

# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

JANUARY, 1934.

### General, Physical, and Inorganic Chemistry.

**Exchange reactions of protium ( $H^1$ ) and deuterium ( $H^2$ ).** R. H. CRIST and G. A. DALIN (J. Chem. Physics, 1933, 1, 677).— $H_2O$  vapour containing 1%  $H^2$  was circulated through a tube at  $800^\circ$  with ordinary  $H_2$  for several days; after drying, the gas gave a spectrum with the  $H^2$   $\beta$  line strengthened.

D. R. D.

**Intensity measurements on the band spectrum of helium.** R. C. JOHNSON and R. C. TURNER (Proc. Roy. Soc., 1933, A, 142, 574—587).—The intensities in the bands 4650, 3676, 3556, 3206, and 3120 Å. of the main "line series" of He have been studied. The predicted distribution is of the correct type, but agreement with observation is not complete. The temp. obtained from intensity factor considerations agree with the vals. found from the position of the max. intensity in the branches. L. L. B.

**Wave functions for the ground state of lithium and three-electron ions.** E. B. WILSON, jun. (J. Chem. Physics, 1933, 1, 210—218).—Improved wave functions and ionisation potentials have been obtained for the configuration  $1s^2 2s$ , and a simple rule is derived by which the wave function of any three-electron ion may be written down without further calculation. A. J. M.

**Effects of pressure on the visible band spectra of nitrogen.** H. S. HARNED and E. R. BROWNS-COMBE (J. Chem. Physics, 1933, 1, 183—185).—The visible band spectrum of  $N_2$  in the electrodeless discharge was studied at pressures from 0.002 to 4 mm. At the lowest pressure all lines of wave-length  $< 5500$  Å. were due to the first negative group of  $N_2^+$  (except 5463 and 4358 Å., due to at. N). With increase of pressure, the first and second positive band systems increased in intensity up to a pressure of 0.2 mm., after which the second positive band system began to fade. A. J. M.

**Structure of the second positive group of nitrogen.** A. GUNTSCHE (Z. Physik, 1933, 86, 262—272).

A. B. D. C.

**Second positive group of the nitrogen spectrum.** D. COSTER, F. BRONS, and A. V. D. ZIEL (Z. Physik, 1933, 86, 411—412).—A correction (cf. A., 1933, 991).

A. B. D. C.

**New  $O_2^+$  bands.** Dissociation energy of  $O_2^+$  and ionisation potential of  $O_2$ . R. S. MULLIKEN and D. S. STEVENS (Physical Rev., 1933, [ii], 44, 720—723).—Three new bands in the first negative and several in the second negative system of  $O_2^+$

are reported. The inconsistency, between ionisation potential and band spectrum data, of vals. for the dissociation energy of  $O_2^+$  and the ionisation potential of  $O_2$  is discussed. N. M. B.

**Triplet spectrum of aluminium hydride.** W. HOLST (Z. Physik, 1933, 86, 338—347).

A. B. D. C.

**Magnetic quenching of fluorescence of diatomic sulphur.** J. GENARD (Compt. rend., 1933, 197, 1402—1404; cf. A., 1933, 1095).—The fluorescence produced in  $S_2$  vapour by Hg light in a field of 40,000 gauss is diminished to varying degrees, or enhanced, according as the exciting light is of  $\lambda < \text{or} > 3126$  Å.

C. A. S.

**Arc spectrum of sulphur in the ultra-violet.** J. E. RUEDY (Physical Rev., 1933, [ii], 44, 757—760).—Data and term vals. are tabulated for the range 100—2600 Å., and include many new lines. S was vaporised in a modified Schüller tube with a discharge in He. N. M. B.

**Spectrum of doubly-ionised argon A III.** T. L. DE BRUIN (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 724—729; cf. A., 1932, 979).—Utilising the changes in intensity and character of the lines produced by the self-induction in the discharge, a no. of A III lines have been detected and analysed. J. W. S.

**Doppler effect in spectra of positive rays of uniform velocity in argon, neon, and helium.** (Miss) A. I. MCPHERSON (Physical Rev., 1933, [ii], 44, 711—716).—The positive-ray spectra in the range 2500—5000 Å., for particles of approx. uniform energy, show Doppler effect. Data for the effect in the  $\lambda 3418$  Ne arc line, the A and Ne spark lines, the He arc lines (faint), and the  $\lambda 4686$  He spark line are given. N. M. B.

**Spectra of potassium in successive stages of ionisation.** M. RAM (Indian J. Physics, 1933, 8, 151—161).—Data and analyses for 32 lines of K III, 30 of K IV, 5 of K V, and 27 of K VI in the extreme Schumann region below  $\lambda 1100$  are tabulated.

N. M. B.

**Pressure effects of nitrogen on potassium absorption lines.** W. W. WATSON and H. MARGENAU (Physical Rev., 1933, [ii], 44, 748—752; cf. A., 1933, 879).—Data for the pressure effects of  $N_2$  up to 30 atm. on the first three doublets of the principal K absorption spectrum series are given. The 4045 and 3446 Å. doublets show shifts of the



absorption max. to the red, and half-widths  $>$  twice those of the resonance lines. Explanations of the non-linear increase with gas density of the shifts and half-widths are discussed. N. M. B.

**Spectra of trebly- and quadruply-ionised calcium.** M. RAM (Indian J. Physics, 1933, 8, 163—170).—Analyses of existing data for the spark lines of Ca, giving 14 terms with 27 lines of Ca IV and 24 terms with 36 lines of Ca V, are tabulated. N. M. B.

**Absorption by thin films of copper, silver, and gold in the visible and ultra-violet regions.** A. SMAKULA (Z. Physik, 1933, 86, 185—194).—All three metals show small absorption maxima between 700 and 186 m $\mu$ , and these may be ascribed to electron transitions in the lattice. No new regions of transparency were observed, and this seems consistent with the presence of an ultra-violet absorption due to bound electrons together with a long-wave absorption region due to free or conductivity electrons. A. B. D. C.

**Emission constants of metals in the near infra-red.** C. HURST (Proc. Roy. Soc., 1933, A, 142, 466—490).—The emissivity of Cu has been determined directly over the wave-length range 1.5—5  $\mu$  for 700° and 850°, and that of Ni over the range 1—6.5  $\mu$  for 850° and 1000°. The method of measurement is described and its advantages are discussed. A comparison of the results with the vals. predicted by the classical theory of Drude and by the quantum-mechanical theory of Kronig (A., 1931, 1209) shows that the former fits the facts better. L. L. B.

**Hyperfine structure of the red line of cadmium (6438), and of the green-yellow (5649) and green (5562) lines of krypton.** (Miss) M. ROMANOVA and (Miss) A. FERCHMIN (Compt. rend. Acad. Sci. U.S.S.R., 1933, 2, 57—63).—The Cd line shows 3 satellites, the 5649 Kr 6, and the 5562 line 8. A. B. D. C.

**Absorption of iodine vapour in presence of other gases.** H. I. AGARBICEANU (Compt. rend., 1933, 197, 1198—1199; cf. A., 1933, 880).—The absorption spectrum of I vapour has been examined in presence of O<sub>2</sub> and N<sub>2</sub> (at 1—760 mm. Hg) between  $\lambda$  4000 and 6700 Å. No new band was observed, but increased absorption occurs in all progressions  $\nu'$ , increasing with  $\nu'$ ; progressions with  $\nu''=0$  are even more affected. O<sub>2</sub> is slightly more active than N<sub>2</sub>. Other mols. apparently deactivate those of I (cf. A., 1932, 787). C. A. S.

**Quenching of iodine fluorescence by iodine and argon.** J. F. KOEHLER (Physical Rev., 1933, [ii], 44, 761—768; cf. Turner, A., 1932, 1183).—Absorption measurements and collision probability calculations were made for fluorescence excited by the green and yellow Hg lines. A does not alter the absorption of I; the yellow excited series is quenched  $>$  the green by both I and A. The complex nature of A quenching is discussed. N. M. B.

**Magnetic extinction of fluorescence of iodine vapour.** J. GENARD (Compt. rend., 1933, 197, 1104—1107).—Using fields up to 42,600 gauss the fluorescence-field curve for I vapour excited by

$\lambda$  5461 of HgI supports Van Vleck's explanation (cf. A., 1932, 787). C. A. S.

**Nuclear moments of xenon.** E. GWYNNE JONES (Nature, 1933, 132, 781).—Hyperfine structures of Xe I confirm Kopfermann's val. (A., 1933, 1096) of  $\frac{1}{2}$  for the nuclear moment (I) of Xe<sup>129</sup>; for Xe<sup>131</sup> (I) is  $> \frac{1}{2}$ , and from the analogy between certain Xe and Hg lines, is probably  $\frac{3}{2}$ . L. S. T.

**Regularities in the spectrum of doubly-ionised cerium.** P. N. KALIA (Indian J. Physics, 1933, 8, 137—145).—Data and analyses for 111 lines in the range  $\lambda$  3544—2203 are tabulated. 38 terms were discovered and partly identified by comparison with the closely similar La II spectrum. N. M. B.

**Polarisation of fluorescence bands of mercury vapour.** G. ZIELINSKI (Compt. rend., 1933, 197, 1109—1111; cf. A., 1932, 891).—Fluorescence excited in Hg vapour by non-polarised light from a Zn spark, examined perpendicularly to the direction of the exciting light, shows 5.6% polarisation. C. A. S.

**Hyperfine structure intensities of the  $2^3S_1$ — $2^3P_{0.1.2}$  triplet in optically excited mercury vapour.** M. L. POOL and S. J. SIMMONS (Physical Rev., 1933, [ii], 44, 744—747).—Photographs and data for the hyperfine structures of  $\lambda$  4047, 4358, and 5461 Hg lines in the arc and in fluorescence are given. The anomalous increase in intensity of the central component in fluorescence is accounted for by the absorption coeffs. of the components of  $\lambda$  4047. N. M. B.

**Positive ion excitation of mercury vapour.** E. J. JONES (Physical Rev., 1933, [ii], 44, 707—710).—A mixture  $3X_2O-Al_2O_3-3SiO_2$  ( $X=Li$  or  $K$ ) was found to be a powerful source of positive ions. Intensity-velocity curves found for the Hg spectral lines resulting from the bombardment of Hg vapour by  $Li^+$  and  $K^+$  ions indicate that velocity rather than energy is the chief factor in the mechanism of collision processes. The spark lines  $\lambda$  2847, 2260, and 2224 appear at 1000 volts for  $Li^+$  ions. N. M. B.

**Experimental test of the spin-maintaining theory for atomic collisions.** R. DÖREL and K. GAILER (Physikal. Z., 1933, 34, 827—831).—There was preferential excitation of Hg triplets by collision with He atoms, without triplet excitation in the He. He rays after passage through Hg vapour were not markedly ionised. In colliding with Hg, the He behaves as an elastic sphere. These results disagree with those to be expected from the theory of electronic rotation impulse maintenance. A. J. M.

**Theory of hyperfine structure.** S. GOUDSMIT (Conv. Fis. Nucl., 1932, 1, 33—49; Chem. Zentr., 1933, ii, 178).—A discussion. A. A. E.

**Analysis of Zeeman patterns.** R. A. FISHER (Physical Rev., 1933, [ii], 44, 724—726).—A simple graphical representation of the line distribution, intensities, polarisation, and  $g$  vals. for Zeeman patterns in all types of spectra, and giving identification and analysis of observed patterns, is described. N. M. B.



**Configuration interaction in complex spectra.** C. W. UFFORD (Physical Rev., 1933, [ii], 44, 732—739; cf. A., 1933, 5).—Mathematical. N. M. B.

**Relative multiplet transition probabilities from spectroscopic stability.** E. U. CONDON and C. W. UFFORD (Physical Rev., 1933, [ii], 44, 740—743; cf. A., 1932, 892).—Mathematical. N. M. B.

**Relative intensity tables for spectrum lines.** H. E. WHITE and A. Y. ELIASON (Physical Rev., 1933, [ii], 44, 753—756).—Calc. relative intensities are tabulated under each resultant spin from singlets to octets, to include all probable  $L$  and  $J$  vals., and can be applied to  $jj$ -coupling, hyperfine structure, and related multiplets. N. M. B.

**Theory of broadening of spectral lines.** H. MARGENAU (Z. Physik, 1933, 86, 523—529).—Fourier and statistical methods of analysing intensity distributions in spectral lines give similar results. A. B. D. C.

**Absorption spectra due to excitation of inner electrons. I. General.** H. BEUTLER (Z. Physik, 1933, 86, 495—515).—Absorption series due to metal vapours were observed between 1200 and 600 Å., and transitions were obtained from electron levels below the valency level, to outer levels which "pre-dissociate" into an electron and ionised atom or mol. A. B. D. C.

**Delay period in sparking.** F. BATH (Z. Physik, 1933, 86, 273—296).—The time required for sparking was observed with an automatic apparatus, using well-defined conditions, with the gases  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{H}_2$  at atm. pressure. A. B. D. C.

**Influence of a magnetic field on a glow discharge.** T. TAKAMINE, T. SUGA, and A. YANAGIHARA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 22, 69—96; cf. A., 1933, 1096).—At pressures of a few mm. the luminosity of a glow discharge in Ne and He is increased generally on application of a magnetic field, the length of the cathode dark space being simultaneously shortened in the same way as by increase of pressure. J. W. S.

**Diffusion theory of the positive column.** R. SEELIGER and A. KRUSCHKE (Physikal. Z., 1933, 34, 883—885).—Theoretical. A. J. M.

**Association of ionic oscillations with the negative glow and anode glow.** K. G. EMELEUS and A. H. GREGG (Phil. Mag., 1933, [vii], 16, 1079—1082). H. J. E.

**Fine structure of residual rays.** M. BLACKMAN (Z. Physik, 1933, 86, 421—447).—Damping of residual ray frequencies is investigated theoretically for one- and three-dimensional lattices (cf. A., 1933, 661). A. B. D. C.

**Explanation of the spectrum of the corona of the sun.** R. FRERICHS (Naturwiss., 1933, 21, 849).—The 6374.72 Å. line in the corona spectrum is bound up with the other O lines, and there is no reason for its isolated occurrence in the spectrum. A. J. M.

**Excess of colour and the K line of calcium in interstellar absorption.** A. COLACEVICH (Atti R. Accad. Lincei, 1933, [vi], 17, 1065—1069).—The relation between the intensity,  $I$ , of the K line of Ca II

and the excess of colour,  $EC$  (the deviation of the colour index from its normal val.), in interstellar light absorption is given by  $I=20EC+4.4$ . O. J. W.

**Spectrum of the night sky and of the zodiacal light.** K. R. RAMANATHAN and J. V. KARANDIKAR (Nature, 1933, 132, 749). L. S. T.

**Zeeman effect in bands of comet tails.** R. SCHMID and L. GERÖ (Z. Physik, 1933, 86, 314—320). A. B. D. C.

**X-Ray spectra in the region 50—250 Å.** M. SIEGBAHN and T. MAGNUSSEN (Nature, 1933, 132, 750).—The more prominent lines in the  $L$  series of the X-ray spectra of the elements 19 (K) to 12 (Mg) are recorded. L. S. T.

**Satellites of the  $K\beta_1$  of potassium.** H. TAZAKI (J. Sci. Hiroshima Univ., 1933, A, 3, 321—325).—The position of the  $K\beta_1$  line of K is independent of the state of chemical combination. With metallic K as the emitting substance,  $K\gamma$ ,  $K\beta'$ ,  $K\beta_1$ ,  $K\beta''$ ,  $K\beta_5$ ,  $K\beta'''$ ,  $K\beta''''$ , and two other lines are observed. These last lie between  $K\beta''$  and  $K\beta_5$ , and between  $K\beta_5$  and  $K\beta'''$ , and are denoted  $K\beta^v$  and  $K\beta^vi$ , respectively. When KCl,  $\text{K}_2\text{SO}_4$ , and  $\text{K}_2\text{CO}_3$  were used as emitting substances,  $K\beta^vi$  was not found,  $K\beta^v$  was observed faintly in the case of  $\text{K}_2\text{CO}_3$ , and the other satellites all occurred without change of wave-length. J. W. S.

**Widths and shapes of the  $K\alpha$  X-ray doublet from Ca (20) to Ni (28).** L. G. PARRATT (Physical Rev., 1933, [ii], 44, 695—702; cf. Allison, A., 1933, 881).—Rocking curves and full widths at half max. intensity are given. Resolution into  $\alpha_1$  and  $\alpha_2$  component lines is attempted; the relative intensities, defined as the ratio of areas under the component curves, is  $2:1\pm2\%$ . The variation of the ratio of peak intensities from element to element compensates for the variation in line width giving a constant ratio for component areas. N. M. B.

**New forbidden lines in the  $L$  series.** S. KAUFMAN (Physical Rev., 1932, [ii], 40, 116).—Lines corresponding with forbidden transitions in elements of at. nos. 78—90 under conditions designed to reveal the  $L\beta_2$  satellites are recorded. L. S. T.

**Atomic factor for X-rays as a dispersion theory problem (K shell).** H. HÖNL (Ann. Physik, 1933, [v], 18, 625—655).—Mathematical. J. W. S.

**Non-relativistic theory of the continuous X-ray spectrum.** F. SAUTER (Ann. Physik, 1933, [v], 18, 486—496).—Theoretical. A. J. M.

**Breakdown potentials for highly purified and dried hydrogen and oxygen at pressures from 1 to 60 tor and distances of 1—35 mm., and their deviations from Paschen's law.** H. FRICKE (Z. Physik, 1933, 86, 464—478). A. B. D. C.

**Calculation of emission potentials from simple material constants.** F. ROTHER and H. BOMKE (Z. Physik, 1933, 86, 231—240). A. B. D. C.

**Heat of volatilisation of electrons in the thermionic effect.** T. FRANZINI (Nuovo Cim., 1933, 10, 57—77; Chem. Zentr., 1933, ii, 21).



**Mass spectrograph study of the ionisation and dissociation by electron impact of *n*-octane.** E. G. LINDER (J. Chem. Physics, 1933, 1, 129—132; cf. A., 1932, 983).—Bombardment by 120-e.v. electrons causes dissociation into fragments, the most numerous containing two or three C atoms (and some H); ions containing odd nos. of H atoms are more numerous than those containing even nos. The dissociation tendency is  $>$  for  $C_6H_6$ .

N. M. B.

**Electronic interference at ground and polished surfaces.** H. RAETHER (Physikal. Z., 1933, 34, 839—840).—The changes taking place when multicryst. metallic surfaces were scratched, ground, polished, pressed, and hammered were investigated by the electron interference method. Similar experiments were carried out with single-crystal surfaces of NaCl,  $CaCO_3$ ,  $CaF_2$ ,  $FeS_2$ , and graphite.

A. J. M.

**Efficiency of electron emission by metastable atoms.** E. W. PIKE (Physical Rev., 1932, [ii], 40, 314—315).—The results of Fould and Langmuir (A., 1932, 315) are discussed.

L. S. T.

**Electron density and electron temperature in freely-burning luminous arcs.** R. MANNKOPFF (Z. Physik, 1933, 86, 161—184).—Ionisation potential, electron density, and degree of ionisation were determined both from diffusion of ions and from the intensity ratio of arc and spark lines. The electron temp. and gas temp. appear to differ by  $< 20^\circ$  at 1 atm.; calculations of at. and electronic collision efficiencies show that electron collisions primarily cause ionisation.

A. B. D. C.

**Polarisation of diffused electrons.** W. M. ELSASSER (Compt. rend., 1933, 197, 1186—1188).—Forster's proof (cf. A., 1933, 1097) that polarisation cannot be produced by reflexion of an electron jet by a unidimensionally varying potential is generalised to show that Born's method never gives as a first approximation a polarisation effect for any potential (cf. A., 1932, 441).

C. A. S.

**Complex electronic impacts.** L. GOLDSTEIN (J. Phys. Radium, 1933, [vii], 4, 576—593).—Mathematical. The quantum theory of perturbations is applied to the mechanism of complex inelastic impacts involving at least two at. electrons.

N. M. B.

**Images of the electron microscope using photo-electrons.** E. BRÜCHE (Z. Physik, 1933, 86, 448—450).

A. B. D. C.

**Scattering of electrons by metal vapour. II. Zinc.** E. C. CHILDS and H. S. W. MASSEY (Proc. Roy. Soc., 1933, A, 142, 509—518).—Measurements have been made of the angular distributions of 4—143-volt electrons scattered elastically in Zn vapour. The scattering curves are compared with those observed for Cd and Hg.

L. L. B.

**Inelastic scattering of slow electrons in gases. IV.** F. H. NICOLL and C. B. O. MOHR (Proc. Roy. Soc., 1933, A, 142, 647—658; cf. A., 1932, 1185).—An extension of previous measurements to  $CH_4$ ,  $N_2$ , Ne, and Hg vapour. The inelastic scattering observed at small angles is discussed with reference to Born's theory, and the gradual disappearance of

the diffraction effects at large angles at the lower voltages is investigated.

L. L. B.

**Total secondary electron emission from metal faces.** S. R. RAO (J. Annamalai Univ., 1933, 2, 249—257).—The shape of the total secondary electron emission curves for metal faces and the differences between the results for multi- and single-cryst. faces can be explained by considering the absorption of secondary electrons by the photo-electric target. The mean velocity of the secondary electrons increases with increasing potential at first rapidly, and then more slowly. The results of Petry on surfaces containing adsorbed gas are confirmed and explained.

A. J. M.

**Physical properties of the positron.** J. THIBAUD (Compt. rend., 1933, 197, 915—917; cf. A., 1933, 993).—By the method previously described it is shown that the sp. charge of the positron is  $< 1/2$ , and  $\approx$  double that of the electron. Positrons are possibly emitted as a spectrum by radon and radiothorium, resulting from internal conversion of  $\gamma$ -radiation. Positrons are produced by the action of  $\gamma$ -rays on Al, Cu, Ag, Pt, Pb, Bi, and U, the more readily the higher is the at. no. of the element acted on (cf. *ibid.*, 549). The coeff. of absorption of positrons is of the same order as that of electrons of the same average energy. The charge of the positron is considered positive, thus rendering unnecessary Dirac's conception of an electron of negative mass (cf. A., 1930, 271).

C. A. S.

**Positive electron.** P. KUNZE (Physikal. Z., 1933, 34, 849—857).—Various methods of production of the positive electron are reviewed, and the possibility of regarding the particle as an unstable one in the Dirac sense is discussed.

