-130^\circ$ , *cinchene*, decomp.  $185-187^\circ$ , and *dihydroquinene cuprichloride*, decomp.  $195^\circ$ , are also obtained. 5-Nitro-6-methoxy ( $+H_2O$ ), efferv.  $187-189^\circ$ , and 2-methyl-quinoline, m.p.  $175-178^\circ$  (decomp.), and *quinoline cuprichloride*, decomp.  $>185^\circ$ , and a compound of 6-methoxyquinoline cupri-tri- and -tetra-chloride, m.p.  $157-159^\circ$ , are described.  
F. R. S.

**Constitution of strychnine.** I. M. KOTAKE and T. MITSUWA (Annalen, 1933, 505, 203—208).—Dihydrostrychnine and  $PhCHO$  in  $EtOH$  containing  $NaOEt$  give benzylidenedihydrostrychnine (I), m.p.  $255^\circ$  (*picrate*, m.p.  $230^\circ$ ). Oxidation of (I) in  $COMe_2-AcOH$  leads to the substance,  $C_{28}H_{28}O_5N_2$ , m.p.  $280^\circ$  [*picrate*, m.p.  $215^\circ$ ; *chloroaurate*, m.p.  $214-217^\circ$  (decomp.)]; *chloroplatinate*, decomp.  $233^\circ$ . Treatment of (I) in  $COMe_2-H_2O$  with  $KMnO_4$  leads to the compound,  $C_{21}H_{22}O_3N_2$ , m.p.  $263^\circ$ , and an acid,  $C_{20}H_{22}O_3N_2$ , m.p.  $300^\circ$ , decarboxylated to the substance  $C_{19}H_{22}O_3N_2$ , m.p.  $268^\circ$  (*hydrochloride*, m.p.  $286^\circ$ ), and transformed by  $Br-H_2O$  into the compound,  $C_{19}H_{20}O_3N_2Br$ , isolated as the acetate, m.p.  $235^\circ$ . Strychnine methiodide in  $EtOH-AcOH$  is converted by  $H_2O_2$  into the periodide, m.p.  $245^\circ$ , and a yellow liquid which yields strychnine methochloride.  
H. W.

**Strychnos alkaloids.** LXXV. Reduction and oxidation of brucinesulphonic acids III and IV and of strychninesulphonic acid III. H. LEUCHS and A. DORNOW (Ber., 1933, 66, [B], 1159—1165).—Hydrogenation of brucinesulphonic acid III ( $PtO_2$ ) gives a  $H_4$ -derivative,  $[\alpha]_D^{20} +77.3^\circ/d$  in  $H_2O$ , whereas oxidation with  $CrO_3$  affords the substance  $C_{16}H_{20}O_3N_2S$ ,  $[\alpha]_D^{20} -193.2^\circ/d$  in  $H_2O$  ( $H_4$ -derivative,  $[\alpha]_D^{20} -56.8^\circ/d$  in  $H_2O$ ), identical with that obtained from aminostrychnine- and brucine-sulphonic acid II. Brucinesulphonic acid III smoothly gives a  $H_2$ -derivative,  $[\alpha]_D^{20} +88.5^\circ/d$  in  $0.1N-NaOH$ , whereas oxidation leads to ill-defined products even when conducted through the aminoquinol hydrate [*perchlorate* ( $+H_2O$ ),  $[\alpha]_D^{20} +3.0^\circ/d$  in  $H_2O$ ]. Hydrogenation of strychninesulphonic acid III leads to partly unchanged material, whilst oxidation with  $CrO_3$  yields little cryst. material. Oxidation with  $14N-$

$HNO_3$  in presence of  $CO(NH_2)_2$  at  $0^\circ$  gives the substances  $C_{21}H_{23}O_7N_3S$  and  $C_{21}H_{24}O_7N_3S$  (I), darkens without melting at  $260-290^\circ$ . (I) is transformed by  $HCl$  into the salt  $C_{21}H_{22}O_6N_2S \cdot HCl \cdot 3H_2O$ . Hydrogenation of (I) leads to the compound  $C_{21}H_{24}O_6N_2S$ ,  $[\alpha]_D^{20} +16^\circ/d$  in  $0.1N-NaOH$ , identical with strychninesulphonic acid hydrate IV. Nitration gives the compound  $C_{21}H_{22}O_{11}N_4S$ . The substance  $C_{21}H_{24}O_{11}N_4S$  is obtained by nitration of the acid  $C_{21}H_{24}O_6N_2S$ .  
H. W.

**Metathebainone.** R. S. CAHN (J.C.S., 1933, 1038—1040).—Thebaine in conc.  $HCl$  is reduced ( $Pd-H_2$ ) to 85% metathebainone and some dihydrocodeine and other non-phenolic bases. This result cannot be reconciled with Schöpf's speculations (A., 1931, 1313).  
F. R. S.

**Solanidine and solanthrene.** F. BERGEL and R. WAGNER (Ber., 1933, 66, [B], 1093—1096).—Treatment of solanine with 2%  $HCl$  leads to solanidine (I), m.p.  $219^\circ$ , for which the formula  $C_{27}H_{43}ON$  is confirmed (*benzoate*, m.p.  $214^\circ$ ; *acetate*, m.p.  $207^\circ$ ), and solanthrene (II),  $C_{27}H_{41}N$ , m.p.  $167^\circ$  (identical with the solanidine of Schöpf). Catalytic hydrogenation of (I) in  $AcOH$  ( $PbO_2$ ) leads only to the absorption of  $2H$  with production of dihydrosolanidine, m.p.  $222^\circ$  (*acetate*, m.p.  $195^\circ$ ). The conception that (II) is formed by loss of  $H_2O$  from (I) is strengthened by the observation that it absorbs  $2H_2$  ( $PtO_2$  in  $AcOH$ ) with production of tetrahydrosolanthrene,  $C_{27}H_{45}N$ , m.p.  $164^\circ$ . Thermal decomp. of dihydrosolanidine palmitate hydrochloride, m.p.  $225^\circ$ , leads to dihydrosolanidine,  $C_{27}H_{43}N$ , m.p.  $165^\circ$ , not identical with Schöpf's solanidine.  
H. W.

**Decomposition of the arsenic acids.** B. ENGLUND (Svensk Kem. Tidskr., 1933, 45, 170—172).—Benzylarsinic acid (I) and  $H_2O$  slowly give  $CH_2Ph \cdot OH + As_2O_3$ . The hydrolysis is catalysed by  $HCl$ , and is then unimol. with respect to (I). The velocity is approx. proportional to the activity of  $HCl$ . The temperature coeff. is normal. Arsinacetic acid (II) in  $H_2O$ ,  $EtOH$ , or  $AcOH$  takes up 2 mols. of  $Br$  per mol., the velocity being proportional to the concn. of (II) and to  $[Br]^{1/2}$ . Distilling the product in vac. gives  $CHBr_3$ ,  $AsBr_3$ , and  $CBr_3 \cdot CO_2H$ .  
R. P. B.

**New derivatives of p-arsanilic acid.** V. p-Arsinomethylmalonanilic acid and related compounds. G. T. MORGAN and E. WALTON (J.C.S., 1933, 1064—1067).—*Me* methylmalonate (improved prep.) is hydrolysed ( $KOH-MeOH$ ) to *Me H methylmalonate*, b.p.  $131^\circ/16$  mm., which with  $SOCl_2$  gives  $\alpha$ -carbomethoxypropionyl chloride, b.p.  $73^\circ/16$  mm.  $\alpha$ -Carbomethoxypropionyl chloride, from *Et* methylmalonate (improved prep.), and atoxyl form *Et p-arsinomethylmalonanilate* [*Na* salt; *Me* ester and its *Na* salt ( $+H_2O$ )], which with the corresponding amine yields methylmalon-anilamide- [ $NH_3$ ; *Na* salt ( $+H_2O$ )], -anilomethylamide- ( $NH_2Me$ ; *Na* salt), -anilethylamide- [ $NH_2Et$ ; *Na* salt ( $+H_2O$ )], and -anilo-n-propylamide-p-arsinic acid [ $NH_2Pr$ ; *Na\_2* salt ( $+H_2O$ )]. The ester gives p-dichloroarsino- (I), m.p.  $158-160^\circ$  (decomp.), which in  $NaHCO_3$  is acidified to p-oxyarsini-, oxidised ( $H_2O_2$ ) to p-arsino-methylmalonanilic acid. (I) in  $SOCl_2$  and  $NH_2Ph$  form p-oxyarsinomethylmalonanilide, oxidised ( $H_2O_2$ ) to

*methylmalonanilide-p-arsinic acid* [Na salt (+2H<sub>2</sub>O)]. Atoxyl and methylmalonyl dichloride yield *methylmalonanilide-pp'-diarsinic acid*. Many of the compounds show marked trypanocidal activity.

F. R. S.

**Constitution of sulpharsphenamine.** W. J. C. DYKE and H. KING (J.C.S., 1933, 1003—1012).—When CH<sub>2</sub>O and NaHSO<sub>3</sub> are added to salvarsan the methylenesulphite groups are attached to the phenolic groups, but when preformed Na formaldehyde H sulphite (I) is used they become attached to the NH<sub>2</sub>. *p*-Aminophenylarsinic acid in NaOH and (I) form *Na p-aminophenylarsino-N-methylenesulphite* (+2·5H<sub>2</sub>O). (I) and 3-amino-4-hydroxyphenylarsonic acid give *Na<sub>2</sub> 3-amino-4-hydroxyphenylarsino-N-methylenesulphite* (+6H<sub>2</sub>O), or in neutral solution, the *Na* salt (+4H<sub>2</sub>O); and the acid with CH<sub>2</sub>O and NaHSO<sub>3</sub> successively forms a *substance*, containing two differing methylenesulphite groups. Samples of commercial sulpharsphenamine have been analysed for total and oxidised S (Elvove's method); it is the Na salt of 3 : 3'-diamino-4 : 4'-dihydroxyarsenobenzene-*OO*'-*N*-trimethylenesulphurous acid. F. R. S.

**Organic compounds of germanium.** II. H. BAUER and K. BÜRSCHKIES (Ber., 1933, 66, [B], 1156—1158).—Ge aryl trihalides are quantitatively prepared from arylgermanic anhydrides and conc. HCl, HBr, or HI in sealed vessels at 100°. The following compounds are described: GePhCl<sub>3</sub>, b.p. 102—103°/13 mm.; GePhBr<sub>3</sub>, b.p. 120—122°/13 mm.; GePhI<sub>3</sub> (III), m.p. 55—56°; *p*-C<sub>6</sub>H<sub>4</sub>Me·GeCl<sub>3</sub> (II), b.p. 115—116°/12 mm.; *p*-C<sub>6</sub>H<sub>4</sub>Me·GeBr<sub>3</sub>, b.p. 155—156°/13 mm.; *p*-C<sub>6</sub>H<sub>4</sub>Me·GeI<sub>3</sub>, m.p. 72°. MgMeI and MgEtI convert (I) into GePhMe<sub>3</sub>, b.p. 182—183°, and GePhEt<sub>3</sub>, b.p. 116—117°/13 mm. The compound *p*-C<sub>6</sub>H<sub>4</sub>Me·GeEt<sub>3</sub>, b.p. 125—126°/12 mm., results from (II) and MgEtI. H. W.

**Action of copper on some aromatic mercuriaceto-compounds.** A. CONTARDI and B. CIOCCA (Annali Chim. Appl., 1933, 23, 362—366).—HgPh<sub>2</sub> and Hg bis-*p*-diethylaminophenyl are conveniently prepared by heating the corresponding mercuriaceto-compounds in PhMe or C<sub>6</sub>H<sub>6</sub> solution in presence of Cu (cf. A., 1925, i, 1341). T. H. P.

**Furan mercurials.** H. GILMAN and G. F. WRIGHT (J. Amer. Chem. Soc., 1933, 55, 3302—3314).—Furan, HgCl<sub>2</sub>, and NaOAc give 2-chloromercuri- (I), m.p. 151°, and 2 : 5-dichloromercuri-furan, and the mother-liquors with KI<sub>3</sub> give tetra- and 2 : 5-di-iodofuran. (I) and BzCl in Et<sub>2</sub>O give a little dibenzoylfuran. (I), with AcCl in COMe<sub>2</sub>, gives furyl Me ketone (21%), with furfuryl chloride in Et<sub>2</sub>O *difurylmethane* (II), b.p. 94°/22·5 mm., with I 2-iodofuran (5-HgCl-derivative, m.p. 173°), with Me<sub>2</sub>SO<sub>4</sub> at 160—170° furan, with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> *Hg difuryl*, m.p. 114°, b.p. 156°/7 mm. [also prepared from (I) and I in COMe<sub>2</sub>, or N<sub>2</sub>H<sub>4</sub>, and from Mg 2-furyl iodide and HgCl<sub>2</sub> in Et<sub>2</sub>O], with HCl-H<sub>2</sub>O-EtOH at 100° furan (82%), and with SOCl<sub>2</sub> in Et<sub>2</sub>O at 20° a little 2-chlorofuran. (II) is stable to KMnO<sub>4</sub> and EtNO<sub>2</sub>-NaOMe, and gives the 5-HgCl-derivative, m.p. 149·5°, which regenerates (II) with hot acid and with aq. I (best with CaCO<sub>3</sub>) gives a 70% yield of 5-iodo-2 : 2'-*difurylmethane*, b.p. 123°/9 mm. 2-Furonitrile and Mg 2-furyl iodide in

Et<sub>2</sub>O give 2-furyl-2-furylmethane, m.p. 33°, b.p. 113°/6 mm. (73·3% yield), which with N<sub>2</sub>H<sub>4</sub> and KOH-MeOH gives (II) in 92% yield. Mg 5-iodo-2-furyl iodide and Me<sub>2</sub>SO<sub>4</sub> give a 72% yield of 2-iodofuran, also obtained in 60% yield from 2 : 5-di-iodofuran and Al-Hg. 2-Methylfuran gives the 5-HgCl-derivative (III), m.p. 127°, by way of an intermediate compound (IV), C<sub>5</sub>H<sub>6</sub>O·Hg(OH)Cl, HgCl<sub>2</sub>. (IV) with KI<sub>3</sub> gives 5-iodo- (V), b.p. 59°/18 mm., and (?)-*di*-iodo-2-methylfuran (unstable). The latter with Al amalgam in Et<sub>2</sub>O-MeOH gives β-(? 3-iodo-2-methylfuran, b.p. 57°/28 mm. (5-HgCl-derivative, m.p. 193·5°). (III) with KI<sub>3</sub> gives (V) (48%), the Grignard reagent from which affords 5-methyl-2-furoic acid (33%) and 5-methyl-2-furoyl- $\alpha$ -naphthalide, m.p. 149·5° (also obtained from  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub> and 5-methyl-2-furoyl chloride, b.p. 93°/20 mm.). Na furoate and hot aq. HgCl<sub>2</sub> give 2-chloromercuri- and 2 : 5-dichloromercuri-furan; the appropriate Na salts give similarly good yields of 5-iodo-, 5-bromo- (VI), m.p. 177°, and 5-methyl-2-chloromercurifuran, m.p. 134°; the 5-NO<sub>2</sub>-compound (VII), m.p. 208°, was obtained in 25% yield at 150—160°. (VI) and (VII) with aq. HCl give quant. yields of 2-bromo- and 2-nitro-furan, respectively. Furoic acid (VIII), its 5-Br- and other  $\alpha$ -substituted derivatives (but not the 5-NO<sub>2</sub>-acid) are decarboxylated by hot, aq. HgCl<sub>2</sub> to furan etc. (VII) and NaI<sub>3</sub> give 2-iodo-5-nitrofuran, m.p. 76°, lachrymatory, also obtained from 2 : 5-di-iodofuran and HNO<sub>3</sub> (*d* 1·52) in Ac<sub>2</sub>O at -5° to -10°. Similar nitration of 2 : 5-dibromofuran gives a quant. yield of fumaric acid. (VIII) and aq. Hg(OAc)<sub>2</sub> give *acetoxymercury furoate*, which at 110—135° gives a mixture whence AcOH and NaCl yield 3-chloromercurifuran, m.p. 184·5°. This with hot HCl-aq. EtOH gives (I) (63% yield), with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> *Hg* 3 : 3'-*difuryl* (72%), m.p. 73°, and with KI<sub>3</sub> 3-iodofuran, b.p. 132·2°/732 mm. (62%) (also obtained from tetra-iodofuran and Al-Hg in Et<sub>2</sub>O-MeOH). Mercurials could not be obtained from 2 : 5-di-iodo- or 2-nitro-furan, or 2-nitrothiophen. In general  $\alpha$ - are more reactive than  $\beta$ -mercurials. R. S. C.

**Organic derivatives of silicon.** XLVIII. **Steric effects of the cyclohexyl group.** N. W. CUSA and F. S. KIPPING (J.C.S., 1933, 1040—1043).—SiPhCl<sub>2</sub> and C<sub>6</sub>H<sub>11</sub>·MgBr give *cyclohexyloxycyclohexylphenylsilicane*, m.p. 103—104°, and, in absence of O<sub>2</sub>, *dicyclohexylphenylsilicane*, b.p. 180—185°/4 mm. The non-formation of quaternary hydrocarbon is probably due to steric hindrance. *Dicyclohexylphenylsilicyl bromide* and MgEtBr form *dicyclohexylphenylethylsilicane*, b.p. about 370°, decomposed by Br to a mixture of condensation products of *dicyclohexylsilicane*. F. R. S.

**Hydrolysis of proteins during denaturation.** M. A. LISSITZIN and N. S. ALEXANDROVSKAJA (Biochem. Z., 1933, 264, 35—39).—The chemical changes which occur in proteins (legumin, phaseolin, glycinin) on denaturation (acid and alkali) do not go beyond a certain point and are not continued on repeating the treatment. The denatured products closely resemble Hammarsten's caseinogen. W. McC.

**Dipeptide phosphoric acid from caseinogen.** P. A. LEVENE and D. W. HILL (J. Biol. Chem., 1933,

101, 711—718).—*Brucine glutamylserinephosphate* (I),  $C_{31}H_{39}O_{13}N_4P$ , m.p. 171—172° [*Ba* salt,  $(C_8H_{10}O_9N_2Ba)_2Ba$ ], is isolated from the brucine salt of the ppt. obtained by hydrolysing caseinogen-phosphopeptone with 2*N*-HCl and treatment with  $Ba(OH)_2$ . Two possible structures are suggested for (I). A. L.

Reversibly oxidisable substance from irradiated protein. P. WELS [and M. JOKISCH] (Arch. exp. Path. Pharm., 1933, 171, 480—495).—Ultra-violet irradiation of aq. ovalbumin in  $N_2$  gives a reversibly oxidisable substance containing SH (possibly glutathione). F. O. H.

Isolation of tyrosylserylprolyltyrosine in the stepwise degradation of silk-fibroin (*Bombyx mori*). E. ABDERHALDEN and A. BAHN (Z. physiol. Chem., 1933, 219, 72—81).—Tyrosylserylprolyltyrosine [ $Bz_4$  and  $Bz_3$  (by loss of serine- $Bz$ ) derivatives] was isolated from the fraction of the hydrolysis products of silk-fibroin pptd. by Hopkins' reagent. Tryptic hydrolysis gave tyrosine, *serylproline*, froths at 110—150°, solidifies, m.p. 215—225°, and *tyrosylserylproline* [dibenzenesulphonyl and phenylcarbimido- (I) -derivatives; benzylamine derivative of (I)]. 1-Tyrosylglycine, froths at 150—170°, solidifies, m.p. 255—265° (decomp.),  $[\alpha]_D^{20} +69.7^\circ$  in  $H_2O$ , was synthesised from *dicarbobenzyloxytyrosine chloride*, m.p. 73°, by interaction with glycine to give *dicarbobenzyloxytyrosylglycine*, m.p. 168°. J. H. B.

Cleavage of nitrogen linkings in protein and peptides by the light of the quartz lamp. H. C. ECKSTEIN and F. LIEBEN (Biochem. Z., 1933, 263, 366—370).—Irradiation of feebly acid solutions of globin, gelatin, and caseinogen by means of the quartz lamp causes an increase of  $NH_2-N$  (Van Slyke) partly due to the formation of  $NH_3$  and partly of free  $NH_2$  groups. This is not due either to the hydrolysis of the peptide linking nor to arginine, and it appears probable that the newly-formed  $NH_2$  groups and  $NH_3$  are derived from the N-containing nuclei of histidine, proline, and hydroxyproline. P. W. C.

Viscosity of ovalbumin and hæmoglobin in carbamide solutions. C. S. LIU (Chinese J. Physiol., 1933, 7, 107—116).—In 40%  $CO(NH_2)_2$  solution,  $\eta$  of ovalbumin (I) increases with denaturation; this is not due to  $p_H$  change. (I) shows a min. at  $p_H$  5.7 and hæmoglobin at  $p_H$  7.4, the isoelectric points of the denatured proteins. By determining the shift of  $p_H$  by citrate buffers these vals. were calc. to be 5.2 and 6.9. H. G. R.

Formation of carbamide from prolysin, citrullin, hydantoin, and protein by the action of hydrogen sulphide. M. WADA and N. HAYAMA (Proc. Imp. Acad. Tokyo, 1933, 9, 305—308).— $CO(NH_2)_2$  (I) results when prolysin, citrullin, and other hydantoin are treated with  $H_2S$  and weak alkali. The amounts of (I) so obtained from some proteins are reported. A. L.

Dilatometric studies of the fission of proteins and dipeptides. P. RONA and FISCHGOLD (Klin. Woch., 1933, 12, 113; Chem. Zentr., 1933, i, 1953).—Vol. changes on fission of proteins with pepsin at 37° and of peptides with conc. HCl at 50° or 1.5*N*-

NaOH at 37° have been determined. The diminution in vol. on fission of ovalbumin (but not of caseinogen) is proportional to the degree of degradation. A similar proportionality holds for the cleavage of dipeptides; NaOH causes an increase, and HCl a decrease, in vol. Hence vol. changes are considerably influenced by the different ionic conditions of the amphoteric dipeptides or  $NH_2$ -acids. A. A. E.

Semimicro-determination of carbon and hydrogen. E. P. CLARK (J. Assoc. Off. Agric. Chem., 1933, 16, 414—418).—Procedure, using an electric combustion furnace and a  $CeO_2$  catalyst, is described. J. S. A.

Rapid colorimetric determination of total carbon and nitrogen in the same sample. E. M. EMMERT (J. Assoc. Off. Agric. Chem., 1933, 16, 424—427).—The substance is oxidised by heating with  $NaClO_3 + H_2SO_4$ , C being oxidised to  $CO_2$ , and N to  $HNO_3$  which is distilled over.  $CO_2$  is determined colorimetrically by means of Na phenolphthalein (cf. A., 1931, 1142), and  $HNO_3$  by means of phenoldisulphonic acid (cf. B., 1930, 372). J. S. A.

Micro-determination of sulphur and phosphorus in organic compounds. A. ELEK and D. W. HILL (J. Amer. Chem. Soc., 1933, 55, 3479—3482).—This is effected by fusion with  $Na_2O_2$  in a micro-bomb and subsequent determination as  $BaSO_4$  and  $NH_4$  phosphomolybdate, respectively, 3.5 mg. of substance being required. R. S. C.

Determination of aldehydes by quantitative application of Cannizzaro's reaction. L. PALFRAY, S. SABETAY, and (MLLE.) D. SONTAG (Chim. et Ind., 1933, Spec. no., 1037—1038; cf. A., 1930, 318; 1931, 856; 1932, 867).—The Cannizzaro change is quant. with aromatic but only with certain aliphatic aldehydes (*e.g.*, heptaldehyde). The method is applicable to mixtures (oils of bitter almond, cumin). H. W.

Determination of cholesterol. I. Colorimetric methods. A. S. RUIZ and I. TORRES (Anal. Fis. Quim., 1933, 31, 370—377).—The methods of Myers and Wardell (I), Grigaut (II), Bloor (III), and Autenrieth and Funk (IV) are compared. Preference is given to (I), and (II) is satisfactory, but (III) gives high vals. and in (IV) extraction is incomplete. R. K. C.

[Organic] colour reactions. II. I. M. KORENMANN (Z. anal. Chem., 1933, 93, 438—447; cf. A., 1932, 717).—The influence of temp. and concn. on various org. colour reactions with conc.  $H_2SO_4$  or HCl has been investigated, the importance of these factors being emphasised. The following colour reactions are considered: vanillin test for phloroglucinol,  $COMe_2$ , and pinene; Schryver's test for  $CH_2O$ ; the  $K_2Cr_2O_7$  test for  $NH_2Ph$  and  $NHAcPh$ ; the  $KClO_3$  test for  $NH_2Ph$ ; the  $KNO_3$  test for  $m-C_6H_4(OH)_2$ ; the brucine test for  $HNO_3$ . D. R. D.

Bromometric determination of novocaine and anæsthesin by Fijalkow's method. W. HOFFMANN (Apoth.-Ztg., 1932, 47, 686—687; Chem. Zentr., 1932, ii, 3925).—Sources of error are discussed. L. S. T.

Volumetric potassium bromate-bromide titration of furfuraldehyde. Effect of temperature.

O. C. MAGISTAD (Ind. Eng. Chem. [Anal.], 1933, 5, 253).—Theoretical results are obtained at 18°, but not at higher temp. E. S. H.

Antimony trichloride reaction with compounds containing 5-membered monoheterocyclic rings. V. E. LEVINE and E. RICHMAN.—See this vol., 987.

Micro-determination of proline and oxyproline. K. LANG (Z. physiol. Chem., 1933, 219, 148—154).—Proline and oxyproline are oxidised to pyrroline (I) and hydroxypyrroline (II) by means of  $\text{OCl}'$ . (I) and (II) are isolated by steam distillation and determined together by  $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ . (II) is determined separately by condensation with isatin in dil.  $\text{H}_2\text{SO}_4$ . J. H. B.

Volumetric determination of very small amounts of nicotine. L. NAGY and A. DICKMANN (Z. anal. Chem., 1933, 94, 12—17).—Nicotine is pptd. by silicotungstic acid. The ppt. is dissolved in a known amount of 0.01N-NaOH and excess of NaOH is titrated with 0.01N-HCl in presence of Me-red. The procedure can be carried out in presence of  $\text{C}_5\text{H}_5\text{N}$ . E. S. H.

Spectrophotometric investigation of the Jaffé-Folin reaction for creatinine. H. MOHLER and F. ALMASY (Z. anal. Chem., 1933, 94, 17—18).—The absorption spectra of solutions of creatinine (I),  $\text{K}_2\text{Cr}_2\text{O}_7$  (II), and Na picrate (III) have been compared. Those of (I) and (III) are identical in the ultra-violet. (II) is most suitable as a colour comparison at 4650—5100 Å. E. S. H.

Identification of organic compounds. XIV. Gen-alkaloids [*N*-oxides of alkaloids]. L. ROSENTHALER (Pharm. Ztg., 1933, 78, 926—928; cf. this vol., 844).—Pptn. tests are described for the *N*-oxides of atropine (orange), hyoscyamine (pale orange), eserine (very pale yellow), scopolamine (orange), strychnine (yellow), and morphine (yellow). The colours in parentheses are those given in boiling  $\text{Ac}_2\text{O}$  (cf. lit.). R. S. C.

Concentrated sulphuric acid without and with addition of other substances as reagents for colour reactions of alkaloids. R. LILLIG (Pharm. Ztg., 1933, 78, 910—913, 921—926).—Lists of the reactions are given and various corrections of lit. statements are made. R. S. C.

## Biochemistry.

Method of gas analysis for respiration trials. M. KLEIBER (J. Biol. Chem., 1933, 101, 583—594).—To avoid the error, in the Haldane apparatus, due to effusion of  $\text{O}_2$  from the KOH to the sample, determinations of  $\text{CO}_2$  and  $\text{CO}_2 + \text{O}_2$  are carried out simultaneously in two separate apparatus. In the determination of  $\text{O}_2$ , distillation of  $\text{H}_2\text{O}$  from the measuring pipette to the pyrogallol is decreased to a min. H. G. R.

Precise analysis of air from respiration chambers. T. M. CARPENTER (J. Biol. Chem., 1933, 101, 595—601).—The accuracy of the author's modification (A., 1929, 1113) of the Haldane apparatus is demonstrated. No evidence of the diffusion of gases through KOH solution was obtained. H. G. R.