A. J. M.

**Ionisation function of argon in atomic argon radiation of a few hundred ion-volt-equivalents.** O. BEECK (Physikal. Z., 1933, 34, 840—841).—A method for the production of a powerful, const. beam of at. rays has been devised, and used for determination of the ionisation function of A. The no. of electrons produced per atom, in a distance of 1 cm., under a pressure of 1 mm., and at  $0^\circ$  is 4.5 for 350, and 6.5 for 650 ion-volt-equivs.

A. J. M.

**Polarisation of positive-ray glow.** W. ROMBERG (Ann. Physik, 1933, [v], 18, 515—528).—Theoretical.

A. J. M.

**Atomic mass of sodium. II. Sodium chloride-silver ratio.** C. R. JOHNSON (J. Physical Chem., 1933, 37, 923—933; cf. A., 1932, 922).—Six titrimetric NaCl:Ag ratios give  $Na=22.994$  ( $Cl=35.457$ ,  $Ag=107.880$ ). The same val. is obtained from five gravimetric NaCl:AgCl ratios.

F. L. U.

**At. wts. of radioactive substances.** F. WESTERN and A. E. RUARK (J. Chem. Physics, 1933, 1, 717—722).—Vals. are deduced for the probable at. wts. of the Pb isotopes and from these the at. wts. of radioactive substances are calc. allowing for the mass and energy lost in disintegration. It is considered that the chemical at. wt. of Ra is too low, whilst those of Th and U are too high.

H. S. P.

**Isotope of hydrogen. II.** P. ZEEMAN and J. DE GIER (Proc. K. Akad. Wetensch. Amsterdam, 1933,



36, 716—717; cf. A., 1933, 1099).—Positive-ray analysis of  $H_2$  containing 10%  $H^3H^2$  shows additional parabolas with  $m/e=6$  and 20, and ascribed to  $H_3^+$  and  $OH_2^+H_2^+$  ions, respectively. J. W. S.

**Isotopes of sodium and caesium.** C. B. DOLLINS and E. R. BISHOP (J. Amer. Chem. Soc., 1933, 55, 4372—4374).—The magneto-optical method shows the presence of three isotopes in Na, one heavier and one lighter than 23, and of six isotopes in Cs, three lighter and two heavier than 133. E. S. H.

**Manganese isotopes.** I. G. OTTO and E. R. BISHOP (J. Amer. Chem. Soc., 1933, 55, 4371—4372).—The magneto-optical method of analysis indicates that Mn has seven isotopes, three of which are lighter and three heavier than 55, the most abundant. E. S. H.

**Separation of isotopes.** H. EYRING and A. SHERMAN (J. Chem. Physics, 1933, 1, 345—349).—Theoretical. The relative importance of effusion processes, the half quanta due to van der Waals forces, and half quanta associated with homopolar linkings is considered with respect to the separation of isotopes. Calculations are given of the rôle of zero-point energy in the separation of the isotopes. Only in the neighbourhood of liquid  $H_2$  temp. are van der Waals forces important. Processes involving the breaking of homopolar linkings at moderate or low temp. are more efficient than effusion processes. Catalysts, light, electric discharges, and electrolysis, which at low temp. provide atoms which enter into subsequent reactions, are particularly effective. J. W. S.

**Name and symbol for  $H^2$ .** H. C. UREY, I. M. MURPHY, and F. G. BRICKWEDDE (J. Chem. Physics, 1933, 1, 512—513).— $H^1$  and  $H^2$ , and the names protium and deuterium, respectively, are proposed. F. L. U.

**Thorium- $C''$ .** (MLLE.) C. CHAMÉ (Compt. rend., 1933, 197, 1037—1039).—To obtain Th- $C''$  by the recoil method on a Au plate spread with Th active deposit a circular ring of ebonite maintained at negative potential was used; the air within the ring was freed from charged dust by laying a metal plate on the ring. This was replaced for about 10 sec. by the collecting plate for Th- $C''$ . Saturation was obtained with a field of about 700 volts per cm. Th- $C''$  free from any trace of Th- $C$  and giving a half-life period of 3.1 min. was obtained with 270 volts per cm. Slight anomalies in the beginning of the decay curve of Th- $C''$  were possibly connected with the fine structure of  $\alpha$ -rays from Th- $C$ . C. A. S.

**Interaction of hard  $\gamma$ -rays with atomic nuclei.** C. Y. CHAO and T. T. KUNG (Nature, 1933, 132, 709).—The scattering experiments described for the action of hard  $\gamma$ -rays (I) on Pb are interpreted as evidence for the disintegration of Pb by (I). L. S. T.

**Interaction of hard  $\gamma$ -rays with atomic nuclei.** (LORD) RUTHERFORD (Nature, 1933, 132, 709).—The experiments described (preceding abstract) provide additional evidence of the creation of negative and positive electrons by the conversion of a hard  $\gamma$ -ray in the strong electric field of a nucleus, and are best interpreted as such rather than as a nuclear disintegration. L. S. T.

**Nuclear  $\gamma$ -ray absorption.** T. HEITING (Naturwiss., 1933, 21, 800; cf. A., 1933, 1100).—When bombarded with hard  $\gamma$ -radiation, Al, Fe, Cu, and Pb give out secondary  $\gamma$ -radiation of wave-length 24 X independent of at. no. The process is, therefore, not a nuclear photo-process, where the wave-length should vary with at. no. There is a second component ( $\lambda = 6.6$  X) which belongs to nuclear resonance or a nuclear photo-process, and of which the intensity is very small. The secondary radiation of const. wave-length may be regarded as a recombination radiation, due to the recombination of positrons and electrons arising from the absorption of the  $\gamma$ -rays. A. J. M.

**Absorption of penetrating  $\gamma$ -rays.** W. GENTNER (Compt. rend., 1933, 197, 1111—1112; cf. A., 1933, 995).—The difference between the coeff. of absorption per electron of Pb and that calc. by the Klein-Nishina formula for Pb, namely  $\mu_e - \mu_{\text{calc}}$ , shows a much less marked min. for  $\lambda$  6.6 X than the differences  $\mu_{\text{Pb}} - \mu_{\text{Al}}$  or  $\mu_{\text{Pb}} - \mu_{\text{Ag}}$  determined by Chao (cf. A., 1932, 318). C. A. S.

**Use of a high-pressure ionisation chamber for the study of  $\gamma$ -radiation and neutrons.** P. SAVEL (J. Phys. Radium, 1933, [vii], 4, 609—612).—Ionisation current-pressure curves for the pressure range 1—30 atm. are given for  $\gamma$ -rays from Ra and complex radiation emitted by Be irradiated by  $\alpha$ -particles from Po, the chamber being successively filled, in each case, with  $H_2$ ,  $N_2$ , and A. N. M. B.

**Disintegration of lithium under proton bombardment.** P. I. DEE (Nature, 1933, 132, 818—819).—The proton beam is passed into the gas of the expansion chamber through a thin mica window and then allowed to fall on a thin target of  $Li_2O$ . A dense sphere of ionisation is produced by scattering of the protons in the gas, but in addition short-range particles mostly emitted in opposite pairs, can be observed. Further work is necessary to decide whether the reaction in question is  ${}^7Li + {}^1H \rightarrow {}^4He + {}^4He + \gamma$ -radiation or  ${}^7Li + {}^1H \rightarrow {}^8Be$ . L. S. T.

**Disintegration of lead by means of penetrating radiation.** B. ROSSI (Atti R. Accad. Lincei, 1933, [vi], 17, 1073—1077).—The secondary particles obtained by the action of penetrating cosmic radiation on Pb are produced not singly, but in groups of several particles at once, due to nuclear disintegrations. O. J. W.

**Wave-statistical theory of radioactive disintegration.** K. C. KAR and A. GANGULI (Phil. Mag., 1933, [vii], 16, 1097—1109).—A relation between the disintegration const. and the velocity of the emitted  $\alpha$ -particle is derived, and is compared with experimental vals. H. J. E.

**Mechanism of the Geiger-Müller counter.** G. STETTER (Physikal. Z., 1933, 34, 886).—A criticism of the experimental conditions in the work of Christoph and Hanle (A., 1933, 996). A. J. M.

**Mechanism of the Geiger-Müller counter.** W. CHRISTOPH and W. HANLE (Physikal. Z., 1933, 34, 886).—A reply to Stetter (preceding abstract). A. J. M.

**Neutrons and positrons.** W. BOTHE (Naturwiss., 1933, 21, 825—831).—A review.



**New artificial source of neutrons.** H. R. CRANE, C. C. LAURITSEN, and A. SOLTAN (Compt. rend., 1933, 197, 913—915; cf. A., 1933, 1225).—Using the same apparatus, LiCl and Be were bombarded with ions (deutons and protons) from a mixture of 5%  $H^2$  with 95%  $H^1$ , which yielded very many more neutrons than were obtained when bombardment was with He ions (the no. was reduced by  $> 50\%$  if the internal coating of the electroscope with paraffin was omitted). Bombardment with protons has no effect on Be and but little on LiCl (cf. A., 1933, 883). The disintegrations may be assumed to be  $Be^9 + H^2 \longrightarrow B^{10} + n^1$  and  $Li^7 + H^2 \longrightarrow 2He^4 + n^1$ .

C. A. S.

**Collisions of neutrons with light nuclei.** II. N. FEATHER (Proc. Roy. Soc., 1933, A, 142, 689—709; cf. A., 1932, 790, 981).—The method previously described has been applied to neutron- $O_2$  nucleus encounters, and series of photographs of the tracks produced in  $O_2-H_2$  and  $C_2H_2-He$  gas mixtures have been obtained. Evidence is adduced for the presence of recoil protons due to neutrons produced in the resonance disintegration of Be, and also of C recoil atoms due to neutrons of high energy. Disintegration collisions have been observed in  $O_2$ , and one case of C-nucleus disintegration by the neutrons from Po-Be.

L. L. B.

**Materialisation by interaction of photon and electron.** F. PERRIN (Compt. rend., 1933, 197, 1100—1102).—The min. energy,  $h\nu$ , of a photon that enables it on meeting an electron of mass  $m$  to materialise as a pair of electrons,  $+$  and  $-$ , is  $4mc^2$ , or approx.  $2 \times 10^6$  e.v., of which half appears as the two electrons and half as kinetic energy, or double that required for the photon to materialise on a nucleus; the resultant electrons (two negative and one positive) have a velocity of about  $4c/5$  in the direction of the incident photon. If the energy of the photon is  $> 4mc^2$  the electrons will have different velocities. The result should appear as a triple fork in an expansion chamber, and should be discernible in a gas of high at. wt., e.g., Xe.

C. A. S.

**Materialisation of electrons at the time of collision of two electrons: annihilation of positive electrons.** F. PERRIN (Compt. rend., 1933, 197, 1302—1304; cf. preceding abstract).—The collision between an electron of kinetic energy  $> 2mc^2$  (about  $10^6$  e.v.) and an at. nucleus should produce a pair ( $+$  and  $-$ ) of electrons, as also should one between two electrons, one at (relative) rest, the other with kinetic energy  $6mc^2$ , in which case the colliding and the materialised electrons should all move in the direction of the incident electron with velocity  $\sqrt{3/2}c$ ; if the energy of the incident electron is  $> 6mc^2$  the velocities and directions will be various. Conversely, a pair ( $+$  and  $-$ ) of electrons should be dematerialisable with emission of two photons each of energy  $mc^2$ ; if this happens in presence of a third electron, then with propulsion of the electron and emission of one photon with energies of  $2mc^2/3$  and  $4mc^2/3$ , respectively; or if in presence of two other electrons, with propulsion of each of these with energy  $mc^2$ . Such phenomena should be recognisable in a Wilson chamber photograph.

C. A. S.

**Exchange of energy between inert gas atoms and a solid surface.** J. M. JACKSON and A. HOWARTH (Proc. Roy. Soc., 1933, A, 142, 447—456).—The theory of the thermal accommodation coeff. (Jackson and Mott, A., 1932, 1074) is extended by removing the restriction that all the solid atoms should oscillate with the same frequency. Good agreement is obtained with the experimental results of Roberts for the accommodation coeff. of He on a clean surface of W (*ibid.*, 316, 680).

L. L. B.

**Exchange of energy between gas atoms and solid surfaces.** III. Accommodation coefficient of neon. J. K. ROBERTS (Proc. Roy. Soc., 1933, A, 142, 518—524; cf. A., 1932, 316, 680).—The accommodation coeff. of Ne with a W surface free from films of adsorbed gas is 0.07 at  $295^\circ$  abs., and varies little with temp. down to  $79^\circ$  abs. With a surface covered with adsorbed films the val. is 0.6. Applying Jackson and Mott's theory of the interchange of energy between monatomic gas atoms and the atoms of a solid surface (*ibid.*, 1074) to the experimental results for He and Ne, it is shown that the repulsive forces between W atoms and the gas atoms are not similar to the forces between elastic spheres.

L. L. B.

**Energy distribution in cosmic rays.** W. G. POLLARD (Physical Rev., 1933, [ii], 44, 703—706).—Mathematical. Cosmic rays probably preserve their energy distribution of original emission.

N. M. B.

**System of the elements.** I. Vector model of the free atom. II. Periodic classification. III, IV. Interpretation of chemical properties in terms of atomic theory. V. Investigation of the atomic nucleus. VI. Structure of atomic nuclei. A. J. RUTGERS (Chem. Weekblad, 1933, 30, 602—606, 632—635, 642—646, 654—657, 671—674, 682—684).—A lecture.

H. F. G.

**Pauli's principle in nuclei.** W. M. ELSASSER (J. Phys. Radium, 1933, [vii], 4, 549—556).—The addition of a neutron or proton to a nucleus is considered; it gives rise to a system from the energy distribution of which various nuclear properties are explained.

N. M. B.

**Bond energies and mass defects in atomic nuclei.** W. M. LATIMER and W. F. LIBBY (J. Chem. Physics, 1933, 1, 133—136).—The interpretation of the mass defect curve is discussed in reference to the coupling of protons and electrons (cf. A., 1931, 544). Gamow's equation is modified by making the attractive energies the sum of the linking energies. The calc. vals. for the mass defect of the symmetrical nuclei of O, A, Zn, Xe, and Po are in good agreement with experiment.

N. M. B.

**Characteristic values of the two minima problem and quantum defects of  $f$  states of heavy atoms.** T. Y. WU (Physical Rev., 1933, [ii], 44, 727—731).—Mathematical. An application of the characteristic vals., solved by an approx. method, explains the fact that the calc. quantum defects are all very close to 1.

N. M. B.

**Constitutive parts of atomic nuclei.** D. IVANEKO (Compt. rend. Acad. Sci. U.S.S.R., 1933, 2, 52—56).—Theoretical (cf. A., 1932, 981).

A. B. D. C.



**Normal state of hydrogen molecule-ion.** B. N. DICKINSON (J. Chem. Physics, 1933, 1, 317—318).—Rosen's treatment for  $H_2^+$  (A., 1932, 211) was found not suitable for  $H_2^+$ . D. R. D.

**Lifetimes of unstable molecules.** N. ROSEN (J. Chem. Physics, 1933, 1, 319—326).—The lifetime of a mol. containing surplus energy is derived from consideration of internal energy transitions and compared with data for  $HO_2$ . D. R. D.

**Lifetimes of unstable molecules.** O. K. RICE (J. Chem. Physics, 1933, 1, 625—626).—A note on Rosen's paper (preceding abstract). H. J. E.

**Normal state of the hydrogen molecule.** S. WEINBAUM (J. Chem. Physics, 1933, 1, 593—596).—The calc. dissociation energy of normal  $H_2$  is 4.00 e.v. H. J. E.

**Quantum mechanics of seven and eight electrons with spin degeneracy.** H. EYRING and G. E. KIMBALL (J. Chem. Physics, 1933, 1, 239—246).—Calculations and proofs are given for assumptions previously made (A., 1933, 213) using an extension of Slater's method (A., 1931, 548) for 3 and 4 atoms. M. S. B.

**Calculation of matrix elements for Lewis electronic structures of molecules.** L. PAULING (J. Chem. Physics, 1933, 1, 280—283).—A simple graphical method is developed for calculating the coeff. of the integrals occurring in the matrix elements involved in Slater's treatment (A., 1931, 1356) of the electronic structure of mols. M. S. B.

**Calculation of matrix elements between linking eigenfunctions.** H. EYRING and G. E. KIMBALL (J. Chem. Physics, 1933, 1, 626).—Mathematical (see above). H. J. E.

**Dispersion theory in metallic conductors. II.** Y. FUJIOKA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 22, 202—215). R. S.

**Self-forces of elementary particles. I.** G. WENTZEL (Z. Physik, 1933, 86, 479—494).—Theoretical. A. B. D. C.

**Density of energy in the theory of light.** L. DE BROGLIE (Compt. rend., 1933, 197, 1377—1380; cf. A., 1932, 1184).—Mathematical. The classical form  $(\mathcal{E}^2 + \mathcal{H}^2)/2$  for the density of electromagnetic energy is approx., as is  $mv^2/2$  for the kinetic energy in relativistic dynamics. C. A. S.

**Atomic eigenfunctions in the impulse space.** G. RUMER (Compt. rend. Acad. Sci. U.R.S.S., 1933, 104—105). H. J. E.

**Relativistic theory of the Dirac electron in a nul field.** A. PROCA (Ann. Physique, 1933, [x], 20, 347—440).—Mathematical. A relativistic form of the Dirac theory is approached by the introduction of a "proper time" analogous to classical proper time. The functions and physical interpretation of a new type of ternary operator are examined. N. M. B.

**Heights of nuclear potential barriers.** E. W. POLLARD (Phil. Mag., 1933, [vii], 16, 1131—1141; cf. A., 1933, 443).—For Li, Be, B, N, F, C, and Al the height is a linear function of the at. no. The theoretical significance of the rule is discussed. H. J. E.

**Zeeman effect in solids.** F. H. SPEDDING (J. Chem. Physics, 1933, 1, 144—154; 287, errata).—Crystal photographs and microphotometer curves are given for the transverse Zeeman effect on the absorption lines of monoclinic  $GdCl_3 \cdot 6H_2O$ . Results can be explained on the assumption that if an electron is excited as a first approximation, only its spin can orient in a magnetic field. N. M. B.

**Photochemistry of solid lithium hydride.** F. BACH and K. F. BONHOEFFER (Z. physikal. Chem., 1933, B, 23, 256—264).—Solid LiH has a marked absorption max. at 2517 Å., which is taken to correspond with transfer of an electron from  $H'$  to an adjacent Li<sup>+</sup> giving neutral unexcited atoms. The quantum yield, measured by the evolution of  $H_2$ , is about 0.05, which is ascribed to the bulk of the H formed remaining in the LiH lattice. LiH becomes greyish-blue on exposure to ultra-violet light, but may be decolorised by heating or exposure to visible light of long wave-length. R. C.

**Spectroscopic evidence for the molecule PN.** J. CURRY, L. HERZBERG, and G. HERZBERG (J. Chem. Physics, 1933, 1, 749).—An extensive system of diat. bands in the region 2400—2900 Å. has been found when a discharge is passed through  $N_2$  containing P. The fine structure shows that the system is a  $^1\Pi \rightarrow ^1\Sigma$  transition, and so cannot be due to PO or CP. The rotational and vibrational consts. point to PN. H. S. P.

**Spectroscopic proof and structure of the PN molecule.** J. CURRY, L. HERZBERG, and G. HERZBERG (Z. Physik, 1933, 86, 348—366).—The  $^1\Pi \rightarrow ^1\Sigma$  band system due to PN (see above) has been analysed and the nuclear separations are 1.487 and 1.542 Å. for the  $^1\Sigma$  and  $^1\Pi$  levels. A. B. D. C.

**New band systems in the gadolinium oxide spectrum.** G. PICCARDI (Nature, 1933, 132, 714).—A correction (cf. A., 1933, 1102). L. S. T.

**Band spectrum of tin oxide.** F. C. CONNELLY (Proc. Physical Soc., 1933, 45, 780—791).—The emission and absorption spectra of a  $H_2$  flame containing traces of  $SnCl_4$  have been investigated, and the  $SnO$  bands have been analysed.  $SnO$  is the emitter, since the spectrum can be obtained with a Sn arc in air, but not in  $H_2$  or  $N_2$ . Vibrational analysis of Mahanti's A system (A., 1931, 544) is extended to  $v'=8$ , and approx. vals. of the vibrational consts. are calc. from the band head data. The lower electronic level of this system is the ground state and its energy of dissociation is 5.7 volts. J. W. S.

**Band spectrum of bismuth oxide.** C. GHOSH (Z. Physik, 1933, 86, 241—248).—The vibrational structure of bands between 4300 and 6700 Å. has been analysed. A. B. D. C.

**Molecular spectra of some indium and gallium halides.** A. PETRIKALN and J. HOCHBERG (Z. Physik, 1933, 86, 214—230).—Absorption and emission spectra in the ultra-violet were observed for  $InCl_2$ ,  $InCl$ ,  $InBr$ ,  $GaCl_2$ ,  $GaBr_3$ , and  $GaI_3$  at different temp. A. B. D. C.

**Change in the absorption spectrum of cobalt chloride in aqueous solution with increasing concentration of hydrochloric acid.** O. R. HOWELL



and A. JACKSON (Proc. Roy. Soc., 1933, A, 142, 587—597).—From a study of the variation of the extinction coeffs. of the four principal bands 695, 666, 626, 610 m $\mu$  of solutions of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (12 g. per litre) with increasing concn. of HCl, it is shown that no blue constituent is formed until a crit. concn. of acid (5.0N) is reached, and its amount then increases rapidly with increasing concn. of acid, the relation becoming linear at 7.1N. The state of the Co atom is determined only by the environment and is independent of the relative concn. of the Co to the other constituents. The intensity of absorption of the blue complex ion is 92.5 times that of the red.

L. L. B.

**Rotation analysis of the  $^2\Sigma \rightarrow ^2\Sigma$  and  $^2\Pi \rightarrow ^2\Sigma$  bands of  $\text{CO}^+$ .** R. SCHMID and L. GERÖ (Z. Physik, 1933, 86, 297—313).

A. B. D. C.

**Spectrum of the afterglow of carbon dioxide.** A. FOWLER and A. G. GAYDON (Proc. Roy. Soc., 1933, A, 142, 362—369).—The spectrum of the  $\text{CO}_2$  afterglow differs from those given by oxides of C in vac. tubes, but resembles that given by the flame of CO burning in air or  $\text{O}_2$ . It is probable that the bands of the  $\text{CO}_2$  afterglow and of the CO flame are produced by the direct combination of CO and  $\text{O}_2$ , without dissociation into atoms of C and O or mols. of C. The extreme complexity of the spectrum, as revealed by spectrographs of adequate resolving power, also suggests that the bands of the afterglow originate in  $\text{CO}_2$  mols.