Continuous recorder of respiratory metabolism. H. REIN (Arch. exp. Path. Pharm., 1933, 171, 363—402).—The apparatus, which is electrically controlled, records the %  $\text{O}_2$  consumption, the %  $\text{CO}_2$  of the expired air, the vol. of inspired air, and the frequency of respiration. Its application to men and animals is described. F. O. H.

Mammalian life without red blood-corpuses. W. R. AMBERSON, A. G. MULDER, F. R. STEGGERDA, J. FLEXNER, and D. S. PANKRATZ (Science, 1933, 78, 106—107).—Experiments which show that hæmoglobin (I) can perform its respiratory function in solution much as it does within red corpuscles are described. The chief function of the vertebrate red corpuscles is to keep (I) in the blood-stream by means of impermeable membranes. L. S. T.

Diet and its effect on blood formation. F. S. ROBSCHT-ROBBINS (J. Amer. Dietet. Assoc., 1933, 8, 387—395).—The increase in hæmoglobin produced in dogs by various foods has been determined. CH. ABS.

Combination of methæmoglobin with hydrogen sulphide. D. KEILIN (Proc. Roy. Soc., 1933, B, 113, 393—404).—The necessity of  $\text{O}_2$  for the formation of sulphohæmoglobin (I) (A., 1926, 314) from hæmoglobin (II) and  $\text{H}_2\text{S}$  is confirmed. (I) appears to be an irreversible  $\text{Fe}^{\text{II}}$  derivative of (II) + an oxidation product of  $\text{H}_2\text{S}$ . (II) cannot be recovered from (I). Acid methæmoglobin (III) and  $\text{H}_2\text{S}$  [1 mol. per atom of Fe of (III)] combine to form "H<sub>2</sub>S-hæmoglobin" (IV), distinct from (I), with absorption bands at 578 (weak) and 545  $\mu$  (stronger), and a dissociation const. of approx.  $1.3 \times 10^{-5}$ . Treatment of (IV) with  $\text{Pb}(\text{OAc})_2$  yields (III), reduction gives (II). A. C.

Preparation of hæmatoporphyrin. M. A. KAPLAN (J. Lab. Clin. Med., 1932, 18, 309—312).—Oxalated blood is mixed with an equal vol. of conc.  $\text{H}_2\text{SO}_4$ , cooled, and diluted with 4 vols. of  $\text{H}_2\text{O}$ . The filtrate is neutralised with NaOH and the brown ppt. repeatedly dissolved and repptd. until the filtrate gives no biuret test. The ppt. is then suspended in  $\text{H}_2\text{O}$  and dialysed until free from Fe and  $\text{SO}_4$ ". CH. ABS.

Lipin content of white blood-cells in normal young women. E. M. BOYD (J. Biol. Chem., 1933, 101, 623—633).—The total lipin content (I) is 1—3%, composed of phospholipin 47, neutral fat 31, free cholesterol 11, and cholesteryl ester 11%; the total fatty acid is approx. 2/3 of the total lipin. White blood-cells are intermediate between body-tissues and blood-plasma with respect to (I). H. G. R.

Determination of serum-cholesterol adapted to the Man and Gildea fatty acid method. Determination of lipin-phosphorus. E. B. MAN and J. P. PETERS (J. Biol. Chem., 1933, 101, 685—695).—Serum-cholesterol is determined in the solution

from the determination of serum-fatty acids by the Man and Gildea method (this vol., 295). Lipin-P is determined in an aliquot of the EtOH-Et<sub>2</sub>O extract of serum by a modification of the Fiske and Subbarow method (A., 1926, 443).  
H. G. R.

Hourly and daily variations in the blood-cholesterol [of dogs]. J. M. MUÑOZ (Rev. Soc. Argentina biol., 1932, 8, 595—603).—The average hourly variation was 6.5%; daily variations (11 or 18%) depended on the diet.  
CH. ABS.

Determination of the ratio cholesteryl esters to total cholesterol in blood-serum. L. VELLUZ (Bull. Soc. Chim. biol., 1933, 15, 845—846).—A modification of the method of Bloor (A., 1916, ii, 650) in which a more conc. final solution facilitates the colorimetric determination.  
A. L.

Effect of the removal of lipins on the precipitability of serum-proteins by neutral salts. H. WU (Chinese J. Physiol., 1933, 7, 125—134).—The proteins are more easily pptd. by Na<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub> from the reconstituted lipin-free serum than from the original serum.  
H. G. R.

Determination of serum-proteins. S. L. MALOWAN (Biochem. Z., 1933, 264, 224—227).—At the isoelectric point the proteins of human and animal blood-serum (I) are quantitatively pptd. by heating to 75—80°. The (I) from tumours in rats and mice contains only half as much protein as does that from the healthy animals. In guinea-pigs the colloidal nature of the (I) is altered and pptn. of protein made difficult by life in a low-pressure (260—630 mm.) atm., but such life results in slight increase in the protein content of the (I).  
W. McC.

Distribution of indole between plasma and red corpuscles. J. GARCÍA-BLANCO and O. VIDAL (Anal. Fis. Quím., 1933, 31, 392—393).—Greater adsorption of indole (I) by red corpuscles occurs when the latter are suspended in 0.95% NaCl containing (I) than when (I) is added to whole blood.  
R. K. C.

Micro-determination of indole in blood-plasma. J. GARCÍA-BLANCO and O. VIDAL (Anal. Fis. Quím., 1933, 31, 390—391).—Least indole (I) is removed by adsorption on pptd. protein when the latter is pptd. by EtOH. 1 c.c. of oxalate plasma, treated with 4.5 c.c. of EtOH, is centrifuged, and to 4 c.c. of the liquid are added 10 drops of 5% *p*-NMe<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CHO and 2 c.c. of conc. HCl. In a concn. of 0.01—0.04 mg. per c.c. 65% of added (I) is accounted for in the colorimetric determination.  
R. K. C.

Glutathione and the non-glucose reducing substances of blood. M. RAWSON and J. PICKARD (Bull. Soc. Chim. biol., 1933, 15, 781—789; cf. A., 1932, 960).—There is no relationship between the non-glucose reduction (I) and the amount of hæmoglobin. (I) is due to unknown substances the amount of which increases in pathological blood and to glutathione (II) which represents approx. half of (I) in normal blood. The (II) is present only in the corpuscles.  
A. L.

Creatinine as a source of error in blood-sugar determination by the Crecelius-Seifert method. G. GRUBER and A. F. PELLEGRINI (Wien. med. Woch.,

1932, 82, 1253—1255; Chem. Zentr., 1932, ii, 3923—3924).—Owing to the high creatinine content of blood, this method for blood-sugar yields results which are much too high.  
L. S. T.

Physiology, pathology, and pharmacology of blood-magnesium. K. LANG (Z. klin. Med., 1932, 122, 206—243; Chem. Zentr., 1933, i, 797—798).—A survey.  
L. S. T.

Electrodialysis of the electrolytes of blood-serum. E. DI BENEDETTO (Rev. Soc. Argentina biol., 1932, 8, 497—504).—From horse and dog serum all the Cl, 97% of the Na, 80—83% of the K, and 55—63% of the Ca were separated.  
CH. ABS.

Determination of iodine in blood. H. J. PERKIN (Biochem. J., 1933, 27, 1078—1081).—Blood (10 c.c.) is heated with K<sub>2</sub>CO<sub>3</sub> (2 g.) in a 50-c.c. Ni crucible for 4 hr. at 500°; the ash, made into a paste with H<sub>2</sub>O, is extracted 4 times with EtOH (7 c.c. of 95%) and the extracts are filtered and evaporated to dryness without boiling. The residue, dissolved in H<sub>2</sub>O (1 c.c.), is treated with Br in slightly acid solution to oxidise I' to IO<sub>3</sub>', excess of Br removed by boiling, and IO<sub>3</sub>' determined by addition of I' and micro-titration of the liberated I. The error is < 10%. Rabbit's blood contains 8.0 × 10<sup>-6</sup> g. and human blood 6.5—9.0 × 10<sup>-6</sup> g. of I per 100 g.  
W. O. K.

Rapid method for obtaining protein-free ultrafiltrates of blood and plasma. C. WILSON and E. R. HOLIDAY (Biochem. J., 1933, 27, 1095—1098).—An ultra-filtration apparatus suitable for obtaining protein-free filtrates from blood, plasma, and serum is described. The prep. of two types of collodion membrane for the apparatus is given.  
A. W.

Loss of weight of fibrinogen on coagulation. C. H. HSU and H. WU (Chinese J. Physiol., 1933, 7, 117—124).—The fibrin obtained on coagulation is approx. 6.7% < the fibrinogen from which it is derived.  
H. G. R.

Thrombin. I. Fractionation and purification. II. Components. III. Coupling of the components. A. FISCHER (Biochem. Z., 1933, 264, 169—177, 178—183, 184—191; cf. this vol., 522).—I. A method for the determination of thrombin (I) is described. (I) is pptd. by half-saturation with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, is very sol. in acids, has its isoelectric point near neutrality, and is rapidly denatured by acidifying or heating. Fifty-fold purification of the (I) in muscle extract is attained by acidifying, rapidly neutralising, and centrifuging, or by heating at 50° for 1 min. The coagulating power of (I) so purified differs from that of the original material in being only slightly sensitive to the action of heparin (II). The difference is probably due to partial denaturation.

II. (I) has two components: a protein and an Et<sub>2</sub>O-sol substance (III). The ultra-violet absorption spectrum of (III) from purified (I) exhibits a band at 250—260 mμ, the degree of activity of (I) being proportional to the magnitude of the absorption in this region. Blood-serum exhibits an absorption min. at 255 mμ, but the greater is the activity of (I) the less pronounced is this min.

III. Although neither the protein component nor (III) has any coagulating power, they combine to

produce an active coagulant which is very sensitive to the action of (II), but is rendered insensitive by treatment for a short time with acid. (I) is a lipo-protein containing Ca and (III) is possibly cephalin. The activity of samples of (I) is proportional to their content of (III). W. McC.

**Stability of glycerinated hæmolysin.** R. A. KILDUFFE (J. Lab. Clin. Med., 1933, 18, 571).—Anti-sheep hæmolysin with an equal vol. of glycerol showed practically no loss in titre after 16 years. CH. ABS.

**Effect of organ extracts on hæmolysis.** L. PINCUS (Z. klin. Med., 1933, 123, 55—62; Chem. Zentr., 1933, i, 1469).—Hæmolysis is inhibited by thymus, heart, and liver extracts. A. A. E.

**Isolation of antibodies from immunised serum-globulin.** T. ASABA (Arb. med. Fak. Okayama, 1933, 3, 467—486).—Pptn., electro dialysis, and the biological method are discussed. CH. ABS.

**Relationship between structure of antigen and specificity of antibody. VI. Relation between mol. wt. of haptenes and their affinity for antibodies.** E. BERGER and H. ERLÉNMEYER (Biochem. Z., 1933, 264, 113—119; cf. this vol., 846).—The power of antigens (I) (aromatic sulphonic acids) containing the same active group ( $\text{SO}_3\text{H}$ ) to bind antibodies *in vivo* (rabbits) does not increase with increasing mol. wt. of (I), but increases suddenly when a certain mol. wt. (tyrosinebisazosulphanilic acid) is reached. W. McC.

**Parallel action of neutral salts on the inhibition of complement and on the dispersion of gelatin.** J. GORDON and F. C. THOMPSON (Brit. J. Exp. Path., 1933, 14, 33—42).—The action of neutral, non-hydrolysable Na and K salts on the inhibition of complement is in the order:  $\text{CNS}' > \text{I}' > \text{Br}' = \text{NO}_3' > \frac{1}{2}\text{SO}_4'' > \text{Cl}'$ ; this is the lyotropic series for the salt effects in the swelling of purified gelatin at low concns. of salts. Dispersion of the serum-proteins is probably the cause of the observed inhibition. CH. ABS.

**Physico-chemical properties and solubility in ethyl alcohol of egg-yolk oil.** M. G. VITA and C. L. BRACALONI (J. Pharm. Chim., 1933, [viii], 18, 104—108). H. D.

**Elementary composition and caloric value of the fatty acids of the phospholipins of human skeletal muscle.** D. P. CUTHBERTSON (Biochem. J., 1933, 27, 1099—1102).—Phospholipins derived from the skeletal muscle of normal men yielded fatty acids which gave C 76.03, H 11.98, O 11.99%. The average R.Q. of the acids was 0.709 and the average caloric val. 9.521 g.-cal. per g. at const. pressure. The equiv. of 1 litre of  $\text{O}_2$  at const. pressure was 4.75 g.-cal. and the I val. was 111. These vals. are similar to those previously recorded for the triglycerides of subcutaneous fat, and differ from those for the triglycerides of skeletal muscle. A. W.

**Degree of unsaturation of the fats of human adipose tissue in relation to depth from skin surface.** D. P. CUTHBERTSON and S. L. TOMPSETT (Biochem. J., 1933, 27, 1103—1106).—The fats of the panniculus adiposus abdominalis, omental, peri-

nephric, epicardial, and liver tissues of three normal human cadavers gave average I val. of 70, 63.5, 63, 63.5, and 127, respectively. The corresponding average vals. for the fats of six obese female cadavers were 70, 69, 63, —, and 89, respectively. Distinct differences in the composition of the storage fat at different depths from the skin surface are not found in man. A. W.

**Insect wax. VI. Synthesis of di-acid triglycerides of palmitic and myristic acids.** F. N. SCHULZ and M. BECKER (Biochem. Z., 1933, 264, 87—93; cf. this vol., 736).— $\alpha$ -Palmito- $\alpha'$ - $\beta$ -dimyristin and  $\alpha$ -myristo- $\alpha'$ - $\beta$ -dipalmitin, prepared from  $\text{COMe}_2$ -glycerol, have m.p. 53.2° and 56.5°.  $\beta$ -Palmito- $\alpha'$ -dimyristin and  $\beta$ -myristo- $\alpha'$ -dipalmitin, from  $\alpha$ -iodohydrin, have m.p. 54.8° and 56.8°. The mixtures of acids obtained from the triglycerides by hydrolysis have m.p. 45—46°, 53.5°, 45—46°, and 44°, respectively.  $\beta$ -Lauro- $\alpha'$ -dimyristin has m.p. 47.6°.  $\alpha\beta$ -Dimyristoiodydrin and  $\alpha\alpha'$ -dimyristin have m.p. 42.5° and 63.8°, respectively. A mixture of 2 mols. of myristic and 1 mol. of palmitic acid has m.p. 45—46°, whilst the acid obtained from *Schizoneura* wax by hydrolysis has m.p. about 38°. The wax is consequently not identical with any of these glycerides. W. McC.

**Determination of the total carbohydrate content of the liver tissue in the fasting rabbit.** C. TSAI (Chinese J. Physiol., 1933, 7, 91—102).—Total carbohydrate (I) is determined by determination of the reducing sugar, after HCl hydrolysis and removal of non-carbohydrate reducing substances by  $\text{HgSO}_4$ . Under fasting conditions (I) and glycogen (II) vary considerably, whereas the non-(II) fraction is approx. const. H. G. R.

**Determination of total sugar in liver tissue. Reply to C. Tsai.** A. CARRUTHERS (Chinese J. Physiol., 1933, 7, 103—106; cf. preceding abstract).—The supernatant fluid, obtained by centrifuging a boiling  $\text{H}_2\text{O}$  extract of ground liver tissue, is in equilibrium with the sugar in the tissue residue. H. G. R.

**Determination of lactic acid. I. Comparison of the method of Fürth and Charnass with the modification of Friedemann, Cotonio, and Shaffer. II. Determination in urine, milk, blood, and organs.** J. A. COLLAZO and A. S. RUIZ (Anal. Fis. Quím., 1933, 31, 458—493).—The presence of  $\text{MnSO}_4$  is necessary in the oxidation of lactic acid to  $\text{MeCHO}$ , and the  $\text{MeCHO}$ -H sulphite compound is best determined by Clausen's method, but direct distillation of  $\text{MeCHO}$  is simplest, and the aëration method is unnecessary (cf. Friedemann *et al.*, A., 1927, 800; 1929, 677; this vol., 488). R. K. C.

**Occurrence of a substance resembling acetylcholine in skeletal muscle. III.** F. PLATNER (Pflüger's Archiv, 1932, 230, 705—716; Chem. Zentr., 1933, i, 1969).—EtOH extracts of the muscle of various animals contained detectable quantities of a substance resembling acetylcholine (I) which does not originate in the (I)-sensitive apparatus. A. A. E.

**Tissue-acetylcholine. I. Origin, significance, and fate of acetylcholine in human placenta.**

H. C. CHANG and A. WONG. II. Acetylcholine content of Collip's oestrogenic placental extract. H. C. CHANG (Chinese J. Physiol., 1933, 7, 151—169, 171—178).—I. The amount of acetylcholine (I) in placenta appears to be directly related to the activity of the uterus (II). (I)-like substance of human placenta is not liberated into the natural circulation in any appreciable quantity.

II. Collip's extract (A., 1930, 646) exhibits (I)-like action in addition to its oestrogenic effect.

H. G. R.

Approximate determination of spermine in single human organs. G. A. HARRISON (Biochem. J., 1933, 27, 1152—1156).—The dry organ is freed from fat (Et<sub>2</sub>O) and then extracted with 2.5% CCl<sub>3</sub>·CO<sub>2</sub>H; the clear extract is treated with picric acid and the pptd. spermine picrate converted through the hydrochloride into the phosphate. The amounts of spermine (I) in individual normal prostates obtained *post mortem* vary enormously and are probably fortuitous. The approx. amounts of (I) in testes, pancreas, and other human organs are reported; they are of the same order as found in all organs other than the prostate.

H. B.

A constituent of adrenal cortex. E. SCHMITZ and G. HILGETAG (Naturwiss., 1933, 21, 626—627).—By a modification of the method described previously (this vol., 642), a cryst. neutral substance, C<sub>35</sub>H<sub>74-76</sub>O<sub>8</sub>N<sub>2</sub>S, m.p. 242° (decomp., brown at 200°), is obtained which depresses blood-cholesterol in dogs.

R. K. C.

Salmenic acid, a carotenoid of the salmon. H. VON EULER, H. HELSTRÖM, and M. MALMBERG (Svensk Kem. Tidskr., 1933, 45, 151—152).—Et<sub>2</sub>O extracts of salmon muscle or roe yield on hydrolysis the sparingly sol. Na salt of salmenic acid, with absorption bands at 485 mμ and 525 mμ. R. K. C.

I. Carotenoids of marine invertebrates. II. Carotenoid pigments of fishes. E. LÖNNBERG (Ark. Zool., 1933, 25A, No. 1, 1—17; No. 2, 1—8).—I. Carotene and xanthophyll were detected spectroscopically and with the SbCl<sub>3</sub> test in certain echinoderms and molluscs. In the crustacea, polychæta, nemertines, and anthozoa examined, xanthophyll appeared to predominate.

II. Xanthophyll appeared to be widely distributed in the skin and fins of various fishes, being also, apparently, the predominant carotenoid in the bodies of the prey.

NUTR. ABS. (b)

A lyochrome from ova of *Myxine glutinosa*. H. VON EULER and H. HELSTRÖM (Svensk Kem. Tidskr., 1933, 45, 180).—A yellow, fluorescent colouring-matter, with absorption from 500 mμ into the ultra-violet, and a band at 275 mμ, is obtained by extracting the fat-free ova with H<sub>2</sub>O. It gives the murexide reaction and oxidises leucomethylene-blue.

R. K. C.

Enzymes of the skin. X. Catalase of human skin. J. WOHLGEMUTH and E. SZÖRÉNYI (Biochem. Z., 1933, 264, 94—103; cf. A., 1925, i, 203).—The decomp. of H<sub>2</sub>O<sub>2</sub> at 0° (but not at higher temp.) by catalase (I) from human skin is a unimol. reaction. The activity (II) of (I) alters only slightly between p<sub>H</sub> 6.5 and 8.0, the optimum being at neutrality.

Low concn. of FeSO<sub>4</sub> partly and of NaCN completely inhibits (II), but, although probably identical with them, (I) differs from blood- and liver-catalase in that its (II) is not affected by O<sub>2</sub>, CO, or CO<sub>2</sub>. The preps. used contained Cu, but it is possibly not a constituent of (I).

W. McC.

Chloride and water in the constitution of tissues. H. G. CLOSE (Biochem. J., 1933, 27, 967—975).—At room temp. the Cl' and H<sub>2</sub>O contents of human *post-mortem* tissue remain const. for at least 24 hr. The tissues form three groups according to their H<sub>2</sub>O content: (I), body-fluids (90—99%); (II), nuclear tissues (75—85%); and (III), anuclear tissues (10—73%). (I) have an average Cl' content > that of (II) or (III). The tissues arranged in order of descending p<sub>H</sub> give a series almost identical with that of descending Cl' content. The chief characteristics, including metabolic rate and the Na, K, and protein contents, of the three groups are discussed.

F. O. H.

Micro-determination of calcium in tissues rich in iron. R. WOLFF (Bull. Soc. Chim. biol., 1933, 15, 814—819).—The method is a modification of that of Guillaumin (A., 1931, 248), the Ca being pptd. as oxalate at p<sub>H</sub> 5.0. Fe does not interfere provided there are < 6 mg. per 10 c.c. of solution, and the determination can be made when the amount of Fe is 50 times that of Ca.

A. L.

Micro-determination of magnesium in animal tissues. R. WOLFF and M. TRAIN (Bull. Soc. Chim. biol., 1933, 15, 820—832).—The tissue is ashed and extracted with aq. HCl. Ca is pptd. at p<sub>H</sub> 5.0 as oxalate and Mg as MgNH<sub>4</sub>PO<sub>4</sub> in presence of NH<sub>4</sub> citrate. After washing with aq. EtOH, the NH<sub>4</sub> in the ppt. is determined by the Kjeldahl method. The separation of Ca is necessary only when the amount present is > thrice that of the Mg, and the method can be used to determine 0.02 mg.

A. L.

Vanadium in certain organisms. A. P. VINOGRADOV (Trav. lab. biogéochim. acad. sci. U.R.S.S., 1932, 2, 1—7).—*Ciona intestinalis*, L., and *Ascidella aspersa*, Müll., contained, respectively, 1.3 × 10<sup>-3</sup> and 4.9 × 10<sup>-3</sup>% V. V was detected in ash of *Sarcobotrylodes aurea*, but not in that of *Pyura*, *Styela*, *Molpadia affinis*, or *Cucumaria frondosa*.

CH. ABS.

Daily variations in the f.p. of milk. H. A. SCHUETTE and E. O. HUEBNER (Trans. Wisconsin Acad. Sci., 1933, 28, 267—274).—The f.p. of the milk, determined by the Hortvet method (cf. B., 1933, 40), of a well-fed cow over a period of 30 days does not vary individually or from that of the herd. With two cows, the vals. 0.542—0.563° (average 0.551°) and 0.542—0.557° (average 0.549°) were obtained. The presence of colostrum depresses the f.p., due to increased salt concn. and probably also to retardation of freezing by the high protein content. With the approach of parturition there is a decrease in the lactose content and a corresponding increase in the inorg. salts.

F. O. H.

Amount and properties of fat-globules in Siberian cow's milk at different periods of lactation. A. GHURAUSKAYA (Trans. Omsk Inst. Dairying, 1931, 1, 60).

NUTR. ABS. (b)

**Peroxidase reaction. XLII. Arakawa's reaction and toxicity of human milk.** K. ASAKURA and H. OHSAKO (Tôhoku J. Exp. Med., 1933, 20, 429—433).—Although human milk (I), negative to Arakawa's reaction, is deficient in vitamin-B<sub>1</sub>, this deficiency is not the cause of death when (I) is injected into mice receiving a diet of H<sub>2</sub>O and well-polished rice, since milk with a positive Arakawa reaction, in which the vitamin has been destroyed by heat or oxygenation, has no toxic effect when injected.

NUTR. ABS. (m)

**Action of sodium thiocyanate on milk. II. Bactericidal action of NaCNS.** W. WITTHOLZ (Milch. Forsch., 1933, 15, 315—320).—In acid solution *B. bulgaricum*, *S. thermophilus*, and *Diploc. lacticus* were destroyed. The destruction of *B. bulgaricum* required least NaCNS, whilst *D. lacticus* required most.

E. B. H.

**Inorganic constituents of cerebrospinal fluid. IV. Potassium in serum, serum-ultra-filtrate, and cerebrospinal fluid.** E. WATCHORN and R. A. McCANCE (Biochem. J., 1933, 27, 1107—1112).—Serum-K is wholly ultra-filterable, and thus the agreement between this val. and the K level of hydrocele, pleural, and ascitic fluids is explained. The K level of cerebrospinal fluid (I) is, at the most, only 65—70% of the serum-K, and this suggests that (I) does not, as far as K is concerned, represent a serum-ultra-filtrate.

A. W.

**Correlation of the p<sub>H</sub> of the cerebrospinal fluid and blood in rabbits.** A. M. PETRUNKIN, M. L. PETRUNKIN, and A. P. ZAVYALOVA (Arch. Sci. biol., U.S.S.R., 1932, 32, 61—67).—Vals. are parallel normally and during Et<sub>2</sub>O anæsthesia.

CH. ABS.

**Reducing property of aqueous humour.** H. K. MÜLLER (Nature, 1933, 132, 280).—The reduction of methylene-blue by the aq. humour (I) of the rabbit and of cattle depends, not on an enzyme, but on a reducing substance (II) present in the CCl<sub>3</sub>-CO<sub>2</sub>H filtrate [1 c.c. of (I) = 1 c.c. 0.002N-I, approx.]. (II) is sensitive to O<sub>2</sub> only in alkaline solution, and the reduction of the dye by (I) is accelerated by increased alkalinity and addition of NaCN. Substances containing SH are not demonstrable in (I). (II) is probably vitamin-C which is closely related to the metabolism of the lens and to the genesis of cataract.

L. S. T.

**Determination of cholesterol in bile and duodenal fluid.** V. DEULOFEV and J. E. BAVIO (Anal. Fis. Quím., 1933, 31, 206—209).—The fluid is dried on plaster of Paris, which is then extracted with Et<sub>2</sub>O, and the cholesterol is determined in the extract by Grigaut's method, using the Liebermann-Burchard reaction.

R. K. C.

**Gastric mucus. I. Determination.** F. BALTZER (Biochem. Z., 1933, 264, 28—34).—Ultra-filtration, treatment with colloidal Fe(OH)<sub>3</sub>, determination of N (total, NH<sub>2</sub>, NH<sub>3</sub>), and observation of changes in viscosity due to alteration in reaction show that the mucus probably consists of mucins containing NH<sub>2</sub>-compounds in colloidal solution.

W. McC.

**Inverse concentration ratios for sodium and potassium in gastric juice and blood-plasma.**

R. C. INGRAHAM and M. B. VISSCHER (Proc. Soc. Exp. Biol. Med., 1933, 30, 464—466).—The Na content of blood-plasma of etherised or amyralised dogs is 1.6 times that of their gastric juice secreted after histamine injection; the K content is < half that in the gastric juice.

NUTR. ABS. (m)

**Gastric pepsin. I. Methods of measurement and factors which influence it.** A. E. OSTERBERG, F. R. VANZANT, and W. C. ALVAREZ (J. Clin. Invest., 1933, 12, 557—556).—Gilman and Cowgill's method gives accurate vals. Blood, mucin, blood-proteins, peptones, and alkalis markedly reduce peptic activity.

CH. ABS.

**[H<sup>+</sup>] of gastro-intestinal contents of vegetarian and omnivorous rats.** S. WAN (Chinese J. Physiol., 1933, 7, 179—184).—No significant difference was found in the p<sub>H</sub> of fæces and gastro-intestinal contents of rats on omnivorous and vegetarian diets.

H. G. R.

**Gastric secretion and alkaline tide in urine.** R. S. HUBBARD, S. A. MUNFORD, and J. TYNER (J. Biol. Chem., 1933, 101, 781—785).—A comparison of the p<sub>H</sub> of urine from patients with normal gastric juice with that from patients with achlorhydria indicates that the secretion of HCl by the stomach is the main cause of the alkaline tide. The urine of the last-named group showed a regular increase in acidity after the meal.

A. L.

**Chloride content of glomerular urine and plasma of frogs.** B. B. WESTFALL and A. N. RICHARDS (Amer. J. Med. Sci., 1933, 185, 148).—The max. difference in Cl content is 6% (average 2%). As regards Cl', glomerular urine of frogs is an ultra-filtrate from plasma.

CH. ABS.

**Glyoxaline derivatives in urine.** O. FÜRTH and E. H. MAJER (Biochem. Z., 1933, 264, 142—156; cf. A., 1932, 1056).—Glyoxaline derivatives (I) in urine are best pptd. with Hopkins' reagent and are then colorimetrically determined (as histidine) by the method of Weiss and Sobolev (A., 1914, ii, 155) using histidine (II) as standard. Other otherwise satisfactory methods are untrustworthy when applied to urine. Normal human urine contains 8—18 mg. of (I) per 100 c.c. In tuberculosis, diseases of the liver, and pregnancy the amounts are respectively 10—32, 13—16, and 14—53 mg. Only exceptionally does (II) constitute the chief part of the (I) of pregnancy urine.

W. McC.

**Detection of protein in human urine.** R. HIROHATA, H. SHIMOKAWA, and O. KAMIZAWA (Biochem. Z., 1933, 264, 126—130).—Filtered urine (5 c.c.) is acidified if necessary with AcOH and 10% aq. flavianic acid (0.5—1.0 c.c.) is added. Presence of protein (I) is indicated by production of a turbidity or ppt. insol. in excess. 0.003% of (I) can be detected. All usual constituents of urine do not interfere, and a ppt. due to substances other than (I) (quinine, K, Ca) is dissolved by diluting or heating.

W. McC.

**Determination of indican in urine.** J. BROEKMEYER (Klin. Woch., 1932, 11, 1713—1715; Chem. Zentr., 1932, ii, 3924).—A modification of Obermeyer's method is described.

L. S. T.

**Blood in unexplained gastric anacidity.** W. S. POLLAND (J. Clin. Invest., 1933, 12, 599—611).—No abnormalities were observed. CH. ABS.

**Electrolyte balance studies in adrenalectomised dogs with particular reference to the excretion of sodium.** R. F. LOEB, D. W. ATCHLEY, E. M. BENEDICT, and J. LELAND (J. Exp. Med., 1933, 57, 775—792).—Blood-Na, -Cl, and  $\text{-HCO}_3'$  decrease in Addison's disease, and in adrenalectomised animals. Blood-K increases after adrenalectomy. Loss of Na from the body results from increased urinary excretion of Na, vomiting, and diarrhoea. CH. ABS.

**Influence of iodine, and its mode of action, in experimental adrenaline arteriosclerosis. I, II.** K. KAGAWA (Folia Pharmacol. Japon., 1933, 15, No. 4, 309—320, 321—331).—Small doses of KI prevent adrenaline arteriosclerosis in normal, but not in thyroidectomised, rabbits. CH. ABS.

**Effect of thyroid preparations on experimental hypercholesterolaemia and atherosclerosis. I. B.** FRIEDLAND (Z. ges. exp. Med., 1933, 87, 683—702).—Administration of cholesterol to rabbits leads to rapid development of atherosclerosis (I) which does not run parallel with the degree of hypercholesterolaemia (II). Simultaneous administration of thyreoidin (III) (50—250 mg. per kg. per day) reduces or prevents the (II) and development of (I) even when large doses of cholesterol (IV) are given for long periods. When the blood-(IV) is normal (III) has little effect on it. Male rabbits are more susceptible than females to the action of (III). NUTR. ABS. (m)

**Anæmia of infancy from maternal iron deficiency in pregnancy.** M. B. STRAUSS (J. Clin. Invest., 1933, 12, 345—353).—Fe given during pregnancy to mothers with hypochromic anæmia prevents the development of anæmia in infants during the first year of life. Apparently the foetus of Fe-deficient mothers does not store sufficient Fe to carry the infant through this period. CH. ABS.

**Cholesterol and lecithin-phosphorus in the plasma of anæmia other than pernicious anæmia.** G. L. MULLER and C. W. HEATH (Arch. Int. Med., 1933, 52, 288—305).—In anæmia (I) due to chronic loss of blood the plasma-cholesterol (II) and the lecithin-P (III) decrease with increasing severity of (I), whilst in (I) due to acute loss of blood the (II) and (III) remain normal or increase. In (I) associated with cancer of the stomach the (II) and (III) tend to be low. In chronic myelogenous leucæmia (II) is usually below normal, whilst (III) is normal. In aplastic (I) (II) and (III) are high. Irregular results are obtained in ideopathic hypochromic (I). W. O. K.

**Glycolysis in the blood of patients with pernicious anæmia.** S. M. GOLDHAMER (J. Clin. Invest., 1933, 12, 538—588).—Retarded glycolysis is proportional to red-cell decrease. CH. ABS.

**Gastro-intestinal studies. II. Pancreatic enzymes in pernicious anæmia.** O. M. HELMER, P. J. FOUTS, and L. G. ZERFAS (J. Clin. Invest., 1933, 12, 519—532).—Pancreatic enzymes were present in the duodenum. Determination of these enzymes in gastric contents during fasting is of no val. in estimat-

ing pancreatic activity. There is no impairment of functional secretion of enterokinase in pernicious anæmia. Liver feeding had little effect on the activity of the pancreatic enzymes. CH. ABS.

**Relationship between anti-anæmic principles in stomach and liver.** J. F. WILKINSON and L. KLEIN (Lancet, 1933, 125, 629—632).—The prep. of different concentrates containing hæmopietin (I), the active anti-anæmic substance in hog's stomach, is described. (I) is less stable than, and has different properties from, the anti-anæmic principle in liver (II). When stomach fractions containing the thermo-labile (I) are incubated with beef or stomach muscle, a relatively heat-resistant, hæmopoietically-active material is obtained; a substance similar to or identical with (II) is probably synthesised. The enzyme (I), by acting on some substance present in protein food, may produce *in vivo* a substance which is stored as (II) until it is required for red-cell formation. (I) is present in the normal stomach of man, of carnivorous and omnivorous animals, but not in those of herbivorous animals. Pernicious anæmia is a type of deficiency disease characterised by absence of a sp. enzyme, (I), and pepsin and HCl from gastric secretion. Experimental evidence for the enzymic nature of (I) is adduced. L. S. T.

**Increased potency of liver-extract by incubation with human gastric juice.** O. M. HELMER, P. J. FOUTS, and L. G. ZERFAS (Proc. Soc. Exp. Biol. Med., 1933, 30, 775—778).—One case of pernicious anæmia showed no response when treated daily for 10 days with liver-extract No. 343 (I), derived from 100 g. liver. Another showed no improvement during a 10-day control period in which 150 c.c. of normal human gastric juice (II) were taken by mouth daily. Both cases responded well when treated daily for 10 days with (I), from 100 g. of liver, after incubation of the extract at 40° for 4 hr., with 100 c.c. of (II). NUTR. ABS. (b)

**Effect of injected liver-extracts on blood-cholesterol and -cholesteryl esters.** F. GEBHARDT and J. KLEIN (Klin. Woch., 1933, 12, 494—497).—The concn. of free cholesterol and of cholesteryl esters in the blood was raised by the injection of liver-extract in all cases investigated, including patients with pernicious and secondary anæmia, liver disease, and healthy subjects. NUTR. ABS. (b)

**Biochemistry of asthmatic conditions with special reference to the urinary "proteose."** G. H. ORIEL (Lancet, 1933, 125, 406—409).—The differences in biological activity of urinary proteose in different phases of asthma are described. Normal proteose gives one fraction only, whilst asthmatic proteose can be separated into three fractions. L. S. T.

**Arterial and venous blood-sugar response to adrenaline in normal individuals and in biliary tract disease.** A. CANTAROW (Amer. J. Med. Sci., 1933, 185, 449—450). CH. ABS.

**Influence of the endocrine system in blood disorders.** D. HUBBLE (Lancet, 1933, 125, 113—119).—Evidence relating to the effect of the thyroid, the adrenals, and the pituitary on hæmopoiesis is

reviewed. The thyroid hormone stimulates the production of red cells (I) and lymphocytes, and depresses the formation of granular leucocytes (II); the adrenal cortical hormones stimulate the production of (II), and possibly of (I), whilst the basophile cells of the anterior lobe of the pituitary stimulate all types of circulating cells. Blood disorders are discussed in relation to disorders of the endocrine system.

L. S. T.

**Cancer : application of the Rupp-Schied-Thiel thiocyanate reaction to urine.** M. X. SULLIVAN and W. C. HESS (J. Washington Acad. Sci., 1933, 23, 378—380).—The test, which consists in the determination in the 24-hr. urine of the apparent CNS', is not sp. for, or necessarily positive in, cancer.

W. O. K.

**Metabolism of normal and tumour tissue. IX. Ammonia and urea formation. X. Effects of lactate, pyruvate, and deprivation of substrate.** F. DICKENS and D. G. GREVILLE (Biochem. J., 1933, 27, 1123—1133, 1134—1140).—X. Aërobic formation of  $\text{NH}_3$  by kidney, spleen, Jensen sarcoma, and embryo tissue was large, but was completely inhibited by glucose or fructose. Anaërobic elimination of  $\text{NH}_3$  is generally < aërobic. Judged by  $\text{NH}_3$ +urea formation, protein oxidation, in a glucose medium, is so small as to have no influence on the R.Q.

X. The inhibitory effect of *l*-lactate on anaërobic glycolysis (I) is about half that of *d*-lactate. After preliminary substrate-deprivation, (I) recovers completely with tissue other than brain, which recovers to only 12% of the normal val. Pyruvate tends to keep the glycolysis of tissues at max. H. G. R.

**Phosphatase content of the muscle of animals with tumours.** J. WIENBECK (Z. physiol. Chem., 1933, 219, 164—172).—Striped muscle of rats with tumours can liberate  $\text{H}_3\text{PO}_4$  from thymonucleic acid, although in normal animals the power is lacking (cf. Edlbacher and Kutscher, A., 1931, 1180). In mice the difference is less marked, since muscle of the normal animal shows nucleophosphatase action. After 4 hr. products are formed which favour a synthetic  $\text{PO}_4$  metabolism, and hence mask the phosphatase effect. J. H. B.

**Enzymes in tumours. I.** E. WALDSCHMIDT-LEITZ, E. McDONALD, and collaborators (Z. physiol. Chem., 1933, 219, 115—127).—The amount of cathepsin (I), phosphatase (II), and deamidase in experimental tumours falls, but of arginase (III) rises, with increasing necrosis. The amounts of amino- and dipeptidase are independent of the ageing of the tumour. The (I) and (III) of the liver are diminished, the kidney-(II) is increased, in the diseased animals. Generally the enzyme content of the tumour is similar to that of normal organs, but differs from that of muscle-tissue, although the high catalase content of the liver forms an exception. The degree of activation of (I) in tumours, independent of ageing, is similar to that of the liver, but whilst active (III) in tumours alters only slightly with age, the total enzyme, determined after cysteine-Fe activation, increases greatly. The incomplete activation, like the lowered respiration, is attributed to a lack of heavy metal.

J. H. B.

**Alleged activators of proteolysis in tumours.** L. Pozzi (Atti R. Accad. Lincei, 1933, [vi], 17, 865—868).—Aq. and EtOH extracts of liver have no accelerating effect on proteolysis, but, on the contrary, an inhibitory action. Similar extracts of rat tumours have neither accelerating nor inhibitory effects. Liver and tumour extracts mixed together appear to exert a mutual inhibition. R. N. C.

**Activation of fructose fermentation by Jensen sarcoma with pyruvic acid and various oxidising agents.** O. ROSENTHAL (Z. Krebsforsch., 1932, 38, 216—240; Chem. Zentr., 1933, i, 1475).— $\text{AcCO}_2\text{H}$ , methylene-blue, Lauth's violet, Capri-blue,  $\text{K}_3\text{Fe}(\text{CN})_6$ , and  $\text{C}_5\text{H}_{11}\text{NO}_2$ , which activate lactic acid fermentation of fructose in Jensen rat sarcoma, are reduced by the tissues and act as H acceptors. A. A. E.

**Action of chlorophyll on blood-corpuses normally and in cancer.** A. H. ROFFO (Z. Krebsforsch., 1933, 38, 312—325; Chem. Zentr., 1933, i, 1469).—In cancer, red blood-corpuses are hæmolyzed more readily than normally by irradiated chlorophyll. A. A. E.

**Is methylene-blue anti-carcinogenic?** M. COPISAROW (Science, 1933, 78, 212).—A discussion. L. S. T.

**Treatment of cancer with connective tissue extracts.** H. S. BAKER (Lancet, 1933, 125, 643—645).—Intravenous administration of an extract, presumed to contain a principle inhibiting cell overgrowth, of connective tissue from an area in the pig or cow corresponding with that of the primary growth, diminishes the size and vigour of carcinomata in human beings. L. S. T.

**Potassium content of benign uterine tumours.** L. C. SCOTT (Amer. J. Cancer, 1933, 17, 924—931).—The average val. is 0.166 (normal, 0.188) g. per 100 g. of moist tissue. Tumour-K decreases as growth progresses. CH. ABS.

**Heat cramps.** J. H. TALBOTT and J. MICHELSEN (J. Clin. Invest., 1933, 12, 533—549).—Cramp is probably caused by loss of base,  $\text{Cl}'$ , and  $\text{H}_2\text{O}$ , principally from the sweat glands. CH. ABS.

**Substances formed in decay of dental pulp (gangrene).** I. H. SCHMALFUSS and G. FISCHER [with W. MÖRING] (Zahnärztl. Rund., 1932, 41, No. 28, 6 pp.; Chem. Zentr., 1933, i, 1144).—Indole substances and volatile bases are present in decayed, but not in normal, dental pulp. A. A. E.

**Quebrachitol as a sweetening agent for diabetics.** R. A. McCANCE and R. D. LAWRENCE (Biochem. J., 1933, 27, 986—989).—Whilst quebrachitol (*l*-methylinositol) has a sweetness approx.  $\frac{1}{3}$  that of sucrose, it has no influence on insulin hypoglycæmia and neither raises the blood-sugar nor causes deposition of liver-glycogen in normal animals. That it readily produces colic or diarrhœa, however, militates against its use in diabetes. F. O. H.

**Post-insulinic blood-sugar levels.** I. F. FERNÁNDEZ and J. M. CLAVERA (Anal. Fis. Quim., 1933, 31, 364—369).—In 22 patients, contrary to Burger, there was no relation between initial post-insulinic hypoglycæmia and functional state of the liver. R. K. C.

**Virus obtained from influenza patients.** W. SMITH, C. H. ANDREWS, and P. P. LAIDLAW (*Lancet*, 1933, 125, 66—68).—Filtrates of throat washings from influenza patients produce a disease (I) in ferrets. Human sera, especially those from influenza convalescents, contain antibodies which neutralise the virus of (I). Swine influenza virus produces in ferrets a disease indistinguishable from (I), and the pig and human viruses have close antigenic relationships.

L. S. T.

**Low excretion of nitrogen and rise of basal metabolic rate in hypertonus.** A. HELD (*Z. ges. exp. Med.*, 1933, 87, 578—584).—In patients (I) with high blood-pressure (II) who are pale, the urinary output of N on a diet containing min. amounts of protein is > in patients who are florid. In (I) the basal metabolism was high, especially when the high (II) was fixed. X-Ray irradiation of rabbits leads to an increase of protein decomp. products in the blood and a rise of (II). The output of creatinine accounts for a large part of the urinary N but does not run parallel with it.

NUTR. ABS. (m)

**Relation of liver function to the amount of guanidine and sugar in the blood.** N. ARAKAWA (*Nagoya J. Med. Sci.*, 1932, 6, 96—99).—Blood-sugar was inversely, and -guanidine directly, proportional to the severity of hepatic injury in rabbits.

CH. ABS.

**Hæmorrhagic tendency in jaundice.** Blood-fibrin, sedimentation rate, coagulation time, and other blood factors. C. F. BURKE and J. F. WEIR (*J. Lab. Clin. Med.*, 1933, 18, 657—668).—Blood-fibrin and -protein, serum viscosity, and sedimentation rate of erythrocytes are normal in obstructive or intrahepatic jaundice. Increase in serum-bilirubin and prolongation of coagulation time are the best criteria of hæmorrhagic tendency.

CH. ABS.

**Determination of amino-nitrogen in endocrine and joint disease.** G. PERÉMY and K. FELEDY (*Magyar Orvosi Arch.*, 1932, 33, 296—302; *Chem. Zentr.*, 1932, ii, 3907).—Blood- and urinary  $\text{NH}_2\text{-N}$  were determined fasting and after a meat meal.

A. A. E.

**Quinoline derivatives for the treatment of malaria.** O. MAGIDSON, I. STRUKOV, N. DELEKTORSKAYA, and I. LIPOVICH (*Khim. Farm. Prom.*, 1933, 9—14).—Of the derivatives synthesised 6-methoxy-8-N-dimethylaminopropylquinoline was the most efficient.

CH. ABS.

**Changes in distribution ratio of constituents of blood and cerebrospinal fluid in meningitis.** S. J. KOPETZKY and E. H. FISHBERG (*J. Lab. Clin. Med.*, 1933, 18, 796—801).—Cerebrospinal fluid (I)-lactic acid is increased; (I)-Cl: blood-plasma (II)-Cl, and (I)- $\text{CO}_3$ : (II)- $\text{CO}_3$  are decreased.

CH. ABS.

**Irradiation treatment in mongolism; effect on the cholesterol of blood-serum.** E. BINGENHEIMER (*Z. ges. exp. Med.*, 1933, 87, 592—612).—The blood-cholesterol (I) has a higher val. in warm than in cold-blooded animals. In man it is lowest at birth, rises quickly until the third month, and then gradually reaches the adult val. at puberty; it is lower and shows a slower rise in the premature than

in the full-term infant. In normal children the val. varies between 120 and 170 mg. per 100 c.c., whilst in children with mongolism it is much less, the lowest normal (120) figure being reached in the tenth year. Children with other types of mental deficiency have normal (I) val. X-Ray irradiation of the skull or trunk of mongols leads to an increase in (I) and perhaps to a decrease in susceptibility to infection, but otherwise causes no improvement clinically. The typical (I) curve found after irradiation of the skull suggests that the pituitary may influence cholesterol metabolism.

NUTR. ABS. (m)

**Experimental muscle degeneration.** IV. Carbohydrate metabolism in muscle repair. V. Nitrogen metabolism of degenerated muscle in acute injury and repair. D. K. FISHBACK and H. R. FISHBACK (*J. Lab. Clin. Med.*, 1933, 18, 777—781, 781—788).—IV. The lactic acid (I) content of striated muscle in rabbits increases rapidly during acute mol. degeneration, and diminishes after 4 hr. Glycogen (II) decreases during 48 hr. and then tends to become normal. There is no const. ratio between the changes in (I) and (II). A decrease in the phosphocreatine content and a retarded increase in inorg. P are observed throughout degeneration and repair.

V. The decrease in total N in mol. degeneration is approx. proportional to the degree of cedema. Diminished non-protein- and  $\text{NH}_2\text{-N}$  increase rapidly during repair. Variations in urea-N are not const.

CH. ABS.

**Urine- and serum-proteins in nephritis.** E. M. WIDDOWSON (*Biochem. J.*, 1933, 27, 1321—1331).—Determination of the N distribution, optical rotation and racemisation, osmotic pressure, and sp. refraction of the urine- and serum-albumin and -globulin of nephritics shows no difference between the proteins from the two sources.

H. D.

**Cystine and nephrotoxicity.** M. E. BELL (*Biochem. J.*, 1933, 27, 1267—1270).—The feeding of young rats with synthetic diets containing 1—2% of free cystine failed to produce acute nephrosis (cf. A., 1929, 720). The condition is probably due to an infection which is partly dependent on the altered oxidation-reduction potential in the intestines.

F. O. H.

**Urea secretion.** VIII. Effects on urea clearance of changes in protein and salt contents of the diet. C. L. COPE (*J. Clin. Invest.*, 1933, 12, 567—572).—NaCl, or increase in protein intake from 75 to 120 g., had little effect on urea clearance in normal or nephritic patients. Depressed clearance followed a decrease in protein intake to 40 g.

CH. ABS.

**Biochemical changes in the blood in intestinal obliteration.** J. GARCÍA-BLANCO and F. COMESAÑA (*Anal. Fis. Quim.*, 1933, 31, 394—398).—In rabbits blood-sugar increased very rapidly after ligation of the gut below the pylorus (I), but changed little after ligation below the duodenum (II) or at the rectum. The non-protein-N increased rapidly after ligation below (I) or (II), and less rapidly after rectal ligation.

R. K. C.

**Ætiology of pellagra.** H. CHICK (*Lancet*, 1933, 125, 341—346).—A discussion. The hypothesis that

pellagra is caused by a toxic substance derived from maize and can be corrected by foodstuffs such as meat, milk, eggs, and green vegetables, or perhaps by sufficient vitamin- $B_2$ , is advanced. L. S. T.

**Plasma-protein changes and suspension stability of the blood in lobar pneumonia.** J. K. MOEN and H. A. REIMANN (J. Clin. Invest., 1933, 12, 589—598).—Plasma-total protein is usually decreased during the febrile period; the fibrinogen and globulin fractions are increased. CH. ABS.

**Excretion of sodium thiosulphate during uncomplicated human pregnancy after intravenous administration in large amounts.** A. BOLLIGER and M. S. S. ERLAM (J. Obstet. Gynaecol., 1933, 40, 289—298).—The % excretion was subnormal in the later months of pregnancy and during the puerperium. CH. ABS.

**Effect of pregnancy and lactation on blood-serum of cattle, with remarks on milk fever.** W. FREI and M. DEMMEL (Schweiz. Arch. Tierheilk., 1932, 11, 525—538).—A small decrease in serum-glucose was observed during pregnancy (86—91 mg.) as compared with oestrus and interoestrus (99—110 mg. per 100 c.c.). The  $n$  of the serum was not significantly different in lactating cows as compared with non-lactating animals. The composition of the blood is not materially altered in normal cows during lactation. Milk fever, associated with hypocalcaemia or hypoglycaemia, arises more from disturbances of the endocrine and vegetative nervous system associated with parturition than from the onset of lactation. NUTR. ABS. (b)

**Relation between pancreas and eclampsia. Significance of diastase in normal and pathological pregnancy, birth, and confinement.** W. SPITZER (Arch. Gynaecol., 1932, 150, 681—685; Chem. Zentr., 1932, ii, 3899).—No increase in the diastase content of blood or urine was detected during normal pregnancy, parturition, and confinement. In many pathological cases the diastase val. is raised. L. S. T.

**Nitrogen metabolism in pituitary insufficiency.** B. BRAIER (Anal. farm. bioquim., 1932, 3, 61—76, 97—106).—Normal dogs eliminate 0.24 and hypophysectomised 0.14 g. N per kg. per day. Equilibrium through gradual elimination of N from the diet is reached at 0.30 and 0.20 g., respectively. Fasting dogs eliminate 0.36 and 0.25 g. N per day. Vals. for creatinine elimination are also given. CH. ABS.

**Magnesium rickets.** G. M. ZU HÖRSTE (Klin. Woch., 1932, 11, 1796; Chem. Zentr., 1932, ii, 3910).—Addition of  $MgCO_3$  to a non-rachitic diet causes a P-deficiency rachitis in rats and rabbits, as does an excess of  $CaCO_3$ . L. S. T.

**Factors involved in malformation of the bones of growing chickens. I. Value of egg-yolk and chicken fat.** E. W. HENDERSON (Poultry Sci., 1933, 12, 91—96).—The type of rickets not cured by these additions probably results from high dietary Ca and/or P. CH. ABS.

**Trypanosomiasis and avitaminosis. I. Rickets and *T. lewisi*. II. Scurvy and *T. brucei*.** B. BORGHI (Atti R. Accad. Lincei, 1933,

[vi], 17, 574—577, 665—671).—I. The symptoms of rickets in rats are greatly aggravated by infection with *T. lewisi*, death being hastened. The splenomegalic effect of *T. lewisi* is not shown.

II. Scurvy is aggravated in guinea-pigs by infection with *T. brucei*, whether applied at early or late stages of the avitaminosis, but death is not hastened. The splenomegalia produced by the trypanosome in normal animals does not appear. R. N. C.

**Proteolytic enzymes in the organs of scorbutic guinea-pigs.** L. POZZI (Atti R. Accad. Lincei, 1933, [vi], 17, 583—586).—Extracts of the liver and kidneys of scorbutic guinea-pigs showed a catheptic activity (I) > those of normal animals; the activity of the liver extract was > that of the kidney extract, which is the reverse of the normal condition. Extracts from scorbutic animals cured with adrenal cortex extract showed a decrease in (I). The dipeptidase activity of such extracts was unaltered in scurvy. R. N. C.

**Oxygen consumption of scorbutic and normal guinea-pigs.** N. SÖDERSTRÖM and N. TÖRNBLÖM (Upsala Läkareförenings Förhandl., 1932, 38, 1—6).—Five out of six guinea-pigs on a scorbutic diet showed a lower  $O_2$  consumption than controls on an antiscorbutic diet. NUTR. ABS. (b)

**Seborrhoea in the rat caused by feeding with whale oil.** E. SOMEKAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 21, 149—157).—Rats fed on a diet containing 15% of sperm-head oil or arctic-sperm oil developed seborrhoea (I), growth was retarded, and death occurred in a few weeks. Additions of yeast prolonged the life of the animals, but (I) was even more conspicuous. The saponification products of the whale oil were toxic, but caused no (I). Synthetic oleyl oleate produced (I); oleyl palmitate and cetyl oleate were without effect. A. L.

**Treatment of parathyroid tetany with calcium chloride, parathyroid extract, and vitamin-D.** P. SCHULTZER (Acta med. scand., 1932, 79, 11—22; Chem. Zentr., 1933, i, 797).—The fallen Ca-level in parathyroid tetany was raised by administration of parathyroid hormone, vitamin-D, and  $CaCl_2$ . L. S. T.

**Behaviour of the anterior pituitary hormone in a case of teratoma testis.** R. S. FERGUSON (Amer. J. Roentgenol., 1933, 29, 443—449).—In testicular teratoma the hormone is excreted in the urine. Irradiation of the tumour with X- or  $\gamma$ -rays diminishes the output. CH. ABS.

**Blood in tuberculosis.** D. M. TELANG (J. Univ. Bombay, 1933, 1, No. 5, 181—201).—The sedimentation rate (I) of the red blood-corpuscles is faster in acute stages of osteomyelitis, pneumonia, amebic dysentery, and malaria than in all tuberculous conditions (II) and the rate in (II) is > that in normal health. (I) is faster in pulmonary and bone tuberculosis than in glandular or intestinal types, the rate increasing as the disease progresses and *vice versa*. In pulmonary tuberculosis systolic and diastolic blood-pressure and blood-Ca are lower than normal, whilst blood-sugar, -urea, and -Cl show no deviation from normal. A. L.

**Accumulation of iron in tuberculous areas.** III. V. MENKIN (Amer. J. Med. Sci., 1933, 185, 40—49).—Repeated intravenous injection of  $\text{FeCl}_3$  is followed by accumulation of Fe in caseous areas of tubercles. CH. ABS.

**Gastric pepsin.** II. Secretion of pepsin in cases of duodenal ulcer and pseudo-ulcer. F. R. VANSANT, A. E. OSTERBERG, W. C. ALVAREZ, and A. B. RIVERS (J. Clin. Invest., 1933, 12, 557—565).—Pepsin is increased in peptic ulcer; high vals. are also found in certain nervous patients who present some of the symptoms of ulcer. CH. ABS.

**Protein content of normal and pathological serum in cattle.** M. DEMMEL (Münch. tierärztl. Woch., 1932, 83, 457—460).—The  $n$  of serum is taken as a measure of its protein (I) content, calculations being made from Reiss tables on the assumption of 0.00277 as index component for the non-protein constituents and 0.00172 for each 1% of (I). Comparative figures are thus provided for healthy and diseased cattle. Chronic infections and chronic organic disorders cause a rise in (I). In diseases associated with nutritional disturbance and poor condition, and in inflammatory conditions with oedema, there is a distinct decrease in (I). In general (I) is raised in cases of sterility. NUTR. ABS. (b)

**Some chemical aspects of life.** (Sir) F. G. HOPKINS (Nature, 1933, 132, 381—394).—Presidential address to the British Association, 1933. L. S. T.

**Intracellular oxidation-reduction studies.** V. Comparison of intact and cytolysed starfish eggs by the immersion method. R. CHAMBERS, L. V. BECK, and D. E. GREEN (J. Exp. Biol., 1933, 10, 142—152).—The aerobic apparent oxidation-reduction potential for intact and cytolysed starfish eggs at  $p_{\text{H}}$  6.8—7.0 is approx. —0.06 volt; the anaerobic val. is < 0.167 volt. Cytolysis results in a lowered reduction rate.  $\text{Et}_2\text{O}$  and phenylurethane do not affect the reduction rate of intact eggs;  $\text{EtOH}$  and  $\text{Et}_2\text{O}$  inhibit that of cytolysed eggs. KCN has no effect;  $\text{HgCl}_2$  destroys the reducing power.  $\text{PbCO}_3$  retards the reducing power of intact eggs and destroys that of cytolysed eggs. CH. ABS.