L. L. B.

**Absorption spectra of uranium compounds.** F. EPHRAIM and M. MEZENER (Helv. Chim. Acta, 1933, 16, 1257—1272).—Spectral absorption lines for a large no. of U compounds are given. A parallel is drawn between the spectra of U compounds and those of the rare earths.  $\text{UCl}_5$ , the only known compound of  $\text{U}^{\text{V}}$ , gives no absorption lines even in liquid air. Heavy metal *uranates* have been prepared by digesting  $\text{UO}_2$  salts with the metallic hydroxides, but  $\text{CdO} \cdot 2\text{UO}_3$  and  $\text{ZnO} \cdot \text{UO}_3$  only have been obtained as clearly defined compounds. The uranates do not give a linear absorption spectrum.

M. S. B.

**Predissociation and the crossing of molecular potential energy curves.** O. K. RICE (J. Chem. Physics, 1933, 1, 375—389; cf. A., 1931, 271, 1077, 1078).—Theoretical. The calculation of the width and shape of a line broadened on account of predissociation is extended to include perturbations of such size that the lines of given rotational quantum no. belonging to two adjacent vibrational levels do not overlap appreciably. The theory is applied to predissociation phenomena in  $\text{ICl}$ , and two groups of sharp and diffuse levels are ascribed respectively to  $\text{ICl}^{35}$  and  $\text{ICl}^{37}$ .

J. W. S.

**Colours of copper salts.** W. D. BANCROFT and H. W. ROGERS (J. Physical Chem., 1933, 37, 1061—1073).—The colour of  $\text{Cu}^{\text{II}}$  salts is the same in the solid, solution, and vapour states if the chromophoric groups are the same.  $\text{Cu}^{\text{II}}$  with  $2\text{H}_2\text{O}$  is green and with  $\leq 3\text{H}_2\text{O}$  blue. The  $\text{NH}_3$  mol. has practically the same effect as the  $\text{H}_2\text{O}$  mol., but the blue shade is different. Anhyd.  $\text{Cu}^{\text{II}}$  is probably colourless, but may be red. The red or brown colour of  $\text{CuCl}_2$  alone and in certain double salts is probably due to a  $\psi$ -salt. X-Ray

analysis has shown that the group  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  probably exists in some of the green double salts. Cu produces a blue colour in borate and silicate glasses. The reasons for the various colours are unknown.

H. S. P.

**Ultra-violet absorption and chemical reactivity of organic compounds.** M. GRUNFELD (Ann. Chim., 1933, [x], 20, 304—370).—A full account of work previously published (A., 1930, 838; 1932, 371, 444).

F. L. U.

**Continuous absorption spectrum of polyatomic molecules. III.** Y. HUKUMOTO (Sci. Rep. Tôhoku, 1933, 22, 868—878).—Dissociation energies of  $\text{C}_2\text{Cl}_4$ ,  $\text{C}_2\text{HCl}_3$ ,  $\text{C}_3\text{H}_5\text{Cl}$ ,  $\text{Bu}^n\text{Br}$ ,  $\text{Bu}^n\text{I}$ ,  $\text{CCl}_4$ ,  $\text{SiCl}_4$ ,  $\text{TiCl}_4$ , and  $\text{SnCl}_4$  have been calc. from the long wavelength limits of the continuous absorption bands.  $\text{Bu}^n\text{I}$  has two regions of absorption. The shift of the absorption limits on liquefaction is attributed to changes in the unstable potential energy states of some of the mols.

J. G. A. G.

**Ultra-violet absorption of aldehydes.** H. CONRAD-BILLROTH (Z. physikal. Chem., 1933, B, 23, 315—318).—Measurements have been made with aliphatic aldehydes in hexane solution. With the normal aldehydes the max. is displaced by  $1350\text{ cm}^{-1}$  compared with the corresponding ketone. With both classes of compound the position of the band seems to depend only on the no. of groups, other than  $\cdot\text{CHO}$  or  $\text{COMe}$ , attached to the C atom adjacent to the  $\cdot\text{CHO}$ .

R. C.

**Ultra-violet absorption of some organic substances.** J. DABROWSKI and L. MARCHLEWSKI (Bull. Soc. chim., 1933, [iv], 53, 946—950).—The absorption spectrum of isatin (I) is very close to that of the *N*-Me ether (II) and totally different from that of the *O*-Me ether (III), the resemblance of the (I) and (II) spectra thus confirming the observations of Hartley and Dobbie (J.C.S., 1899, 75, 640). This is contrary to the statement of Morton and Rogers (cf. A., 1926, 9), and it is suggested that these authors worked with (III) which had undergone a change to a substance more closely resembling (I), since (III) is known to be unstable. It is concluded that the study of absorption spectra in this series can be used to determine the constitution of the tautomeric substance, as was stated by Hartley and Dobbie.

R. S.

**Light absorption of *p*-nitrosodimethylaniline.** J. F. H. CUSTERS and C. J. DIPPEL (Z. Physik, 1933, 86, 516—520).—The region investigated was 250—550 m $\mu$  before and after addition of an equiv. amount of HCl.

A. B. D. C.

**Absorption spectra of diphenols in alkaline medium.** A. SAINT-MAXEN and E. DUREUIL (Compt. rend., 1933, 197, 1411—1413).—The absorption spectra of quinol (I), pyrocatechol (II), and resorcinol (III) in aq. and alkaline solution have been compared for  $\lambda$  2200—5800 Å. The changes in presence of alkali for the spectra of (I) and (II) indicate quinone formation; in (III), where this is impossible, they are negligible (cf. A., 1909, ii, 374).

C. A. S.

**Spectral absorption of methylated xanthines and constitution of the purine nucleosides.** J. M.



GULLAND and E. R. HOLIDAY (Nature, 1933, 132, 782).—The ultra-violet spectral absorption of xanthine (I) and certain Me derivatives may provide a method of distinguishing between derivatives of (I) substituted in the 7 or 9 positions, and this method can be used to assign to these positions the carbohydrate radical (II) in the natural and synthetic purine glucosides. (I) and its Me derivatives can be divided into two groups: (i) the absorption curves show two bands in alkaline solution, viz., (I), 1-, 8-, and 9-methyl-, 3:9-dimethyl-, and 1:3:9-trimethyl-purine, and (ii) the curves show one band in both acid and alkaline solution, viz. 3-, 7-methyl-, 1:3-, 1:7-, 3:7-dimethyl-, and 1:3:7-trimethyl-purine. Me at position 7 thus inhibits the appearance of the second band. A comparison of the spectra of methyl-purines with those in which the H of the NH of the glyoxaline ring is unsubstituted suggests that in 3-methylpurine and in theophylline (Me at 1 and 3) this H is at position 7, whereas in (I) and 1- and 8-methylpurine it is at position 9, the reverse of the usual arrangement. The formula of (I) and of the hypothetical isopurine would therefore have to be interchanged. In xanthinose from yeast-nucleic acid it is probable that (II) is attached at position 9, whilst the synthetic arabinoside and glucoside of theophylline contain (II) in position 7 (cf. A., 1933, 838). L. S. T.

**Absorption spectra of molecular organic compounds.** W. H. HUNTER and E. H. NORTHEY (J. Physical Chem., 1933, 37, 875—887).—Measurement of the absorption spectra of fused chloro-, benzo-, tolu-, xylo-, and duro-quinone, and of equimol. mixtures of them with aromatic hydrocarbons, ethers, and amines permits the latter to be arranged in order of increasing effect, ranging from mere solvent action to mol. compound formation. This order is independent of the quinone used. The change in the spectrum produced by a substance capable of forming a mol. compound increases with increasing oxidation-reduction potential of the quinone.

F. L. U.

**Polarisation of the fluorescent band.** S. M. MITRA (Current Sci., 1933, 2, 176—177).—The fluorescence band obtained with solutions of various dyes in glycerol and in gelatin, and with solutions of Na salicylate, BzOH, and  $\beta$ -C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub> in glycerol was found to be equally polarised throughout.

A. J. M.

**Structure of the ultra-violet spectrum of various proteins.** F. VLÈS and M. PRAGER (Arch. Phys. biol., 1932, 10, 5—20; Chem. Zentr., 1933, i, 2219).—Narrow bands in the region 275 m $\mu$  exist in the absorption spectra of serum and of various proteins, but not in the same band in that of COME<sub>2</sub>. The nature of the groups responsible is considered.

A. A. E.

**Spectrochemical investigation of the viscose reaction.** K. ATSUKI and H. SOBUE (J. Soc. Chem. Ind. Japan, 1933, 36, 589—595B).—Absorption data are recorded for cellulose xanthate for visible and ultra-violet light. There is a max. at 3000—3100 Å. for the xanthate and at 3300 Å. for the reaction products of NaOH and CS<sub>2</sub> alone.

A. G.

**Vibration frequencies and other constants of the H<sub>2</sub>O molecule.** J. H. VAN VLECK and P. C. CROSS (J. Chem. Physics, 1933, 1, 357—361).—The calculation is based on the Slater-Pauling theory of directed valency, supplemented by data from the band spectrum of the OH mol. The heat of dissociation and valency angle agree with experiment. Two fundamentals should fall near 2.8  $\mu$ , this being in agreement with Mecke's interpretation of the H<sub>2</sub>O spectrum, but not with that of Johnston and Walker.

J. W. S.

**Infra-red absorption spectra of NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub>.** R. SCHAFFERT (J. Chem. Physics, 1933, 1, 507—511).—Measurements have been made between 3° and 150°. Frequencies of bands due to NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub>, respectively, are tabulated. The simplicity of the spectrum of N<sub>2</sub>O<sub>4</sub> suggests a symmetrical structure of the mol.

F. L. U.

**Rotation vibration spectrum of methane.** H. VEDDER and R. MECKE (Z. Physik, 1933, 86, 137—156).—This spectrum was photographed between 0.7 and 1  $\mu$ . The rotational structure was measured but not analysed. The known vibration bands of CH<sub>4</sub> can be allotted to four normal frequencies at 3015, 2945, 1530, and 1320 cm.<sup>-1</sup> The problem of the normal modes is investigated, assuming a general potential field having the symmetry of the molecule. The observed frequencies indicate that the particular case of a valency force field fits the mol., and that the force consts. for C-H, angular, and H-H displacements are as 5.5 : 1 : 0.12.

A. B. D. C.

**Transmission of infra-red radiation by a thin layer of horn.** J. H. TAYLOR (Proc. Roy. Soc., 1933, A, 142, 598—605).—A layer of horn 0.022 mm. thick was used. Marked absorption was found in the region of 3.4  $\mu$ , and also in the region beyond 6  $\mu$ .

L. L. B.

**Discovery of molecular diffusion of light in pure liquids.** A. TURPAIN (Compt. rend., 1933, 197, 1107—1109).—The mol. diffusion of light by a pure liquid and its polarisation were described, and the Raman effect was foreshadowed, by Lallemand 65 years ago (cf. *ibid.*, 1869, 69, 189; 1874, 79, 694).

C. A. S.

**Raman effect of aluminium salts.** A. DA SILVA VEIRA (Compt. rend., 1933, 197, 1035—1037).—Raman lines of Al(NO<sub>3</sub>)<sub>3</sub> and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> occur between 270 and 1639 cm.<sup>-1</sup>, but lines of higher frequency of the sulphate were concealed by a continuous background. NO<sub>3</sub>' lines are at 721, 1052, 1312, and 1414, that at 819 being an inactive frequency; 721, 1312, and 1414 are forbidden; 721 is doubly and 1312 and 1414 are singly degenerate; 1639 is due to H<sub>2</sub>O. Of the sulphate lines 461, 612, 981, and 1109 are due to SO<sub>4</sub>''; 396 in both is ascribed to Al'''. There are some indications that Al''' is hydrated (cf. A., 1932, 983). The origin of nitrate lines at 446, 537, 627, 1241, and 1530 and of sulphate lines at 270, 527, and 686 is doubtful.

C. A. S.

**Evidence from Raman effect for electrolytic dissociation in sulphuric acid.** I. R. RAO (Indian J. Physics, 1933, 8, 123—135).—A qual. study gave Raman lines 416, 742, 1043, 562, 910, 1171, and



1365  $\text{cm}^{-1}$ . The four last-named decrease in intensity with dilution, whilst the 1043 line increases, being attributed to the  $\text{HSO}_4$  ion, and due to dissociation on dilution. At lower concns., a new line 980  $\text{cm}^{-1}$ , attributed to the  $\text{SO}_4$  ion, appears; it increases in intensity with dilution, indicating further dissociation of  $\text{HSO}_4$  into  $\text{H}^+$  and  $\text{SO}_4^{2-}$ . The lines 562, 1171, and 1365 are stated to be evidence of mols. of the type  $\text{SO}_2(\text{OH})_2$  in the pure acid. The successive dissociation stages are  $\text{H}^+ + \text{HSO}_4^-$  and  $2\text{H}^+ + \text{SO}_4^{2-}$ .  
N. M. B.

**Raman bands of water.** G. BOLLA (Nuovo Cim., 1933, [ii], 10, 101—107; Chem. Zentr., 1933, ii, 989).—Five new bands, max. at  $\Delta\nu=510$ , 780, 1645, 2150, and 3990  $\text{cm}^{-1}$ , have intensities < those at 3200 and 3435  $\text{cm}^{-1}$ . The band at 1645  $\text{cm}^{-1}$  is narrower and sharper than the others. A. A. E.

**Raman spectrum of water vapour.** D. H. RANK (J. Chem. Physics, 1933, 1, 504—506).—The displacements 1648 and 984  $\text{cm}^{-1}$  reported by Johnston and Walker (A., 1933, 1102) were not observed.  
F. L. U.

**Raman effect in solutions of ammonium nitrate in nitric acid.** L. MÉDARD and (Mlle.) T. PETITPAS (Compt. rend., 1933, 197, 1221—1222).—The Raman spectra for  $\text{NH}_4\text{NO}_3 + 2\text{HNO}_3$  (i.e., 38.7%  $\text{NH}_4\text{NO}_3$ ) and for solutions of 0—55%  $\text{NH}_4\text{NO}_3$  in  $\text{HNO}_3$  contain lines previously reported (cf. A., 1933, 1228) with variations indicating that dilution of  $\text{HNO}_3$  with  $\text{NH}_4\text{NO}_3$  has a similar effect to dilution with  $\text{H}_2\text{O}$ . 3100—3300  $\text{cm}^{-1}$  is referred to vibration of H in the mol.  $\text{NO}_2\cdot\text{OH}$ .  
C. A. S.

**Vibration spectra and structure of the cyanogen halides.** W. WEST and (Miss) M. FARNSWORTH (J. Chem. Physics, 1933, 1, 402—405).—The Raman spectra of CN halides, in the liquid state or in EtOH solution, contain three frequencies,  $\nu_1=2201$ , 2187, 2158  $\text{cm}^{-1}$ ;  $\nu_2=729$ , 580, 470  $\text{cm}^{-1}$ ;  $\nu_3=397$ , 368, 321  $\text{cm}^{-1}$ , for CNCl, CNBr, and CNI, respectively. The order of intensity of Raman transitions is  $\nu_1 > \nu_2 > \nu_3$ . The relative vals. of the frequencies indicate a linear arrangement of the nuclei in the lowest electronic state of these mols., and the data accord with the structure  $\text{X}\cdot\text{C}\cdot\text{N}$  rather than  $\text{X}\cdot\text{N}\cdot\text{C}$ .  
J. W. S.

**Raman spectrum of tetramethylmethane.** D. H. RANK (J. Chem. Physics, 1933, 1, 572—575).—Data for  $\text{CMe}_4$ , *n*-amyl chloride, and  $\text{CMe}_3\text{Cl}$  are recorded. A vibrational frequency of 415  $\text{cm}^{-1}$  for  $\text{CMe}_4$ , predicted by Kohlrausch and Barnes (A., 1933, 7), was observed.  
H. J. E.

**Complete Raman spectrum of benzene from 4100 to 5100 Å.** P. GRASSMANN and J. WEILER (Z. Physik, 1933, 86, 321—337).—Using high dispersion, 41 Raman lines were observed and allocated to combinations of 10 fundamental frequencies. The displacement at 984  $\text{cm}^{-1}$  is ascribed to  $\text{C}^{13}$ .  
A. B. D. C.

**Raman spectra of dichlorobenzenes.** J. W. SWAINE and J. W. MURRAY (J. Chem. Physics, 1933, 1, 512).—Raman frequencies for the three isomerides are given.  
F. L. U.

**Raman spectra of ring compounds. I. Mono-substituted benzene compounds.** J. W. MURRAY

and D. H. ANDREWS (J. Chem. Physics, 1933, 1, 406—413).—An improved apparatus for study of Raman spectra is described. The use of filters, e.g.,  $\text{PhNO}_2$ ,  $\text{NaNO}_2$ , or  $\text{Cu}(\text{NO}_3)_2$ , for removing violet, ultra-violet, and red light, respectively, is suggested, this aiding the location of the weaker lines of the spectrum. Raman spectra of *n*- $\text{C}_4\text{H}_{10}$ , PhCl, PhBr, and PhI have been reinvestigated and the results are tabulated. Several new lines have been found. The Raman spectrum of 2-chloropyridine has been found to be analogous to that of PhCl. J. W. S.

**Raman spectrum of some substituted cyclenes.** M. GODCHOT, E. CANALS, and (Mlle.) G. CAUQUIL (Compt. rend., 1933, 197, 1407—1409).—The Raman spectra of seven Me and an Et derivative of cyclopentene, -hexene, or -heptene are compared with those of the corresponding unsubstituted cyclenes. The differences are slight, the chief being that in the Me derivatives the line near 800  $\text{cm}^{-1}$  is replaced by two. 825 of cyclohexene becomes 821 and 758 in 1-methylcyclohexene; the line near 1440 is thickened in the Et derivative, and replaced by a doublet in the  $\text{Me}_2$  and  $\text{Me}_3$  derivatives.  
C. A. S.

**Depolarisation of light; depolarisation by organic colloids and by kaolins.** V. PETRESCU (Ann. Sci. Univ. Jassy, 1933, 18, 318—336).—Suspensions of birefringent particles > the wave-length of light can cause depolarisation. With casein, legumin, fluorescein, rhodamine, and benzopurpurin depolarisation occurs, but with kaolins the effect is irregular, probably owing to impurities. H. S. P.

**Diffusion of light and rotations of molecules in liquids.** A. ROUSSET (Compt. rend., 1933, 197, 1033—1035).—The depolarisation factor  $\rho$ , measured at the centre of the spectrum, has been determined for  $\text{C}_6\text{H}_6$ ,  $\text{CS}_2$ ,  $\text{AcOH}$ , and  $\text{SO}_2$ , as a function of the width (25—2500  $\mu$ ) of the slit of the spectrograph, whence are deduced the relative intensities of the *P*, *Q*, and *R* branches, the distribution of intensities in *P* and *R*, and also  $\rho_0$ , the depolarisation factor of the *Q* branch. The differences between the results and those previously obtained are discussed (cf. A., 1932, 107, 898; 1933, 446, 448).  
C. A. S.

**Quenching of light from flames produced by various chemicals.** C. D. CHILD (Phil. Mag., 1933, [vii], 16, 1141—1150).—Addition of salts and acid (e.g.,  $\text{HNO}_3$  or  $\text{AlCl}_3$ ) to aq. Ca, Sr, Na, or K salts sprayed into otherwise non-luminous flames generally diminishes the characteristic radiation. Results are attributed to dissociation of the added mols. in the flames.  
H. J. E.

**Theory of the phosphorogen.** A. A. GUNTZ (Compt. rend., 1933, 197, 1030—1033).—The conclusion (cf. A., 1931, 998; 1932, 11; 1933, 579) that in the production of phosphorescent ZnS total absence of any phosphorogen may be compensated by the high temp. (about 3000°) of prep. is disputed on the ground that solid ZnS could not exist at a temp. >1500°, and that a concn. of  $10^{-5}$  Cu is the optimum at 2000°. Some factor other than temp. must intervene (cf. A., 1926, 885).  
C. A. S.

**Thermo-luminescence spectra of fluorites. I. Thermo-luminescence spectra of fluorites from**



Obira. E. IWASE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 22, 234—241).—Specimens showing greater no. of thermo-luminescence bands in the short-wave region have greater photo-sensitivity and rare-earth content. R. S.

**Triboluminescence of mercurous halides.** J. H. KRÉPELKA and D. F. NOVOTNY (Časopis českoslov. Lék., 1933, 13, 26—35, 85—95; Chem. Zentr., 1933, i, 3542).—Pure, solid  $\text{Hg}^{\text{I}}$  halides, but not complex Hg compounds, exhibit triboluminescence; the sensitivity is  $>$  that of ultra-violet fluorescence.  $\text{Hg}^{\text{II}}$  compounds free from  $\text{Hg}^{\text{I}}$  cannot be obtained by direct synthesis from Hg and  $\text{Cl}_2$ ; crystallisation in the dark in an inert atm. is necessary. The intensity of the phenomenon depends on degree of dispersion, presence of impurities, temp., and  $\text{H}_2\text{O}$  content. A. A. E.

**Ionisation potentials and energies of formation of non-polar molecules.** J. SAVARD (Compt. rend., 1933, 197, 1122—1123, and J. Phys. Radium, 1933, [vii], 4, 650—664).—The relation  $D=2n(I_m-I_a)$  or  $2nI_m-n_aI_a$ , according as  $D$  is the energy of dissociation of the mol.  $\text{A}_2$  or  $\text{AB}_p$  (provided that in  $\text{AB}_p$  the no. of linking electrons is even and they are in one envelope), where  $2n$  is the no. of linking electrons in the mol.,  $n_a$  the no. of electrons in A,  $I_m$  the first ionisation potential of the mol., and  $I_a$  that of the atom, is deduced theoretically, and verified for  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{C}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ , and  $\text{C}_2\text{N}_2$ , and also for the energies of the single, double, and triple linkings of C. C. A. S.

**Photo-electric sensitisation of caesium.** W. KLUGE (Physikal. Z., 1933, 34, 844—846).—By means of a special photo-cell experiments were carried out with compact Cs layers down to  $-39^\circ$ , and studied at 600 m $\mu$ . Experiments in the ultra-violet were made with cells of the type  $\text{M}-\text{Cs}_2\text{O}-\text{Cs}$ , where M is the carrier metal (Ag, Cu, Ni, or Au). In all cases two short-wave max. were observed. The electronic emission from a cell of this type comes from the immediate surface (adsorbed Cs layer) in the visible and infra-red, but in the ultra-violet from the intermediate layer. A. J. M.