**Manometric analysis of the metabolism in avian ontogenesis.** III. Respiratory quotient of the yolk-sac and allantois during the last two weeks of development. J. NEEDHAM (Proc. Roy. Soc., 1933, B, 113, 429—459; cf. this vol., 87).—The R.Q. of the allantois (I) falls from 0.95 on the fifth to 0.82 on the twentieth day of development; that of the yolk-sac (II) from 0.9 on the second to 0.6 on the seventh, remaining at 0.56 until the fourteenth day. The vals. for (I) are reduced by 0.1 if glucose is absent from the medium. The low vals. for (II) at mid-development are not due to (a) tissue damage, (b) conversion of fat into carbohydrate, (c) desaturation of fatty acids, or (d) ketogenic processes, but probably to the low R.Q. of protein catabolism ending in uric acid and to synthetic use of C and  $\text{O}_2$ . During the last week of development respiration of (II) is irreversibly inhibited by  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ , but is unaffected by quinine or atoxyl. A. C.

**Metabolism of tissues.** H. LASER (Biochem. Z., 1933, 264, 72—86; cf. A., 1932, 1058; Lipmann, this vol., 741).—The metabolism of hen fibroblast *in vitro* is similar to that of surviving tumour tissue. Extensive glycolysis takes place under anaerobic conditions (I) and also under aerobic conditions when respiration is strong and unaffected. Embryonic connective (II) and epithelial tissue and leucocytes live and grow for several days under (I). The increase in wt. of (II) in 4—6 days under (I) is the same as in  $\text{O}_2$ .

W. McC.

**Physiology of normal and Frizzle fowl: basal metabolism.** F. G. BENEDICT, W. LANDAUER, and E. L. FOX (Storrs Agric. Exp. Stat. Bull., No. 177, April 1932).—In fowls, parts of the body without feathers lose heat as much as do the feathered areas. Observations of the course of the R.Q. and the total metabolism immediately following the ingestion of food indicate that the fowl must fast 48 hr. before the fat quotient is reached and its metabolism is basal. When the fat quotient obtains, the total metabolism reaches a const. level for at least 24 hr. more of fasting. The heat production of normal fasting hens (between 15 and 28°) averages 866 g.-cal. per sq. m. body-surface ( $K=10$ ) per 24 hr. and that of normal cocks 838 g.-cal. At night metabolism is much lower. The heat production of normal moulting hens at 28° is 844 g.-cal. and at 17—19° 1291—1611 g.-cal. In the Frizzle fowl (a type characterised by very scanty feathering), even at 28° fasting heat production is > in the normal, and nearly in proportion to the defective nature of the plumage. At about 17° the Frizzles have much greater heat production (twice normal). Metabolism is lower at night, and night measurements only are valid in determinations of basal metabolism in the fowl. The heat lost in the form of  $\text{H}_2\text{O}$  vapour is 49% in the normal and 17% in the Frizzle. NUTR. ABS. (m)

**$\alpha$ -Oxidation of fatty acids.** H. FASOLD (Klin. Woch., 1932, 11, 1151; Chem. Zentr., 1932, ii, 3912).—Ingestion of  $\text{NaHCO}_3$  increases, and of free org. acids decreases, urinary org. acids. A. A. E.

**Specificity of cholesterol resorption and its biological significance.** R. SCHOENHEIMER (Klin. Woch., 1932, 11, 1793—1796; Chem. Zentr., 1932, ii, 3913).—Cholesterol, but not sitosterol, is resorbed by rabbits. A. A. E.

**Liver-lipins after splenectomy.** S. MARINO (Arch. Farm. sperim., 1933, 56, 327—342).—Following splenectomy in dogs the level of the lipins of the liver fluctuates considerably; this is most marked with the total sterols and the phosphorylated fatty acids. Thus the liver, in common with other organs (cf. this vol., 304, 739), can partly replace the spleen, the function of which in fat metabolism is discussed. F. O. H.

**Lipin metabolism.** V. Blood-lipase of Carnivora and Herbivora during experimental lipaemia. VI. Effect of cholesterol on secretion of pepsin. I. REMESOV, N. TAVASTSTYERNA, and D. MATROSSOVITSCH (Z. ges. exp. Med., 1933, 87, 613—622, 623—634).—V. Hypercholesterolemia in dogs leads to a reduction of blood-lipase activity (I) due to adsorption of the lipase by the colloidal

cholesterol (II) particles, the ester being more powerful than free (II). Mn sol and to a greater extent Ni sol partly prevent the reduction of (I), whilst addition of Ca oleate has little effect. Lecithin, which *in vitro* has no action on blood-lipase, reduces its activity when present in excess in the blood-stream. Injection of insulin leads to an increase in (I) which reaches its max. when the blood-sugar and (II) are at their lowest. Injection of adrenaline or nicotine reduces (I), an effect possibly only partly due to increase of (II). (II) is an important regulator of enzyme action in the body owing to its property of adsorbing enzymes.

VI. Investigation of peptic activity of the gastric juice obtained from dogs with a gastric fistula shows that max. peptic activity occurs just before the stomach is emptied; this has the purpose of clearing the stomach of undigested food. Oral administration of (II) with meat broth reduces peptic activity; the effect is more marked when sunflower oil is given with (II). When a colloidal solution of (II) in bouillon is given, peptic activity increases. The toxic effect of high (II) feeding may be primarily due to its action on alimentary enzymes. NUTR. ABS. (m)

Induction substance in the development of the embryo. F. G. FISCHER and E. WEHMEIER (Naturwiss., 1933, 21, 518).—The substance which in amphibian embryos controls the induction of the medulla plate is probably glycogen. W. O. K.

Glycogen metabolism of the organisation centre in amphibian gastrula. I. C. P. RAVEN (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 566—569).—The decrease in glycogen content of invaginating cells during gastrulation of the axolotl embryo is a direct result of the involution process. A. C.

Site of formation of the principal glycogen reserve on ingestion of carbohydrate. I. S. SCHWARTZ (Arch. sci. biol., U.S.S.R., 1932, 32, 68—71).—In dogs, glycogen is synthesised largely in the liver and to only a small extent in the intestinal wall. CH. ABS.

Pentose metabolism. III. Absorption of *l*-rhamnose and formation of glycogen in the rat. A. K. SILBERMAN and H. B. LEWIS (J. Biol. Chem., 1933, 101, 741—751).—The absorption coeffs. of *l*-rhamnose (I) administered orally from the gastrointestinal tract of the rat were found to be 41, 20, and 12 mg. per 100 g. of rat per hr. for 1, 2, and 3 hr. absorption periods, respectively. As these results indicate that no significant absorption took place after the first hr., a mixture of glucose and (I) was fed with a view to find if (I) had a toxic effect. The absorption of glucose, however, was normal. The absorption of (I) fed to phloridzinised animals decreased to about 50% of the above vals., and in no case after (I)-ingestion was glycogen deposition apparent in the liver. A. L.

Fate of pentose in the healthy and the diabetic system. E. GRAFE (Klin. Woch., 1932, 11, 1742—1744; Chem. Zentr., 1933, i, 805).—The effect of *l*-xylose (I), especially, on dogs and diabetic men, has been investigated. 20—60% of added pentose appears in the urine without distinction between

men and dogs or normal and diabetic cases. Diuresis is markedly increased. Glucose never appears or increases in the urine. Glucose and pentose metabolism proceed independently. Blood-sugar always increases after addition of (I), depending mainly on the dose and conditioned only by excess of pentose. L. S. T.

Diuretic action and elimination of intravenously injected pentoses. P. THOMAS and A. GRADINESCU (Compt. rend. Soc. Biol., 1933, 112, 415—416).—In dogs with catheterised ureters, injection of pentose (0.4 g. per kg. body-wt.) first results in a transitory increase in arterial blood-pressure. Diuresis commences as soon as the blood pressure rises by 10 mm. Hg. Xylose (I) has a greater effect than arabinose (II). The urine contains 3—5% of sugar in 15 min. and up to 8% in 1 hr. (II) is eliminated more quickly than (I). NUTR. ABS. (m)

Relation of lactic acid and alanine to glycogen formation. T. H. HODGSON (Biochem. J., 1933, 27, 1158—1162).—Young rabbits form liver-glycogen from Na *dl*-lactate injections, but not from *dl*-alanine. H. G. R.

Lactic acid of the blood during experimental glycaemia due to ingestion of glucose. J. A. COLLAZO, J. PUYAL, and I. TORRES (Anal. Fis. Quim., 1933, 31, 454—457).—In 20 healthy, fasting, human subjects given 50 g. of glucose the rise and fall of the lactic acid and glucose of the blood in the next 2 hr. was parallel. R. K. C.

Intermediate products and the last stages of carbohydrate breakdown in the metabolism of muscle and in alcoholic fermentation. O. MEYERHOF (Nature, 1933, 132, 337—340, 373—375).—A lecture. L. S. T.

Absorption of glucose by rectum. W. S. COLLENS and L. C. BOAS (Arch. Int. Med., 1933, 52, 317—324).—When glucose, dissolved in distilled H<sub>2</sub>O, is administered, per rectum, to normals or diabetics, resorption (up to 90% in 2 hr.) takes place and a rise in blood-sugar usually occurs. W. O. K.

Absorption of glucose from intestinal loops. I. S. RAYDIN, C. G. JOHNSTON, and P. MORRISON (Amer. J. Med. Sci., 1933, 185, 303). CH. ABS.

Metabolism of amino-acids in animal tissues. H. A. KREBS (Klin. Woch., 1932, 11, 1744—1748; Chem. Zentr., 1933, i, 806—807).—Large amounts of NH<sub>2</sub>-acids (I) obtained by keeping tissues of man, dogs, rats, and cats in physiological saline in presence of O<sub>2</sub> at 37.5° are decomposed under suitable conditions with formation of NH<sub>3</sub>. Deamination occurs mainly in the kidneys, and these (I) are the chief source of urine-NH<sub>3</sub>. Keto-acids, which result from deamination of the natural  $\alpha$ -(I), have been isolated. Oxidative deamination is practically the only way in which deamination of (I) occurs in animal organisms. L. S. T.

Growth-promoting properties of homocystine and proof of the structure of homocystine. V. DU VIGNEAUD, H. M. DYER, and J. HARMON (J. Biol. Chem., 1933, 101, 719—726).—The structure of homocystine (I) suggested by Butz and Vigneaud (this vol., 151) is proved by its conversion into meth-

ionine (II) by reduction in liquid  $\text{NH}_3$  with Na and subsequent methylation. Feeding experiments in which additions of (I) were made to a basal diet containing caseinogen 5.0, dextrin 38.0, sucrose 15.0, lard 19.0, cod-liver oil 5.0, salt mixture 4.0, agar 2.0, and milk vitamin concentrate 12.0, showed that (I) could support the growth of rats in lieu of (II).

A. L.

**Cystine and wool production.** C. REMINGTON, J. G. BEKKER, and J. KELLERMAN (*Nature*, 1933, **132**, 63—64).—A reply to criticism (cf. A., 1932, 646).

L. S. T.

**Metabolism of sulphur. XX. Rate of absorption of *dl*-methionine from the gastrointestinal tract of the rat.** B. W. CHASE and H. B. LEWIS (*J. Biol. Chem.*, 1933, **101**, 735—740).—The absorption coeff. of *dl*-methionine (I) from the gastro-intestinal tract of the rat was 53 mg. per hr. per 100 g. of rat, slightly > the rate observed for cystine by other workers. No deposition of glycogen in the liver was observed after absorption of (I) for 3 hr. The urines of rats receiving (I) gave the cyanide-nitroprusside test for the S-S linking.

A. L.

**Absorption of certain sulphur compounds from intestinal loops of dogs.** J. C. ANDREWS and C. G. JOHNSTON (*J. Biol. Chem.*, 1933, **101**, 635—640).—Relative rates of absorption from isolated jejunal loops (I) of the dog were: cysteic acid > cysteine > *dl*-cystine > *l*-cystine and  $\text{Na}_2\text{SO}_4$ . No reduction of cystine occurred during 4 hr. in (I).

H. G. R.

**Relation of thiol concentration to size inheritance in the rabbit.** P. W. GREGORY and H. GOSS (*Amer. Naturalist*, 1933, **67**, 180—185).—Average glutathione concns. (mg. per 100 g.) were 43.78 (large race) or 30.8 (small race).

CH. ABS.

**Energy of urea synthesis. II. Effect of varying hydrogen-ion concentration with different metabolites.** H. BORSOOK and G. KEIGHLEY (*Proc. Nat. Acad. Sci.*, 1933, **19**, 720—725).—1 mol. of  $\text{O}_2$  is required for every mol. of urea synthesised. In absence of  $\text{NH}_3$ , the rate of respiration, with lactate or succinate as metabolite, was > when no metabolite or glucose was added.

H. G. R.

**Uric acid excretion on diet low in purines.** J. MELKA (*Pfuger's Archiv.*, 1933, **232**, 61—65).—The summer and winter excretion of uric acid (I) was determined when the subject was on a diet containing 87 mg. of purine substances daily. There was a reduction of (I) within 2 days of the commencement of the diet; 6 weeks later the output increased. It is concluded that man can synthesise nucleoprotein over long periods. The output of (I) was relatively higher in winter.

NUTR. ABS. (b)

**Variations in the plasma- and blood-potassium during alimentation and fasting.** R. GERSCHMAN and A. D. MARENZI (*Anal. farm. bioquim.*, 1932, **3**, 128—133).—For dogs, starvation vals. are approx. const., whilst on a meat diet they vary considerably from day to day.

CH. ABS.

**Fasting and specific dynamic action [of meat proteins] in dogs with lesion of the tuber cinereum**

**or in hypophysectomised dogs.** P. MAZZOCCO (*Rev. soc. argentina biol.*, 1932, **8**, 621—627).

CH. ABS.

**Changes in body composition with various diets and with starvation.** DITTMAR (*Arch. exp. Path. Pharm.*, 1933, **171**, 496—518).—With starved rats the ratio body-wt./organ-wt. varies considerably. Thus the liver suffers a relatively greater loss in wt., whilst the heart decreases proportionately with the body. With carbohydrate-fed rats, starvation for 1—2 days produces a rapid diminution in liver-glycogen (I) and -sugar formation, an increased amount of fat and protein being used for production of sugar. Fat deposition also occurs, a process which in phloridzinised animals is therefore due to rapid deprivation of (I). With 3 days' starvation, storage of (I) and decomp. of fats are increased. The periodic variations in (I) and liver-fat occur also with rats fed on a fat and protein diet. Prolonged starvation diminishes the fat content of all the organs and of the muscle.

F. O. H.

**Bacteria as food for vertebrates.** V. BURKE (*Science*, 1933, **78**, 194—195).—Common  $\text{H}_2\text{O}$  bacteria contain all the food factors, including vitamins, necessary for normal development of the larval stage of *Rana pretiosa*. Bacteria also serve as direct and indirect factors in determining the food supply of higher animals.

L. S. T.

**Detoxication of phenylacetic acid.** A. M. AMBROSE, F. W. POWER, and C. P. SHERWIN (*J. Biol. Chem.*, 1933, **101**, 669—675).—About 95% is detoxicated with glutamine and about 5% with glycuronic acid; on continued ingestion the ratio is shifted in favour of the latter.

H. G. R.

**Growth of pigs. I. Calcium and phosphorus metabolism in young growing pigs.** L. S. SPILDO (*Rep. Res. Lab. Roy. Vet. Agric. Coll., Copenhagen*, 1933, No. 151).—Pigs 6—8 weeks old were fed on a basal ration of barley, maize, soya-bean meal, and dry or skimmed milk. With a high  $\text{P}_2\text{O}_5$ :CaO ratio (above 2.5) blood-Ca fell and -P rose, change in composition of the blood always being the first sign of an abnormal ration. The skeleton showed osteoporotic changes ("osteitis fibrosa") and tetany occurred. With a low  $\text{P}_2\text{O}_5$ :CaO ratio (about 0.4) reverse changes in the blood were noted and osteoporosis with rickets developed. Tetany did not occur. The Ca:P ratio appeared to be the most important factor governing metabolism, but if the total CaO intake fell below 0.2% of the dry matter of the ration, normal growth and composition of the blood were not maintained even with a good ratio of Ca:P. The utilisation of CaO in the ration was about 60% and that of  $\text{P}_2\text{O}_5$  50%. For 100 g. growth, 1.4 g. CaO and 2.6 g.  $\text{P}_2\text{O}_5$  were required. Addition of inorg. salts to a ration of cereals and skimmed milk to make the  $\text{P}_2\text{O}_5$ :CaO ratio about 1.6 and the Ca intake about 4.6 g. per kg. of dry matter gave excellent results. Without vitamin additions and without direct light the pigs remained normal. Administration of vitamin-D with a high  $\text{P}_2\text{O}_5$ :Ca ratio improved the absorption of Ca, but did not greatly affect the composition of the blood; with a low

$P_2O_5$ : Ca diet, it was definitely unfavourable. Addition of vitamin-A had no definite effect. Light had a beneficial action, but could not altogether counteract the effect of a badly balanced ration.

NUTR. ABS. (b)

Calcium and phosphorus metabolism of normal pre-school children. I. T. PORTER-LEVIN (J. Amer. Dietet. Assoc., 1933, 8, 482—488).—The increase in mineral retention from the use of irradiated cereals was within experimental error. CH. ABS.

Toxicity of methyl alcohol. I. Comparison with formaldehyde and formic acid on the isolated frog's heart. II. Comparison with formaldehyde and formic acid on the posterior vessels of the frog. U. SAMMARTINO (Arch. Farm. sperim., 1933, 56, 311—319, 320—326).—I. The toxicities of  $HCO_2H$ ,  $CH_2O$ , and  $MeOH$  as shown by the isolated frog's heart are in the mol. ratio of 1430 : 187 : 1.

II. All three substances in extreme dilution (1 : 10<sup>6</sup>) produce vasodilation, whilst with larger doses  $HCO_2H$  and  $CH_2O$ , but not  $MeOH$ , produce vasoconstriction.

F. O. H.

Toxicity of methyl alcohol. III. Minimum delayed [lethal] intravenous dose of methyl alcohol, formaldehyde, and formic acid. IV. Critical review; mode of action of methyl alcohol. U. SAMMARTINO (Arch. Farm. sperim., 1933, 56, 351—363, 364—371; cf. preceding abstract).—III. In rabbits the min. lethal doses and times of death after intravenous injection are:  $MeOH$ , 4.2 g., 104 hr.;  $CH_2O$ , 0.7 g., 8 hr.;  $HCO_2H$ , 0.24 g., 21 hr. The paralysis caused by  $MeOH$  is preceded by convulsions, whilst  $CH_2O$  and  $HCO_2H$  are consistently depressant.  $MeOH$  alone causes ocular lesions.

IV. Experiments on the isolated frog's heart, on the posterior venous system of the frog, and on rabbits, indicate that the toxicity of  $MeOH$  is due to the alcohol itself and not to its oxidation products.

R. K. C.

Epivan: an intravenous anaesthetic. R. JARMAN and A. L. ABEL (Lancet, 1933, 125, 18—20).—Epivan, the Na salt of *CC-cyclohexenylmethyl-N-methylbarbituric acid*, produces all stages of general anaesthesia in a few sec. when intravenously injected into human beings.

L. S. T.

Determination of toxicity constants and activity of some barbituric derivatives. L. LAUNOY (J. physiol. path. gén., 1932, 30, 364—378).

CH. ABS.

Habituation and accumulation phenomena. II. Phanodorm, luminal, and prominal. M. R. BONSMANN (Arch. exp. Path. Pharm., 1933, 171, 612—618).—Daily administration of phanodorm (I) to dogs produces a continuous inhibition of the secretion of urine, whilst with prominal (II) or luminal (III) the inhibition is only temporary. Preliminary treatment with (II) inhibits the diminution of urine due to (III) and *vice versa*, whilst that due to (I) is inhibited by (II) or (III), but not *vice versa*. Dogs become habituated to the narcotic effects of (I) and (II). Whilst the inhibition of diuresis rapidly follows administration in each case,

the onset of the effects on the nervous system varies with the three narcotics. F. O. H.

Narcotic potency in paraldehyde series. P. K. KNOEFEL (J. Pharm. Exp. Ther., 1933, 48, 488—491).—Paraldehydes produced by the polymerisation of  $CH_2O$ ,  $EtCHO$ ,  $Pr^cCHO$ , and  $Pr^bCHO$  are unsuitable as narcotics. H. D.

Influence of iodoacetic acid on the blood-sugar level. J. T. IRVING (Nature, 1933, 132, 315).—Perfusion experiments with rabbit's legs show that Na iodoacetate (1 in 2000 to 1 in 6000, calc. as free acid) impairs the utilisation of blood-sugar both in presence and absence of insulin. L. S. T.

Vesicant action of halogenated sulphides. W. R. KIRNER (J. Amer. Chem. Soc., 1933, 55, 3501—3502).—Dawson's conclusion (this vol., 709) is not new (cf. A., 1928, 1214). R. S. C.

Vesicant action of chloroalkyl sulphides. T. P. DAWSON (J. Amer. Chem. Soc., 1933, 55, 3506).—Kirner's priority (cf. preceding abstract) is admitted. R. S. C.

Action of furfuraldehyde on respiratory and blood gas. I. HAYASHI, Z. KANDA, T. SATO, and I. MATSUMIYA (Nagoya J. Med. Sci., 1932, 6, 141—149).—In rabbits the  $CO_2$  in the expired air was decreased and the  $O_2$  increased. The  $CO_2$ -combining power of the blood was decreased. CH. ABS.

Inhibition of esterification by phloridzin. E. LUNDSGAARD (Biochem. Z., 1933, 264, 209—220; cf. Wilbrandt and Laszt, this vol., 630).—Phloridzin (I) in concn. of 0.005—0.02M inhibits phosphorylation (II), dephosphorylation (III), and production of lactic acid from glucose or glycogen. Since (I) likewise inhibits glycolysis in brain, the views of Ashford and Holmes (A., 1929, 1124) receive no support. In rabbits receiving injections of (I) in doses required to result in diabetes the concn. of (I) necessary for causing inhibition of (II) and (III) is reached in the kidneys only. The diabetes caused by (I) which acts by inhibiting the (II) believed to accompany reabsorption of glucose in the tubuli of the kidneys is probably a purely renal disease. W. McC.

Effect of phloridzin on the absorption of glucose. E. LUNDSGAARD (Biochem. Z., 1933, 264, 221—223).—Phloridzin (0.02M), injected directly into the intestine of the rabbit or cat, specifically inhibits resorption of glucose, but does not affect resorption of  $NH_2$ -acids (glycine, glutamic acid). W. McC.

Biological determination and standardisation of some cardiac glucosides. Ouabain, digitalin, scillaren, and cymar. J. LÉVY and R. CAHEN (Bull. Sci. pharmacol., 1932, 38, 23—37, 85—108; Chem. Zentr., 1932, ii, 3926).—Min. lethal doses for dogs are recorded. Ouabain, international standard, is the cryst. glucoside of *Strophanthus gratus*, 19.94%  $H_2O$ ,  $\alpha_D$  —30.6° for the anhyd. substance. L. S. T.

Cumulative poisoning by squill derivatives and ouabain. E. W. WALLACE and H. B. VAN DYKE (J. Pharm. Exp. Ther., 1933, 48, 430—444).—In the dog scillonin (I) is cumulatively < half as potent as ouabain (II), and <  $\frac{1}{3}$  as toxic as scillaren-A and -B,

scillicin, and digitalis. The lethal doses of (I) and (II) are approx. the same for mammals, whereas in the frog (I) was the least toxic. H. D.

**Pharmacological action of peimine and peiminine.** K. K. CHEN, A. L. CHEN, and T. Q. CHOU (J. Amer. Pharm. Assoc., 1933, 22, 638—641; cf. A., 1932, 178).—Both peimine and peiminine when perfused through the inferior vena cava in frogs produce the same effect and in the same degree, i.e. decrease in heart rate, complete A-V block, and periodicity. They cause a fall of blood-pressure (cats) and inhibit the activity of rabbits' isolated intestine (concn. 1:10,000). There is a moderate hyperglycæmic action in rabbits. The min. lethal dose to white mice is 9 mg. per kg. E. H. S.

**Relation between tetanus symptoms and the calcium and inorganic phosphorus content in the serum of parathyroidectomised dogs.** A. BEZNAK (Magyar Orvosi Arch., 1932, 33, 253—262; Chem. Zentr., 1932, ii, 3907).—Strychnine convulsions raise the inorg. P of blood-serum in normal and in parathyroidectomised dogs. The increase comes from the contracted muscles. In tetanus the creatine-P of muscle decreases, whilst the inorg. P increases. The Ca concn. in blood-serum decreases in tetanus convulsions, but increases in those produced by strychnine. L. S. T.

**Modification in the lipin content of the central nervous system in the convulsive state.** V. SANGIRARDI (Atti R. Accad. Lincei, 1933, [vi], 17, 861—864).—The convulsive state produced by strychnine, nicotine, picrotoxin, PhOH, BaCl<sub>2</sub>, etc. is accompanied by a fall in the lipin content of the spinal cord, the extent of which varies with the lipin concerned, and in the cholesterol content. R. N. C.

**Enteral absorption of ergot alkaloids and their specific action on the circulation.** E. ROTHLIN (Arch. exp. Path. Pharm., 1933, 171, 555—591).—Direct duodenal or jejunal administration of ergot alkaloids (I) is followed after a latent period of approx. 10 min. by rapid absorption, a max. effect being attained after 40 min. With 0.25 and 0.50 mg. per kg. the action persists for 2—4 and 4—6 hr., respectively. Aq. ergotamine is readily absorbed from the rectum. Following intestinal administration, (I) are absorbed from both normal and defatted ergot preps. F. O. H.

**Detection of morphine in urine of addicts.** F. PANSE (Fort. Therapie, 1932, 8, 629—633; Chem. Zentr., 1932, ii, 3924).—Urine is treated with NaOH and NaHCO<sub>3</sub>, and an EtOAc extract is evaporated to 1—2 c.c. and fractionally sublimed for the identification of morphine. L. S. T.

**Detection of quinine in urine by erythroquinine reaction.** R. MONNET (J. Pharm. Chim., 1933, [viii], 18, 94—96).—0.01 mg. of quinine (I) per c.c. of urine is detected by the addition of 1% aq. AcOH to a CHCl<sub>3</sub> extract of urine made alkaline with aq. NH<sub>3</sub>, shaking, and adding successively Br-H<sub>2</sub>O, aq. K<sub>4</sub>Fe(CN)<sub>6</sub>, and dil. aq. NH<sub>3</sub>. The red colour in the CHCl<sub>3</sub>-layer indicates the presence of (I). H. D.

**Action of ultra-violet rays of various frequencies on solutions of alkaloids.** Q. MINGOIA (Annali Chim. Appl., 1933, 23, 318—330).—The behaviour of certain alkaloid salts, alterable by heating, is recorded. Wood's light (I) does not affect aq. solutions of heroine, cocaine, or codeine hydrochloride, or atropine sulphate, when exposed either freely or in quartz tubes. Moreover, the same solutions, when inoculated with *Aspergillus fumigatus*, *B. tumefaciens*, *B. coli*, etc., are not sterilised by (I). Hence, ultra-violet rays (II) offer no advantage over other sterilising agents for the sterilisation of solutions used in hypodermo-therapy, as the more refractive (II) usually change the solutions and (I) does not ensure asepsis. T. H. P.

**Pharmacology of substances from yeast.** K. ZIPF and J. BRÄKLING (Arch. exp. Path. Pharm., 1933, 171, 603—611).—Abs. EtOH, COMe<sub>2</sub>, or Et<sub>2</sub>O extracts of pressed or dried brewer's yeast contain no substance acting on the rabbit's blood-vessels or intestine or on the guinea-pig's uterus. Aq. and aq.-EtOH extracts have an action characteristic of the adenosine and/or the choline type of substances; acetylcholine, histamine, and the depressor substance of Euler and Gaddum (A., 1932, 1061) are not detectable. F. O. H.

**Inactivation of biogenic amines etc. by formaldehyde.** K. ZIPF and E. BAETSCHER (Arch. exp. Path. Pharm., 1933, 171, 592—602).—The following are inactivated by CH<sub>2</sub>O: histamine, posterior pituitary gland extract, tyramine, phenylethylamine, isoamylamine, muscle- and yeast-adenylic acid, acetylcholine, carbamylcholine chloride (A., 1932, 301), pilocarpine, and BaCl<sub>2</sub>. Inactivation is due to actual combination of ·NH<sub>2</sub> or ·NH with CH<sub>2</sub>O and/or to intracellular action of CH<sub>2</sub>O on the substrate concerned. The detection of histamine by CH<sub>2</sub>O is applicable only to tissue extracts. F. O. H.

**Relationship between chemical constitution and physiological action.** V. Molecular dissymmetry and physiological activity. L. H. EASSON and E. STEDMAN (Biochem. J., 1933, 27, 1257—1266).—The mitotic action, the degree of inhibiting the hydrolysis of PrCO<sub>2</sub>Me by liver-esterase (cf. A., 1931, 1190), and the action on the intestine of a no. of methylurethanes of the type *m*-NHMe·CO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CRR'·NMe<sub>2</sub> (R=H, Me, and R'=H, Me, Et, Pr<sup>n</sup>, Ph) and similar compounds (this vol., 1046) support the theory that, assuming that three of the groups linked to the asymmetric C in an optically active drug are concerned in its attachment to its sp. receptor in the tissues, mol. dissymmetry and its associated optical activity have no direct influence on the magnitude of the physiological activity of a drug. This theory is further supported by the fact that *d*-adrenaline has approx. the same pressor activity as 3:4-dihydroxy-β-phenylethylmethylamine. F. O. H.

**Dinitro-*o*-cresol as a stimulator of metabolism.** E. C. DODDS and (SIR) W. J. POPE (Lancet, 1933, 125, 352—353).—Subcutaneous injection and oral administration of dinitro-*o*-cresol (I) increase the

O<sub>2</sub> consumption of guinea-pigs. (I) is three times as active as 2 : 4-dinitrophenol in this respect.

L. S. T.

[Pharmacological] actions of dinitrophenol. M. L. TAINTER and W. C. CUTTING (J. Pharm. Exp. Ther., 1933, 48, 410—429).—Administration of 2 : 4-dinitrophenol to rabbits, cats, dogs, rats, pigeons, and men, in doses from 3 to 40 mg. per kg. body-wt., produces an increase in body-temp. up to 7°; this increase is independent of the central nervous system and of contractions of the skeletal muscles, and is not prevented by ergotamine, adrenalectomy, or thyroidectomy. Death may result from direct circulatory depression, hyperpyrexia, or acidosis and anoxæmia.

H. D.

Experimental apiol poisoning in animals. L. KALBFLEISCH (Arch. exp. Path. Pharm., 1933, 171, 439—442).—The toxicity of apiol is at least partly due to (*o*-C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>PO<sub>4</sub> (I). That the latent period between the time of administration of (I) to rabbits is hyperbolically related to the dose and that (I) produces neuritis indicate a combination occurring with certain phosphorylated lipins of the body at a rate dependent on the concn. of (I) in the blood.

F. O. H.

Chemicals active in increasing tissue permeability and enhancing certain infectious processes. A. CLAUDE (Science, 1933, 78, 151—152).—Diazo-compounds are the only synthetic substances so far discovered which are able to increase tissue permeability, and to enhance the lesions resulting from infectious agents, thus resembling certain tissue extracts and virulent bacteria. *p*-Ph-N<sub>2</sub>-SO<sub>3</sub>H, but not sulphanilic acid, is suddenly and completely diffused when intradermally injected; coupling with serum- or ov-albumin gives an active prep. of greater spreading power, and one which enhances infectious processes.

L. S. T.

Efficiency of intravenously injected medicaments as a function of time. W. GEHLEN (Arch. exp. Path. Pharm., 1933, 171, 541—554).—Mathematical considerations indicate that a max. content of an intravenously injected drug is attained after a period which is characteristic for the drug and is independent of the dose. A characteristic period also occurs with continuous administration.

F. O. H.

Action of lymphagogues of the first class. Y. TAKAYANAGI (Nagoya J. Med. Sci., 1932, 6, 113—131).—In narcotised dogs peptone, Na nucleate, and adrenaline increased the *d*, viscosity, and total solids.

CH. ABS.

Changes in blood concentration incident to shock. V. H. MOON and P. J. KENNEDY (Amer. J. Med. Sci., 1933, 185, 447—448).—In dogs, determinations of *d*, erythrocytes, and hæmoglobin indicate increase in blood concn.

CH. ABS.

Blood-potassium and -calcium in electric shock. I. R. PETROV and S. F. LIBIKH (Arch. Sci. Biol., U.S.S.R., 1932, 32, 229—239).—In most rabbits (surviving) blood-serum-K is greatly increased and -Ca decreased; in dogs and some rabbits (killed) -Ca was increased whilst -K was unchanged or slightly

decreased. In man (one experiment) -K was slightly increased and -Ca was decreased.

CH. ABS.

Influence of variations in systematic acid-base balance on carbohydrate tolerance in normal subjects. G. THOMPSON, D. M. MITCHELL, and L. C. KOLB (Biochem. J., 1933, 27, 1253—1256).—Ingestion of 15—25 g. of NH<sub>4</sub>Cl by men reduces the alkali reserve of the blood-plasma to a level comparable with that found in diabetic coma and raises the urinary excretion of acid by 100—200% and of NH<sub>3</sub> by 300%. The acidosis is accompanied by a failure in glucose tolerance, but administration of glucose does not produce any trace of glycosuria even when the blood-sugar level exceeds the normal threshold val. Ingestion of 20—70 g. of NaHCO<sub>3</sub> reduces the urinary excretion of acid and NH<sub>3</sub> to zero, but does not produce a marked increase in the CO<sub>2</sub>-combining power of the plasma. Such alkalosis causes only a slight variation in the blood-sugar response to ingestion of glucose.

F. O. H.

Effect of feeding fluorides on the composition of the teeth and bones of rats. M. C. SMITH and E. M. LANTZ (J. Biol. Chem., 1933, 101, 677—683).—With 0.05% NaF in the diet there was no significant alteration in the composition of teeth and bones. With 0.1% NaF, ash and P were lower, Ca was higher, and Ca : P ratio increased.

H. G. R.

Effect of fluorine on the nutrition of swine, with special reference to bone and tooth composition. C. H. KICK, R. M. BETHKE, and B. H. EDGINGTON (J. Agric. Res., 1933, 46, 1023—1037).—Administration to pigs of < 0.3% F as natural phosphate rock or as NaF reduced growth, food consumption, and the efficiency of utilisation of the ration. The femurs of the pigs showed an increased diam., decreased breaking strength, and loss of normal colour and lustre. Affected bones contained normal proportions of ash, Ca, and P, increased Mg and F, and decreased CO<sub>3</sub>". These changes were directly correlated with the amount of F fed. Enlargement of the mandibles following F feeding was due to an increase in the diam. of the marrow cavity rather than to thickening of the walls. The type of marrow was also changed. Prolonged feeding of excessive amounts of F caused softening of the teeth. The % of ash, Ca, P, Mg, and CO<sub>3</sub>" was not appreciably affected, but the F content was directly proportional to the amount consumed. The F of natural phosphate rock and of NaF produced similar physiological effects except that the former induced certain pathological changes in the kidneys.

A. G. P.

Biochemistry of silicic acid. I. Micro-determination of silica. E. J. KING and H. STANTIAL. II. Presence of silica in tissues. III. Excretion of administered silica. E. J. KING, H. STANTIAL, and M. DOLAN. IV. Relation of silica to the growth of phytoplankton. E. J. KING and V. DAVIDSON (Biochem. J., 1933, 27, 990—1001, 1002—1006, 1007—1014, 1015—1021).—I. A method is described based on the formation of a silicomolybdic acid complex (I) (A., 1923, ii, 507), reduced by 1 : 2 : 4-aminonaphtholsulphonic acid giving a blue colour which is compared with suitable standards. Form-

ation of (I) is max. at an acidity of 0.08*N*.  $\text{PO}_4^{''}$  and  $\text{Fe}^{''}$  interfere with the reaction and are removed by  $\text{CaCl}_2 + \text{CaCO}_3$  (A., 1932, 34). Blood (2 c.c.) is deproteinised by basic  $\text{Fe}^{\text{III}}$  acetate. Typical data for blood, urine, and tissues are given.

II. The  $\text{SiO}_2$  content of the urine of carnivorous and omnivorous animals is < that of herbivorous animals; in all cases it is markedly influenced by the diet. Human urine contains 0.7—2.2 mg. per 100 c.c., a level considerably increased by silicosis. Human blood has an average content only approx.  $\frac{1}{17}$  that found by Kraut (A., 1931, 378). Small but significant amounts occur in fetal tissues, whilst with adult tissues wide variations occur, the highest content being found in the lungs.

III. Introduction of finely-ground  $\text{SiO}_2$  or of gelatinous  $\text{H}_2\text{SiO}_3$  into the stomachs of dogs produces an increase in the urinary excretion (I) of  $\text{SiO}_2$  without any concomitant increase in the blood level (II). Intravenous injection of aq.  $\text{Na}_2\text{SiO}_3$  produces a large increase in (I) and a moderate increase in (II). The amount excreted is < that injected. With suspensions of finely-divided  $\text{SiO}_2$ , intravenous injection causes death, there occurring only a slight increase in (I). The highest val. of (II) is attained by injection of "silistren" (a glycol silicate), death ensuing within 5 days. Spraying of aq.  $\text{Na}_2\text{SiO}_3$  into the lungs appears to lead to increased (I). Animals possess a very low renal threshold for  $\text{SiO}_2$ .

IV. The addition of  $\text{Na}_2\text{SiO}_3$  (up to 100 mg. of  $\text{SiO}_2$  per litre) to diatoms growing in sea- $\text{H}_2\text{O}$  containing an abundance of nutrient salts causes increased growth, whilst higher concns. have an unfavourable effect. That dissolution of  $\text{SiO}_2$  appears to be more rapid in an autolysing suspension of diatoms containing  $\text{CHCl}_3$  than in one which has been boiled indicates the probability of the existence of a silicatase.

F. O. H.

Silica content of lungs. A. F. SLADDEN (Lancet, 1933, 125, 123—125).—The  $\text{SiO}_2$  contents (I) of the lungs of 60 industrial workers are recorded. When (I) is > 1.0% of dried lung substance, extensive fibrosis (II) is usually present. When (I) is > 1.6%, (II) is severe.

L. S. T.

Toxicity of arsenious oxide. L. COHEN (Rep. Austral. Assoc. Adv. Sci., 1933, 21, 42—46).—The solubility of relatively pure commercial  $\text{As}_2\text{O}_3$  in 5—7% glucose or sucrose is about  $\frac{1}{3}$  (or less) of its solubility in  $\text{H}_2\text{O}$ . The variable toxicity to animals of  $\text{As}_2\text{O}_3$  may be due to differences in the concn. of sugars in the alimentary tract.

W. O. K.

Toxicity of nearsphenamine. I. Increase on exposure to air. II. Characteristic curve for rats. C. A. MORELL and C. W. CHAPMAN (J. Pharm. Exp. Ther., 1933, 48, 375—390, 391—409).—I. Solutions of nearsphenamine (I) in glass-distilled  $\text{H}_2\text{O}$ , kept in air for 20 min., increase in toxicity by 107% > those kept under oil. The latter show no increase in toxicity after 2½ hr.

II. A characteristic curve for the toxicity of (I) for rats is constructed. Individual variations of 211% in one colony of rats were observed.

H. D.

Dissociation and local irritating effects of calcium salts. B. BEHRENS and J. WAJZER (Bio-

chem. Z., 1933, 264, 120—125; cf. Weilguny, A., 1932, 964).—The degrees of local irritation produced by org. Ca salts (propionate, lactate, valerate, hexoate, gluconate) on injection are to some extent related to the degree of their dissociation.

W. McC.

Toxicity and deposition of thallium in birds. P. A. SHAW (J. Pharm. Exp. Ther., 1933, 48, 478—487).—The lethal doses of Tl for quail, geese, and ducks are respectively 12, 15, and 30 mg. per kg. body-wt. Tl accumulates in the muscles. In the dog > 100 days are required for the complete elimination of a dose of Tl.

H. D.

Mercury poisoning. II. Influence of diuretin and theocin. M. KUSE (Folia Pharmacol. Japon., 1933, 15, No. 4, 333—340).—When administered to rabbits with novasurol, diuretin and theocin have a favourable effect.

CH. ABS.

Antidotal action of sodium thiosulphate and dihydroxyacetone in cyanide poisoning, and alleged antidotal action of glucose. B. B. TURNER and H. R. HULPIEU (J. Pharm. Exp. Ther., 1933, 48, 445—469).—The fatal dose of NaCN for rabbits is approx. 2 mg. per kg. body-wt. The blood-sugar curve of rabbits given NaCN is of the same form as one of severity of symptoms plotted against time; no antagonistic action of glucose to NaCN is observed.  $\text{Na}_2\text{S}_2\text{O}_3$  and dihydroxyacetone (I) administered together enable the rabbit to recover from thrice the lethal dose of NaCN, whereas the action of  $\text{Na}_2\text{S}_2\text{O}_3$  alone is too slow to be effective and that of (I) is of too brief duration.

H. D.

Sodium tetrathionate and methylene-blue in cyanide and carbon monoxide poisoning. J. H. DRAIZE (Science, 1933, 78, 145).— $\text{Na}_2\text{S}_4\text{O}_6$  (I) and methylene-blue (II) are both effective antidotes for CN' or CO poisoning in rabbits. (I) is more effective than (II) in each case.

L. S. T.

Sodium nitrite and sodium hyposulphite in potassium cyanide poisoning. A. BUZZO and R. E. CARRATALÁ (Semana méd., 1933, i, 1224—1229).

CH. ABS.

Chronic radium poisoning in rats. H. E. THOMAS and F. H. BRUNER (Amer. J. Roentgenol., 1933, 29, 641—663).—Injection of  $\text{RaCl}_2$  leads to decrease in calcification of the central portions of all bones, and a concn. of Ca salts in the parts of bones nearest the joints. > 99% of the retained Ra is present in the bones. Organs dealing with Ca metabolism contained more Ra than did other soft tissues.

CH. ABS.

Action of radium emanation on single cells or groups of cells. A. FOÀ (Atti R. Acad. Lincei, 1933, [vi], 17, 578—582).—Cells exposed to Ra needles undergo a series of irreversible changes, involving increased refractivity of the nuclear membrane, granulation and shrivelling of the protoplasm, and ending in complete fracture of the cell. The effects are due entirely to the  $\alpha$ -particles.

R. N. C.

Reaction in the skin occurring during the latent period following X-radiation. J. C. MOTTRAM (Nature, 1933, 132, 317).—Some hr. after exposure

of the skin of rats, inoculated with pyrrole-blue, to X-rays a blue colour appears at the area of irradiation.

L. S. T.

**Chemical nature of enzymes.** E. WALDSCHMIDT-LEITZ (Science, 1933, 78, 189—190).—A discussion.

L. S. T.

**Respiration co-enzyme.** F. E. ALLISON, S. R. HOOVER, and D. BURK (Science, 1933, 78, 217—218).—A factor, designated co-enzyme R (I), which is sp. and essential for respiration has been obtained by extracting commercial sucrose with abs. EtOH. Certain organisms fail to reproduce or grow in absence of (I) because of inability to respire; adequate addition of (I) causes respiration to reach the normal max. in  $> 1$  hr. (I) is sol. in H<sub>2</sub>O and in abs. EtOH, but insol. in the ordinary fat solvents; it is readily dialysable and heat-stable, and contains no inorg. element. *Azotobacter vinelandii* synthesises (I), which is discharged into the culture medium. (I) appears to be widely distributed throughout the animal and vegetable kingdoms.

L. S. T.

**Peroxidase reaction and metals.** W. GRIMMER and S. RAUSCHNING (Milch. Forsch., 1933, 15, 381—383).—The effect of the presence of Cu, Fe, Ni, and Mn on the various types of peroxidase reactions was studied. Apparent positive results were obtained in all cases with *p*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> and Rothenfusser's reagent, whilst with guaiacol, benzidine, and guaiacum tincture results were negative.

E. B. H.

**Catalase. VII. Synthetic hæmin-catalases.** K. G. STERN (Z. physiol. Chem., 1933, 219, 105—114; cf. this vol., 862).—The parahæmatins (I) and hæmochromogens (II) of various NH<sub>2</sub>-acids and proteins show a lower catalase activity (III) than free hæmin. Piperazine, on the other hand, especially in the Fe<sup>III</sup> complex, activates strongly, although quinoline and isatin inhibit. (II) are almost always less active than (I), and have a lower optimum *p*<sub>H</sub>. Adsorption of the (I) and (II) of arginine, histamine, and nicotine on animal charcoal affects the *p*<sub>H</sub> max., but not the (III).

J. H. B.

**Digestion of raw starch.** E. POZERSKI (Bull. Soc. sci. Hyg. aliment., 1933, 21, 1—29).—Starch dissolved by heat, or broken up mechanically, is digested *in vitro* by saliva and pancreatic juice, crude starch only slightly. Pre-treatment with dil. HCl aids digestion by enzymes. Starch in the form of cereal grains is completely digested by fowls and pigeons, but when given as a powder with non-carbohydrates is scarcely digested at all.

NUTR. ABS. (b)

**Amylase and sisto-amylase in malts from various grains.** T. CHRZĄSZCZ and J. JANICKI (Biochem. Z., 1933, 264, 192—208; cf. this vol., 749, 982).—Malt from various grains (barley, wheat, rye, millet, buckwheat, oats, and maize) contains greatly varying amounts of sisto-amylase (I) and of eleuto-substances (II). The amount of amylase (III) which passes into aq. malt extracts (IV) depends on the amounts of (I) and (II) present, on the concn. of (IV), and on the manner in which they are diluted. The different powers (*e.g.*, liquefying) of (IV) vary independently and are affected in different degrees by the

type of malt, the concn. of (IV), and the amounts of (I) and (II) present.

W. McC.

**Barley diastase.** R. H. HOPKINS, G. F. COPE, and J. W. GREEN (J. Inst. Brew., 1933, 39, 487—493).—Barley diastase, either EtOH-pptd. (I) or barley extract (II), has the most rapid saccharifying action on Lintner sol. starch (III) at *p*<sub>H</sub> 4.5—4.7 for range of action within 45% conversion at 37°. The *p*<sub>H</sub>-activity curve resembles that of malt diastase at the same temp. The normal limit of maltose production, 60—65%, is not substantially modified between *p*<sub>H</sub> 4.3 and 7.5. The enzyme is not activated by Meyerhof's activator (A., 1927, 590) or Pringsheim's complement (A., 1923, i, 965), but both (I) and (II) are activated in the presence of living yeast. (I) degrades glycogen 1/3 as rapidly as it does (III). (III) was degraded to 3% of the original dry wt. by the repeated addition of large doses of (I) to the redispersed undegraded dextrin.

R. H. H.

**Biolase.** R. WEIDENHAGEN and B. KOROTKYJ (Z. Ver. deut. Zucker-Ind., 1933, 83, 262—272).—The authors failed to confirm the statement of Pringsheim and Schapiro (A., 1926, 715) that the main product of starch conversion by biolase at 70° is a trisaccharide (I). The main fractions were dextrinous and had  $<$  half the reducing power of maltose. Small quantities of glucose and probably isomaltose were isolated as osazones, but no (I).

J. H. L.

**$\beta$ -*D*-Fructosidase [invertase]. II.** R. WEIDENHAGEN (Z. Ver. deut. Zucker-Ind., 1933, 83, 376—389).—A further study of the method of prep. already described (A., 1932, 91). Products 1000 times as active as the original yeast can be obtained. By the use of large amounts of the enzyme, irisin, like inulin (*ibid.*, 543; B., 1933, 280), has been quantitatively converted into fructose.

J. H. L.

**Production of lactic acid in liver pulp.** J. S. L. BROWNE and R. GRANT (Biochem. Z., 1933, 264, 163—168).—When liver pulp (I) is digested at 37—38° its lactic acid content (II) increases only slightly and its total carbohydrate content does not decrease. When (I) contains many blood-corpuses the increase in (II) is  $>$  when it contains few. Possibly (I) itself exerts no glycolytic action.

W. McC.

**Production and transformation of  $\alpha$ -glycerophosphoric acid during enzymic hydrolysis of carbohydrates.** O. MEYERHOF and W. KIESSLING (Biochem. Z., 1933, 264, 40—71; cf. this vol., 528, 742).— $\alpha$ -Glycerophosphoric acid (I) and AcCO<sub>2</sub>H (II) are produced in equiv. amounts in muscle extracts (rabbit, frog) when enzymes and sulphite are present. The detection, determination, and isolation of (I) are described. The Me<sub>2</sub> ester of its Me<sub>2</sub> ether has  $[\alpha]_D^{20} -4.46^\circ$ . Lactic acid (III) is produced from (I) and (II) according to the scheme proposed by Embden *et al.* (Klin. Woch., 1933, 12, 213). In presence of NaF the yield of (III), which is not decreased, is equiv. to the amount of (II) consumed, but in absence of NaF this yield is equiv. to twice the amount of (II) consumed. Since NaF inhibits the hydrolysis of phosphoglyceric acid (IV), H<sub>2</sub>PO<sub>3</sub>·O·CH<sub>2</sub>·CH(OH)·CO<sub>2</sub>H, it appears that (I) and (II) react to produce an acid probably identical with glyceraldehyde- $\gamma$ -phosphoric acid. The -form

only of (I) reacts thus.  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$  does not inhibit the hydrolysis of (IV) to (II) and  $\text{H}_3\text{PO}_4$ , but inhibits the reaction between (I) and (II). When adenylyl pyrophosphate is absent this reaction produces only half the usual amount of (III), which is equiv. to the amount of (II) consumed. In yeast maceration juice similar changes occur. W. McC.

**Phosphatase activity of tissue extracts.** H. BAKWIN and O. BODANSKY (J. Biol. Chem., 1933, 101, 641—656).—In rat-bone extracts the reaction velocity (I) of phosphatase activity is proportional to the enzyme concn. In intestinal extracts of cattle and rats there is < direct proportionality, due to the presence of proteolytic autolysis products. In cattle-bone extracts there is > direct proportionality, due to insufficient concn. of Mg and other accelerants. H. G. R.

**Glucosulphatase. VI. Natural substrates of the enzyme.** T. SODA and J. YAMAZAKI (Bull. Chem. Soc. Japan, 1933, 8, 207—212; cf. this vol., 749).—The distribution of org. sulphates in various parts of *Viviparus japonicus*, Martens, and the total org. sulphates in four other shell-fish, are recorded. The substrate of glucosulphatase exists in sol. and insol. form in some shell-fish. R. S. C.

**Comparison of the choline-esterase activities of the blood-sera from various species.** E. STEDMAN, (MRS.) E. STEDMAN, and A. C. WHITE (Biochem. J., 1933, 27, 1055—1060).—Choline-esterase (I), determined by a new modification of the method previously described (this vol., 315), could not be detected in sera (II) of tortoise, frog, hedgehog, goose, rat, rabbit, goat, ox, sheep, and ferret. A small but definite amount was detected in (II) from pig, fowl, mouse, pigeon, and duck, whilst relatively large quantities existed in (II) from cat, fox, guinea-pig, dog, man, horse, and monkey (order of increasing amount). The (I), Me butyrate esterase (III), or tributyrin lipase (IV) activities of these (II) showed no relationship. (I) and (III) are distinct enzymes, although their action may not be absolutely sp. Certain (II) probably also contain (IV) as a third enzyme. W. O. K.

**Digestibility of proteins *in vitro*. V. Rate of liberation of cystine on hydrolysis of caseinogen.** Observations on colorimetric tests for cystine when applied to peptic and acid digests of caseinogen. D. B. JONES and C. E. F. GERSDORFF (J. Biol. Chem., 1933, 101, 657—667).—After 30 min. hydrolysis with 20% HCl, 20% of the cystine (I) content of caseinogen was liberated, as determined by Sullivan's method (II) (A., 1930, 1604), and after  $3\frac{1}{2}$  hr. 50%. No increase was obtained after 6 hr. Folin and Marenzi's method (III) (A., 1929, 1039) first gives abnormally high vals. (0.55% after 15 min. hydrolysis) which slowly decrease, becoming 0.33% after 18 hr. hydrolysis. Using (II) on peptic digests no appreciable quantity of (I) was detected; using (III) an early rise and fall, becoming const. at 0.25% after 5 hr., was observed. The colour obtained with peptic digests is not due to free  $\text{NH}_2$ -acid. H. G. R.

**Rate of ammonia liberation in tryptic and peptic digestion of caseinogen.** I. KRAUS-RAGINS (Proc. Soc. Exp. Biol. Med., 1933, 30, 452—457).—Liberation of  $\text{NH}_3$  in tryptic digestion of caseinogen (*in vitro*) is due to the action of the enzyme, but in peptic digestion  $\text{NH}_3$  is liberated by HCl without pepsin. NUTR. ABS. (m)

**Activation of propepsin.** R. EGE and P. MENCK-THYGESEN (Biochem. Z., 1933, 264, 13—23).—Pepsin is determined by measuring its coagulating effect on caseinogen in circumstances where no activation (I) of propepsin occurs. (I) becomes measurable at  $40^\circ$  when the  $p_{\text{H}}$  exceeds 5.1. A change of  $p_{\text{H}}$  from 5 to 4 results in a ten-fold increase in the rate of (I) and a temp. rise of  $10^\circ$  doubles the rate. W. McC.

**Antipepsin; determination.** A. SLIVE (J. Lab. Clin. Med., 1933, 18, 801—805).—Rabbit's blood and tissues, particularly the liver, often contain an antipeptic substance. Antipeptic activity is produced by intravenous injection of pepsin. The detection and determination of antipepsin is described. CH. ABS.

**Cathepsin and papain.** E. MASCHMANN and E. HELMERT (Z. physiol. Chem., 1933, 219, 99—104).—The inactivation of cathepsin (I) and papain (II) by  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$  is due to a sp. action on the enzyme and not to oxidation of the thiol activator (cysteine). When HCN is added to (I) or (II) solutions a Na nitroprusside reaction develops. The activating power of HCN may be due to its power of converting  $\cdot\text{S}\cdot\text{S}\cdot$  into  $\cdot\text{SH}$  groups. Fully active (I) giving a negative test for thiol is inhibited by  $\text{O}_2$ . J. H. B.

**Aminopolypeptidase. II.** A. K. BALLS and F. KÖHLER (Z. physiol. Chem., 1933, 219, 128—137; cf. A., 1932, 543).—When aminopolypeptidase (I) solution is dialysed against  $\text{H}_2\text{O}$ , activity and P are lost at the same rate. Against  $0.005M\text{-PO}_4'''$  the loss of activity is much slower. The partly inactivated enzyme is incompletely reactivated on addition of the evaporated dialysate, but not by  $\text{PO}_4'''$  or  $\text{P}_2\text{O}_7''''$ . (I) is not attacked by phosphatase. Preps. of (I) obtained by different methods show the same affinity relations towards various polypeptides, indicating the homogeneity of the enzyme. J. H. B.

**Action of polyhydric phenols on urease; influence of thiol compounds.** J. H. QUASTEL (Biochem. J., 1933, 27, 1116—1122).—*o*- (I) and *p*- (II)  $\text{-C}_6\text{H}_4(\text{OH})_2$  are very toxic to jack-bean or soya-bean urease, but *m*- is not. Adrenaline, protocatechuic acid, protocatechualdehyde, gallic acid, and pyrogallol are toxic, but less so than (I); phloroglucinol is inactive.  $\text{CN}'$  and  $\text{NH}_2$ -acids do not protect urease against (I) or (II), and thus this toxicity differs from that of metals or of dyes. Serum or egg-white gives no protection, but boiled egg-white does, probably due to liberated SH groups. SH compounds (cysteine, glutathione, thioacetic acid,  $\text{H}_2\text{S}$ ) and  $\text{Na}_2\text{S}_2\text{O}_4$  reduce or eliminate the toxic action of (I) etc. It is suggested that the high toxicity of (I) and (II) is probably due to the presence in these solutions of the corresponding quinone; benzoquinone is more toxic than (II). Protection by SH

compounds is probably due to the reduction of the quinone to the dihydric phenol. A. W.