**External photo-electric effect at low temperatures.** R. SUHRMANN (Physikal. Z., 1933, 34, 877).—The sensitivity curve at low temp. deviates considerably from expectation based on the classical theory, and agrees with the theory of Sommerfeld. A. J. M.

**Power loss phenomena in liquid dielectrics.** W. JACKSON (Proc. Roy. Soc., 1933, A, 142, 606—620).—A series of dielectric loss measurements have been made on samples of  $\text{C}_6\text{H}_6$ , PhMe, PhCl, and  $\text{PhNO}_2$ , for frequencies of  $2 \times 10^5$  to  $2 \times 10^6$  cycles per sec., before and after the application of d.c. voltage. The dielectric loss over this frequency range can be accounted for in terms of ionic conduction. On the application of steady voltage an "electrical cleaning" process occurs which affects the magnitude of this loss. A theory is proposed to explain the phenomena observed. L. L. B.

**Influence of surface charge on conductivity measurements for poor conductors.** F. SEIDL

(Z. Physik, 1933, 86, 274).—Former results (A., 1932, 899) agree with those of Goldhammer (cf. A., 1933, 888). A. B. D. C.

**Diffusion and electrolytic conduction in crystals. (Ionic semi-conductors.)** W. JOST (J. Chem. Physics, 1933, 1, 466—475; cf. A., 1933, 353).—Theoretical. Calculations based on the assumption that atoms or ions are displaced to metastable positions in the interlattice space agree in order of magnitude with observed data regarding the influence of polarisation and the energy of activation. F. L. U.

**Dielectric constant and ionisation potential of gases.** A. GÜNTHER-SCHULZE (Z. Physik, 1933, 86, 249—252).—A logarithmic relation between ionisation potential and dielectric const. is shown to hold with great accuracy for inert gases, and mol. gases lie irregularly about this relation. A. B. D. C.

**Dependence of the dielectric constants of gases on temperature and density.** H. H. UHLIG, J. G. KIRKWOOD, and F. G. KEYES (J. Chem. Physics, 1933, 1, 155—159).—Data for the dielectric consts. of  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{NH}_3$  over a wide range of temp. and density are tabulated. Molar polarisation, plotted as a function of the density, increases slowly for  $\text{CO}_2$  and  $\text{NH}_3$ , but is quite independent for the others. For  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2$ , and  $\text{N}_2$  it is independent of the temp., indicating that these mols. have no permanent dipoles; for  $\text{NH}_3$  it varies widely. The calc. dipole moment of  $\text{NH}_3$  is  $1.48 \times 10^{-18}$  e.s.u. N. M. B.

**Dielectric constant of  $\text{H}^2\text{H}_2\text{O}$ .** G. N. LEWIS, A. R. OLSON, and W. MARONEY (J. Amer. Chem. Soc., 1933, 55, 4731).—The ratio of the dielectric const. of  $\text{H}^2\text{H}_2\text{O}$  to that of  $\text{H}^1\text{H}_2\text{O}$  at  $25^\circ$  is 0.990. The divergence increases with falling temp. E. S. H.

**Dielectric constant of liquid sulphur.** H. J. CURTIS (J. Chem. Physics, 1933, 1, 160—165).—The dielectric const. and power factor were measured for the temp. range  $118$ — $350^\circ$ ; the former at  $118^\circ$  was  $3.520 \pm 0.010$ . Polarisation curves show that liquid S is non-polar, whereas absorption bands in the infra-red spectrum indicate polar mols. No explanation is available. N. M. B.

**Dielectric constants of substances containing water.** J. TAUSZ and H. RUMM (Kolloid-Beih., 1933, 39, 58—104).—The dielectric consts.,  $\epsilon$ , of several powders and fibrous materials (including sugar, starch, silicic acid, borax, and tobacco) have been determined by an isodielectric method, and the influence of temp., frequency, structure, and  $\text{H}_2\text{O}$  content has been examined. The vals. obtained for dry sugar and starch (3.71 and 4.01, respectively) are  $<$  those in the literature. The presence of  $\text{H}_2\text{O}$  increases  $\epsilon$ , whilst the variation of  $\epsilon$  with temp. shows in some cases that the  $\text{H}_2\text{O}$  is in two different states; a portion of the  $\text{H}_2\text{O}$  (bound) has little influence, whilst the remainder (free) renders  $\epsilon$  sensitive to temp. In starch at  $0^\circ$  most of the  $\text{H}_2\text{O}$  appears to be bound, whilst in  $\text{SiO}_2$  gel a considerable proportion is free. The proportion of free to bound  $\text{H}_2\text{O}$  varies with temp. and with the structure. E. S. H.

**Electric moment as a measure of the ionic nature of covalent linkings.** J. G. MALONE (J. Chem. Physics, 1933, 1, 197—199).—The two-electron



linking with H has the following vals. for the electric moment ( $\mu \times 10^{18}$ ): H-As 0.10; H-P 0.36; H-I 0.38; H-S 0.63; H-Br 0.78; H-Cl 1.03; H-N 1.04; H-O 1.32. These vals. give the position of the elements on an electronegativity scale (Pauling, A., 1932, 1191). The moments of  $\text{SbCl}_3$  ( $3.1 \times 10^{-18}$ ) and of  $\text{SbBr}_3$  ( $2.4 \times 10^{-18}$ ) and of other inorg. halides give vals in agreement with those calc. from the scale. It is predicted that all the trihalides of elements of group V should give appreciable moments, except  $\text{PI}_3$  and  $\text{NCl}_3$ , which should have zero moment. A. J. M.

**Dipole moments of mercaptans and sulphides.** W. S. WALLS and C. P. SMYTH (J. Chem. Physics, 1933, 1, 337—340).—Measurements are reported for thi-anthrene,  $\text{Et}_2\text{S}$ , *n*-amyl sulphide,  $\text{Bu}^n\text{SH}$ , and *n*-amyl mercaptan in  $\text{C}_6\text{H}_6$  at 25° and 50°. The polarisation of the sulphides is dependent on concn., as with the mercaptans. D. R. D.

**Induction between linking moments in some halogenated methanes.** C. P. SMYTH and K. B. McALPINE (J. Chem. Physics, 1933, 1, 190—196).—The dielectric consts. of vapours of  $\text{CHCl}_2\text{F}$ ,  $\text{CHClF}_2$ ,  $\text{CCl}_3\text{F}$ , and  $\text{CCl}_2\text{F}_2$  were measured. To explain the results it is necessary to consider the effects of induction and widening of valency angles by repulsion. Knowing the induction effect, the dipole moments of  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  can be calc.; they agree with experiment. The val. of a linking moment is treated as a function of its environment. Whilst it seems probable that there is a widening of valency angle due to repulsion in all the unsymmetrically substituted methanes, induction is much more important than this in deciding the moments of the  $\text{CH}_4$  derivatives considered. A. J. M.

**Dipole moments and structures of certain long-chain molecules.** C. P. SMYTH and W. S. WALLS (J. Chem. Physics, 1933, 1, 200—204).—The dipole moments of isoprene,  $\text{Br}[\text{CH}_2]_6\text{Br}$ ,  $\text{Br}[\text{CH}_2]_9\text{Br}$ , and  $\text{Br}[\text{CH}_2]_3\text{Br}$ , have been determined. That of isoprene is almost zero, and can therefore play no part in causing this substance to polymerise. Comparison of the vals. obtained with those for other long-chain dibromides shows that the moment of  $\text{Br}[\text{CH}_2]_3\text{Br}$  may be increased by a van der Waals attractive force between the two Br atoms. This effect is not important with other long-chain dibromides, since the force varies inversely as the sixth power of the distance. The moments do not enable a decision to be made between an extended zig-zag C chain and one in which there is free rotation about the C-C linking. A combination of both fits the results, the chain being generally of zig-zag form, but often bent by rotation about certain links in the chain. A. J. M.

**Rotation of polar groups in organic compounds.** J. M. STURTEVANT (J. Amer. Chem. Soc., 1933, 55, 4478—4485).—Theoretical. Quantum methods and classical theory give approx. the same results in certain cases of strong dipole interaction between polar groups capable of rotation about a single linking in org. mols. E. S. H.

**Relation between dipole moment and cohesive forces.** IV. A. E. VAN ARKEL (Rec. trav. chim.,

1933, 52, 1013—1027).—A discussion, with special reference to *cis-trans* isomerism. H. F. G.

**Orientation of non-polar molecules by dipoles.** J. WEIGLE (Helv. phys. Acta, 1933, 6, 68—81; Chem. Zentr., 1933, ii, 508—509).—The effect of the electric field of a dipole on non-polar solvent mols. is calc. If the non-polar mols. are anisotropic they are oriented by the dipole and produce an electric moment which increases that of the dipole. The induced moment is about 1% of that of the original dipole. If the polar mol. is not spherical, polarisation of the neighbouring mols. produces a considerable opposing moment. A. A. E.

**Atomic polarisation.** C. P. SMYTH (J. Chem. Physics, 1933, 1, 247—250).—New vals. of at. polarisation have been calc. from the temp. variations of the dielectric consts. in the vapour state. The vals. are small, but not so small as determined from infra-red intensity data, and the absence of negative vals. indicates that they should not be attributed to experimental errors. The large vals. previously reported for several alkyl halides are probably incorrect, except in the case of complex mols., where dipole orientation may occur within the mol. as indicated by the dielectric const. of the substance in the solid state. M. S. B.

**Relation between apparent at. vol. and the co-ordination centres of insoluble complex compounds.** G. GUTZEIT (Arch. Sci. phys. nat., 1933, [v], 15, 409—417).—If the radius of the atoms is plotted against at. no., only metals lying below a line joining Be, Mg, Ca, Sr, Ba, and Ra form insol. co-ordination compounds, and of these metals, those lying above a line joining Be, Sc, Zr, and Hf form co-ordination compounds with O (in  $\text{:CO}$ ,  $\text{-CHO}$ , etc.) but not with N in  $\text{NH}_3$  and its derivatives. The interpretation of these facts is discussed. H. F. G.

**Calculation of the refractive indices of sodium hydrogen carbonate from the atomic arrangement.** W. H. ZACHARIASEN (J. Chem. Physics, 1933, 1, 640—642).—Vals. calc. from the author's X-ray data (this vol., 16) agree with observed figures to within 0.02. D. R. D.

**Refractive indices of ethylene chloride, *s*-tetrachloroethane, and of their mixture and the molar refractions of these substances.** S. HAMAI (Bull. Chem. Soc. Japan, 1933, 8, 297—308).—*n* shows linear dependence on reciprocal of abs. temp. in every case. Mol. refractions are 20.82 and 31.23, respectively. The dipole moment of  $\text{C}_2\text{H}_4\text{Cl}_2$  is calc. as  $1.375 \times 10^{-18}$  e.s.u. R. S.

**Analysis of rotatory dispersion curves of configurationally related fatty acids.** P. A. LEVENE, A. ROTHEN, and R. E. MARKER (J. Chem. Physics, 1933, 1, 662—676).—Rotatory dispersion curves are given in the visible and ultra-violet for twelve acids and Et esters, and limited rotation measurements on ten other acids, all of the type  $\text{CH}_3\text{-CHR-}[\text{CH}_2]_x\text{-CO}_2\text{H}$  either pure or in *n*- $\text{C}_6\text{H}_{14}$ . Increase of *x* does not alter the direction of the contribution due to R, but reverses that due to the  $\text{CO}_2\text{H}$  between  $x=0$  and  $x=1$ . Change of R between Et and  $\text{C}_{10}\text{H}_{21}$  causes no change in sign of contributions. D. R. D.



**Rotatory power of very dilute solutions.** I. PEYCHÈS (J. Phys. Radium, 1933, [vii], 4, 594—608).—A method for the polarimetric measurement of  $\alpha$  of solutions of the order  $10^{-3}$  mol. per litre is applied to the alkali tartrates.  $\alpha$  of Ru, Cs, and K tartrates increases linearly with concn., but the curves for Na and Li show a max. In all cases the curves converge near the origin, indicating the individuality of the tartrate ion of  $[\alpha] + 45.7^\circ$ . It is concluded that the variation of  $\alpha$  is a linear function of the ionic potential.

N. M. B.

**Influence of neutral salts on rotatory power of *d*- $\alpha$ -phenylethylamine hydrochloride.** YEU-KI-HENG (Compt. rend., 1933, 197, 1316—1318).— $[\alpha]$  of *d*- $\alpha$ -CHPhMe $\cdot$ NH $_2$  $\cdot$ HCl increases rapidly with concn.; it is further increased by addition of a neutral salt. With the same anion the effect depends solely on the concn. of the anion; for different anions it depends on the charge, mass, and composition, large for phthalate or ferrocyanide, smaller for citrate, and still smaller for halides in the order I $^-$ , Br $^-$ , Cl $^-$ , F $^-$ ; that of LiI is abnormally large (cf. A., 1928, 1320).

C. A. S.

**Photo-electric measurement of magnetic rotatory dispersion in the ultra-violet.** G. BRUHAT and A. GUNIER (Compt. rend., 1933, 197, 1028—1030; cf. A., 1933, 448).—The magnetic rotatory dispersion,  $m = \rho_2/\rho_{4358}$ , has been determined for H $_2$ O for 11 vals. of  $\lambda$  (5893—2482 Å.) (cf. A., 1916, ii, 280; 1927, 295), and for heptane, heptene, and heptinene for 8 vals. (5893—2804 Å.). Verdet's consts. and the mol. rotatory powers of the hydrocarbons in the liquid and gaseous states are, for the yellow Hg line, respectively, 1.28, 1.47, and  $1.56 \times 10^{-2}$ ; 1.87, 2.07, and 2.03; and 1.52, 1.66, and 1.62, giving rotations of 27 and  $35 \times 10^{-2}$  for the double and triple linkings, respectively (cf. A., 1933, 1001).

C. A. S.

**Magnetic rotatory dispersion and absorption of the cerous ion in solution.** R. W. ROBERTS, L. A. WALLACE, and I. T. PIERCE (Nature, 1933, 132, 782).—Previous results are confirmed for higher concns. of Ce $_2$ (SO $_4$ ) $_3$ . The rotation of Ce $^{+++}$  throughout the range 5780—3341 Å. is controlled by the two absorption bands 2960 and 2540 Å. The calc. strengths ( $f$  vals.) for certain transitions agree with estimates made directly from absorption data for dil. solutions of Ce $_2$ (SO $_4$ ) $_3$ .

L. S. T.

**Comparison of quantum theoretical formulæ and experimental results for electrical double refraction.** T. NEUGEBAUER (Z. Physik, 1933, 86, 392—410).—Quantum theory gives an interpretation of the Kerr effect for symmetrical mols. where the Kerr const. is not related to degree of depolarisation. This theory also gives an estimate of the internal crystal field in solids.

A. B. D. C.

**Influence of substituents in bases and anions on the co-ordination number of a metal.** A. ABLOV (Ann. Sci. Univ. Jassy, 1933, 18, 297—317).—Co-ordination compounds of Cu salts of various acids with NH $_3$ , C $_5$ H $_5$ N,  $\beta$ -picoline, and C $_2$ H $_4$ (NH $_2$ ) $_2$  (en) have been studied. There is a parallelism between the strength of the acid and the no. of mols. co-ordinated, but the base itself also has influence

on the co-ordination no. The following compounds are described: (NHPh $\cdot$ SO $_3$ ) $_2$ [Cu(C $_5$ H $_5$ N)]; (C $_6$ H $_5$ Br $_2$  $\cdot$ NH $\cdot$ SO $_3$ ) $_2$ [Cu(C $_5$ H $_5$ N) $_4$ ]; (C $_6$ H $_5$ Br $_2$  $\cdot$ NH $\cdot$ SO $_3$ ) $_2$ [Cu(NH $_3$ ) $_4$ ] $\cdot$ H $_2$ O; (OAc) $_2$ [Cu(NH $_3$ ) $_2$  $\cdot$ 2 $\frac{1}{2}$ H $_2$ O]; (CH $_2$ Cl $\cdot$ CO $_2$ ) $_2$ [Cu(NH $_3$ ) $_4$ ] $\cdot$ H $_2$ O; (CH $_2$ Cl $\cdot$ CO $_2$ ) $_2$ [Cu en] $_2$  $\cdot$ 2H $_2$ O; (CN $\cdot$ CH $_2$  $\cdot$ CO $_2$ ) $_2$ [Cu(C $_5$ H $_5$ N) $_2$ ] $\cdot$ 2H $_2$ O; [N(CH $_2$  $\cdot$ CO $_2$ ) $_3$ ] $_2$ Cu $_3$  $\cdot$ 6H $_2$ O; [Cu(C $_6$ H $_7$ N) $_4$ ] $\cdot$ Cl $_2$ .

H. S. P.

**Theory of water and ionic solution, with particular reference to hydrogen and hydroxyl ions.** J. D. BERNAL and R. H. FOWLER (J. Chem. Physics, 1933, 1, 515—548).—Theoretical. Three arrangements of H $_2$ O mols. in liquid water are postulated: an ice-tridymite form below  $4^\circ$ ; a quartz-like form ( $4$ — $200^\circ$ ); an NH $_3$ -like close-packed form ( $200$ — $340^\circ$ ). These forms pass continuously into each other. The theory accounts for the observed crystal structure of ice, the X-ray diffraction curve of water, the total energy of water and ice, the degree of hydration of + and — ions in water, and the heats of dissolution of ions. The abnormally high mobilities of H $^+$  and OH $^-$  are due to transfer of H $^+$  from (OH $_3$ ) $^+$  to OH $_2$  and to transfer of H $^+$  from OH $_2$  to OH $^-$ , respectively. Density changes and dielectric properties of water, and the viscosities of dil. ionic solutions and conc. acids are explained qualitatively. The mobility of (H $^+$ ) is about five times that of (H $_2$ ) in aq. solutions.

H. J. E.

**Theory of structure of CH $_4$  and related molecules.** I. J. H. VAN VLECK (J. Chem. Physics, 1933, 1, 177—182).—The Slater-Pauling and Hund-Mulliken theories of the structure of the CH $_4$  mol., based on localised linkings (electron pairs), are compared with the Heitler-London theory. Both the former, whilst of equal importance, are useful only quantitatively when higher approximations are made.

A. J. M.

**Theory of structure of CH $_4$  and related molecules.** II. J. H. VAN VLECK (J. Chem. Physics, 1933, 1, 219—238).—Calculations are made which show that, according to both the Hund-Mulliken and the Slater-Pauling schemes (see above), the tetrahedral model of CH $_4$  is the most stable. Also in compounds CH $_2$ X $_2$ , CHX $_3$ , and CH $_3$ X the most stable models are tetrahedra of less symmetry than the regular tetrahedron unless the C-H and C-X linkings are of equal intensity. The predicted deviations of the valency angles from  $109.5^\circ$  agree with X-ray diffraction data for CH $_2$ Cl $_2$  and CHCl $_3$ . With  $s$ - $p$  hybridisation and electron pairing two linking axes do not necessarily set themselves at  $109.5^\circ$ . The angle can be anything between  $90^\circ$  and  $180^\circ$ , depending on the relative intensities of the  $s$  and  $p$  linkings. If the  $s$  linking power is not negligible, the angle between an NH axis and the pyramidal axis in NH $_3$  should be somewhat  $> 54.7^\circ$ , the val. when the 3 NH axes are orthogonal, characteristic of pure  $p$  linking. This is in general agreement with experimental data. CH $_4$  $^+$  should be a flattened rather than a regular tetrahedron, or might even be a plane. CH $_3$  should also be a flatter pyramid than NH $_3$ .

M. S. B.



**Allotropy of liquid nitrobenzene.** E. L. LIND and T. F. YOUNG (J. Chem. Physics, 1933, 1, 266—269).—No discontinuities indicating allotropy were found in the density and surface tension curves for  $\text{PhNO}_2$ , whether intensively dried or otherwise, between 6° and 20°. No evidence of delayed transition was observed even on keeping the cooled samples at 6° for 24 hr. M. S. B.

**Occurrence of univalency among the elements.** H. SCHMID (Angew. Chem., 1933, 46, 691—695).—A lecture. H. F. G.

**Theory of multiple linkings.** A. BURAWOY (Z. physikal. Chem., 1933, 166, 393—400; cf. A., 1933, 590).—The proportion of biradical mols. in various org. compounds containing multiple linkings has been calc. from the intensity and width of the  $R$  bands. The difference in energy content between the biradical mol. and the "saturated" mol. represented by the usual formula, which is the energy of rupture of the second or third linking of the multiple linking, is 2.5—9.0 kg.-cal. This small val. accounts for the high reactivity of unsaturated compounds. R. C.

**Electronic structures of polyatomic molecules and valency.** V. MOLECULES  $\text{RX}_n$ . R. S. MULLIKEN (J. Chem. Physics, 1933, 1, 492—503; cf. A., 1933, 339).—The approx. construction, for shared electrons in mols.  $\text{RX}_n$ , of mol. orbitals as linear combinations of at. orbitals is discussed and illustrated by equations for  $\text{RX}_2$ ,  $\text{RX}_3$ , and  $\text{RX}_4$  types. F. L. U.

**Absolute magnetic susceptibility of water and its variation with temperature.** H. AUER (Ann. Physik, 1933, [v], 18, 593—612).—The susceptibility of  $\text{H}_2\text{O}$  as measured by an improved method, which is described in detail, is  $0.72183 \times 10^{-6} \pm 0.067\%$  at 20°, and its temp. coeff.  $(d\chi_i/dt)/\chi_i$  changes from  $2.9 \times 10^{-4}$  at 5° to  $0.62 \times 10^{-4}$  at 70°. J. W. S.

**Magnetic susceptibility of  $\text{MnO}$  as a function of temperature.** R. W. TYLER (Physical Rev., 1933, [ii], 44, 776—777; cf. Li. A., 1932, 900).—The susceptibility-temp. curve for the range 26° to -202° showed a sharp discontinuity at -156°, corresponding with that in the sp. heat-temp. curve, and another at -188°. Mass susceptibility data are given. N. M. B.

**Magnetic permeability of ferromagnetic metals at very high frequency.** G. POTAPENKO and R. SÄNGER (Naturwiss., 1933, 21, 818—819).—A modification of the usual parallel-wire method for determining the permeability of ferromagnetic metals with short waves, requiring only a small quantity of the metal, is described. The permeability of Fe calc. from ohmic resistance agrees with that of Arkadiev (Ann. Physik, 1919, 58, 105), and from self-induction with that of Hoag and Jones (A., 1933, 117). Both vals. decrease with increasing frequency. Similar results are obtained for Ni. Co has a very small permeability,  $< 5$  for waves of  $\lambda$  120 cm. A. J. M.