**Proteolytic enzymes of yeast.** T. F. MACRAE (Biochem. J., 1933, 27, 1229—1236).—By a modification of Willstätter's method (A., 1926, 321) preps. of (a) dipeptidase (I) free from proteinase (II) with traces of aminopolypeptidase (III) and (b) (III) free from (I) and (II) have been obtained from top yeast (IV). (II) free from (I) but not (III) has been obtained from (IV) and Dutch bakers' yeast. H. G. R.

**Molasses-fermenting yeasts.** *Saccharomyces formosensis*, nov. sp. R. NAKAZAWA (J. Agric. Chem. Soc. Japan, 1933, 9, 285—291).—The yeast was isolated from Formosan fermented molasses. CH. ABS.

**Relation between alcohol fermentation, yeasts, and fermentation temperature.** III. R. NAKAZAWA, Y. TAKEDA, and M. ASHIKAGA (J. Agric. Chem. Soc. Japan, 1933, 9, 260—272).—The best source of N for *S. formosensis*, Nakazawa (nov. sp.), was asparagine. The optimum  $p_H$  for EtOH fermentation was 5.0—6.0. Fermentation by various species of *Saccharomyces* is classified in three types according to the relation between max. fermentation temp. and time taken to reach the max. temp. CH. ABS.

**Cozymase of yeast.** K. MYRBACK (Z. physiol. Chem., 1933, 219, 173—176).—Kidney-phosphatase [glycerophosphate activity (I)=1] is about 6 times as active towards cozymase (II) as bone-phosphatase [(I)=0.4]. Heat-inactivated (II) is deaminated by  $HNO_2$  at the same rate as active (II). The  $NH_2$ -group is probably free in both cases. J. H. B.

**Production of glycogen by yeast.** F. T. BRÜCKE (Biochem. Z., 1933, 264, 157—162).—Yeast produces 2—3 times as much glycogen (I) from glucose (II) as from a quantity of EtOH containing an equal amount of C. In concn. of 1 : 5000  $CH_2I \cdot CO_2H$  (III) inhibits the production of (I) from (II), the inhibition being dependent on  $p_H$  in the same way as is the inhibition of the fermentation by (III). (III) also inhibits the production of (I) from EtOH to the same extent as from (II). W. McC.

**Cell-nucleus of yeast and Feulgen's reaction.** E. J. ROCHLINA (Bull. Acad. Sci. U.S.S.R., 1933, 855—858).—A technique is described by means of which the presence in yeast (Berlin Race XII) of a nucleic acid of the thymonucleic type may be demonstrated. T. H. P.

**Agglutination of yeast.** A. MALKOV, A. PETINA, and N. ZWETKOVA (Zentr. Bakt. Par., 1933, 88, II, 193—200).—Agglutination is influenced solely by the  $p_H$  of the medium. The optimum for non-fermenting yeast is within the  $p_H$  range 2.85—3.15. A. G. P.

**Combined action of coal tar and ultra-violet light on the development of yeast.** M. N. MEISEL (Bull. Acad. Sci. U.S.S.R., 1933, 849—853).—The toxicity towards yeasts of coal tar dispersed in a solid or liquid medium increases with the degree of dispersion. *S. cerevisia* is less sensitive to the tar than *S. Ludwigii*, and when grown for a long time (2 years) on tar-containing media, undergoes morphological changes with formation of "saltants." This effect becomes more pronounced if the cultures

are simultaneously exposed to ultra-violet light and results in the appearance of mycelial forms. T. H. P.

**Decomposition of polyuronides by fungi and bacteria.** I. **Decomposition of pectin and pectic acid by fungi and formation of pectolytic enzymes.** S. A. WAKSMAN and M. C. ALLEN (J. Amer. Chem. Soc., 1933, 55, 3408—3418).—*Penicillium*, *A. niger*, and *Fusarium* sp., isolated from soil, decompose pectin and polygalacturonic acids, simple uronic acids being first formed and then decomposed. The three organisms differ in the speed with which they effect each reaction; they produce pectolytic enzymes responsible for these hydrolyses. The amount of enzyme which will hydrolyse 1 mg. of polygalacturonic acid in 1 hr. at 40° and  $p_H$  4.0—6.0 is termed a pectolytic unit. 1 g. of the dry enzyme used contained 4000 such units. A sediment of uncertain nature is formed during the hydrolyses. R. S. C.

**Production of acids by *Aspergillus niger*.** X. **Production of oxalic acid from formic acid.** K. BERNHAUER and F. SLANINA (Biochem. Z., 1933, 264, 109—112; cf. A., 1932, 1168).—*A. niger* converts up to 41% of  $HCO_2Na$  into  $Na_2C_2O_4$ ,  $CO_2$  being produced simultaneously.  $(HCO_2)_2Ca$  likewise yields  $CaC_2O_4$ , but in poorer yield. The results confirm the theory of Chrzaszcz and Zakomorny (this vol., 536). W. McC.

**Biochemistry of micro-organisms.** XXXII. **Cynodontin (1 : 4 : 5 : 8-tetrahydroxy-2-methyl-anthraquinone), a metabolic product of *Helminthosporium cynodontis*, Marignoni, and *Helminthosporium euchlaenae*, Zimmermann.** H. RAISTRICK, R. ROBINSON, and A. R. TODD (Biochem. J., 1933, 27, 1170—1175).—The mycelia of *H. cynodontis* (I) and *H. euchlaenae* (II), when grown on a synthetic culture medium containing glucose as the sole source of C, give *cynodontin* (III),  $C_{15}H_{10}O_6$ , m.p. 260° ( $Ac_4$  derivative, m.p. 224—225°), when extracted with  $CHCl_3$ . (III) is probably 1 : 4 : 5 : 8-tetrahydroxy-2-methylanthraquinone, since it is formed from *helminthosporin* (IV) (this vol., 752),  $MnO_2$ , and conc.  $H_2SO_4$  at 50—60°. A little (IV) is also produced from (I) but not from (II). H. B.

**Biochemistry of micro-organisms.** XXXIII. **Mycelial constituents of *Penicillium brevicompactum*, Dierckx, and related species.** I. **Ergosteryl palmitate.** A. E. OXFORD and H. RAISTRICK (Biochem. J., 1933, 27, 1176—1180).—*Ergosteryl palmitate* (I), m.p. 106—108°,  $[\alpha]_{D_{461}}^{20} -67^\circ$  in  $CHCl_3$ , has been isolated (usually in yields of 0.02%) from the dry mycelia of 14 out of 15 species and strains of *P. brevicompactum* and from *P. italicum*, Wehmer. The mycelium of *P. aurantio-griseum*, Dierckx (var. *Poznaniensis*, Zaleski), contains as much as 0.5% of (I). All the moulds were grown on Raulin-Thom medium and incubated at 24° for 20—30 days; (I) is extracted by light petroleum. H. B.

**Bacterial production of amyl alcohol.** S. FORSMAN (Biochem. Z., 1933, 264, 228—230).—Lindner's *Termobacterium mobile* converts *dl*-valeraldehyde quantitatively into amyl alcohol (67% in the *d*-form).  $MeCHO$  is produced simultaneously in traces. W. McC.

**Enzyme system of Lindner's *Thermobacterium mobile*.** S. FORSSMAN (Biochem. Z., 1933, 264, 231—236; cf. Tankó, A., 1932, 651).—Glucose and, more slowly, sucrose are fermented to the extent of 70% by the fresh bacterium (I), which also converts raffinose (II) (60%) into fructose and melibiose and hydrolyses lactose (93%). The decomp. of (II) by dried (I) reaches 83%. Glucosides ( $\alpha$ - and  $\beta$ -methylglucosides,  $\alpha$ -methylmannoside, amygdalin) are not attacked by (I). W. McC.

**Fermentation of cellulose by thermophilic bacteria. IV. Products of fermentation.** Y. TOMODA and H. YAMAURA (J. Soc. Chem. Ind. Japan, 1933, 36, 436B).—The amounts of EtOH, AcOH, CH<sub>4</sub>, H<sub>2</sub>, CO<sub>2</sub>, butyric and lactic acid formed are recorded. A. A. L.

**Fermentation of polyhydric alcohols by the colon and aërogenes groups of bacteria. I. *d*-Sorbitol.** C. F. POE, J. T. FIELD, and N. F. WITT (Univ. Colorado Bull. Studies, 1933, 20, No. 2—3, 165—171).—The latter group showed greater total acidity and gave greater amounts of org. acids. CHAcMe·OH was not formed. CH. ABS.

**Extracellular fat-formation by a lime-assimilating bacillus.** A. BRUSSOFF (Naturwiss., 1933, 28, 528—529).—From the Aix medicinal springs there has been isolated a CaO-assimilating bacillus the development of which is associated with the extracellular production of fat. There is probably some connexion between the amounts of CaO assimilated and fat produced. R. N. C.

**Lipins of tubercle bacilli. XXXIV. Isolation of a pigment and anisic acid.** R. J. ANDERSON and M. S. NEWMAN (J. Biol. Chem., 1933, 101, 773—779).—The COMe<sub>2</sub>-sol. fat of the tubercle bacillus (strain H-37) was hydrolysed and the fatty acids were removed as Pb salts. The amyl alcohol solution of the residue after extraction with aq. KOH, acidification, and extraction with Et<sub>2</sub>O gave a mixture which was treated with KOH and dried. From this residue COMe<sub>2</sub> extracted the K salt of a pigment, C<sub>11</sub>H<sub>8</sub>O<sub>3</sub>, m.p. 173—174°, and left K anisate. A. L.

**Water-soluble proteins of the tubercle bacillus.** G. A. C. GOUGH (Biochem. J., 1933, 27, 1049—1054).—The bacilli were suspended in abs. EtOH at -10°, transferred to EtOH-Et<sub>2</sub>O mixtures at -3° containing increasing amounts of Et<sub>2</sub>O, and finally extracted with Et<sub>2</sub>O. An aq. extract of the product yielded a globulin- (I) and an albumin-fraction (II) on treatment with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> to half- and full-saturation, respectively. Whilst (I) gave a positive and (II) a negative tryptophan response, the carbohydrate content of (II) (11.7% as glucose) is much > that of (I) (0.3%). Differences also occurred in their immunological reactions. A certain similarity appears to exist between the protein constitution of the tubercle bacillus and that of the *Salmonella* group. F. O. H.

**Chemical composition of the active principle of tuberculin. XVII. Nitrogen partition values of proteins from different acid-fast bacilli and the relationship to biological activity.** F. B. SEIBERT and B. MUNDAY (J. Biol. Chem., 1933, 101,

763—771).—Three different protein preps. made from tuberculin of the human tubercle bacillus and containing almost identical amounts of total N gave similar N partition vals. No significant differences were detected between the above preps. and those similarly made from avian and bovine tubercle bacilli and timothy-grass bacilli filtrates. Using two proteins made from Koch's "old tuberculin" and two denatured protein preps., high vals. for basic N were obtained, but these fractions were less potent in giving the skin reaction on tuberculous guinea-pigs. The presence of much polysaccharide caused an increase in the amide-N vals. A. L.

**Effect of tuberculin on spermatozoa from normal and tuberculous guinea-pigs.** L. C. DONALDSON and A. J. VORWALD (Amer. Rev. Tuberc., 1933, 27, 401—410).—The spermatozoa method is not suitable for testing the potency of tuberculin. CH. ABS.

**Sensitisation of guinea-pigs and the production of allergy and anaphylaxis to tuberculin protein.** H. S. REICHEL and H. GOLDBLATT (Amer. Rev. Tuberc., 1933, 27, 291—307). CH. ABS.

**Effect of the reaction of the medium on the characteristics of bacteria. I. General. Results obtained with *B. coli comm.*, *S. enteritidis*, and *Ps. pyocyanea*. II. Behaviour of *B. subtilis*. III. *B. cereus*.** E. W. STEARN and A. E. STEARN (J. Bact., 1933, 26, 9—35, 37—55, 57—75).—I. Differences in growth and appearance of colonies grown in media of different  $p_H$  persist in certain cases after repeated subculturing in a neutral medium.

II. In media having  $p_H <$  a fairly definite crit. val. a variant "acid strain" develops. By modifying cultural conditions a reversal to the "alkaline" strain may be induced.

III. Characteristic differences in colonies grown on media having  $p_H <$  6.0 are described. A. G. P.

**Use of reduced iron for the cultivation of anaërobic organisms.** J. P. SCOTT and C. A. BRANDLY (J. Bact., 1933, 26, 1—7).—Typical fermentation reactions of anaërobic organisms occur in media containing reduced Fe in place of the customary vaseline seal. Fe causes active partial reduction of methylene-blue. A. G. P.

**Vitamin necessary for the growth of *B. sporogenes*: its relation to auxin and other growth factors.** B. C. J. G. KNIGHT and P. FILDES (Brit. J. Exp. Pathol., 1933, 14, 112—124).—Pressed baker's yeast and urine contain a substance (I) which enables *B. sporogenes* to grow in a purified medium. (I) resembles auxin. NUTR. ABS. (m)

**Chemotherapy of pneumococcus infections. Quinine derivatives.** M. GUNDEL and L. SEITZ (Arch. exp. Path. Pharm., 1933, 171, 519—540).—The *in vitro* and *in vivo* activities of aq. 1% quinine phenylquinolinecarboxylate (I) on pneumococci are > those of aq. 0.5% optochin (II). The Na dehydrocholate derivative (III) is stronger *in vitro*, but somewhat weaker *in vivo*, than (I); under both conditions it is stronger than (II). The SrCl<sub>2</sub> urea derivative has an activity approx. equal to that of (I) or (III). F. O. H.

**Chemical and immunological properties of pneumococci and other heterophile antigens.** G. H. BAILEY and M. S. SHORT (Amer. J. Hyg., 1933, 17, 329—357).  
CH. ABS.

**Properties of pneumocholin, a biochemical antigen.** E. E. ZIEGLER (J. Lab. Clin. Med., 1933, 18, 695—704).—Pneumocholin, produced by lysis of pneumococci in a bile salt, is unchanged in 0.5 hr. at 56°.  
CH. ABS.

**Skin reactions to the specific soluble substances of pneumococcus types I and II.** J. R. ALSTON and A. S. R. LOWDON (Brit. J. Exp. Path., 1933, 14, 1—9).  
CH. ABS.

**Absorption of antitoxins through the skin.** R. RICHOU (Ann. Inst. Pasteur, 1933, 51, 117—145).—In the guinea-pig tetanus antitoxin applied as an ointment to the skin is rapidly absorbed during the first 6 hr., but not to the same extent as by subcutaneous injection. The absorbing power of different areas of the skin varies, that of the stomach being greatest. The difference between various routes of absorption is merely quant.; only 0.1% of the total antitoxin employed is absorbed through the skin.  
P. G. M.

**Skin permeability and anaphylaxis.** R. RICHOU (Ann. Inst. Pasteur, 1933, 51, 146—148).—It is not possible to desensitise the guinea-pig to antitetanus serum by means of skin dressings. Substances penetrating the skin, other than the antitoxin, may give rise to anaphylactic shock.  
P. G. M.

**Red cells and immunity.** R. D. DE LA RIVIERE and N. KOSOVITCH (Ann. Inst. Pasteur, 1933, 51, 149—159).—Diphtheria toxin is adsorbed on red blood-corpuscles both *in vivo* and *in vitro*, although the affinity varies in different species; rat corpuscles show the least affinity. The toxin is adsorbed on the hæmoglobin in the corpuscles, not on the stroma. Tetanus anatoxin adsorbed on red cells acts as a protective agent against hæmolysis by the toxin. The development of antibodies to purified hæmoglobin is highly sp.  
P. G. M.

**Significance of change in antigenic volume as the result of specific agglutination.** F. S. JONES and R. B. LITTLE (J. Exp. Med., 1933, 57, 729—739).  
CH. ABS.

**Bactericidal substance in urine of patients receiving a ketogenic diet.** A. T. FULLER (Biochem. J., 1933, 27, 976—982).—The urine of patients on a ketogenic diet has a marked bacteriostatic action on *B. coli*. This is mainly due to the presence of *l*- $\beta$ -hydroxybutyric acid, although the increased acidity of the urine enhances its action.  
F. O. H.

**Urinary antiseptics. Antiseptic power of urine after administration of urotropine and its derivatives.** D. BOVET and L. DEMANCHE (Ann. Inst. Pasteur, 1933, 51, 237—247).—The drugs were administered intravenously and the bactericidal power of the urine was tested at intervals. The most effective was the  $C_2H_4I-OH$  compound (I) of  $(CH_2)_6N_4$  (II); a urine was obtained lethal to *S. aureus* for 7 hr. and to *B. coli* for 5 hr. after injection of 1 g. per kg. of body-wt. (II) is sensitive to changes of  $p_H$ , being less active on the alkaline side of  $p_H$  5, but (I) is

unaffected. The derivatives were more toxic than (II) itself.  
P. G. M.

**Sterilising action of acids on bacteria. I. Mineral acids.** S. TETSUMOTO (J. Agric. Chem. Soc. Japan, 1933, 9, 67—75).—The action of  $HNO_3$ ,  $HCl$ ,  $H_3PO_4$ ,  $H_3BO_3$ , and  $H_2SO_4$  depends only on the  $p_H$ ; that of dil. aq.  $HCrO_4$  and  $HCNO$  is due to undissociated mols.  
CH. ABS.

**Relation of some physical properties to bactericidal action of some  $\alpha$ -phenyl-substituted acids.** L. H. BALDINGER and J. A. NIEUWLAND (J. Amer. Pharm. Assoc., 1933, 22, 711—716).—The germicidal activity (*B. coli*) of  $BzOH$  and  $\alpha$ -Ph derivatives of the  $C_2-C_7$  aliphatic acids increases with rise of mol. wt. to  $C_6$  and then is limited by the decreasing solubility. Curves showing adsorption by animal C from aq. solution and the distribution coeffs. between oil and  $H_2O$  parallel that of the bactericidal action.  
E. H. S.

**Oligodynamic action of silver, and the rôle of oxygen.** A. VAN ACKER (Natuurwetensch. Tijds., 1933, 15, 93—104).—Various theories are discussed. The oligodynamic action of Ag depends on a chemical action between the Ag and the bacteria, and  $O_2$  plays no part in the process.  
H. F. G.

**Photo-sensitising action of aniline dyes on staphylococci and streptococci.** A. SZÜTS (Magyar Orvosi Arch., 1932, 33, 268—273; Chem. Zentr., 1932, ii, 3903—3904).—The bactericidal action of sunlight and quartz [Hg] light on cultures sensitised by  $NH_2Ph$  dyes has been investigated. Me-violet (I), Nile-blue, phenosafranine, and acridine-orange have the strongest photodynamic action. (I) has an inhibiting action even in the dark, but virulent cultures are destroyed only by irradiation. Eosin, resorufin, and phloxin-red have an inhibiting effect only on staphylococci at higher concn. Neutral-red, fluorescein, rose-bengal, and anthracene-yellow are without effect. Sensitisation increases with an increase in concn. and streptococci are more resistant than staphylococci.  
L. S. T.

**Preparation of purified bacteriophage.** M. SCHLESINGER (Biochem. Z., 1933, 264, 6—12).—The prep. of highly purified bacteriophage in quantity is described. The diam. of the particles is about 90  $\mu$ .  
W. McC.

**Chemical mediators of autonomic nerve impulses.** W. B. CANNON (Science, 1933, 78, 43—48).—A review.  
L. S. T.

**Passage of foetal hormones through the placenta (adrenal and posterior pituitary hormones).** L. CATTANEO (Arch. ital. Biol., 1931, 86, 1—10; Chem. Zentr., 1933, i, 794).—Adrenaline, choline, and pituitary hormone were injected into the foetal heart and subsequently detected in the maternal blood (rabbit).  
L. S. T.

**A lactation hormone of the adrenal cortex.** K. A. BROWNELL, J. E. LOCKWOOD, and F. A. HARTMAN (Proc. Soc. Exp. Biol. Med., 1933, 30, 783—784).—Adrenal cortical extracts prepared by a process involving chilling to  $-12^\circ$  do not support lactation in adrenalectomised rats, although they make possible the successful termination of pregnancy; but the

material separating between 3° and -12° yields an extract, the injection of which enables such animals to suckle their young. The name cortilactin is suggested for this substance. NUTR. ABS. (b)

**Function of the adrenal cortex. VII. Adrenal cortex and glutathione.** K. A. WINTER, M. REISS, and J. VALDECASAS (*Endocrinol.*, 1932, 11, 171—174; *Chem. Zentr.*, 1933, i, 1465).—Injection of the adrenal cortex hormone (I) into rabbits or dogs considerably increases blood-glutathione. Intravenous injection of (I) or glutathione depresses the R.Q. A. A. E.

**Relation between the action of adrenaline on the uterus and the hydrogen-ion concentration of the blood.** F. YAGI (*Folia Pharmacol. Japon.*, 1933, 15, No. 4, 302—308).—Decrease in  $p_{H^+}$  increases, whilst increase diminishes, the min. dose stimulating the uterus of the non-pregnant rabbit. CH. ABS.

**Effect of adrenaline on tissue respiration.** B. WALTHARD and H. VON WATTENWYL (*Biochem. Z.*, 1933, 264, 104—108).—The supposed increase in the respiration of liver (rat, guinea-pig) in Ringer solution produced by adding adrenaline (I) and serum (II) (man, guinea-pig, rat) does not occur, but auto-oxidation of (I), which may be prolonged by (II), takes place. W. McC.

**Mechanism of the antagonistic action of adrenaline and insulin.** W. SCHEER (*Z. klin. Med.*, 1933, 123, 159—167; *Chem. Zentr.*, 1933, i, 1468).—Injection of either or both increases the  $O_2$  requirement. Apparently metabolic changes produced by the two hormones affect different parts of the body. A. A. E.

**Hypoglycaemic effect of insulin in dogs under chloralose.** E. AUBERTIN and E. TRINQUIER (*Compt. rend. Soc. Biol.*, 1933, 112, 316—318).—In chloralosed dogs given 0.25 unit insulin per kg. body-wt., intravenously or subcutaneously, the fall in blood-sugar is more rapid and more prolonged than when no chloralose is given. Subcutaneous injection causes greater relative difference in reaction than intravenous. NUTR. ABS. (m)

**Effect of insulin on blood-sugar after removal of kidneys or ureters.** E. AUBERTIN and E. TRINQUIER (*Compt. rend. Soc. Biol.*, 1933, 112, 318—321).—In dogs insulin, given in doses of 0.25 unit per kg. body-wt., either intravenously or subcutaneously after removal of the kidneys, causes increase in the hypoglycaemic area as compared with normal response. Fall in blood-sugar and prolongation of the hypoglycaemic period increases daily while the animals survive, especially when ligation of the ureters has also been performed. NUTR. ABS. (m)

**Effect of insulin on blood-sugar of rabbits during infection.** L. C. FISHER and H. A. REIMANN (*Proc. Soc. Exp. Biol. Med.*, 1933, 30, 746—747).—The intracutaneous inoculation of 0.1 c.c. of a 1:400 dilution of a culture of Type 1 pneumococci caused healthy rabbits to become more susceptible to the action of insulin. NUTR. ABS. (b)

**Effect of insulin on optical properties of blood-glucose.** J. THOMAS (*Compt. rend. Soc. Biol.*, 1933, 112, 1258—1260).—Lactic acid,  $NH_2$ -acids, glut-

athione, and glycuronates do not affect the  $[\alpha]$  of blood dialysates to an extent  $> 8-10\%$ , whereas differences from the calc. vals. for  $\alpha\beta$ -glucose of 25—30% were observed. The blood of untreated diabetics or of depancreatised dogs is considered to contain only  $\alpha\beta$ -glucose on account of its low  $[\alpha]$ ; insulin restores the much greater differences usually found in normals. NUTR. ABS. (b)

**Influence of insulin on muscle-tissue respiration in polyneuritic pigeons.** T. INAWASHIRO (*Tôhoku J. Exp. Med.*, 1933, 20, 544—552).—Insulin, when added to the cell prep. or injected subcutaneously into the birds 1 hr. before death, caused a diminution in  $O_2$  uptake in strips of pectoral muscle which varied directly with the amount of insulin used, and was more marked with polyneuritic than with normal pigeons. The blood-sugar of normal pigeons averaged 0.155%, that of polyneuritic birds 0.221%. After insulin injection both normal and, to a greater extent, polyneuritic birds showed diminished vals. NUTR. ABS. (b)

**Effect of electrical stimulation of the vagus on secretion of insulin.** R. GAYET and M. GUILLAUMIE (*Compt. rend. Soc. Biol.*, 1933, 112, 1197—1201).—Electrical stimulation of the vagal connexions of pancreatic tissue grafted into the neck of the diabetic dog or of transplanted pancreas, transfused by the blood of another animal in which the adrenal veins were ligatured, was without effect on the blood-sugar. Experiments on animals in which precautions were taken to suppress hepatic glycogenolysis by hepatic denervation and extirpation or denervation of the adrenals, and on animals in which, in addition to hepatic denervation, splanchnic section and extirpation of the essential sympathetic ganglia were performed, were negative. The results do not justify the assumption of a nervous control of insulin output. NUTR. ABS. (b)

**Stimulating action on the pancreatic secretion and hypoglycaemic action of secretin.** J. LA BARRE and J. LEDRUT (*Bull. Soc. Chim. biol.*, 1933, 15, 724—763).—Preps. of secretin (I) which have definite isoelectric points and which give f.-p. curves for their aq. solutions indicative of a pure substance show a hypoglycaemic as well as a stimulating action on the pancreatic secretion. Such preps. treated with  $Et_2O$ , dialysed, or pptd. with homopolar substances still retain their hypoglycaemic action. A double pptn. with heteropolar substances such as  $CCl_3 \cdot CO_2H$  or  $KClO_3$ , however, gives a fraction [excretin (II)] having no hypoglycaemic action. Electrometric titration of (II) indicates that it is a pure substance, and the greater viscosity of aq. solutions of (II) than those of (I) shows that (II) has much larger mols. than (I). A. L.

**Use of albino rats for the assay of the male sex hormone.** Y. WANG and H. WU (*Chinese J. Physiol.*, 1933, 7, 135—149).—The seminal vesicles (I) and preputial glands (II) of rats, castrated at the age of 4 weeks, show a marked decrease in wt. during the first 4 weeks. After two daily injections of the male sex hormone, (I) shows an appreciable gain in wt. in 24 hr. and (II) in 48 hr., which is approx.

proportional to the amount of hormone given. The best results are obtained with rats castrated at 4 weeks and given hormone injections 4 weeks after.

H. G. R.

**Action of the follicular hormone on vegetables.** J. PÁZLER (Z. Zuckerind. Czechoslov., 1933, 57, 421—424).—In sand cultures of oats no sp. effect of the hormone on growth was observed.

A. G. P.

**Stimulation of the reproductive organs of cattle.** P. J. KERR (Indian J. Vet. Sci., 1932, 2, 306—309).—Urine of pregnant cows affords a hormone extract which stimulates the reproductive organs of bulls and cows.

CH. ABS.

**Sex-physiological studies. X. Conservation of prolán in urine.** M. BORST, A. DÖDERLEIN, and D. GOSTIMIROVIĆ (Münch. med. Woch., 1932, 79, 1392—1393; Chem. Zentr., 1932, ii, 3904).—Unchanged prolán can be preserved for 356 days and the follicular-ripening hormone for 424 days by the addition of *m*-cresol or Et<sub>2</sub>O.

L. S. T.

**Prolán in the pituitary. I. Prolán in the pituitary lobes and pars tuberalis in man and the ox. II. Production of prolán in basophilic cells.** B. ZONDEK (Klin. Woch., 1933, 12, 22—25; Chem. Zentr., 1933, i, 957).—In the ox the posterior pituitary lobe contains no prolán; in man the test usually gave positive results. It is present only in the parts adjacent to the anterior lobe, and probably originates in basophilic cells. In the pars tuberalis, but not in other parts of the brain, prolán was detected.

A. A. E.

**Pituitary substance giving increased gonadotropic effects when combined with prolán.** H. M. EVANS, M. E. SIMPSON, and P. R. AUSTIN (J. Exp. Med., 1933, 57, 897—906).—The increased gonadotropic effect obtained by combining prolán with pituitary extracts can be secured equally well by means of preps. which contain large amounts of the growth-promoting or of the gonad-stimulating hormone, neither of which is responsible for the reaction.

CH. ABS.

**Follicular ripening and luteinising hormone in the anterior pituitary lobe of various animals.** H. MAGISTRIS (Pflüger's Archiv, 1932, 220, 835—841; Chem. Zentr., 1933, i, 1464).