**Effect of magnetic field on the energy transfer in paramagnetic gases.** H. SENTLEBEN and J. PIETZNER (Physikal. Z., 1933, 34, 834—835).—To investigate further the effect of a magnetic field on the heat-conductivity of a paramagnetic gas (A., 1931, 31;

1933, 559), experiments were carried out to discover whether the effect is bound up with each single mol. of  $\text{O}_2$ , or whether the conjunction of two mols. by collision is necessary. The variation of the effect by the addition of diamagnetic gases to  $\text{O}_2$  was studied. The  $\text{O}_2$ -He curve is similar to that for pure  $\text{O}_2$ , but the effect is greatly weakened and is not necessarily bound up with the collision of  $\text{O}_2$  mols. The field exerts an influence on the energy transfer between  $\text{O}_2$  and the mols. of the foreign gas. A. J. M.

**Magnetic susceptibility of ions.** K. KIDO (Sci. Rep. Tôhoku, 1933, 22, 835—867; cf. A., 1932, 1077; 1933, 340).—Observed susceptibilities of "inert-gas-like" ions diverge markedly from calc. vals. (cf. A., 1932, 795) and the corresponding differences of paramagnetic susceptibility increase with the no. of valency electrons. Mol. susceptibilities of inorg. compounds are calc. from the observed vals. of the constituent ions. In general, the additive law applies to homopolar and org. compounds, but double linkings depress diamagnetic susceptibility. J. G. A. G.

**Is there a strictly reversible process in the magnetisation of ferromagnetic substances by extremely small alternating currents?** H. WITTKE (Ann. Physik, 1933, [v], 18, 679—700).—For small changes of a magnetic field of finite magnitude, the ratio of the resulting loss to the change in magnetic energy is proportional to the change in field strength, and such small changes give rise to a reversible process. For zero field strength, however, the process is irreversible. J. W. S.

**Magnetisation curve of a ferromagnetic material for very small fields.** R. GANS (Ann. Physik, 1933, [v], 18, 701—704).—Theoretical. J. W. S.

**Thermodynamic relationships.** I. I. PLĂCINTEANU (Ann. Sci. Univ. Jassy, 1933, 18, 10—12).—Formulae are deduced for the influence of temp. on surface tension and for the velocity of propagation of sound in fluids. H. S. P.

**Exchange of energy between polyatomic molecules and a metallic surface.** F. R. WHALEY (J. Chem. Physics, 1933, 1, 186—189; cf. Rice and Byke, A., 1931, 1001).—It has been shown that when fairly complicated mols. ( $\text{CHCl}_3$ ,  $\text{COMe}_2$ ,  $\text{MeOH}$ ,  $\text{CCl}_4$ ,  $\text{EtOAc}$ ) strike a hot surface (Pt) the efficiency of energy transfer from the solid surface to the vibrational degrees of freedom of the impinging mol. is in any case low, and possibly zero. The impinging mols. appear to behave as regards energy transfer like hypothetical gases with six degrees of freedom, translational and rotational. A. J. M.

**Virial and molecular structure.** J. C. SLATER (J. Chem. Physics, 1933, 1, 687—691).—When the total internal energy of a mol. is known, the virial theorem may be used to find the kinetic and potential energies for all configurations of the nuclei. These data may be applied to give an explanation of the formation of a covalent linking. H. S. P.

**Binding forces in alkali and alkaline-earth metals according to the free electron theory.** O. K. RICE (J. Chem. Physics, 1933, 1, 649—655).—The conception of intrinsic ionic vol. is introduced into the free electron theory. Energies of sublimation



calc. from at. vol. data agree well with experiment for alkali metals, but less well for alkaline earths. An extended relationship gives compressibilities in poor agreement with experiment, but the difference is attributed to magnification of small errors rather than to weakness of the theory. D. R. D.

**Dispersion and polarisability and the van der Waals potential in the alkali halides.** J. E. MAYER (J. Chem. Physics, 1933, 1, 270—279).—The ultra-violet absorption of NaCl, KCl, and KI is in agreement with the dispersion of these salts and can be used to calculate the dipole-dipole potential const. for the van der Waals attraction between negative ions. The same const. can also be estimated for the other alkali halides as well as the quadrupole-dipole const. A much greater val. is thus found for the van der Waals potential than previously, and this accounts for the stability of the CsCl type of lattice. The assumption that the polarisability of a given ion varies inversely as the "main frequency" of the crystal is shown to be in approx. agreement with experiment. M. S. B.

**Lattice energies of silver and thallium halides.** J. E. MAYER (J. Chem. Physics, 1933, 1, 327—334).—Theoretical lattice energies calc. from electrostatic considerations agree with experiment, supporting the view that the linking is entirely ionic. Discrepancies with AgI are ascribed to homopolar linking. D. R. D.

**Lattice energies of cuprous halides.** J. E. MAYER and R. B. LEVY (J. Chem. Physics, 1933, 1, 647—648; cf. preceding abstract).—Comparison of theoretical and experimental lattice energies leads to the conclusion that the linking is not entirely ionic, particularly for CuI. D. R. D.

**Nature of the chemical linking. V. Quantum-mechanical calculation of the resonant energy of benzene and naphthalene and the hydrocarbon free radicals.** L. PAULING and G. W. WHELAND (J. Chem. Physics, 1933, 1, 362—374; cf. A., 1932, 561, 1191).—It is concluded that the principal contributions to the structure of  $C_6H_6$  are made by the two Kekulé forms, resonance between them stabilising the mol. to the extent of about 1.35 v.e. over a ring with three double linkings. The excited structures also contribute appreciably both to the energy and to the eigenfunction. The structure of  $C_{10}H_8$  is similar. Dissociation of certain substituted ethanes into free radicals is attributed to the stabilisation of the free radicals resulting from resonance among structures in which the unpaired electron is located on the Me C atom and those in which it is on other atoms. The calc. tendencies towards dissociation are in agreement with experiment, the fact that dissociating power of  $\beta$ - $C_{10}H_7$  is < that of  $\alpha$ - $C_{10}H_7$  and that of  $\cdot C_6H_4 \cdot C_6H_4 \cdot$  < that of  $Ph_2$  being explained. J. W. S.

**Nature of the chemical linking. VI. Calculation from thermochemical data of the energy of resonance of molecules among several electronic structures.** L. PAULING and J. SHERMAN (J. Chem. Physics, 1933, 1, 606—617).—When the normal state of a mol. is represented by only one electronic structure, the total energy of formation of

the mol. equals the sum of the linking energies. If these two energies are unequal, the difference is interpreted as the resonance energy of the mol. among several electronic structures. Data for various aliphatic, aromatic, and heterocyclic mols. are used to calculate the resonance energy. H. J. E.

**Nature of the chemical linking. VII. Calculation of resonance energy in conjugated systems.** L. PAULING and J. SHERMAN (J. Chem. Physics, 1933, 1, 679—686).—The extra resonance energy of conjugation is calc. for dihydronaphthalenes and -anthracenes,  $C_2H_3Ph$ , stilbene, isostilbene,  $C_2HPh_3$ ,  $C_6Ph_4$ ,  $Ph_2$ , *o*-, *m*-, and *p*- $C_6H_4Ph_2$ , and  $C_6H_3Ph_3$ . The calc. vals. agree approx. with the empirical vals. from thermochemical data and enable rules to be deduced for the relative energy of conjugation in various cases. H. S. P.

**Vibration in three-particle systems with special applications to the ethyl halides and ethyl alcohol.** P. C. CROSS and J. H. VAN VLECK (J. Chem. Physics, 1933, 1, 350—356).—The vibrational potential of polyat. mols. is discussed in the light of the theory of directed valency, and the results are applied to the Et halides and EtOH by considering the  $CH_3$ ,  $CH_2$ , and OH groups as dynamic units. Calc. force consts. give approx. the experimental frequencies. J. W. S.

**Statistical theory of low-frequency intermolecular forces.** J. G. KIRKWOOD (J. Chem. Physics, 1933, 1, 597—605).—Mathematical. H. J. E.

**Activation energies for reactions of atoms in different states.** G. K. ROLLEFSON and J. C. POTTS (J. Chem. Physics, 1933, 1, 400—401).—Calculations of activation energy, by a modification of Eyring's method, indicate that normal Cl atoms are much more reactive with respect to ICl than are Cl atoms excited to the  $^2P_{1/2}$  state, in agreement with experiment (A., 1930, 1135; 1931, 578). J. W. S.

**Deflexion of molecular rays in an electric field: electric moment of hydrogen chloride.** I. ESTERMANN and R. G. J. FRASER (J. Chem. Physics, 1933, 1, 390—399).—The mol.-beam method has advantages over the dielectric-const. method for determination of dipole moments in that low gaseous pressures only are required, it is independent of solubility of the compounds in non-polar solvents, and it can detect the effects of relative motions, and especially of the higher rotational states of non-gyroscopic mols. on the moment. Also deviation of the dipolar axis by other than  $90^\circ$  from the axis of rotation is readily detectable, and provides a possible means of deciding between alternative mol. configurations. The application to the detection of temp. variation of the dipole moment is also suggested. An improved apparatus is described, and results for HCl are given, the moment being calc. as  $1.95 \times 10^{-18}$  e.s.u. J. W. S.

**Densities and parachors of vinyl acetate and its liquid polymerides.** C. GREEN, J. MARSDEN, and A. C. CUTHBERTSON (Canad. J. Res., 1933, 9, 396—401).—Densities of monomeric vinyl acetate have been measured from  $9^\circ$  to  $31^\circ$ . The parachor and Ramsay and Shields const. have been determined for the monomeride (I) and some liquid



polymerides (II). Assuming that the (II) are a solution of a dimeride in (I) and using Staudinger's formula to calculate the parachor of the dimeride, the parachors of (II) are calc. from the mixture law and agree with the experimental vals. H. S. P.

**Hydrodynamic equations with capillary terms; theory of surface tension.** Y. ROCARD (J. Phys. Radium, 1933, [vii], 4, 533—548).—Mathematical. Pressures and tensions due to non-uniform density distribution in a fluid in motion or in equilibrium are considered. From the results obtained the Kelvin isotherm theorem, the Ramsay-Shields relation, and the law of corresponding states are deduced.

N. M. B.

**Inherent limitation of Soller multiple slits.** T. N. WHITE (Rev. Sci. Instr., 1933, [iii], 4, 590—592).—The characteristic X-rays reflected from a crystal may, at certain deviations from the Bragg angle, be partly obstructed by the separating strips of the multiple slits, resulting in min. which give to a single line the appearance of a multiplet.

N. M. B.

**Effect of absorption by the crystal on interference phenomena with X-rays according to the dynamic theory.** M. KOHLER (Physikal. Z., 1933, 34, 839).—Theoretical.

A. J. M.

**Lattice constants.** M. C. NEUBURGER (Z. Krist., 1933, 86, 395—422; cf. A., 1931, 1217).

C. A. S.

**Second principle of crystal chemistry.** A. KAPUSTINSKI (Z. Krist., 1933, 86, 359—369; cf. A., 1933, 1001).—The validity of the equation  $U = 256\eta_1\eta_2\Sigma n/(r_K+r_A)$  is demonstrated by plotting  $U/\eta_1\eta_2\Sigma n$  against  $1/(r_K+r_A)$  for many compounds, deviations occurring only with  $\text{Ag}^I$ ,  $\text{Cu}^I$ , and  $\text{Ti}^I$ . Accordingly, as the second principle of crystal chemistry, it is enunciated that the lattice energy of a crystal,  $U$ , and the properties depending thereon are determined by the no. ( $\Sigma n$ ), dimensions ( $r_K$ ,  $r_A$ ), valencies ( $\eta_1$ ,  $\eta_2$ ), and in some cases also the polarisation properties of the constituent ions (or atoms). The above equation is applied to the energetics of a morphotropic series, the calculation of the ionic radius of  $\text{Sn}^{II}$  ( $1.04 \pm 0.02$ ), and heats of reaction, formation, and dissolution (cf. A., 1927, 611).

C. A. S.

**Regularities in the transformation of metals in the solid state.** U. DEHLINGER (Metallwirt., 1933, 12, 207—210; Chem. Zentr., 1933, ii, 493—494).—The transformations (tempering, hardening, and recrystallisation) are discussed in relation to lattice changes.

A. A. E.

**Investigations of amorphous metal layers.** H. ZAHN and J. KRAMER (Z. Physik, 1933, 86, 413—420).—Electrolytically deposited Sb and Pt are transformed into the cryst. state at a definite temp., which is independent of the method of formation of the amorphous layer.

A. B. D. C.

**Submicroscopic distinctions between metals after casting and after recrystallisation.** U. DEHLINGER (Physikal. Z., 1933, 34, 836—838).—Experiments were carried out with 99.8% Al to ascertain if there is any difference in nuclear size between the cast and recryst. metal. It is shown that there is some difference in texture.

A. J. M.

**Molecular structure of ice and liquid water.** E. L. KINSEY and O. L. SPONSLER (Proc. Physical Soc., 1933, 45, 768—779).—The structure proposed regards ice as a lattice of  $\text{H}^+$  cations and complex double pyramidal  $\text{H}_3\text{O}_2^-$  anions, which form neutral chains parallel to the  $c$  axis. At the m.p. rearrangement occurs, producing large nos. of  $\text{H}_2\text{O}$  mols., in temp. equilibrium with the  $\text{H}_4\text{O}_2$  mols., which are prevented from dissociating into  $\text{H}^+$  and  $\text{H}_3\text{O}_2^-$  by the large polarising fields present in the liquid state. The theory permits a qual. explanation of many abnormal properties of water and ice.

J. W. S.

**Lattice constant of carborundum.** G. BORRMANN and H. SEYFARTH (Z. Krist., 1933, 86, 472—473; cf. A., 1926, 562).—Modification II of SiC has a  $3.076$ ,  $c$   $15.07$  Å.

C. A. S.

**X-Ray structure of silver amalgam.** A. WERYHA (Z. Krist., 1933, 86, 335—339).— $\text{Ag}_3\text{Hg}_4$  prepared by Reinders' method (cf. A., 1906, ii, 219) or by long immersion of Ag wire in Hg is cubic,  $a$   $10.09$  Å., with 4 mols. in unit cell, space-group  $O_h^2$ ; the point groups of the 12 Ag and 16 Hg atoms are respectively  $V_4$  and  $C_{3v}$ , the former with no parameter, the latter with  $u=0.192$ .

C. A. S.

**X-Ray investigation of  $\text{MgZn}$  and  $\text{MgZn}_5$ .** L. TARSCHISCH (Z. Krist., 1933, 86, 423—438).—The existence of  $\text{MgZn}$  (cf. A., 1929, 873) is established; it has  $d$   $4.24$ ,  $a$   $5.33$ ,  $c$   $8.58$  Å., with 6 mols. in the unit cell; the structure closely resembles that of  $\text{MgZn}_2$ , which is hexagonal with 4 mols. in the unit cell (cf. A., 1927, 190), Mg atoms replacing  $\text{Zn}_2$  in each cell.  $\text{MgZn}_5$ ,  $d$   $6.60$ , has  $a$   $9.92$ ,  $c$   $16.48$  Å., with 16 mols. in the unit cell, space-group  $D_6^2$ .

C. A. S.

**Interatomic distances in crystals of the alkali halides.** M. L. HUGGINS and J. E. MAYER (J. Chem. Physics, 1933, 1, 643—646).—Ionic radii for  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  are calc. from the lattice consts. of the alkali halides.

D. R. D.

**"Alternating" structure of cadmium bromide.** J. M. BIJVOET and W. NIEUWENKAMP (Z. Krist., 1933, 86, 466—470; cf. A., 1929, 1369).—A powder photograph of a crystal of  $\text{CdBr}_2$  from aq. solution implies a unit cell with  $a$   $2.30$ ,  $c$   $6.23$  Å., and containing  $1/3$  mol.; a structure in which layers of  $\text{CdCl}_2$  and  $\text{CdI}_2$  types alternate, or one due to repeated twinning, is deduced. Long-continued trituration alters the structure, and heating at about  $400^\circ$  produces the  $\text{CdCl}_2$  type alone.

C. A. S.

**Crystal lattice of sodium hydrogen carbonate.** W. H. ZACHARIASEN (J. Chem. Physics, 1933, 1, 634—639).— $\text{NaHCO}_3$  forms monoclinic prismatic crystals with 4 mols. in the unit cell, with  $a$   $7.51 \pm 0.04$ ,  $b$   $9.70 \pm 0.04$ ,  $c$   $3.53 \pm 0.03$  Å.,  $\beta$   $93^\circ 19'$ , space-group  $P2_1/n$ ,  $d_{\text{calc}}$   $2.16$ , and  $d_{\text{obs}}$   $2.20$ — $2.22$ . The orientation of the constituent atoms is deduced.

D. R. D.

**Crystal structure of potassium dithionate.** M. L. HUGGINS (Z. Krist., 1933, 86, 384—388).—Two errors in the original paper (cf. J. Min. Soc. Amer., 1931, 16, 580) are corr., but the criticisms of Hägg and Helwig (cf. A., 1932, 1079; 1933, 33) are not accepted.

C. A. S.



**Potassium pentacalcium sulphate.** F. KRÜLL and O. VETTER (Z. Krist., 1933, 86, 389—395).— $\text{K}_2\text{SO}_4 \cdot 5\text{CaSO}_4 \cdot \text{H}_2\text{O}$ , "penta-salt,"  $d^{25}$  2.897, is monoclinic,  $n_a$  1.550,  $n_\beta$  1.585,  $n_\gamma - n_a$  0.033, i.e., intermediate between anhydrite and syngenite ( $n_a$  1.500,  $n_\beta$  1.517,  $n_\gamma - n_a$  0.019). It is slowly decomposed by  $\text{H}_2\text{O}$ , leaving pseudomorphous but porous gypsum (cf. A., 1904, ii, 561; 1905, ii, 319; 1917, ii, 176).  
C. A. S.

**Crystal structure of thallium silicofluoride.** M. TABET (Gazzetta, 1933, 63, 679—680).— $\text{Tl}_2\text{SiF}_6$  has a structure of the  $\text{K}_2\text{PtCl}_6$  type with  $a$  8.60,  $d_{\text{calc.}}$  5.72.  
O. J. W.

**Rhodonitrites of ammonium, potassium, rubidium, calcium, thallium, barium, and lead.** A. FERRARI and C. COLLA (Atti R. Accad. Lincei, 1933, [vi], 18, 45—52; cf. A., 1933, 666).—The following vals. of  $a$  (Å.) and  $d_{\text{calc.}}$ , respectively, have been obtained for the compounds of the general formula  $\text{M}_3[\text{Rh}(\text{NO}_2)_6]$ , where M=metal atom or  $\text{NH}_4$ :  $\text{NH}_4$ ,  $10.91 \pm 0.02$ , 2.214; K,  $10.63 \pm 0.02$ , 2.744; Rb,  $10.83 \pm 0.02$ , 3.321; Cs,  $11.30 \pm 0.02$ , 3.357; Tl,  $10.91 \pm 0.02$ , 5.073. They all have a structure of the  $\text{K}_3\text{Co}(\text{NO}_2)_6$  type.  $\text{Ba}_3[\text{Rh}(\text{NO}_2)_6]$  and  $\text{Pb}_3[\text{Rh}(\text{NO}_2)_6]$ , which are isomorphous with the above salts, are probably cubic with  $a$  10.70 and 10.53 Å., respectively. The Rb, Cs, Tl, and Pb compounds are new.  
O. J. W.

**Structure and swelling of montmorillonite.** U. HOFMANN, K. ENDELL, and D. WILM (Z. Krist., 1933, 86, 340—348).—Montmorillonite being readily hydrolysed occurs in quantity only in arid regions. Analysis:  $\text{SiO}_2$  49.0,  $\text{Al}_2\text{O}_3$  23.0,  $\text{Fe}_2\text{O}_3$  0.3,  $\text{CaO}$  1.6,  $\text{MgO}$  2.9,  $\text{H}_2\text{O}$  23%, of which all but 4 is removed over  $\text{H}_2\text{SO}_4$  or at moderate temp., leaving  $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$  (cf. A., 1909, ii, 736). The crystals are rhombic,  $a$  5.095,  $b$  8.83,  $c$  15.2 Å., and consist of alternate layers of  $\text{AlO}(\text{OH})$  and  $\text{SiO}_2$  extending in the  $a$ - $b$  plane exactly as in kaolin, from which it differs only in dimension along the  $c$  axis. The  $\text{H}_2\text{O}$  occurs between the layers, the  $c$  dimension varying with its amount, thus explaining the swelling on hydration.  
C. A. S.

**Transformation points and softening of glasses.** E. RENCKER (Compt. rend., 1933, 197, 1049—1051; cf. A., 1928, 354; 1933, 1247).—Differential dilatation-temp. curves for  $\text{B}_2\text{O}_3$ , Pollopos, Pyrex, and a glass containing 87%  $\text{SiO}_2$  + 9%  $\text{Na}_2\text{O}$  + 4%  $\text{BeO}$  show that the transformation point coincides with that of the commencement of softening.  
C. A. S.

**X-Ray investigation of tridymite glass.** M. E. NAHMIAS (Nature, 1933, 132, 857—858).—X-Ray analysis of a devitrified glass (78%  $\text{SiO}_2$ , 12%  $\text{CaO}$ , and 10%  $\text{Na}_2\text{O}$ ) gives a pattern of tridymite (I). The use of thermal expansion curves in deciding between (I) and cristobalite is untrustworthy.  
L. S. T.

**X-Ray diffraction of vitreous silica.** B. E. WARREN (Z. Krist., 1933, 86, 349—358).—In vitreous  $\text{SiO}_2$  each Si is tetrahedrally surrounded by 4 O, being 3.1 Å. from each of the four nearest, and 5.0 Å. from each of the twelve nearest Si; each O is shared by two tetrahedral groups. The orientation of such

groups of 16 Si and attendant O is random (cf. A., 1931, 550; 1933, 12). The structure of Pyrex glass is similar.  
C. A. S.

**Crystal morphology of quartz.** I. Vicinal faces of quartz and their significance as regards interpenetrating twins of the Brazil and Dauphinée laws. II. Crystal morphology of  $\alpha$ -(high-temperature) quartz. III. Morphological constants of  $\beta$ -quartz. G. KALB (Z. Krist., 1933, 86, 439—452, 453—457, 458—465).—With the exception of quartz occurring in hollows in effusive rocks all quartz crystals on which vicinal faces occur are of the  $\beta$  (low-temp.) variety. The vicinal faces are of two types: (I) an older, in which the three pyramidal faces are of approx. equal size, and (II) a younger, of recent hydrothermal formation, in which one face is markedly smaller than the others (cf. A., 1933, 140).  
C. A. S.

**X-Ray and electron diffraction of iodine and the di-iodobenzenes.** S. B. HENDRICKS, L. R. MAXWELL, V. L. MOSLEY, and M. E. JEFFERSON (J. Chem. Physics, 1933, 1, 549—565).— $p\text{-C}_6\text{H}_4\text{I}_2$  is orthorhombic bipyramidal ( $a$  17.004,  $b$  7.381,  $c$  6.210 Å.).  $m\text{-C}_6\text{H}_4\text{I}_2$  is rhombic pyramidal ( $a$  17.20,  $b$  7.08,  $c$  6.21 Å.).  $o\text{-C}_6\text{H}_4\text{I}_2$  is monoclinic prismatic ( $a$  8.29,  $b$  12.23,  $c$  7.91 Å.; 4 mols.  $\text{C}_6\text{H}_4\text{I}_2$  per unit cell in each case). From X-ray and electron diffraction measurements the I—I distances are 6.85, 5.97—5.92, and 4.00 Å., respectively. The I—I distance in I vapour is 2.64 Å. The electron diffraction results for  $o\text{-C}_6\text{H}_4\text{I}_2$  require the I—C valency directions to be bent by about  $10^\circ$  from symmetrical positions in the plane of the  $\text{C}_6$  ring.  
H. J. E.

**X-Ray studies of fatty acids.** F. B. SLAGLE and E. OTT (J. Amer. Chem. Soc., 1933, 55, 4396—4404).—Interplanar distances of the (001) planes have been determined for pure  $n$ -fatty acids containing  $\text{C}_{10}$ — $\text{C}_{19}$ . Slight variations with the method of prep. were observed, and a new modification of the  $\text{C}_{14}$  acid was found to be produced by pressing.  
E. S. H.

**X-Ray studies of mixed fatty acids.** F. B. SLAGLE and E. OTT (J. Amer. Chem. Soc., 1933, 55, 4404—4418; cf. preceding abstract).—Data are given for several two-component mixtures of the  $n$ -fatty acids  $\text{C}_{10}$ — $\text{C}_{18}$ , and for complex mixtures containing up to nine components. The existence of solid solutions was established in each case.  
E. S. H.

**Fine structure of structurally isomeric hydrocarbons didiphenyl and triphenylbenzene.** E. HERTEL and G. H. RÖMER (Z. physikal. Chem., 1933, B, 23, 226—234).—Didiphenyl has  $I_a$  8.14,  $I_b$  5.64,  $I_c$  18.4 Å.,  $\beta$   $97^\circ$ , space-group  $C_{2h}^2$ , and 2 mols. in the unit cell.  $s\text{-C}_6\text{H}_5\text{Ph}_3$  has  $I_a$  11.2,  $I_b$  19.8,  $I_c$  7.6 Å., space-group  $V_h^h$ , and 4 mols. in the unit cell.  
R. C.

**Structure of chrysene and 1:2:5:6-dibenzanthracene in the crystalline state.** J. IBALL and J. M. ROBERTSON (Nature, 1933, 132, 750—751).—Chrysene crystallises in the monoclinic system with  $a$  8.34,  $b$  6.18,  $c$  25.0 Å.,  $\beta$   $115.8^\circ$ ; space-group  $C_{2h}^2$ , or, less probably,  $C_2^2$ ; 4 mols. per unit cell. Orientation is discussed. 1:2:5:6-Dibenzanthracene has a face-centred pseudo-orthorhombic lattice, but the



system is actually monoclinic with  $a$  6.59,  $b$  7.84,  $c$  14.17 Å., and  $\beta$  103.5°; space-group  $C_{2h}^2$  or  $C_2^2$  with 2 mols. per unit cell.  
L. S. T.

**Structure of chrysene and 1:2:5:6-dibenzanthracene in the crystalline state.** J. D. BERNAL (Nature, 1933, 132, 751).—Chrysene shows the forms (001), (110), and (100) with a marked tendency to twinning on the  $c$  face. The optic axial plane is (010) with  $\gamma$  making 10° to the  $c$  axis in the obtuse angle: birefringence (I) is high and negative with a fairly large optic axial angle (II). Dibenzanthracene has a high (I), negative, with (II) 78°;  $\alpha$  lies along  $b$  and  $\gamma$  almost or quite perpendicular to (001).  
L. S. T.

**Reflexion of X-rays from anthracene crystals.** B. W. ROBINSON (Proc. Roy. Soc., 1933, A, 142, 422–447).—The abs. intensity of reflexion of X-rays from anthracene crystals for the (001) planes has been measured for the wave-lengths 1.539 and 0.709 Å. The method of measurement is described and the necessary corrections (in particular for extinction in the crystals) are investigated. The final vals. of the structure factor  $F$  for the (001) planes are 30.5 and 32.8, respectively.  
L. L. B.

**Fourier analysis of the durene structure.** J. M. ROBERTSON (Proc. Roy. Soc., 1933, A, 142, 659–674).—A double Fourier analysis has been applied to the structure factors for the three principal crystallographic zones of durene (cf. A., 1933, 1108). The deduced structure shows a regular plane hexagon  $C_6$  ring with the 4 Me groups in the plane of the ring, but slightly displaced towards the unsubstituted positions. The orientation of the mol. in the crystal is given. The C—C distance in the  $C_6$  ring is 1.41 Å.; the distance between the centre of the Me group and the adjacent C atom in the  $C_6$  ring is 1.47 Å.; the shortest distance between the Me groups in neighbouring mols. is 3.93 Å.  
L. L. B.

**Crystalline structure of naphthalene. Quantitative X-ray investigation.** J. M. ROBERTSON (Proc. Roy. Soc., 1933, A, 142, 674–688).—A double Fourier analysis of the experimental data has been carried out for the zones about the  $a$ ,  $b$ , and  $c$  crystal axes. The deduction of the orientation and structure of the mols. closely follows that given for anthracene and durene (A., 1933, 216, 558, and preceding abstract). The C rings are in the form of two regular plane hexagons, with the C—C distance 1.41 Å., and the closest distance of approach between the centres of atoms in adjacent mols. 3.60 Å. The structure differs from that of anthracene chiefly in the larger inclination of the long axis of the mol. to the (010) plane.  
L. L. B.

**Crystallographic study of sucrose. IV.** G. VAVRINECZ (Magyar Chem. Fol., 1933, 39, 40–49; Chem. Zentr., 1933, ii, 210).—The effect of 91 org. and inorg. compounds on the morphology of sucrose crystallised from 70% aq. solution at room temp. has been studied; in most cases small effects are produced.  
A. A. E.

**Transformation of cyclopentadiene into its dimeride.** E. G. V. BARRETT and L. J. BURRAGE (J. Physical Chem., 1933, 37, 1029–1035).—V.p. measurements have been made at various temp. of a

cyclopentadiene during its change from pure monomeride (I) to pure dimeride (II), and also of known mixtures of (I) and (II). Liquid crystals have been noted.  
H. S. P.

**Liquid crystals produced by evaporation or cooling of an aqueous solution of tartrazine.** P. GAUBERT (Compt. rend., 1933, 197, 1436–1438).—Evaporation of a drop of an aq. solution of tartrazine (I) at room temp. produces an outer ring of solid crystals surrounding a birefringent liquid of the unstable nematic and smectic phases (Friedel, A., 1923, ii, 223). In contact with a little  $H_2O$  (I) does not pass into the mesomorphic state.  
J. W. B.

**Electron scattering experiments on the change of semi-conducting crystal surfaces on electron bombardment.** R. SUHRMANN (Physikal. Z., 1933, 34, 878).—Rupp's method was used. Bombardment with electrons causes the disappearance of the crystal lattice for PbS. The bombarding electrons do not form a double layer at the surface. This would require only the shifting of the scattering max. The change in contact potential, and possibly also in the unidirectional effect of electron bombarded surfaces of this type, is due to strong distortion of the lattice.  
A. J. M.

**Investigation of the orientations of thin evaporated metallic films by the method of electron diffraction.** K. R. DIXIT (Phil. Mag., 1933, [vii], 16, 1049–1064).—Vac.-evaporated deposits of Ag on Mo,  $SiO_2$ , and glass, and Al or Zn on Mo, show different orientations according to the temp. (10–650°), and independently of the support. The deposits behave as a two-dimensional gas.  
H. J. E.

**Diffraction of electrons by mica.** J. A. DARBYSHIRE (Z. Krist., 1933, 86, 313–324; cf. A., 1932, 797).—Changes in the diffraction pattern of muscovite with thickness are described (cf. A., 1928, 1174; 1932, 3), and also those in the reflexion pattern with changes in angle of incidence and azimuth (cf. A., 1932, 979). The pseudo-symmetrical effects occur when the incident beam travels along the more important of the zone axes that lie in the cleavage plane.  
C. A. S.

**Electron diffraction and molecular structure.** R. W. DORRTE (J. Chem. Physics, 1933, 1, 566–571).—Data for *cis*- and *trans*- $C_2H_2Br_2$ ,  $C_2HBr_3$ , vinyl bromide,  $C_2Cl_4$ , and  $C_2HCl_3$  are recorded. The structures are planar, with interat. distances C—C 1.3, C—Br 2.0, and C—Cl 1.8 Å.  
H. J. E.

**Determination of the structures of methane derivatives by the electron diffraction method.** R. W. DORRTE (J. Chem. Physics, 1933, 1, 630–633).—In  $CM_3Br$ , the angular distribution of the 3 Me groups and the Br atom around the central C is tetrahedral; the C of the Me is at 1.55 Å. and the Br 2.06 Å. from the central C. The distance between C and halogen is 2.06 Å. in  $MeBr$  and 2.28 Å. in  $MeI$ . In  $CH_2Br_2$  and  $CH_2I_2$ , the angle between the C—halogen linkings is 125° and the interat. distances are C—Br 2.03, Br—Br 3.61, C—I 2.28, and I—I 4.06 Å. In  $CHBr_3$ , the angle between the C—Br linkings is 115° and the interat. distances are C—Br 2.05 and Br—Br 3.46 Å.  
D. R. D.



**Electron diffraction by hydrocarbons.** H. R. NELSON (Physical Rev., 1933, [ii], 44, 717—719).—Diffraction patterns for 25—50-kv. electrons reflected from thin films of vaseline, paraffin, and tap grease indicate that the films are mainly cryst. with the long axes perpendicular to the plane of the film.

N. M. B.

**Variation with temperature of the resistance of nickel wire to stretching.** S. ARZYBASCHEV and V. JUSHAKOV (Z. Physik, 1933, 86, 521—522).—The resistance was investigated between 350° and —190°; it decreased with falling temp. to —83° but at —190° showed an increase.

A. B. D. C.

**Electrical resistance and heat in metals.** C. R. UNDERHILL (J. Franklin Inst., 1933, 216, 629—634).—A method is indicated for a general equation for the temp. coeff. of the resistance of metals for all temp. up to the m.p., starting from determination of the equation of the  $R_m/T$  curve, where  $R_m$  is the mean resistance over the temp. range 0— $T$ .

A. G.

**Fluctuations of molecular field and magnetic equation of state of nickel.** L. NÉEL (Compt. rend., 1933, 197, 1310—1312; cf. following abstract).—Magnetic isotherms of Ni calc. on the assumption of a fixed no. of groups of carriers of magnetic moment give results in accord with experiment near the Curie point, but with still better accord when quantum mechanics is applied. The magnetic equation of state for Ni is consistent with the theory that the no. of magnetic electrons varies with the magnetisation (e.g., 0.83 per atom for  $\sigma=0$ , 0.61 at saturation). (Cf. A., 1932, 901.)

C. A. S.

**Susceptibility of nickel near the Curie point.** L. NÉEL (Compt. rend., 1933, 197, 1195—1197).—A quant. method is described to support the qual. agreement between the magnetisation curves based on the hypothesis of fluctuations of the mol. field and on experimental results previously demonstrated (cf. A., 1932, 901). The  $1/\chi$ - $T$  curves thus calc. for the interval 919.5—634.14° abs., during which the susceptibility varies in the ratio 1:265, agree with experiment (cf. A., 1926, 339).

C. A. S.

**Magnetic anisotropy of crystals of trans-dinitrotetramminocobaltic chloride.** L. W. STROCK (Z. physikal. Chem., 1933, B, 23, 235—238).—On crystallising out in a magnetic field crystals of 1:6-[Co(NO<sub>2</sub>)<sub>2</sub>.4NH<sub>3</sub>]Cl orient themselves with  $\beta = [100]$  parallel to the lines of force. The crystals are magnetically anisotropic and the unit cell contains 16 mols.

R. C.

**Volume magnetostriction for poly- and single crystals.** O. VON AUWERS (Physikal. Z., 1933, 34, 824—827).—Single crystals of the Fe-Ni series and polycryst. specimens of Fe-Co-Ni alloys were investigated. 15 polycryst. Fe-Co-Ni alloys were investigated, including permivar, which has smaller vol. magnetostriction than others.

A. J. M.

**Electronic conduction of cuprous oxide.** W. SCHOTTKY and F. WAIBEL (Physikal. Z., 1933, 34, 858—864).—The Hall effect was investigated for Cu<sub>2</sub>O (a) for plates of the substance containing free O<sub>2</sub>, at low temp. (—180° to 20°), and (b) for outgassed plates at 18—855°. A reversal of the sign of the

Hall potential was found between 400° and 500°, showing that there is an increase of the electron defect conduction over the electron excess conduction with rising temp. The potential increases with decreasing conductivity in both (a) and (b). For (b) there was a very rapid decrease of the Hall const. with fall of temp. The theory is discussed.

A. J. M.

**High strength of thin filaments, the Joffé effect and associated phenomena according to Griffith's theory of rupture.** E. OROWAN (Z. Physik, 1933, 86, 195—213).

A. B. D. C.

**Propagation of sound in nitrogen tetroxide.** W. T. RICHARDS and J. A. REID (J. Chem. Physics, 1933, 1, 737—748).—An extension of previous work (A., 1933, 217). Expressions for the adsorption of sound by dissociating gases are derived from Einstein's theory, and it appears that measurements of the absorption max. should show whether an absorptive region is due to failure of the dissociation reaction or of the heat capacity to follow the adiabatic cycle of the sound wave. Experiments to detect the absorption max. with N<sub>2</sub>O<sub>4</sub> failed owing to inaccuracy of measurement. The acoustical properties of such gases are better investigated by dispersion measurements.

H. S. P.

**Selenium compound of high thermoelectric power.** M. A. LEVITSKAJA and V. J. DLUGAČ (Compt. rend. Acad. Sci. U.R.S.S., 1933, 109—110).—The properties of Cu<sub>2</sub>Se are described.

H. J. E.

**New effect at the occurrence of superconductivity.** W. MEISSNER and R. OCHSENFELD (Naturwiss., 1933, 21, 787—788).—The effect of lowering the temp. below the transition point to superconductivity on the distribution of the lines of force in a cylindrical superconductor placed in a homogeneous magnetic field has been investigated. Although the magnetic field is kept const. the distribution of the lines of force in the external neighbourhood of the conductor changes on lowering the temp. below the transition point. In the interior of a long Pb tube the magnetic field remains the same as it was before lowering the temp. If the field is removed while the Pb is superconducting the field inside the tube remains the same, and the field strength outside does not become quite zero. If the magnetic field is started after the Pb is superconducting the field inside the tube remains zero.

A. J. M.

**Wiedemann-Franz number, thermal conductivity, and thermoelectric force of tellurium.** C. H. CARTWRIGHT (Ann. Physik, 1933, [v], 18, 656—678).—A method is described for the simultaneous measurement of Wiedemann-Franz no. (I), thermal conductivity (II), and thermo-electric force (III). These properties have been examined for single- and poly-crystal 99.99% Te at room temp. and at liquid O<sub>2</sub> temp. (I) is > 100 times the normal figure, but it is shown that this is not contradictory to the theory of electrical conductivity by electrons. At room temp. (III) is greater when (I) is greater. Cooling to liquid O<sub>2</sub> temp. causes a decrease in (III) and an increase in (I). (II) and (III) for pure Te are unaffected by heat-treatment.

J. W. S.



**Purification and physical properties of chemical compounds. IV. Theoretical basis for the behaviour of controlled time-temperature curves.** E. L. SKAU and W. H. LANGDON (Proc. Nat. Acad. Sci., 1933, 19, 943—947; cf. A., 1933, 667).—Mathematical. J. G. A. G.

**Low-temperature specific heats. I. Improved calorimeter for use from 14° to 300° abs. Heat capacity and entropy of naphthalene.** J. C. SOUTHARD and F. G. BRICKWEDDE. **II. Calibration of the thermometer and the resistance of platinum, platinum-10% rhodium, and constantan between -259° and -190°.** J. C. SOUTHARD and R. T. MILNER (J. Amer. Chem. Soc., 1933, 55, 4378—4384, 4384—4391).—I. The adiabatic calorimeter described has a precision of about 0.1% and is particularly suitable for studying slow transitions and thermal changes. The molal heat capacity of  $C_{10}H_8$  increases almost linearly from 1.411 g.-cal. per mol. at 15.14° abs. to 39.55 at 294.68° abs. The entropy and free energy of formation at 298.16° abs. are  $39.89 \pm 0.12$  e.u. and  $+48.5$  kg.-cal., respectively.

**II. A const.-vol. gas thermometer for the calibration of resistance thermometers between 14° and 90° abs. is described.** The electrical resistances of Pt, Pt-10% Rh, and constantan have been determined over this range with an error of about  $\pm 0.02^\circ$ .

E. S. H.

**M.p. of potassium nitrite.** B. VON LENGYEL (Naturwiss., 1933, 21, 848).— $KNO_2$  has m.p.  $419 \pm 3^\circ$ .

A. J. M.

**Physical constants of thioxan, selenoxan, and dithian.** J. D. A. JOHNSON (J.C.S., 1933, 1530).—Vals. of b.p. (corr.) at various pressures and  $n_D^{20}$  are given.

H. B.

**Determination of internal heat of rotation of ethane.** A. EUCKEN and K. WEIGERT (Z. physikal. Chem., 1933, B, 23, 265—280).—The mol. heat has been determined down to 140° abs. by measurements of the thermal conductivity relative to  $C_2H_4$ . From the results the variation with temp. of that part of the mol. heat due to the restricted rotation of the Me groups relative to each other ("internal heat of rotation") has been deduced and the difference in potential energy between the two positions where the H atoms of the Me groups are opposite to each other and where they are twisted through 60° calc. to be 315 g.-cal.  $\pm 20\%$ .

R. C.

**Free rotation in monosilane lattice.** K. CLU-SIUS (Z. physikal. Chem., 1933, B, 23, 213—225).—Measurements of the sp. heat of  $SiH_4$  from 10° abs. to the b.p. have revealed the occurrence of a rotational transformation at 63.4° abs., signalled by a peak on the sp. heat-temp. curve. The peak is unsymmetrical, the fall being much the more abrupt on the higher temp. side, which is ascribed to strong coupling of the rotators in the solid. The solid is weakly doubly refracting above the transition point and strongly doubly refracting below it.

R. C.

**Investigations in the critical region. IV. Critical isotherm and Joule effect of nitrogen tetroxide.** K. BENNEWITZ and J. J. WINDISCH (Z. physikal. Chem., 1933, 166, 416—427; cf. A.,

1929, 873).—With apparatus permitting the measurement of the isothermal Joule effect at high temp. with corrosive substances the crit. Joule isotherm of  $N_2O_4$  has been determined and found to correspond below the crit.  $d$  with the curve deduced from the universal ideal Joule curve and the vals. of  $K_p$ . At higher  $d$  there are deviations ascribed to non-ideality. It is concluded that the ideal Joule curve is valid even for associated mixtures and that van der Waals forces and the chemical forces of association are separable and inherently different.

R. C.

**Vapour pressures of propane and propylene.** A. W. FRANCIS and G. W. ROBBINS (J. Amer. Chem. Soc., 1933, 55, 4339—4342).—An all-glass apparatus for determining v.p.  $> 1$  atm. is described. Data are given for  $C_3H_8$  over the range 27—64° and for  $C_3H_6$  between 29° and 46°.

E. S. H.

**Densities of organic crystals.** A. MUKHERJEE (Indian J. Physics, 1933, 8, 147—149).—The limiting densities of 24 org. crystals determined by the immersion method (cf. Krishnan, A., 1933, 340) are tabulated, and are in good agreement with vals. from X-ray data.

N. M. B.

**Determination of density of corrosive liquids under high pressure, particularly the critical density of nitrogen tetroxide.** K. BENNEWITZ and J. J. WINDISCH (Z. physikal. Chem., 1933, 166, 401—415).—By means of a new apparatus depending on the buoyancy principle, utilising a magnetically controlled float, the orthobaric densities of  $N_2O_4$  have been determined from 17.6° up to the crit. temp. (158.20°). The extrapolated crit.  $d$  is 0.570.

R. C.

**Simplified formulas for the calculation of expansion coefficients and compressibilities of gases at low pressures from the Beattie-Bridgeman equation of state.** J. B. M. COPPOCK (J. Physical Chem., 1933, 37, 995—999).—Simple forms of the Beattie-Bridgeman virial equation have been used to calculate the thermal expansion coeffs. of various gases and also the low-pressure compressibility of  $N_2$  and CO. Agreement with experimental data is good.

H. S. P.

**Viscosity of  $H^2H^2O$ .** G. N. LEWIS and R. T. MACDONALD (J. Amer. Chem. Soc., 1933, 55, 4730—4731).—Viscosity vals., determined by a capillary method over the range 5—35°, are given. The vals. do not agree with those of Selwood and Frost (A., 1933, 1233).

E. S. H.

**Vapour viscosities and the Sutherland equation.** J. H. ARNOLD (J. Chem. Physics, 1933, 1, 170—176).—Vals. of the Sutherland const., in the equation for the temp. variation of the viscosity of a gas, calc. by the use of mol. diameters and viscosity determinations at a single temp. are compared with available data obtained by various methods for the variation of viscosity with temp. for a no. of org. substances.

N. M. B.

**Theory of liquid viscosity.** D. SILVERMAN (Trans. Faraday Soc., 1933, 29, 1285—1294).—Theoretical. Maxwell's equation (Phil. Mag., 1868, [iv], 35, 133) is evaluated, and the resulting expressions are compared with experimental data.

H. J. E.



**Effect of a magnetic field on diffusion of paramagnetic gases.** H. SENTTLEBEN (Physikal. Z., 1933, 34, 835—836).—There is a marked effect on the diffusion of various gases into  $O_2$ , but not for diffusion of one diamagnetic gas into another. A sensitive method for determining the effect is described. A. J. M.