A. A. E.

**Effect of a fat diet and of anterior pituitary extract on the liver-glycogen of thyroidised rats.** H. MAGISTRIS (Compt. rend. Soc. Biol., 1932, 111, 397—399; Chem. Zentr., 1933, i, 1960).—The power of the liver to form glycogen is retained.

A. A. E.

**Effect of the anterior pituitary hormone on the blood-sugar.** F. BÖHM (Z. ges. exp. Med., 1932, 84, 689—694; Chem. Zentr., 1933, i, 1960—1961).—Intravenous injection of prolán (I) into rabbits raises the blood-sugar; when the val. is > 300 mg. per 100 c.c., glycosuria occurs. Ergotamine suppresses (I) hyperglycæmia; insulin hypoglycæmia is diminished by (I). If the liver is free from glycogen, (I) does not produce hyperglycæmia.

A. A. E.

**Pituitary and thyroid glands. Effect of anterior pituitary extract on blood-iodine.** B. A. HOUSSAY, P. MAZZOCCO, and A. BLASOTTI (Compt.

rend. Soc. Biol., 1932, 111, 401—402; Chem. Zentr., 1933, i, 1960).—Injection of anterior pituitary extract into dogs increased the blood-I.

A. A. E.

**Influence of anterior pituitary extract on blood-glutathione.** H. MAVEROFF (Rev. Soc. Argentina biol., 1932, 8, 614—615).—Intraperitoneal injection of the extract increases the erythrocyte-glutathione of normal, thyroidectomised, and hypophysectomised dogs.

CH. ABS.

**Effect of anterior pituitary extract on plasma-protein.** I. GOLDBERG (Rev. Soc. Argentina biol., 1932, 8, 610—613).—In normal dogs daily injection of ox anterior pituitary extract increased the blood-plasma-total protein, -non-protein-N, and -viscosity. In recently thyroidectomised dogs the increase in blood-globulin was proportionally greater.

CH. ABS.

**Distinction between the anterior pituitary hormone having an excito-secretory action on the thyroid gland, and the ovary-stimulating factor in extracts of the anterior lobe.** M. ARON (Compt. rend. Soc. Biol., 1931, 106, 1044—1046; Chem. Zentr., 1932, ii, 3905).

**Adrenotropic hormone of the anterior pituitary lobe.** J. B. COLLIP, E. M. ANDERSON, and D. L. THOMSON (Lancet, 1933, 125, 347—348).—The adrenotropic principle (I) is distinct from the thyrotropic principle.

L. S. T.

**Are the erythrochrome reaction of the minnow and the melanophore reaction of the frog identical?** A. JORES and E. W. LENSSEN (Endokrinol., 1933, 12, 90—101; Chem. Zentr., 1933, i, 1959—1960).—Changes in activity effected by boiling the pigment hormone with NaOH are described. The melanophores of the frog correspond with the alkaline, and the erythrochrome with the acid, form of the hormone. Constituents of the anterior pituitary lobe sensitise the latter, but not the former. The two reactions are not identical.

A. A. E.

**Assaying posterior pituitary extracts for oxytocic activity.** J. M. GULLAND (Biochem. J., 1933, 27, 1216—1217).—Burn's method is simplified. Uterine horns (guinea-pig) can be preserved in Ringer solution.

H. B.

**Oxytocic hormone of posterior lobe of pituitary gland. II. Action of nitrous and nitric acids.** J. M. GULLAND (Biochem. J., 1933, 27, 1218—1228).—The hormone (I) is rapidly converted by HNO<sub>2</sub> at  $p_H$  3 into a derivative *A*, which has 35% of the oxytocic activity of (I) and is stable at  $p_H$  7.4. This is transformed by HNO<sub>3</sub> (formed by aerial oxidation of HNO<sub>2</sub>) or by HNO<sub>2</sub>+HNO<sub>3</sub> into a substance *B* (II) (activity 20%), which is gradually converted by high concns. of HNO<sub>2</sub> into a substance *D* (activity 0.1%). HNO<sub>3</sub> converts (I) into a substance *C* (activity about 90%), which is unstable at  $p_H$  7.2, and is transformed by HNO<sub>2</sub> into a substance probably identical with (II).

H. B.

**Oxytocic hormone of the posterior lobe of pituitary gland. III. Action of preparations of plant proteolytic enzymes.** J. M. GULLAND and T. F. MACRAE (Biochem. J., 1933, 27, 1237—1247; cf. A., 1932, 655; this vol., 539).—The hormone was

inactivated slowly by two aminopolypeptidase (I) preps. and very rapidly by two dipeptidase (II) preps. and by two proteinase preps., both of which contained some (I), whilst one contained a trace of (II). None of these enzymes (all of which were from yeast), however, is responsible for the inactivation, which is due to a fourth enzyme having a  $p_H$  optimum of 7.4 and is present also in papain. Inactivation by the enzyme is never complete, 0.7% of the initial activity remaining; this residual activity is probably due to a derivative of the hormone produced by the action of the enzyme. F. O. H.

**Pharmacological standardisation of parathormone.** C. L. ROSE (J. Lab. Clin. Med., 1932, 18, 300—304).—The unit is 0.01 of the amount required to produce an increase of 5 mg. of Ca per 100 c.c. in the blood of a 20-kg. dog. Blood-Ca is max. 16—18 hr. after subcutaneous injection. CH. ABS.

**Significance of parathyroid hormone for regulation of calcium metabolism. V. Substances which raise and lower blood-calcium.** C. BOMSKOV and J. FALCK (Z. ges. exp. Med., 1933, 87, 662—667).—Intravenous injection of small amounts of substances which stimulate the secretion of adrenaline (nicotine, strychnine, caffeine) leads to a transitory fall in serum-Ca succeeded by a rise; large amounts produce an immediate sharp rise. These results are similar to those following injections of small and large amounts of parathyroid hormone. This hormone stimulates the production of adrenaline.

NUTR. ABS. (m)

**Influence of thyroxine, thyreoglobulin, and paroidin on the reduced glutathione content of blood.** E. ZUNZ (Compt. rend. Soc. Biol., 1932, 110, 1003—1005; Chem. Zentr., 1932, ii, 3907).—Injection of thyroxine into the saphenous vein does not alter the glutathione coeff. (I), but thyreoglobulin (II) raises it. There appears to be no relation between (I) and the accompanying alteration in blood-sugar, nor does the effect of (II) appear to be related to the increased adrenaline secretion. Paroidin (III) increases (I) markedly, and the effect is greatest when the blood-sugar is lowered to the largest extent. (III) has no further effect on (I) when the adrenals are removed. L. S. T.

**Non-thyroid substance with thyroid action. I.** ABELIN and A. FLORIN (Arch. exp. Path. Pharm., 1933, 171, 443—456).—Hydrolysis of iodised protein with aq. Ba(OH)<sub>2</sub> yields an I-containing substance having physiological properties closely resembling those of thyroxine. Thyroidectomy of the animal to which it is administered has no influence on its activity. The method of Leland and Foster (A., 1932, 432) when applied to various iodised proteins yields small amounts of the thyroxine-like fraction. F. O. H.

**Biological action of vitamins and their sequence.** W. KOLLATH (Naturwiss., 1933, 21, 537—542).—A discussion. A. C.

**Vitamin terminology.** J. KÜHNAU (Z. Vitaminforsch., 1932, 1, 184—191; Chem. Zentr., 1933, i, 799). L. S. T.

**Synergism amongst vitamins.** H. J. JUSATZ (Z. ges. exp. Med., 1933, 87, 529—544).—Vitamin-B (I) diminishes the toxic effects produced by feeding excess of irradiated ergosterol (II), but administration of vitamin-A (III) does not modify the toxic effects in hypervitaminosis-D. Symptoms of A- and D-hypervitaminosis in the same animal can be produced simultaneously. (I) increases the catalase index of the blood, but (III) does not. Administration of (II) causes an increase in the blood-catalase, although an excess causes a decrease. In advanced stages of hypervitaminosis-D ability to produce antibodies is diminished. NUTR. ABS. (m)

**Deficiency disorder induced in young suckling rats bred on a purified synthetic diet with "Glaxo casein" (caseinogen) as sole source of protein.** L. W. MAPSON (Biochem. J., 1933, 27, 1061—1068).—The suckling young of rats receiving "Glaxo casein" as sole source of protein develop a disease characterised by failure of growth, loss of fur, and eventual death. The disease is probably the result of a deficiency and is cured by extracts containing physin (cf. A., 1932, 1174) or the Coward factor (cf. A., 1929, 1496). The possible identity of these two factors is discussed. W. O. K.

**Vitamin-A in the retina.** G. WALD (Nature, 1933, 132, 316—317).—The unsaponifiable extracts of the visual purple, intact retinas, and the pigment-choroid layers of frogs, sheep, pigs, and cattle show all the characteristics of vitamin-A-containing oils. An extract of ox retinas cured rats suffering from avitaminosis. L. S. T.

**[Vitamin-A in] rice embryo.** T. MIKI (Arb. med. Univ. Okayama, 1933, 3, 501—504).—The unsaponifiable fraction of the oil extracted from rice embryo contains vitamin-A. NUTR. ABS. (b)

**Carotene content, vitamin-A potency, and anti-oxidants of butter-fat.** C. L. SHREWSBURY and H. A. KRAYBILL (J. Biol. Chem., 1933, 101, 701—709).—The colorimetric determination of carotene (I) by comparison with a dichromate standard is possible with (I) dissolved in light petroleum. When butter-fat is used as solvent the results are consistently high, although the spectrophotometric method is trustworthy. Treatment of butter-fat with charcoal destroys its colour, vitamin-A activity, and the natural anti-oxidants which protect (I) from oxidation. A. L.

**Seasonal variation in butter-fat. I. Seasonal variations in carotene, vitamin-A, and the antimony trichloride reaction.** R. G. BOOTH, S. K. KON, W. J. DANN, and T. MOORE (Biochem. J., 1933, 27, 1189—1196).—Blue val. (I) of the untreated butter-fat (II) was valueless as a guide to the vitamin-A (III) content, being 0.2—0.1 of the unsaponifiable matter. Variations in (I) between winter and summer butter were due to a higher concn. of inhibitory substance in the latter. When assaying total (III) by colorimetric methods, both (III) and carotene (IV) should be accounted for. Total (III) of (II) in summer is about thrice that in winter, and the activity due to (IV) is also > in winter.

H. G. R.

**Threshold of activity of carotene.** L. RANDOIN and R. NETTER (Bull. Soc. Chim. biol., 1933, 15, 706—723).—A study of the change in wt. and the preventive and curative effect with respect to xerophthalmia brought about by administration of carotene to young rats deprived of vitamin-A indicates that a daily dose of  $4 \times 10^{-6}$  g. is the amount  $< 10 \times 10^{-6}$  g. which has the greatest relative effect. Administration of  $10 \times 10^{-6}$  g. daily does not bring about normal growth as obtained by the daily addition of 1 drop of cod-liver oil, and the effect is not distinctly superior to that of  $4 \times 10^{-6}$  g. daily. A. L.

**Method of enhancing the vitamin-A value of cod-liver oil.** E. R. JANES, H. F. GROVER, and E. J. QUINN (Proc. Soc. Exp. Biol. Med., 1933, 30, 516—519).—The growth of rats depleted of vitamin-A is stimulated by giving combined malt extract and cod-liver oil emulsion, but rats given the same dose of the oil alone or of the emulsion and malt extract separately fail to grow and show symptoms of vitamin-A deficiency. Vitamin-A is therefore best utilised in the malt and oil emulsion. NUTR. ABS. (m)

**Evaluation of the vitamin-A concentrate "Vogan."** Avitaminosis-A. T. MOLL, F. DOMAGK, and F. LAQUER (Klin. Woch., 1933, 12, 465—467).—"Vogan," a vitamin-A (I) concentrate derived from fish-liver oils, contains 40,000 rat units (approx. Sherman units) of (I) per c.c. Massive doses of (I) (0.02 c.c. daily of Vogan) were deleterious for mice, causing excessive storage of lipins (II) in epithelial cells. (I) deficiency, on the other hand, caused the epithelial cells to be completely depleted of (II), and it is therefore suggested that (I) is concerned in the metabolism of (II). NUTR. ABS. (b)

**Comparison between the spectrophotometric and biological assay for the vitamin-A content of fish-liver oils.** M. A. MAGILL and W. R. BRODE (Ohio J. Sci., 1933, 33, 127—134).—Some agreement was obtained within certain groups of commercial samples. Several closely allied compounds may be responsible for both colour reactions and vitamin properties. Peppermint oil contains a colour-forming compound which has a similar chromogen to that in oils known to contain vitamin-A. CH. ABS.

**Value of ferrous iodide administered directly and indirectly.** H. C. CAMERON (Proc. Soc. Exp. Biol. Med., 1933, 30, 762—765).—No vitamin-A-substituting effect is observed on giving  $\text{FeI}_2$  alone or combined with linoleic acid. NUTR. ABS. (m)

**Blood-cholesterol in dogs on a vitamin-A-deficient diet.** E. P. RALLI and A. WATERHOUSE (Proc. Soc. Exp. Biol. Med., 1933, 30, 519—523).—In dogs fed on a vitamin-A- (I) -deficient diet the blood-cholesterol (II) increases when symptoms of (I)-deficiency appear. On giving (I), (II) diminishes. Hence the metabolism of cholesterol appears to be affected by the amount of (I) in the body. NUTR. ABS. (m)

**Fat-soluble vitamins and nutrition.** ANON. (Nature, 1933, 132, 304).—A summary of a lecture on the significance of vitamins-A and -D in human nutrition and in certain diseases. L. S. T.

**A- and D-Avitaminosis in the guinea-pig. Combined action of the vitamins. Composition of diet and scurvy in the guinea-pig.** P. E. SIMOLA (Acta Soc. med. Fennicæ "Duodecim," 1932, A, 16, No. 1, 16 pp., 12 pp., 8 pp.).—A. Carotene prevents the onset of symptoms in guinea-pigs receiving a diet deficient in vitamin-A. On a modified McCollum diet, guinea-pigs remain alive for relatively long periods with no marked rachitic changes, but a diet with excess of P is tolerated very badly.

B. The course of B-avitaminosis in young rats is not appreciably influenced by varying the amounts of the A-, C-, and D-factors in the diet nor is the course of C-avitaminosis in guinea-pigs influenced by varying the A- and D-factors. The vitamin-A content of the livers of half-grown rats with vitamin-A deficiency is not influenced by the amount of vitamin-D supplied.

C. In guinea-pigs receiving different deficient diets wt. loss is least when a modification of McCollum's rachitogenic diet is used. The shortest life spans are observed with Zilva's scorbutic diet. Scurvy symptoms are most marked with diets containing abundant carbohydrate or fat. Carotene or vigantol exerts no marked effect on the progress of the scurvy. NUTR. ABS. (m)

**Effect of vitamins on growth, length of life, and fertility.** F. GROEBBELS (Klin. Woch., 1933, 12, 215—217).—In rats receiving a diet of caseinogen, rice starch, palmin, salt mixture, and yeast additions of "ossin" (I) (cod-liver oil and egg yolk), cod-liver oil (II), or irradiated ergosterol (III) diminish the fertility of the females (as judged by the no. of young per litter) and the rate of growth and survival of the young. The unfavourable effect on the growth of the young is less with (I) than with (II) or (III). NUTR. ABS. (m)

**Vitamin-D. IV. Ergosterol in soya-bean oil.** S. IZUME, Y. YOSHIMARU, and T. HIDAKA (J. Agric. Chem. Soc. Japan, 1933, 9, 246—253).—The sterol, m.p. 136—137° (acetate, m.p. 131—132°), contains 19.8—20.0% (by absorption spectrum) of ergosterol. CH. ABS.

**Isomerides of cholesterol and experimental rickets.** U. SAMMARTINO (Arch. Farm. sperim., 1933, 56, 343—350).—Rats were fed on a normal diet and on a rachitogenic diet supplemented with either cholesterol (I) or the isocholesterol (II) of De Fazi (this vol., 710), both non-irradiated and irradiated. With irradiated, but not with non-irradiated, (I) and (II), bone-calcification approaches that occurring with the normal diet. F. O. H.

**Effect of high doses of irradiated and non-irradiated ergosterol on the albino rat.** J. T. HAUCH (Proc. Soc. Exp. Biol. Med., 1933, 30, 475—477).—Toxic effects (I) are observed only with high doses. The (I) recorded by others with comparatively small doses were due to the presence of a toxic substance other than vitamin-D. NUTR. ABS. (m)

**Action and therapeutical importance of the water-soluble derivatives of vitamin-D.** E. BECART (Arch. internat. Pharmacodyn. Thérap., 1933, 44, 164—172).—Rickets in rats can be cured by  $\text{H}_2\text{O}$ -sol. K vitamin-D phthalate. NUTR. ABS. (m)

**Calcium-phosphorus metabolism in the chicken. IV. Ergosterol requirements of growing chicks.** E. J. KING, H. HULL, and G. E. HALL (Poultry Sci., 1933, 12, 129—132).—Growing chicks consuming a diet with a Ca : P ratio of 1.91 : 1 needed 10 times as many rat-units of vitamin-D in the form of irradiated ergosterol (I) as in the form of cod-liver oil (II) to produce leg bones with approx. the same ash content. (I) and (II) were mixed with the diet; the same amount of (I) given separately by mouth produced a higher ash content.

NUTR. ABS. (b)

**Free fatty acids in cod-liver oils and vitamin-D.** O. SCHULTZ (Z. Vitaminforsch., 1932, 1, 287—289; Chem. Zentr., 1932, ii, 3910).—Six oils containing 1—20% of free fatty acid showed agreement in respect of vitamin-D content; this deteriorated by about 30% during 2 years. Methods of prep., with the exception of bleaching, had no marked influence on the vitamin content.

L. S. T.

**Vitamin-D activity of butter. I. Chemical differentiation of antirachitic factor of autumn and winter butter from irradiated ergosterol and vitamin-D of cod-liver oil.** S. K. KON and R. G. BOOTH (Biochem. J., 1933, 27, 1302—1309).—Autumn and winter butters saponified with aq.-alcoholic KOH lose > 80% of their antirachitic potency. Irradiated ergosterol (I) and cod-liver oil (II) treated in the same way both in the presence and absence of butter are unaffected by the treatment, indicating a chemical difference between the antirachitic factor of butter and those of (I) and (II).

H. D.

**Lactic bacteria, lactose, and the international vitamin-D standard as calcification factors in rachitic rats.** R. LECOQ and H. VILLETTE (Ann. Falsif., 1933, 26, 409—416).—The Randoin-Lecoq method (A., 1928, 556) produces a rapid development of rickets without greatly affecting the wt. increase of the rats, and this is accompanied by a rise in faecal  $p_{H}$  which is not necessarily an indication of rickets, although it is corrected by addition to the diet of irradiated ergosterol. The curative dose of international vitamin-D standard is 1.4 and the preventive dose 0.7 units per 35—45-g. rat per day. Lactic bacteria oppose the rise in  $p_{H}$ , but do not prevent the incidence of rickets, whilst lactic acid (in place of sucrose) lowers the  $p_{H}$  and frequently produces a change in alimentary equilibrium which results in rickets. In biological analyses the effects of vitamin-D and P compounds should be distinguished, although the latter may be expressed in terms of the former if experimental conditions are identical.

J. G.

**Biological detection of vitamin-D.** E. BECCARI (Giorn. Biol. appl. Ind. Chim., 1932, 2, 174—181; Chem. Zentr., 1933, i, 1964).—Intensive growth and change in ash constituents of bones are not exact criteria for vitamin-D.

A. A. E.

**Bone-ash method of determining effectiveness of vitamin-D supplements.** J. L. ST. JOHN, C. KEMPF, and L. BOND (Poultry Sci., 1933, 12, 34—36).—Ash of cartilage-free bone is > that of the whole tibia; cartilage ash (I) in rachitic is much < in

non-rachitic chicks. (I) may be a better criterion than bone ash of the effectiveness of vitamin-D supplements.

CH. ABS.

**Antineuritic vitamin. II.** A. WINDAUS, R. TSCHESCHE, and H. RUHKOPF (Nachr. Ges. Wiss. Göttingen, Math.-Phys. Kl., 1932, 342—346; Chem. Zentr., 1933, i, 1311—1312).—The substance is not  $C_{12}H_{17}ON_3S$ , but  $C_{12}H_{16}ON_4S$  [hydrochloride, m.p. 250° (decomp.); chloroaurate, sinters 190°, decomp. 198°; rufianate (+H<sub>2</sub>O), m.p. 291° (decomp.)]. Hot aq. Ba(OH)<sub>2</sub> affords NH<sub>3</sub> and H<sub>2</sub>S. Hot 2N-HCl affords NH<sub>3</sub> only. Cold dil. KMnO<sub>4</sub> and hot conc. HNO<sub>3</sub> give H<sub>2</sub>SO<sub>4</sub>. OMe, NMe, guanidino-, and C(SH)·NH groups could not be detected.

A. A. E.

**Isolation of oryzanin, antineuritic vitamin. II.** S. OTAKE (J. Agric. Chem. Soc. Japan, 1933, 9, 186—196; cf. A., 1932, 657).—Oryzanin hydrochloride,  $C_{12}H_{16}O_2N_4S_2HCl$ , m.p. 250°, was obtained (1.6 g.) from rice bran (11,500 kg.) by pptg. "oryzanin extract" with AgNO<sub>3</sub> and Ba(OH)<sub>2</sub> at  $p_{H}$  4.5—6.8, hydrolysing the ppt. with HCl, repptg. with phosphotungstic acid, preparing the Pt salt, and removing the Pt with H<sub>2</sub>S.

CH. ABS.

**Antineuritic vitamin from rice polishings. VIII. Polyneuritis in experimental animals.** A. G. VAN VEEN (Meded. Volksgesond. Ned.-Ind., 1932, 21, 184—195).—A formula very similar to those put forward by Otake and Windaus is ascribed to "cryst. vitamin-B<sub>1</sub>" (I). In rats, a daily dose of 4—6 × 10<sup>-6</sup> g. produced a normal rate of growth up to 100—130 g. Increase of dose up to 10—15 × 10<sup>-6</sup> g. produced normal growth up to 200 g. It is concluded that the (I) tested also contained vitamin-B<sub>4</sub>. (I) stimulated the appetite of polyneuritic animals. 4 mg. of (I) had the same potency as 1 g. (100 international units) of Jansen and Donath's acid clay adsorption product. For the prevention of polyneuritis, "rice-birds" required a daily dose of 0.4—0.5 unit, pigeons 2—3, and rats 1—2 units.

NUTR. ABS. (m)

**Crystalline [picrolonate of] antineuritic vitamin (B<sub>1</sub>).** A. SEIDELL and M. I. SMITH (J. Amer. Chem. Soc., 1933, 55, 3380—3383).—Gradual addition of picrolonic acid in MeOH to an aq. solution of the vitamin prep. from brewers' yeast concentrates the vitamin-B<sub>1</sub> into the more sol. portions of the pptd. picrolonate, which after crystallisation from MeOH has m.p. 227° (efferv.) and is curative for polyneuritic rats in doses of 0.015 mg.

R. S. C.

**Extraction of vitamin-B<sub>1</sub> from fresh yeast.** A. SEIDELL (Ann. Brass. Dist., 1933, 31, 24—26).—Preliminary treatment of yeast with sucrose seemed to permit a more complete extraction of the antineuritic vitamin from the liquefied mass by means of 60—70% EtOH than either Pirie's method or treatment with NaCl.

NUTR. ABS. (b)

**Irradiated adenine sulphate and antineuritic vitamin (B<sub>1</sub>).** F. SCHULTZ and F. LAQUER (Z. physiol. Chem., 1933, 219, 158—163).—Neither irradiated nor non-irradiated adenine nor its salts have an antineuritic (B<sub>1</sub>) action on pigeons (cf. Guha and Chakravorty, A., 1932, 1294).

J. H. B.

**Evaluation of food and drugs containing vitamin. II. Vitamin-B complex.** A. JUNG (Z. Vitaminforsch., 1932, 1, 192—214; Chem. Zentr., 1933, i, 804).—Vals. for various materials are given. The % vitamin- $B_2$  requirements of man and rats are approx. identical. A. A. E.

**Phosphorylation and phosphatase action in avitaminosis-B.** J. BODNÁR and A. KARELL (Magyar Orvosi Arch., 1932, 33, 348—350; Chem. Zentr., 1933, i, 1316).—Phosphorylation in the muscle and liver of a pigeon with avitaminosis-B is 77—146% > the normal. No difference was observed in phosphatase action. A. A. E.

**Apparent effect of thymus-nucleic acid on the incidence of rat polyneuritis.** F. F. HEYROTH (Bull. Basic Sci. Res., 1932, 4, 125—127).—Addition of thymus-nucleic acid to a  $B_1$ -free diet restricts the growth of rats and results in an earlier incidence of polyneuritis. CH. ABS.

**Gaseous exchange in pigeons in avitaminosis [ $B_1$ ]. Action of pilocarpine on this exchange in avitaminosis.** G. SARZANA (Arch. internat. Physiol., 1933, 36, 1—12, 13—17).—A. The basal metabolism (I) of pigeons averages 5 g.-cal. per kg./hr. At 29—30° there is no substantial difference in (I) between normal and avitaminous pigeons, but at 12—13° avitaminous birds (II) show a diminished  $O_2$  consumption because (II) cannot adapt themselves to the changed conditions as efficiently as can normal birds.

B. Pilocarpine causes a slight increase in  $O_2$  consumption in pigeons kept for a short time on a diet of polished rice, but when they are in an advanced stage of avitaminosis, there is sometimes a decrease, due to inanition, in this consumption.

NUTR. ABS. (m)

**Avian polyneuritis. Action of vitamin- $B_1$  concentrates *in vitro*.** A. P. MEIKLEJOHN (Biochem. J., 1933, 27, 1310—1320).—Addition of vitamin- $B_1$  (I) concentrate to the minced cerebrum of a (I)-deficient pigeon in the presence of lactate (II) increases the  $O_2$  consumption, but fails to increase the amount of (II) removed. The minced cerebrum of a (I)-deficient pigeon readily removes (II). H. D.

**Vitamin-B-deficient ration.** B. SURE (Proc. Soc. Exp. Biol. Med., 1933, 30, 779—780).—The diet consisted of caseinogen (purified by washing with acidulated  $H_2O$  and with 25% EtOH) 10, salts 4, butter-fat 10, and dextrin 61, together with vitamin- $B_2$  as beef steak (autoclaved for 6 hr. at 20 lb. pressure, and dried at 100°) 15. Rats fed on this diet were depleted of vitamin- $B_1$  in 4—6 weeks.

NUTR. ABS. (b)

**Vitamin- $B_2$  in fruits.** P. L. DAY and W. J. DARBY (J. Home Econ., 1933, 25, 319—323).—The vitamin- $B_2$  content of apples and oranges is low and that of avocados and pears somewhat higher.

NUTR. ABS. (m)

**Vitamin- $B_2$ .** P. GYÖRGY, R. KUHN, and T. WAGNER-JAUREGG (Naturwiss., 1933, 21, 560—561).—Ovoflavin and lactoflavin (this vol., 298, 522, 847) possess the highest vitamin- $B_2$  potency recorded, when administered to rats on a diet supple-

mented by yeast extracts freed from vitamin- $B_2$  or by cryst. vitamin- $B_4$  preps. Flavins and associated vitamin- $B_2$  activity are found both free and bound to material of high mol. wt. Irradiation destroys the vitamin activity. R. K. C.

**Vitamin content of mango fruit.** M. E. F. CRAWFORD and E. O. V. PERRY (Biochem. J., 1933, 27, 1290—1293).—The contents of three varieties of mango in vitamins-A, -C, and -D were assayed.

H. D.

**Vitamin-C in Citrus juices.** A. H. BENNETT and D. J. TARBERT (Biochem. J., 1933, 27, 1294—1301).—Ascorbic acid was determined in Citrus juices by titration with dichlorophenol-indophenol at  $p_H$  6. Individual variations in reducing power up to 60% were observed in lemons. The presence of preservatives, strong acidification, or boiling causes the reducing power of oranges and lemons to decrease and ultimately to vanish during storage. H. D.

**Regeneration of reducing properties of oxidised lemon juice.** S. W. JOHNSON (Biochem. J., 1933, 27, 1287—1289).—Tillmans' observation (A., 1932, 658) that lemon juice oxidised with indophenol, I, or  $H_2O_2$  can regain its reducing capacity when treated with  $H_2S$  immediately after oxidation is confirmed.