**Complex formation due to polarisation. I. System krypton and hydrogen chloride.** G. GLOCKER, C. P. ROE, and D. L. FULLER. **II. System propane and hydrogen chloride.** G. GLOCKER, D. L. FULLER, and C. P. ROE (J. Chem. Physics, 1933, 1, 703—708, 709—713).—I. The rare gases may form loose compounds with dipoles due to polarisation forces. If the  $p$ - $v$ - $T$  relation for a mixture of gases is determined, evidence of interaction may be deduced from a study of the second virial coeff. This method has been used to show that interaction occurs between Kr and the dipole HCl.

**II. Saturated hydrocarbons resemble the rare gases and evidence of interaction between  $C_3H_8$  and HCl has been obtained by the above method.** H. S. P.

**Refractive index of liquid mixtures containing pyridine.** N. A. PUSHIN and P. G. MATAVULJ (Bull. Soc. Chim. Yougoslav., 1933, 4, 63—69).—The  $n$ -composition curves of the systems  $C_5H_5N$ -PhOH,  $o$ - and  $p$ - $C_6H_4Cl$ -OH,  $o$ -,  $m$ -, and  $p$ -cresol, thymol, and guaiacol indicate formation of 1:1 compounds in every case. R. T.

**Partial vapour pressures and refractivities of mixtures of benzene with nitrobenzene, phenol, benzyl alcohol, or  $p$ -dichlorobenzene.** A. R. MARTIN and C. M. GEORGE (J.C.S., 1933, 1413—1416).—The partial v.p. at  $70^\circ$  and the refractivities at  $25^\circ$  of the binary mixtures are recorded and discussed in reference to inter-dipole and van der Waals forces. The OH-compounds are associated to a much greater degree than the others, but  $p$ - $C_6H_4Cl_2$  appears to be slightly associated. H. F. G.

**Application of Henglein's equation to liquid mixtures and solutions.** V. A. KIREEV (J. Gen. Chem. Russ., 1933, 3, 622—627).—The v.p. calc. from Henglein's equation (A., 1920, ii, 732) agree with the experimental data for aq.  $COMe_2$  and  $H_2SO_4$ . R. T.

**Rapid determination of vapour-pressure isotherms of liquid mixtures and solutions.** V. A. KIREEV, E. N. SERPIONOVA, and N. S. MATJUSCHIN (J. Appl. Chem. Russ., 1933, 6, 769—771).—Measured vols. of one component are added at const. temp. to a fixed vol. of the other, and the v.p. is measured after each addition. R. T.

**Binary systems. IV. Ethane systems.** F. E. C. SCHEFFER and J. SMITTENBERG (Rec. trav. chim., 1933, 52, 982—986).—Temp.-pressure data are recorded for  $C_2H_6$ + $p$ - $C_6H_4Cl_2$  (I), 1:3:5- $C_6H_3Cl_3$  (II),  $p$ - $C_6H_4ClBr$  (III), and  $p$ - $C_6H_4Cl$  (IV). For (I) the miscibility is complete throughout the range studied ( $5$ — $78^\circ$ ), whereas (II) is only partly miscible between about  $40^\circ$  and  $50^\circ$ . For (III) the 3-phase line intersects the heterogeneous area, the quadruple point being at about  $40^\circ$  and 52 atm.

(IV) exhibits very limited miscibility, and  $dP/dt$  for the 3-phase line is negative throughout. H. F. G.

**Boiling of fused reciprocal salt-pairs. System (NaK)(ClI).** E. JANECKE (Z. anorg. Chem., 1933, 215, 49—65).—A space model is constructed from the experimental data of Greiner and Jellinek (A., 1933, 770). F. L. U.

**Investigation of the gold-copper system by determination of resistance at low temperatures.** V. POSPIŠIL (Ann. Physik, 1933, [v], 18, 497—514).—Alloys containing 10—100% Au have been investigated in the chilled and tempered conditions by finding the ratio of their resistances at  $-195^\circ$  and  $-252.4^\circ$  to that at  $0^\circ$  (the  $r$ -val. method). This method is regarded as more trustworthy than the determination of sp. resistance. The concn.-resistance curves for the chilled alloys are similar to those for a binary system with a complete series of mixed crystals. The curves for the tempered alloys, however, show sharp min. at 25 and 50% Au, corresponding with  $AuCu_3$  and  $AuCu$ . At 75% Au the curve for the tempered alloy rises above that for chilled alloys, showing that some modification of the mixed crystal system in the former is brought about by the tempering in this region. The results agree with those of Grube (A., 1931, 1364). No indication of  $Au_2Cu_3$  was found. A. J. M.

**Compounds of aluminium with silver.** F. E. TISCHTSCHENKO (J. Gen. Chem. Russ., 1933, 3, 549—557).—A study of the fusion diagram and of the microcryst. structure of ordinary and chilled alloys affords evidence of the compound  $\alpha$ - $AlAg_3$  (I) which is formed at the peritectic temp.  $771^\circ$ , and undergoes transformation into  $\beta$ - $AlAg_3$  (II) at  $606^\circ$ , and of the compound  $Al_2Ag_3$ , m.p.  $751^\circ$ , which decomposes below  $711^\circ$  to yield  $AlAg_2$  (III). (I) does not form solid solutions, but (II) can dissolve  $> 10.2\%$  Al (at  $722^\circ$ ), and (III) can dissolve  $> 1.3\%$  Ag or  $3.2\%$  Al. R. T.

**Iron-rich iron-silicon alloys.** C. P. YAP (J. Physical Chem., 1933, 37, 951—967; cf. A., 1932, 1206).—Thermoelectric characteristics, electrode potentials, and X-ray photographs of Fe-Si alloys containing 13—32% Si suggest that  $Fe_3Si$  ( $\phi$ ) is present. The existence of  $Fe_3Si_2$  and  $FeSi$  is also indicated. A study of existing f.-p. data indicates that  $\phi$  should be formulated as  $Fe_6Si_2$ . F. L. U.

**Electrical conductivity and equilibrium diagram of binary alloys. VIII. System lithium-zinc.** G. GRUBE and H. VOSSKÜHLER (Z. anorg. Chem., 1933, 215, 211—224).—The complete equilibrium diagram has been examined by thermal analysis and transformations in the solid state determined by temp.-resistance measurements. There are five series of homogeneous mixed crystals:  $\alpha$ , 0—1.5% Li;  $\beta$ , 8.5—24%;  $\gamma$ , 26.5—29%;  $\delta$ , 33—50%;  $\epsilon$ , 98—100%. The existence of  $Li_2Zn_3$  has been confirmed. With excess of Li or Zn it forms  $\delta$  mixed crystals. On cooling it changes at  $174^\circ$  into another form which gives  $\delta'$  mixed crystals with either component. A new compound,  $LiZn_2$ , is formed at  $93^\circ$  from  $\gamma'$  and  $\delta'$  mixed crystals. The existence of a compound  $LiZn$  is doubtful. M. S. B.



**Conclusions from rules on concentration of valency electrons in binary intermetallic alloys.** H. PERLITZ (J. Chem. Physics, 1933, 1, 335—336).—The empirical rules governing the formation of intermetallic phases of the types of  $\beta$ -,  $\gamma$ -, and  $\epsilon$ -brass are expressed algebraically. These phases are not to be expected when the metals have the same no. of valency electrons, but may be expected if the concn. of valency electrons of one component is  $>$ , and of the other  $<$ ,  $3/2$ ,  $21/13$ , or  $7/4$  electrons per atom. Since the same conditions govern the appearance of  $\beta$ -,  $\gamma$ -, and  $\epsilon$ -phases, all these may be expected when any one is found. D. R. D.

**Magnesium-zinc-silicon alloys rich in magnesium.** E. ELCHARDUS and P. LAFFITTE (Compt. rend., 1933, 197, 1125—1127).—The thermal diagram of the system Mg-Zn-Si has been determined within the limits Mg-Mg<sub>2</sub>Si-MgZn<sub>2</sub>. Over most of the range the melt forms two phases, the limit for ternary solid solution having the composition 94.5 Mg+5.25 Zn+0.25% Si; that of the ternary eutectic, m.p. 335°, is 53.3 Mg+43.5 Zn+3.2% Si (cf. B., 1923, 892; A., 1929, 398). C. A. S.

**Solubility of cupric chloride in water and transition points of its hydrates. The tetrahydrate.** E. BOYE (Z. anorg. Chem., 1933, 215, 75—80).—Equilibria in the system CuCl<sub>2</sub>-H<sub>2</sub>O have been determined. The tetrahydrate forms blue needles, the colour of which is not changed by H<sub>2</sub>O. The cryohydric point is at -43.4°. Transition temp. are as follows:  $4 \rightleftharpoons 3$ , 15.0°;  $3 \rightleftharpoons 2$ , 25.7°;  $2 \rightleftharpoons 1$ , 42.2°. F. L. U.

**Solubility of thallous iodate and thallous chloride in the presence of amino-acids.** C. F. FAILEY (J. Amer. Chem. Soc., 1933, 55, 4374—4378).—The solubility of TlIO<sub>3</sub> and TlCl in H<sub>2</sub>O in presence of glycylglycine, glycine,  $\alpha$ -alanine,  $\alpha$ -amino-*n*- and -*iso*-butyric acid,  $\alpha$ -amino-*n*-valeric acid, carbamide, and diketopiperazine, respectively, has been determined. For TlIO<sub>3</sub> the logarithm of the solubility is approx. a linear function of the concn. of the added substance. The dielectric consts. of the solutions do not explain the differences observed among the NH<sub>2</sub>-acids. E. S. H.

**Rule for the expression of the partition of associating substances.** M. J. ALMQUIST (J. Physical Chem., 1933, 37, 991—994).—A distribution equation agreeing with experimental data and having a theoretical basis is given. The degree of association is assumed to be equal in both solvents. H. S. P.

**Fractional crystallisation of radiferous barium chloride.** (MME.) B. E. MARQUES (Compt. rend., 1933, 197, 1314—1315; cf. A., 1933, 562).—The relative quantities of Ra<sup>++</sup> and of Ba<sup>++</sup> in the solution before and after crystallisation are slightly different. C. A. S.

**Diffusion of hydrogen through platinum and nickel and through double layers of these metals.** W. R. HAM (J. Chem. Physics, 1933, 1, 476—481).—Direct experiments on double layers of Pt and Ni show that the temp. coeff. of flow depends wholly on the outgoing surface. The work of Borelius (A., 1927, 195, 727) is confirmed for single sheets. F. L. U.

**Sorption of oxygen by nickel catalysts.** W. W. RUSSELL and L. G. GHERING (J. Amer. Chem. Soc., 1933, 55, 4468—4474; cf. A., 1932, 332).—Considerable amounts of O<sub>2</sub> are instantaneously and irreversibly adsorbed by Ni catalysts even at -190°. The degree of irreversible adsorption increases with rising temp.; considerable reversible adsorption occurs only at -190°. The rates of slow sorption increase with rising temp. Activated adsorption probably occurs at -190° and accounts for most of the O<sub>2</sub> sorbed at 0°. E. S. H.

**Possible magnitude of the sorption error in measurements involving easily sorbable gases at low pressures.** M. FRANCIS (J. Physical Chem., 1933, 37, 1019—1027).—Measurements with SO<sub>2</sub> at <0.1 mm. show that the amount of gas sorbed on the walls of a simple apparatus may exceed that in the free space. Care must therefore be taken in interpreting pressure changes with a sorbable gas at low pressures. H. S. P.

**Sorption of iodine vapour by various inorganic substances.** E. BEUTEL and A. KUTZELNIGG (Monatsh., 1933, 63, 99—116).—Although sorptive power (*s*) is widely observed, the velocity of sorption of I vapour at room. temp. by numerous inorg. powders (not previously evacuated) from all groups of the periodic table is, in general, small, but is increased (1) by trituration with I, (2) by previous heating of the powder, and (3) by heating with I, and is therefore hindered by the absorbed air. *s* depends on the surface area of the sample and hence on its method of prep.; with ZnO there is a definite relation between *s* and the nature of the compound from which it is prepared by thermal decomp. Vigorous grinding of the powder sometimes increases (fibrous Al<sub>2</sub>O<sub>3</sub>) and sometimes hinders (SiO<sub>2</sub> gel) sorption. Most rapid sorption occurs with MgO, ZnO (from basic ZnCO<sub>3</sub> at 300°), Ca(OH)<sub>2</sub>, and Sb<sub>2</sub>O<sub>3</sub>. The colour (*c*) of the sorbate varies from yellow to red, becoming almost black for high I content (*i*), the relation of *c* to *i* varying with different substances and samples. Optical analysis of the reflected light and of the absorption curves for different thicknesses of I shows that *c* is related to the light transmission of the (thin) layers of adsorbed I, and is also influenced by the optical behaviour of the sorbing material. J. W. B.

**Adsorbabilities of ions.** K. S. G. DOSS (J. Indian Chem. Soc., 1933, 10, 503—508).—Theoretical. E. S. H.

**Adsorption of thorium-B by thallium halide crystals in presence of ions. II.** J. F. KING and P. R. PINE (J. Physical Chem., 1933, 37, 851—874; cf. A., 1933, 899).—Adsorption of Th-B<sup>++</sup> on TlBr and TlI is increased by I<sup>-</sup>, CrO<sub>4</sub><sup>2-</sup>, CNS<sup>-</sup>, and Br<sup>-</sup>, the effect decreasing in the order named. It is diminished by Cl<sup>-</sup> and C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, and by Pb<sup>++</sup>, Cu<sup>++</sup>, Ag<sup>+</sup>, and Tl<sup>+</sup>. Anions are adsorbed on the crystal surfaces, conferring a negative charge on them, and the subsequent adsorption of Th-B<sup>++</sup> is favoured by insolubility of the salt formed by it with the ion concerned. This rule is strictly followed among the halide anions, but the effectiveness of other ions is partly determined by their deformability. Cations



diminish adsorption of Th-B'' by competing with it. In the latter case Tl' is most effective because it is more readily attached than foreign ions to the Tl halide lattice. No "neutral" (*i.e.*, non-adsorbing) specimen of TlBr or TlI could be prepared.

F. L. U.

**Effect of alkali and alkaline-earth ions on the adsorption of thorium-B by silver bromide crystals.** J. F. KING and U. T. GREENE (*J. Physical Chem.*, 1933, 37, 1047—1059).—The adsorption (I) of Th-B ions on AgBr crystals in presence of alkali and alkaline-earth bromides has been measured. At const. [Br'] and with different cations, the (I) of Th-B changes as a result of the simultaneous (I) of the cations. A relation appears to exist between the adsorbability of the cations and their heats of hydration, ionic size, and the solubility of the bromides.

H. S. P.

**Adsorption systems of kaolins and clays with liquids in relation to plasticity.** E. GRUNER (*Z. anorg. Chem.*, 1933, 215, 1—18).—V.p.-composition isotherms have been determined for systems of kaolins and clays with various liquids. Liquids which do not form plastic mixtures give a v.-p. curve consisting of vertical and horizontal parts with a sharply curved connecting portion, whilst those which confer plasticity show a gradual transition. Parallelism exists between the degree of plasticity and the extent of the inclined part of the curve. The latter group includes only those liquids which possess asymmetric dipoles, such as H<sub>2</sub>O, NH<sub>3</sub>, and their simple derivatives. Liquid NH<sub>3</sub> dehydrates allophane present in clays but is without action on kaolinite. The results are discussed with reference to the chemical constitution of kaolinite.

F. L. U.

**Elementary deduction of Gibbs' adsorption theorem.** F. O. KOENIG and R. C. SWAIN (*J. Chem. Physics*, 1933, 1, 723—730).—Theoretical. An exact elementary deduction of Gibbs' adsorption theorem and of related equations is given.

H. S. P.

**Preparation and properties of thin lead sulphide layers, with special reference to their detector action. II.** G. BRÜCKMANN (*Kolloid-Z.*, 1933, 65, 148—161; cf. A., 1933, 1113).—The layers have a stoichiometric composition and well-defined crystal structure; their optical properties depend on the film thickness. Detector action is observed with the purest PbS and is independent of the material under the PbS layer, but varies with the thickness of the film, and is favoured by a coarse cryst. structure. The existence of a solid, insulating layer at the point of contact is improbable. The electrons pass in the direction from contact material to PbS, except when contact with graphite is made; no difference is shown by various metals and alloys as contact materials. Theories of rectifying action are discussed.

E. S. H.

**Surface phenomena at the interface solid-solution. Change in heats of wetting of solutions of surface-active substances on addition of electrolytes.** B. ILJIN, V. SEMENTSCHENKO, and V. IVANOV (*Z. physikal. Chem.*, 1933, 166, 382—392).—The heat of wetting,  $Q$ , of non-activated wood charcoal in aq. solutions of NaCl, Pr<sup>3</sup>OH, and

Bu<sup>3</sup>OH is  $>$  in pure H<sub>2</sub>O and increases with the concn. In mixed solutions of either alcohol and NaCl the increase in  $Q$  compared with pure H<sub>2</sub>O is  $>$  the sum of the effects caused by the two solutes separately.

R. C.

**Vaporous state of myristic acid films on aqueous solutions.** S. A. MOSS and E. K. RIDEAL (*J.C.S.*, 1933, 1525—1528).—A new type of Langmuir trough is described in which the film pressure ( $F$ ) rotates a floating barrier against the torsion of a wire. Myristic acid spread on H<sub>2</sub>O is found to obey the equation  $FA=0.5RT$ , where  $A$ =area of the film, and it is deduced that the mols. are associated in pairs even when  $A$  is large.

D. R. D.

**Influence of foreign substances on the wettability of chemicals by water.** L. J. WEBER and A. C. CHATTERJI (*Kolloid-Beih.*, 1933, 38, 412—438).—The wettability of C<sub>10</sub>H<sub>8</sub>, anthracene, and phenanthrene by aq. solutions of org. substances has been determined (with an accuracy of  $\pm 3\%$ ) by a simple sedimentation method. In series of fatty acids, alcohols, esters, and amines the wettability increases with increasing mol. wt. or surface activity. Traube's rule is valid for the lower homologues. Non-polar substances (paraffin, CS<sub>2</sub>, CCl<sub>4</sub>, pentane) have little influence on the wettability of C<sub>10</sub>H<sub>8</sub>, whilst small amounts of polar substances (oleic acid, NH<sub>2</sub>Ph, PhOH, toluidine, xylydine, CH<sub>2</sub>Ph-OH) increase the wettability. Similar phenomena are observed when the org. substances are added to molten C<sub>10</sub>H<sub>8</sub>. The great influence exerted by small amounts of impurities suggests that the wettability of a substance may be used as an indication of its purity.

E. S. H.

**Experiments with wetting agents.** H. A. NEVILLE and C. A. JEANSON (*J. Physical Chem.*, 1933, 37, 1001—1008).—The surface tensions of aq. solutions of various concns. of the Na sulphonates of C<sub>6</sub>H<sub>5</sub>, PhMe, xylene, cymene, PhEt, PhPr<sup>2</sup>, PhBu, and of a commercial wetting agent (sulphonate) have been measured. Two substituting groups increase the surface activity  $>$  a single group with the same no. of C atoms. The absorption of the wetting agents by wool runs parallel with the potential curve of the wool in acid solution and is negligible in alkali. These agents increase the sorption of dye in acid and decrease it in alkaline solution.

H. S. P.

**Surface tension of film-covered liquids at saturation.** H. BROWN (*J. Amer. Chem. Soc.*, 1933, 55, 4521—4523).—A discussion (cf. A., 1933, 899).

E. S. H.

**New method of studying electrical properties of unimolecular films on liquids.** H. G. YAMINS and W. A. ZIZMAN (*J. Chem. Physics*, 1933, 1, 656—661).—The surface potential of unimol. films of some fatty acids and glycerides on pure H<sub>2</sub>O and 0.01N-H<sub>2</sub>SO<sub>4</sub> was measured by a potentiometer and a condenser comprising the surface under study and a metal plate vibrating above it. Reproducible results are obtained which agree with those of earlier workers.

D. R. D.

**Surface chemistry. Nobel lecture.** I. LANGMUIR (*Angew. Chem.*, 1933, 46, 719—733).—A summary of Langmuir's published work.

E. S. H.



**Electrokinetic phenomena in capillaries.** H. REICHARDT (Z. physikal. Chem., 1933, 166, 433—452; cf. A., 1931, 795).—Since the streaming potential,  $\zeta$ , at a liquid-solid interface may change with time when the liquid remains stationary, the variability of  $\zeta$  with the streaming velocity,  $v$ , at low vals. of  $v$  is explained. The field due to  $\zeta$  retards the flow in the double layer. If surface conduction is predominant the transport back of the charges set free at the ends of the capillary will occur principally by backward streaming of the part of the double layer in immediate proximity to the wall, which will reduce the mean  $v$ . If the cross-section of the double layer is a not negligible fraction of the total liquid cross-section the effective resistance of the capillary to the flow of liquid under the influence of a pressure difference,  $p$ , may be considerably increased by the field due to  $\zeta$ . The fundamental electrokinetic equations for narrow capillaries are deduced. The equation for the convection current is valid for wide tubes within which there is turbulent flow. Turbulence within the double layer is impossible. Saxeen's relation  $\zeta/p$ =(amount of liquid transported electro-osmotically)/(current strength) is valid also for systems of capillaries where convective surface conduction plays a part. R. C.

**Capillary ascension of hydrosols and solutions of dyes: influence of concentration and of electrolytes.** A. BOUTARIC and M. PEYRAUD (Compt. rend., 1933, 197, 1218—1220).—When strips of filter-paper are suspended with one end dipping into various hydrosols, and sols or solutions of colloidal or semi-colloidal dyes, the  $H_2O$  rises first at a rate which is independent of the solute and is followed more slowly by the colloid etc. Decrease of humidity or rise in temp. increases the rate. When these are const. the rate is independent of concn. for negative colloids etc., but increases linearly with the concn. for positive colloids, thus affording a means of determining the electric character of the colloid. The effect of an electrolyte added to the sol varies mainly according to the cation or anion as the colloid is negative or positive, respectively. C. A. S.

**Water filtration through membranes and membrane resistance.** V. V. LEPESCHKIN (Kolloid-Z., 1933, 65, 184—186).—At pressures < 100 cm.  $H_2O$  the velocity of filtration of  $H_2O$  through parchment and dried collodion membranes decreases with decreasing pressure, until a pressure is reached (the "membrane resistance") at which filtration stops. Membrane resistance increases as the pore size decreases, but is practically independent of the thickness of the membrane. The observed phenomena are ascribed to the force required to overcome the attraction between the  $H_2O$  mols. and the walls of the membrane. E. S. H.