H. D.

**Vitamin studies on pears. I. Vitamins-A and -C in Winter Nelis and d'Anjou [pears] after prolonged storage.** I. A. MANVILLE and F. G. CHUINARD (J. Amer. Dietet. Assoc., 1933, 8, 504—516).—Vals. for -A are 2, 5, and for -C 2, 3 Sherman units, respectively. CH. ABS.

**Vitamin-C content of Baldwin apples and apple products.** C. R. FELLERS, M. M. CLEVELAND, and J. A. CLAGUE (J. Agric. Res., 1933, 46, 1039—1045).—A sufficiency of vitamin-C (I) for guinea-pigs was obtained by feeding approx. 4 g. of apples per 300 g. live wt. During storage for 8—10 months the loss of (I) from the apples was approx. 40%. Fresh expressed juice contained nearly as much (I) as did fresh whole fruit. Benzoated or pasteurised cider retained practically no (I) after 48 hr. Canned apple sauce was a poor source of (I). A. G. P.

**Vitamin-C. VIII. Chemical properties. Isolation from cabbage juice.** T. MATSUOKA (J. Agric. Chem. Soc. Japan, 1933, 9, 197—206).

CH. ABS.

**Vitamin-C. IX.** T. MATSUOKA (J. Agric. Chem. Soc. Japan, 1933, 9, 311—315).—Vitamin-C from cabbage juice ( $p_H$  5) is not extracted from aq. solution by oxide-free  $Et_2O$ ; after neutralisation with  $Na_2CO_3$  to  $p_H$  7.3 part is extracted by  $Et_2O$ . CH. ABS.

**Vitamin-C in blood and urine?** M. VAN EEKELLEN, A. EMMERIE, B. JOSEPHY, and L. K. WOLFF (Nature, 1933, 132, 315—316).—Experiments which indicate that the reducing factor in blood and urine is probably vitamin-C are described. Cerebrospinal fluid also yields a substance which reduces 2:6-dichlorophenol-indophenol and gives max. absorption at 2650 Å. as does ascorbic acid. L. S. T.

**Vitamin-C in sea fish and invertebrates.** B. VON EULER and H. VON EULER (Svensk Kem. Tidskr., 1933, 45, 173—180).—Vitamin-C (I) was determined

by titration in organs of the following fish: *Salmo salar* (II), *Gadus callarias* (III), *G. virens*, *Raniceps raminus*, *Squalus acanthias*, and *Myxine glutinosa*. The kidneys contained 0.46–0.8 mg. of (I) per g. fresh wt., whilst livers contained < half this amount, and the muscle none. The lens of (II) contained 4.5 mg. and that of (III) 2.3 mg. per g. In 12 species of marine invertebrates the liver, ovaries, or gonads contained on the average 0.26 mg. per g. The algæ *Enteromorpha elaterata* and *Ulva lactuca* contained 0.05 mg. and 0.04 mg., respectively. No parallelism between (I) content and catalase vals. was found.

R. K. C.

**Ascorbic acid as the antiscorbutic factor.** E. L. HIRST and S. S. ZILVA (Biochem. J., 1933, 27, 1271–1278).—Various specimens of ascorbic acid (I) show a marked disparity in antiscorbutic activity when tested on guinea-pigs. Oxidation of (I) with I gave a product only slightly less active than (I) (cf. A., 1927, 702), whilst oxidation with Cl<sub>2</sub> destroyed the activity. The theory that the antiscorbutic activity is a property of (I) *per se* is discussed.

F. O. H.

**Silver nitrate staining reaction for ascorbic acid in the adrenal, pituitary, and ovary of various species of animals.** J. GOUCHER and S. S. ZILVA (Biochem. J., 1933, 27, 1279–1286).—The adrenal cortex (I), anterior (II) and intermediate pituitary lobes, and ovary from various animals [man, ox, dog, cat, guinea-pig (III), rat], whether susceptible to scurvy or not, reduce AgNO<sub>3</sub> in the dark. The (I) of (III) on a scorbutic diet supplemented with high doses of decitrated lemon juice does not react with AgNO<sub>3</sub> despite complete protection from scurvy. The (II) of oxen when tested on (III) was twice as active as (I), indicating a content of 40–50 international units of vitamin-C per g. of fresh tissue. With 42 persons free from clinical scurvy, (I) only occasionally reacted with AgNO<sub>3</sub>, whilst (II) did so in most cases.

F. O. H.

**Determination of the vitamin-C value of ascorbic acid.** K. M. KEY and B. G. E. MORGAN (Biochem. J., 1933, 27, 1030–1035).—Guinea-pig tests indicate an equivalence of 7–4 international units of vitamin-C per mg. ascorbic acid (I). With graded doses, a response curve is obtained with (I) which is approx. identical with that obtained with orange juice. The trustworthiness of lemon juice as a standard for vitamin-C appears to be doubtful; the stability of (I) indicates it to be more suitable. Guinea-pigs vary in their response to (I).

F. O. H.

**Disappearance of vitamin-C from adrenals of scorbutic guinea-pigs.** A. E. SIEHRS and C. O. MILLER (Proc. Soc. Exp. Biol. Med., 1933, 30, 696–698).—The staining capacity of guinea-pig adrenals with AgNO<sub>3</sub> was reduced on the second day on Sherman's scorbutic diet, and had practically disappeared on the sixth. The daily administration of 3 c.c. of orange juice from the eighteenth day restored the max. staining power in four days. Some time elapsed between the disappearance of vitamin-C from the adrenals and the appearance of gross scorbutic lesions.

NUTR. ABS. (b)

**In what form is chlorine retained in the organism deprived of the antiscorbutic vitamin?** A.

MICHAUX (Bull. Soc. sci. Hyg., 1932, 20, 345–358; Chem. Zentr., 1933, i, 1314).—On a rachitogenic diet the blood- and tissue-Na, but not -K, of guinea-pigs is increased.

A. A. E.

**Treatment of scurvy in man with intravenous injection of ascorbic acid.** P. SCHULTZER (Lancet, 1933, 125, 589–590).—Daily intravenous injections of 40 mg. of ascorbic acid cured scurvy in a man receiving a diet deficient in vitamin-C.

L. S. T.

**Photosynthesis.** R. D. ASANA (J. Univ. Bombay, 1933, 1, No. 5, 21–34).—A review.

A. L.

**Variations in the nightly production of carbon dioxide in higher plants.** P. JACCARD (Planta [Z. wiss. Biol.], 1933, 19, 713–728).—Irregular variations are recorded which are unrelated to the environmental [CO<sub>2</sub>], temp., light intensity, or rate of assimilation during the day.

A. G. P.

**Plant respiration. II. Variations in respiratory quotient during germination of seeds with different food reserves.** W. STILES and W. LEACH (Proc. Roy. Soc., 1933, B, 113, 405–428; cf. A., 1932, 1176).—The R.Q. of germinating seeds of *Zea mais*, in which starch is the main reserve, falls from an initial val. of about 1.0 to 0.75 in 2 days, and then rises slowly to 1.0. Other starchy seeds, *Lathyrus odoratus*, *Pisum sativum*, and *Vicia faba*, behave similarly at slightly different levels. In *Fagopyrum esculentum*, however, the R.Q. rises steadily from 0.5 to 1.0. In *Lupinus luteus*, containing much hemicellulose and a little fat, the R.Q. falls after 2 days at 0.92. *Tropaeolum majus*, a similar seed with more fat, has the val. 0.75 for 10–11 days. Of seeds with high fat content, *Ricinus communis* shows a fall in R.Q. from 0.85 to 0.5 in 5 days, *Helianthus annuus* an initial increase from 0.75 to 0.85 in 1 day, followed by a continuous fall, and *Cucurbita pepo* similar changes at a higher level. The results are discussed in relation to the nature of the seed reserve. A low or falling R.Q. is ascribed to the utilisation of O<sub>2</sub> for the conversion of fat into carbohydrate.

A. C.

**Swelling of seeds. III. Respiratory quotient of swelling seeds.** E. G. PRINGSHEIM [with JEDLITSCHKA and GÖRLICH] (Planta [Z. wiss. Biol.], 1933, 19, 653–712).—Changes in the R.Q. of seeds after swelling under H<sub>2</sub>O and in atm. of varying CO<sub>2</sub> and O<sub>2</sub> content are examined and discussed. Modifications of technique are described.

A. G. P.

**Germination behaviour of *Magnolia grandiflora*.** C. R. EVANS (Bot. Gaz., 1933, 94, 729–754).—Pretreatment of seed for germination is examined. Cells of the endosperm contain oil and protein reserves but no starch. Traces of reducing sugars and sol. proteins occur in cells near the embryo. The embryo contains oil and traces of reducing sugars and short-chain proteins, but no protein granules or starch. With the initiation of the germination process, oil decreases and sol. proteins increase in endosperm cells near the embryo. Considerable proportions of starch appear in the cotyledons. No oil disappears from the embryo prior to this stage. Fe is present in all parts of the seed and is abundant in the root tips of the seedling. Epidermal cells of the embryo steadily increase in acidity, and neighbouring cells of the

endosperm change from alkaline to acid. Oxidase is not apparent before the protrusion of the hypocotyl. Glutathione is present in seed during soaking in  $H_2O$ , initially in the endosperm, and subsequently throughout the embryo. Peroxidase and catalase occur in the dry seed and increase during germination. A. G. P.

**Radial growth of the xylem and the starch reserves of *Pinus sylvestris*: preliminary survey.** W. WRIGHT (New Phytol., 1933, 32, 77—96).—Relationships are traced between growth and the starch content (I) of various organs. In the aerial parts (I) shows a min. in winter (total absence in January) and a max. from April to July with a slight break in May. Fluctuations of (I) in roots are apparently independent. Appearance and disappearance of starch begins first in leaves and branches and is uniform throughout the length of branches and trunk. A. G. P.

**Morphological and physico-chemical changes accompanying proliferation of *Bryophyllum* leaves.** R. O. FREELAND (Amer. J. Bot., 1933, 20, 467—480).—During the initial formation of foliar shoots the  $[H^+]$ , total acidity, and osmotic pressure of the margins of the proliferating leaves increase. Acidity and  $[H^+]$  decline later. There is also an accumulation of starch, an increase of reducing sugars and of oxidase, catalase, and diastase around the foliar buds, and, in the entire leaf, an increase in total sugars and sucrose,  $NH_2$ -, amide-, and  $NO_3$ -N and a decrease in total polysaccharides. A. G. P.

**Rôle of organic acids in plant metabolism.** II. T. A. BENNET-CLARK (New Phytol., 1933, 32, 128—161; cf. this vol., 758).—Current theories are reviewed. In the conversion of sugar into malic acid in *Crassulaceae*, 1 mol. of sugar yields  $\frac{1}{2}$  mol. of acid. The remaining C atoms are probably utilised for the re-formation of polysaccharide.  $CO_2$  is produced from some intermediate product in the conversion of sugar into malic acid and the decreased acidity involved results from the reaction  $R \cdot CO_2H \rightarrow RH + CO_2$ . A. G. P.

**Nitrogen and plant nutrition.** N. W. BARRITT (Nature, 1933, 132, 279—280).—A criticism (cf. *ibid.*, 49). L. S. T.

**Leguminous bacteria and plants.** XIII. Nitrogen economy of oats in mixed culture with peas. U. WARTIOVAARA (Z. Pflanz. Düng., 1933, 31, A, 353—359).—In mixed crops on soil poor in N the protein content of oats increased with the proportion of peas in the mixture. Differences were more apparent in the early stages of growth than later (cf. Virtanen, A., 1931, 1100). A. G. P.

**Metabolic unity between stock and scion.** K. SILBERSCHMIDT (Planta [Z. wiss. Biol.], 1933, 19, 729—780).—Comparison is made of N changes in homoplastic (I) and heteroplastic (II) grafts of tobacco with those in untreated plants. Accumulation of N began in the base of the scion (III) approx. 2 weeks after grafting, vals. for (II) being  $>$  for (I). The increase, especially in (II), consisted largely of protein-N. There was a corresponding reduction in the N of the apical portion of the stock (IV). A reverse translocation of N from (III) to (IV) was induced by

darkening the leaves of (III) or by cutting (IV) and re-rooting in sand. A. G. P.

**Carbohydrate character of the first generation of pea hybrids.** C. BOURDOUIL (Bull. Soc. Chim. biol., 1933, 15, 790—792).—The crossing of pure strains of peas having smooth and wrinkled seeds gives a first generation of seeds in which the content of free reducing sugar is small, and that of sol. glucosides and starch likewise corresponds with that of the parent having smooth seeds. The pollen of the smooth variety therefore causes an activation of starch synthesis in the ovule of the wrinkled, although the pollen of the wrinkled causes no change in the ovule of the smooth. A. C.

**Leaf diagnosis of the potato.** II. H. LAGATU and L. MAUME (Ann. Agron., 1933, 3, 1—52; cf. B., 1933, 36).—Experimental data are discussed in relation to the mechanical and mineralogical analysis of soils and their nutrient vals. The development and applications of the authors' method are indicated. A. G. P.

**Salazic acid and the constituents of the lichen, *Labaria pulmonaria*.** T. J. NOLAN and J. KEANE (Nature, 1933, 132, 281).—Methylation of salazic acid (I) with  $Ag_2O$  and MeI gives a  $Me_3$  derivative of (I),  $C_{18}H_9O_{10}Me_3$ , and a  $Me_5$  derivative of hydrated (I),  $C_{18}H_9O_{11}Me_5$ . Asahina and Asano's constitutional formula for (I) (this vol., 823) is not accepted. *Sticta pulmonaria* (L. *pulmonaria*, Hoffm.) contains no gyrophoric acid, but a pentahydric alcohol, m.p.  $102^\circ$  (acetate, m.p.  $74-75^\circ$ ), believed to be arabitol, is present, as well as an acid (stictaic?),  $C_{15}H_{14}O_9$  (acetate, m.p.  $239^\circ$ ). L. S. T.

**Globularia alyoum.** J. V. SÁNCHEZ (Anal. Fís. Quím., 1933, 21, 361—363).—The aq.  $Na_2CO_3$  extract yielded cinnamic acid and a little (?) protocathectic acid. No truxillic acid was found. R. K. C.

**Carbohydrates of sunflower seeds.** A. GOLDOVSKI and A. BOZHENKO (Masloboino-Zhir. Delo, 1932, No. 7, 30—34).—58% of the carbohydrates consists of sol. mono-, di-, and tri-saccharides. The kernels do not contain starch or dextrins. CH. ABS.

**Phosphorus-containing compounds in sunflower seeds.** A. GOLDOVSKI and A. BOZHENKO (Masloboino-Zhir. Delo, 1932, No. 10, 21—27).—Of the phosphatides 66.26% is combined with other constituents of the protoplasm. Phytin, combined with inositol, contains 84.61% of the  $H_3PO_4$  present. For the determination of phytin in vegetable materials containing tannins, preliminary oxidation of the latter with  $KMnO_4$  is necessary. CH. ABS.

**Tannins of sunflower seeds.** A. GOLDOVSKI and M. PODOLSKAYA (Masloboino-Zhir. Delo, 1932, No. 12, 20—27).—The tannins (chlorogenic acid) are not present in the hulls. CH. ABS.

**Nucleic acid of rice embryo (oryza-nucleic acid).** I. M. KIMURA (Bull. Waseda Appl. Chem. Soc., 1933, 19, 14—21).—*Oryza-nucleic acid* (N 14.42, P 6.81%) gave on hydrolysis pentose, guanine, adenine, and uracil, but not cytosine. CH. ABS.

**Search for alkaloid-free lupins.** N. N. IVANOV and M. I. SMIRNOVA (Bull. Appl. Bot., Russia, 1932,

54, 5—24).—Alkaloid-free lupins, suitable as fodder, have the same protein content as lupins rich in alkaloids. Bouchard's ( $KI_3$ ) and Dragendorff's reagents are employed. CH. ABS.

Search for alkaloid-free lupins. V. S. FEDOTOV (Bull. Appl. Bot., Russia, 1932, 54, 29—38).—*L. luteus*, *pilosus*, and *polyphyllus* had a variable, whilst *L. angustifolius*, *albus*, and *mutabilis* had a const., alkaloid content. CH. ABS.

Use of colour reaction in the search for alkaloid-free lupins. N. N. IVANOV and M. I. SMIRNOVA (Bull. Appl. Bot., Russia, 1932, 54, 50—51).—The crushed seed is tested with Bouchard's  $KI_3$  reagent. CH. ABS.

Chinese citrus fruit. II. Analysis of the edible portion of Fu Chu (Chinese tangerine). P. P. T. SAH and S. Y. HSIUNG (J. Chinese Chem. Soc., 1933, 1, 96—99).—Reducing and total sugar, acid val., protein, solids, and volatile matter are determined. J. L. D.

Syringoside from the bark of *Philyrea latifolia*, L., and *P. decora*, L. A. KRAMER (Bull. Soc. Chim. biol., 1933, 15, 764—780).—Phileoside, the glucoside isolated from *P. latifolia* and *P. decora* (this vol., 544), is identical with syringoside. A. L.

Constituents of Wu Chū Yü (*Evodia rutæcarpa*). A. L. CHEN and K. K. CHEN (J. Amer. Pharm. Assoc., 1933, 22, 716—719).—Rutæcarpine,  $C_{18}H_{13}ON_3$ ; evodiamine,  $C_{19}H_{17}ON_3$ ; evodin,  $C_{26}H_{30}O_8$ ; and *wuchuyine*,  $C_{13}H_{15}O_2N$  (?), m.p. (corr.) 237.5°,  $[\alpha]_D^{25} -68^\circ$ , have been isolated from the fruit. E. H. S.

Ether-soluble substances in polished rice and their physiological action. Y. SAHASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 21, 178—219).—Neither the EtOH extract (I) of polished rice nor the Et<sub>2</sub>O-sol. portion (II) of (I) when administered to dogs and pigeons *per os* was harmful; both extracts, however, possessed strong hæmolytic power and were toxic when injected. The aq.  $Na_2CO_3$  extract of (II) acidified and extracted with Et<sub>2</sub>O gave a mixture of palmitic (III), oleic (IV), and linoleic (V) acids, (V) causing death when injected into rats. The unsaponifiable portion of (II) gave phytosterol and other substances having no toxicity. (III), (IV), (V), hiragonic and clupanodonic acids were all toxic when injected, particularly the two last-named, which do not occur in polished rice. A. L.

Formation of oil in Niger seed (*Guizotia abyssinica*). D. L. SAHASRABUDDHE (Indian. J. Agric. Sci., 1932, 3, 57—88).—A discussion of theories of fat synthesis. Proteins appear in the seed 15 days after the flower opens, and oil a few days later. Between the 26th and 40th days half the total oil makes its appearance. The % of reducing sugars is greatest about the 27th day, decreases rapidly until the 40th day, and finally disappears at the 45th day when the oil content is at a max. Lower fatty acids are first synthesised and later the higher fatty acids; hexoses and pentoses rather than polysaccharides are the source of the fats. The I val. increases throughout the ripening period (89.5—126.2), whilst the Ac val. decreases (62.4—23.2). An esterase is present

which shows max. activity when the oil content is rapidly increasing. P. G. M.

Liquid wax of seeds of *Simmondsia californica*. R. A. GREENE and E. O. FOSTER (Bot. Gaz., 1933, 94, 826—828).—The const. of the wax were similar to those of sperm oil and arctic sperm oil. The wax may consist largely of fatty acid esters of decyl alcohol. A. G. P.

Volatile oil and resin of *Cynomarathrum nuttallii*. E. K. NELSON (J. Amer. Chem. Soc., 1933, 55, 3400—3402).—The ground root contains 6% of volatile oil (of which 95% is  $\beta$ -pinene) and yields to EtOH 15% of a non-volatile resin, containing a neutral substance,  $C_{16}H_{28}O_2$ , m.p. 74—76°, angelic and possibly valeric acid. R. S. C.

Sulphur and phosphorus in various parts of the wheat grain. G. BERTRAND and L. SILBERSTEIN (Compt. rend., 1933, 197, 285—288).—Wheat grain contains the following % (dry) of S and P, respectively: bran 1.23 and 13.68, flour 1.9 and 1.83, embryo 2.31 and 12.98. The EtOH-sol. part of gluten contains 3.49 and 5.05, and the insol. part 10.02 and 3.04% of S and P, respectively. P is, therefore, probably contained in org. combination at least in part. R. S. C.

Silica of the wheat plant. E. BLANCHARD and J. CHAUSSIN (Compt. rend., 1933, 197, 188—190).—Wheat contains the largest amount of  $SiO_2$  of all cultivated plants, a large % of which is not sol. Oats and maize have also been examined. It is suggested that the  $SiO_2$  diminishes the quantity of org. acid present in the plant. F. R. S.

Constituents of mulberry leaves. II. Reaction of ash. Y. KISHI (J. Agric. Chem. Soc. Japan, 1933, 9, 160—164).—The ash content and alkalinity increase directly with the degree of maturation. CH. ABS.

Selective absorption of ions not confined to young rootlets. F. J. CRIDER (Science, 1933, 78, 169).—Selective absorption is not confined to young, elongating rootlets; that of  $PO_4'''$  and  $NO_3'$  occurs in the woody parts of the roots, but in seedling and in large trees over a wider temp. range than that of root elongation. L. S. T.

Biochemistry of water containing hydrogen isotope. G. N. LEWIS (J. Amer. Chem. Soc., 1933, 55, 3503—3504).—Tobacco seeds do not germinate in pure  $H^2H^2O$ , and growth in 50%  $H^2H^2O$  is retarded. J. G. A. G.

Rôle of peroxidase in the deterioration of frozen fruits and vegetables. M. A. JOSLYN and G. L. MARSH (Science, 1933, 78, 174—175).—Changes occurring in frozen fruits and vegetables are described. Vegetable peroxidases may not be the chief cause involved in the deterioration. L. S. T.

Effect of yeast extract on the growth of plants. A. I. VIRTANEN and S. HAUSEN (Nature, 1933, 132, 408—409).—An aq. extract of yeast markedly stimulates the development of blossoms in peas. Follicular hormone has no such effect. L. S. T.

Growth-promoting substances in plants. F. HODER (Med. Klinik, 1932, 28, 1430—1432; Chem.

Zentr., 1933, i, 1959).—Addition of small quantities of red beet or tomato juice or especially coconut "milk" to nutrient agar markedly promotes bacterial growth thereon. The activity was unaffected after removal of vitamins-A and -D. The "cubiotic" principle is probably complex. A. A. E.

**Growth hormone of plants. III. Inhibiting action on bud development.** K. V. THIMANN and F. SKOOG. **IV. Mechanism of the action.** J. BONNER (Proc. Nat. Acad. Sci., 1933, 19, 714—716, 717—719).—III. The growth hormone, when supplied to plants with the terminal bud removed, inhibits the development of lateral buds.

IV. The hormone (I) acts on the cell-wall through the protoplasm. With low. concn. of (I), respiration (II) of coleoptile sections is stimulated, but is inhibited with high concn. (I) inactivated for growth by  $H_2O_2$  does not stimulate (II). H. G. R.

**New eosin-effect on plants.** F. BOAS (Ber. Deut. bot. Ges., 1933, 51, 274—275).—Seedlings of *Lolium perenne*, from seed soaked in eosin solution (1 : 1000) for 48 hr. in darkness, showed modifications of both geotropic and phototropic responses. A. G. P.

**Factors affecting the sporulation of *Phyllosticta solitaria* in artificial culture.** A. J. MIX (Phytopath., 1933, 23, 503—524).—Spore production was largely influenced by nutrient conditions and occurs most freely in media of moderate concn. The suitability of N sources for growth and sporulation was in the order,  $KNO_3$  > albumin > asparagine > peptone. Glucose, fructose, and sucrose were favourable C sources. Mannose was unfavourable to growth and sporulation, and xylose did not support growth. Fertile pycnidia were formed in media having initial  $pH$  4.2—5.8. A. G. P.

**Pathology of tobacco blackshank.** F. T. WOLF (Phytopath., 1933, 23, 605—612).—The wilting of plants infected with *Phytophthora nicotiana* is due to the presence of a toxin which is thermostable, non-volatile, and probably a protein. Acids other than  $H_2C_2O_4$  are produced by the fungus, but these do not induce wilting. The organism secretes enzymes which enable it to utilise the middle lamella, secondary membranes, starch, sucrose, glucose, and maltose. A. G. P.

**Parasitism of *Cuscuta chinensis*.** T. SASAKI (Keijo J. Med., 1933, 4, 261—269).—The high carbohydrate (I) and low chlorophyll contents of *C. chinensis* (II) indicate that (I) is obtained from its host, *Glycine soja*, Benth.; this is confirmed by the high diastase content of (II). The distribution of enzymes, Fe, etc. in (II) is correlated with its parasitic habits. F. O. H.

**Micro-determination of water in biological fluids.** K. KURODA (Keijo J. Med., 1933, 4, 270—290).—By the use of a capillary container, the  $H_2O$  content of 10—30 mg. of fluid can be determined with an accuracy of 0.01—0.03%. Desiccation is by heating at 90° for 3 hr. F. O. H.

**Determination of the hydrogen-ion concentration of biological liquids.** G. GOLLNOW (Med. Welt, 1932, 6, 1544; Chem. Zentr., 1932, ii, 3923). L. S. T.

**Micro-vessel for glass electrode determinations of hydrogen-ion activity of biological fluids.** I. R. TAYLOR and J. H. BIRNIE (Science, 1933, 78, 173—174). L. S. T.

**Lipins of mammalian liver. IV. Extraction apparatus for biochemical purposes.** E. FRÄNKEL and A. POLLANZ (Z. physiol. Chem., 1933, 218, 153—156).—A continuous extraction apparatus of Ni (percolator type) dealing with 12—15 litres of powdered solid is described. J. H. B.

**Determination of cholesterol.** B. EWERT (Biochem. Z., 1933, 263, 149—165).—The material (e.g., suprarenal glands) containing 2—20 mg. of cholesterol (free and bound) is ground with sand, extracted with EtOH and  $Et_2O$ , and dissolved in  $CHCl_3$ , which is then removed. Dissolution in EtOH and pptn. with digitonin follow. The error is negligible, but a correction must be applied. W. McC.

**Determination of histidine in biological fluids.** R. KAPELLER-ADLER (Biochem. Z., 1933, 264, 131—141; cf. Hunter, A., 1922, ii, 885).—Histidine (I) reacts with Br in dil. AcOH giving a substance which acquires a deep bluish-violet colour when treated with aq.  $NH_3$  and  $(NH_4)_2CO_3$  and warmed. A colorimetric method (II) for the determination of (I) based on this sp. reaction (sensitivity 1 : 50,000) is described. The reaction depends on the presence of an intact alanyl group in the side-chain. When (II) is applied to protein hydrolysates interfering substances are removed by oxidation with 0.1N- $KMnO_4$  and the (I) is pptd. with Hopkins' reagent. Horse haemoglobin, caseinogen, and fibrin contain, respectively, 7.32—7.45, 4.09—4.14, and 3.33—3.73% of (I). Pregnancy urine contains 6—74 mg. per 100 c.c. of (I), which also occurs, in very small amount, in male urine, but rarely in normal or pathological female urine. W. McC.

**Determination of creatinephosphoric acid.** O. RIESSER and A. HANSEN (Z. physiol. Chem., 1933, 219, 57—61).—The method of Fiske and Subbarow gives, in frog muscle, vals. slightly, in rat muscle 50%, < the Lohmann and Jendrassik method, which is more trustworthy. J. H. B.

**Ureometer.** D. GANASSINI (Arch. Ist. Biochem. Ital., 1933, 5, 111—118).—The ureometer gives exact micro-determinations of the urea and  $NH_3$  of urine and blood by the NaOBr method. Its use avoids two common causes of error, viz., the error from variable external temp., and the gas error from slow decomp. of NaOBr. R. N. C.

**Micro-determination of iodine in blood and other fluid.** J. EYCKERMAN (Z. Kinderheilk., 1933, 54, 435—439).—The method is a modification of Pfeiffer's acid- $H_2O_2$  method for ashing. NUTR. ABS. (b)

**Micro-determination of iodine in thyroid gland and other organic compounds.** H. J. VAN GIFFEN (Pharm. Weckblad, 1933, 70, 910—914).—Satisfactory results are obtained by fusing 0.05 g. of thyroid gland with 0.8 g. of nitrate-carbonate fusion mixture, dissolving in  $H_2O$ , oxidising the I' to  $IO_3'$  with HOCl, and titrating the liberated I after treatment with KI with 0.0005N- $Na_2S_2O_3$ . S. C.