**Stationary, checked, and other states of osmotic systems.** II. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 717—723; cf. A., 1933, 900).—Theoretical. J. W. S.

**Influence of  $p_H$  on speed of diffusion of the chlorine ion across collodion membranes.** C.

HRYNKOWSKI (Bull. Soc. Chim. biol., 1933, 15, 1146—1153).—The rate of diffusion of  $Cl^-$  in solutions of KCl, NaCl,  $CaCl_2$ , and mixtures of these salts increases with decreasing  $p_H$  of the solutions. A higher  $p_H$  or  $[Ca^{++}]$  decreases the time required for equilibrium to be established. H. D.

**Mol. wts. of dissolved substances.** A. W. POUND and J. R. POUND (J. Physical Chem., 1933, 37, 969—972; cf. A., 1931, 843).—Results of cryoscopic determinations of the mol. wt. of 11 substances in various org. solvents are given. F. L. U.

**F.p. and osmotic pressures of lactose solutions.** E. O. WHITTIER (J. Physical Chem., 1933, 37, 847—849).—Results of f.p. measurements from 4.7% to saturation are given. Since the vals. agree within 1% with those for sucrose, it is inferred that one may be substituted for the other without influence on osmotic effects. F. L. U.

**Lambert-Beer law and the nature of absorbent particles in solution.** E. DARMOIS (Compt. rend., 1933, 197, 1120—1121).—Absorption curves which deviate from the Lambert-Beer law, and are supposed to indicate the presence of two or more isomerides, are similar to those for rotatory power under similar circumstances, and deductions relative to the no. of isomerides present can be similarly made (cf. A., 1911, ii, 352; 1928, 589). C. A. S.

**Absorption spectra of glycine solutions and their interpretation.** G. A. ANSLOW, M. L. FOSTER, and C. KLINGLER (J. Biol. Chem., 1933, 103, 81—92).—Absorption spectra for  $H_2O$ , HCl, and NaOH solutions of glycine (I) have been determined for the range 6000—1850 Å. F.p. determinations before and after irradiation have also been made. The results indicate that the cation  $^+NH_3\cdot CH_2\cdot CO_2H$  exists in both  $H_2O$  and HCl solution. Determinations of the frequency at which dissociation (II) occurs in the  $CO_2H$  group show that (I) behaves like other  $NH_2$ -acids (cf. A., 1932, 896). Hence (II) takes place by the separation of  $H^+$  from the mol. ion giving the zwitter-ion. In aq. NaOH the (I) cation exists as  $^+NH_3\cdot CH_2\cdot CO_2Na$  and (II) takes place by the separation of  $Na^+$  leaving the zwitter-ion. The energies of (II) in ergs and volts, and the heats of (II) in cal., have been calc. Polymerisation increases with increasing concn. and also with irradiation of the solutions with ultra-violet light. The results confirm the theory of the zwitter-ion structure of the (I) mol. M. S. B.

**Molecular refraction in dilute solutions.** II. Interferometric precision measurement of refractive indices. W. GEFFCKEN and A. KRUIS (Z. physikal. Chem., 1933, B, 23, 175—192; cf. A., 1933, 587).—By using monochromatic light with a modified form of Haber-Loewe apparatus, interferences of the order of several thousand can be observed. The difference in  $n$  between solution and solvent can be determined with an abs. precision ranging from 0.05 in the more conc. solutions to 0.03 for dil. solutions. For aq.  $NH_4NO_3$  at 25° the apparent mol. refraction of the solute falls linearly with increasing concn., but with aq. NaCl and KCl the curve exhibits a max. R. C.



**Specific influence of the solvent in electrolytic dissociation.** D. J. G. IVES (J.C.S., 1933, 1360—1365).—Conductometric titration of solutions of Cu, Ni, and Zn sulphates and malonates and Cu oxalate containing  $C_5H_5N$  (which may be expected to provide a more stable solvation sheath) supports the view previously put forward (A., 1931, 1126). It is suggested that the behaviour of salts of the Cu malonate type is governed by the electron-accepting tendency of the cation and its influence on the competing co-ordinating tendencies of the anion and the solvent; if the solvent has the greater co-ordinating tendency the differences of the degrees of ionisation of a series of salts having a common anion or cation may almost completely disappear, whereas if the tendency is greater for the anion the differences due to sp. properties of the other ions will be apparent.

H. F. G.

**F.p. of aqueous solutions. IV. Potassium, sodium, and lithium chlorides and bromides.** G. SCATCHARD and S. S. PRENTISS (J. Amer. Chem. Soc., 1933, 55, 4355—4362; cf. A., 1932, 912).—Refinements of technique are described. The bromides show greater deviations from the limiting law than the corresponding chlorides. Deviations for salts of the same anion increase in the order  $K < Na < Li$ , except in very dil. solutions of LiCl.

E. S. H.

**Optical determination of ionic equilibria in dilute ethyl alcoholic solution.** P. GROSS, A. JAMÖCK, and F. PATAT (Monatsh., 1933, 63, 117—126).—Under conditions ensuring rigid exclusion of  $H_2O$  the mol. extinction coeffs. ( $\epsilon$ ) of  $NH_4$  and  $NEt_4$  picrates at 4360 Å. and 20° for dil. EtOH solutions ( $c = 2.5 \times 10^{-6}$  to  $2.9 \times 10^{-3}$  mol. per litre) are const. ( $4019 \pm 3$  and  $4026 \pm 8$ , respectively), indicating complete dissociation. Picric acid under such conditions gives a val. for the activity coeff. almost identical with that previously obtained (A., 1930, 992), but the thermodynamic dissociation const. ( $k_0$ ) deviates slightly from the previous val. (cf. below). Measurements of  $\epsilon$  for picric acid and  $NH_4$  picrate in the visible and ultra-violet regions confirm the complete dissociation of the salt and the assumption that undissociated picric acid does not absorb between the visible region and 3600 Å. Increasing concn. of  $H_2O$  in EtOH causes a linear increase in  $\epsilon$  for  $NEt_4$  picrate until at 0.8 mol. per litre it reaches the val. for the picrate ion in  $H_2O$ , but its effect on  $\epsilon$  for the free acid is greater owing to alteration in the dissociation const. conditioned by the equilibrium  $(EtOH, H)^+ + H_2O \rightleftharpoons H_3O^+ + EtOH$  (equilibrium const. calc. =  $0.0524 \pm 0.001$ ), whence the deviation in  $k_0$  noted above would be caused by  $< 0.1\%$  of  $H_2O$  in the EtOH previously used.

J. W. B.

**Dielectric properties of solutions of electrolytes in a non-polar solvent.** C. A. KRAUS and G. S. HOOPER (Proc. Nat. Acad. Sci., 1933, 19, 939—943; cf. A., 1933, 1120).—In harmony with the view that electrolytes in non-polar solvents are in the form of ion pairs which unite to form more complex aggregates at higher concn., the rise of dielectric const.,  $k$ , at 25°, with increase of concn. of  $C_6H_6$  solutions of tetraisoamylammonium picrate (I) and bromide (II), triisoamylammonium picrate

(III), and  $AgClO_4$  (IV) is  $\gg$  with  $m\text{-}C_6H_4(NO_2)_2$  (V) in  $C_6H_6$ . At high concn.,  $k$  is related to the symmetry of the ions. Electric moments are: (I) 18.0, (II) 14.7, (III) 12.91, (IV) 11.97, and (V)  $4.0 \times 10^{-18}$  e.s.u.

J. G. A. G.

**Investigation of influence of solute on solvent by means of infra-red absorption spectra. II. Effect of hydrogen and hydroxyl ions on state of association of water.** R. SUHRMANN and F. BREYER (Z. physikal. Chem., 1933, B, 23, 193—212; cf. A., 1933, 348, 998).—Extinction coeff. measurements have been made between 0.85 and  $2.3 \mu$ . The absorption max. of  $H_2O$  at 0.98, 1.20, and  $1.45 \mu$  are depressed by dissolved HCl or  $H_2SO_4$ , and the absorption on the long-wave side of these bands and that at  $1.96 \mu$  is increased. These effects are ascribed to the addition of  $H^+$  to  $H_2O$  mols., and to depolymerisation of the  $H_2O$ . From the depression of the max. at  $1.45 \mu$  by HCl it is calc. that each  $H^+$  binds approx. 1  $H_2O$  mol. The absorption curve of  $H_3O^+$ , calc. from absorption data for aq. HCl, shows no distinct banded absorption, which suggests that  $H^+$  forms no definite compound with  $H_2O$  but merely a short-lived complex in which the at. vibrations of  $H_2O$  are modified in varying degree by the electric field of  $H^+$ . All the absorption max. of  $H_2O$  are depressed by KOH. Here each  $OH^-$  binds approx. 2  $H_2O$  mols. The absorption curve of  $H_2O$  mols. under the influence of  $OH^-$  is similar in character to that of  $H_3O^+$ , and it is probable that  $OH^-$  forms no definite compound with  $H_2O$  but merely influences the  $H_2O$  to a variable extent.

R. C.

**Limiting laws of the interionic attraction theory of strong electrolytes.** P. VAN RYSELBERGHE (J. Chem. Physics, 1933, 1, 205—209).—The general form of the limiting laws can be obtained by combining the Gibbs-Helmholtz equation and the virial theorem of Clausius. The equations of Debye and Hückel and of Kramers represent special forms of the general laws.

A. J. M.

**Influence of soluble phosphates on viscosity of kaolin suspensions.** V. A. PLOTNIKOV and E. M. NATANSON (J. Appl. Chem. Russ., 1933, 6, 839—844).—The viscosity  $\eta$  of kaolin (I) suspensions is reduced to the same extent by 0.062N- $Na_2HPO_4$  (II), 0.063%  $Na_2SiO_3$  (III), 0.36%  $Na_2CO_3$ , 0.24%  $K_2CO_3$ , 0.33%  $K_2CrO_4$ , and 0.24%  $(NH_4)_3PO_4$ ; at higher concns.  $\eta$  rises again in all cases. The action of the above electrolytes is due to adsorption on (I), which is at a max. at the concns. given. The  $p_H$  of the suspensions varies very little with increasing concn. of (II) or (III), owing to the buffer action of (I), and variations in  $\eta$  cannot be attributed to change in  $p_H$ .

R. T.

**Mechanism of the formation of Kohlschütter's silver sol.** H. B. WEISER and M. F. ROY (J. Physical Chem., 1933, 37, 1009—1018).—Kohlschütter's Ag sol may be obtained by the action of  $H_2$  on suspensions of  $Ag_2O$  at 50° or 60° provided these have not been ultra-filtered. Soft glass, Pyrex, or quartz vessels may be used and the presence of alkali or sulphide is unnecessary. With Pt, deposition of Ag crystals occurs owing to the activation of H at



the Pt surface. Mirror formation on glass is due to deposition of  $\text{Ag}_2\text{O}$  by the alkali in the glass, followed by the reduction of  $\text{Ag}_2\text{O}$  by H activated at a Ag or Ag- $\text{Ag}_2\text{O}$  surface. H. S. P.

**Significance of gas phase in formation of emulsions.** F. ROGOWSKI and K. SÖLLNER (Z. physikal. Chem., 1933, 166, 428—432).—The formation of emulsions either by the action of supersonic waves or by shaking is promoted and the emulsions are rendered more stable by the presence of a foreign gas, the action of which is apparently not sp. R. C.

**Determination of the amount of bound water in disperse systems. I. Refractometry and polarimetry.** A. DUMANSKI (Kolloid-Z., 1933, 65, 178—184).—A sucrose solution of known concn. is added to the colloid system containing a known amount of total  $\text{H}_2\text{O}$ . After shaking and keeping, the solution is filtered, and sucrose is determined in the filtrate refractometrically or polarimetrically. The amount of bound  $\text{H}_2\text{O}$  is calc. from the difference between the concn. of sucrose found and the concn. it would possess if it were dissolved in the total  $\text{H}_2\text{O}$  present. E. S. H.

**Composition of arsenic trisulphide sol and its variation with age and under the influence of light.** V. KRESTINSKAJA and V. JAKOVLEVA (Kolloid-Z., 1933, 65, 187—191).—The micelles of  $\text{As}_2\text{S}_3$  sols contain excess of  $\text{As}_2\text{O}_3$  or  $\text{H}_2\text{S}$  according to the conditions of prep. Ageing phenomena are due to hydrolysis of  $\text{As}_2\text{S}_3$  and oxidation of  $\text{H}_2\text{S}$ . By adsorption of  $\text{H}_2\text{AsO}_3$  and loss of  $\text{H}_2\text{S}$ , the relative As content of the micelles increases. The ageing process is accelerated by light. E. S. H.

**Phase volume theory and homogenisation of concentrated emulsions.** J. B. PARKE (J.C.S., 1933, 1458—1459).—Emulsions containing > 74% disperse phase (I) by vol. must contain drops of non-uniform size (cf. J.C.S., 1907, 91, 2001); such emulsions of  $\text{C}_6\text{H}_6$  and PhMe in Na and K oleate solutions are broken down by homogenisation to emulsions of about 70% (I) in which the drops are microscopically uniform, whilst more dil. emulsions are unaltered. D. R. D.

**Optics of white sols. II. Diffuse side rays.** T. CASPERSSON (Kolloid-Z., 1933, 65, 162—170; cf. A., 1932, 993).—The optical relations of colloidal particles of different diameters are discussed theoretically. E. S. H.

**Colloid-chemical foundations of photoanisotropy. I. General problem.** F. WEIGERT and J. MATULIS (Kolloid-Beih., 1933, 38, 384—411).—An introductory discussion. E. S. H.

**Rôle of dielectric constant, polarisation, and dipole moment in colloid systems. XI. Stabilisation of metal organosols.** Wo. OSTWALD, J. F. EHLERS, and H. ERBRING (Kolloid-Beih., 1933, 38, 337—383; cf. A., 1932, 462).—The sol-forming power and sol stability of Ag dispersed in org. media by the oscillating electrical discharge can be measured by the "Umschlagszeit" ( $U$ ), which is the time in sec. during which dispersion can occur before the onset of coagulation. The dependence of  $U$  and the corresponding concn. of sol on the applied potential

and temp. has been investigated and the existence of a crit. temp. is confirmed. The conditions of dispersion of Hg in (a) mixtures of polar and non-polar liquids ( $\text{Et}_2\text{O}$ ,  $\text{PhNO}_2$ , MeOH, EtOH, PrOH, Bu<sup>o</sup>OH, and  $\text{COMe}_2$  in  $\text{C}_6\text{H}_6$ ) and (b) mixtures of two polar liquids ( $\text{PhNO}_2$ ,  $\text{H}_2\text{O}$ , MeOH, EtOH, PrOH, Bu<sup>o</sup>OH, isoamyl and *n*-hexyl alcohols in  $\text{Et}_2\text{O}$ ) have been examined. In the simplest case ( $\text{Et}_2\text{O}$ - $\text{C}_6\text{H}_6$ ),  $U$  varies with the proportion of one component in the mixture  $c$  according to the relation  $U = k\sqrt{c(1/\epsilon_c)}$  or  $U = k_1\sqrt{c(\mu^2/\epsilon_c)}$ , where  $\epsilon_c$  is the dielectric const.,  $\mu$  the dipole moment, and  $k$  and  $k_1$  are consts. With  $\text{PhNO}_2$ - $\text{C}_6\text{H}_6$  the expression  $U = k\sqrt{cP''}$  is valid, where  $P'' (=k_1\mu^2)$  is the orientation polarisation.  $U$  is increased when a polar liquid is added to a non-polar liquid but is not altered when a non-polar liquid is added to a polar liquid. These results are discussed in relation to the degree of dissociation of the mols. of liquid. E. S. H.

**Magneto-optical investigations on ferric oxide sols. I. General.** W. HELLER (Kolloid-Beih., 1933, 39, 1—57; cf. following abstract).—The variable, complex magneto-optical behaviour observed with  $\text{Fe}_2\text{O}_3$  sols is due to the presence of several constituents ( $\alpha$ - $\text{Fe}_2\text{O}_3$ ,  $\alpha$ - $\text{Fe}_2\text{O}_3$ , and a basic salt of unknown composition), which have different properties.  $\alpha$ - $\text{Fe}_2\text{O}_3$  gives a positive effect, which increases with increasing field strength in a characteristic way. Goethite sols give at first a positive effect, changing to negative with ageing of the sol. The intermediate stage between positive and negative double refraction is isotropic when the sol is homodisperse, but gives a positive-negative (alternating) effect when heterodisperse. The change of sign with time is more rapid in sols having small particles. In general, with rise of temp. negative effects tend to diminish and positive effects to be enhanced. The temp. coeff. in very fresh positive or aged negative sols is relatively small (3—6%), but is considerable in the intermediate stage. Magnetic double refraction is reduced by all processes that bring about coagulation. E. S. H.

**Transverse magneto-optic anisotropy of some colloidal solutions. II. Ferric oxide sol. (Summary.)** W. HELLER and H. ZOCHER (Z. physikal. Chem., 1933, 166, 365—381; cf. A., 1933, 461).—A study of the Majorana phenomenon.  $\alpha$ - $\text{Fe}_2\text{O}_3$  sols have a const. double refraction,  $\delta$ , independent of the field strength,  $H$ , whilst with  $\alpha$ - $\text{Fe}_2\text{O}_3$  sols  $\delta$  varies with  $H$  and may become negative on keeping, a change ascribed to diminishing form anisotropy of the particles. Sols containing supposedly a colloidal basic salt have positive  $\delta$ . The magneto-optical data indicate that the active substance in most  $\text{Fe}_2\text{O}_3$  sols prepared by the usual methods at room temp. is goethite primary particles. The only types of coagulation producing anisotropic particle aggregates are coagulation by shaking or stirring and very slow pptn. by electrolytes. The double diffraction passes through a max. with increasing degree of dispersity. With fresh goethite sols  $\delta$  decreases with rise of temp.,  $T$ , whilst with very old sols the negative  $\delta$  decreases, becomes positive, and passes through a max. These variations are ascribed to rapid decrease in the inner



anisotropy of the particles as  $T$  rises. The form of the  $H$  function of the anisotropy of goethite sols varies with  $T$ . Orientability decreases rapidly in the order  $\alpha\text{-Fe}_2\text{O}_3 > \text{goethite} > \text{basic salt}$ . Orientation and de-orientation in the magnetic field are extremely rapid compared with  $\text{V}_2\text{O}_5$  sols. Under the influence of light the rate of variation of  $\delta$  with time increases materially, and moderate warming has an even more marked effect. In light of short wavelength all the sols are strongly dichroic. All natural  $\text{Fe}_2\text{O}_3$  sols exhibit a positive, usually weak, streaming double refraction. R. C.

**Change of stability of sols of various concentrations with their purity.** S. GHOSH and R. N. MITTRA (J. Indian Chem. Soc., 1933, 10, 471—476).—Experiments with  $\text{ThO}_2$  sols show that if the sol contains large amounts of stabilising electrolyte it may behave abnormally on dilution towards coagulation by univalent electrolytes, although additive effects are shown when the sol is coagulated by a mixture of electrolytes. E. S. H.

**Kinetics of slow coagulation. I, II.** D. N. GHOSH (J. Indian Chem. Soc., 1933, 10, 509—516, 517—527).—I. Smoluchowski's equation is not applicable to the slow coagulation of a monodisperse S sol which is free from ionogenic impurities. The difference between rapid and slow coagulation is ascribed to the almost complete discharge which occurs in the rapid process.

II. The S-shaped slow-coagulation curves are explained on the ground that the rate at any stage depends on (a) the no. of primary particles, and (b) the no. of multiple particles. The adherence factor  $\epsilon$  in Smoluchowski's theory is not a const., but is a function of time, increasing as the size of the multiple particles grows. E. S. H.

**Viscosity of cellulose solutions.** (MME.) A. DOBRY and J. DUCLAUX (Compt. rend., 1933, 197, 1318—1320).—The influence of the nature of the solvent on the viscosity of cellulose nitrate solutions has been examined. C. A. S.

**Heat development and work performance in the dilution of lyophilic sols.** I. OKAMURA (Kolloid-Z., 1933, 65, 175—178).—The heat of dilution and osmotic pressure of solutions of cellulose nitrate and acetate and ethylcellulose in  $\text{COMe}_2$  and  $\text{MeOAc}$  respectively have been determined. The differential work of swelling is  $>$  the differential heat of dilution. E. S. H.

**Lyophilic colloids. XIX. Influence of neutral salts and non-electrolytes on isoelectric gelatin sol.** L. W. J. HOLLEMAN, H. G. B. DE JONG, and R. S. T. MODDERMAN (Kolloid-Beih., 1933, 38, 439—463; cf. A., 1933, 23).—Determinations of the viscosity of isoelectric gelatin sols show that  $(\eta_r - \eta_0)/\eta_0$  is increased by small amounts of electrolytes, the effect increasing with increasing valency of the anion. The lyotropic series is also encountered, but in the reverse order. The results are explained by assuming that the electrophoretic null point at the isoelectric point represents a compensation of two weak, opposite charges. A similar effect is observed with  $\text{MeOH}$ ,  $\text{EtOH}$ ,  $\text{PrOH}$ , and methane. E. S. H.

**Lyophilic colloids. XX. Capillary-electric charge and hydration as state variables of hydrophilic gels. Formation of starch paste.** J. A. VAN DER HOEVE, H. G. B. DE JONG, and H. R. KRUYT (Kolloid-Beih., 1933, 39, 105—138; cf. A., 1933, 779).—The influence of electrolytes and non-electrolytes on the temp. at which potato-starch forms a paste with  $\text{H}_2\text{O}$  has been investigated. At low concns. of electrolyte the temp. rises with increasing concn., the effect being the greater the higher is the valency of the cation; at higher concns. lyotropic influences come into play. Non-electrolytes favour the formation of paste when positively adsorbed (tannin), but have the opposite effect when negatively adsorbed ( $\text{EtOH}$ ). The influence of electrolytes or non-electrolytes on the formation of paste bears no relation to their influence on sols of starch. A mechanical theory of the formation of starch paste is developed. E. S. H.

**Odometer observation as an aid in the elucidation of gel structure.** K. VON TERZAGHI (Kolloid-Z., 1933, 65, 129—148).—A discussion of published work on the pressure and heat of swelling of gels and the pressure-vol. relations of coarsely disperse gel models. The heat developed is due partly to the internal friction of  $\text{H}_2\text{O}$  streaming through the structure, and partly to the change of state of  $\text{H}_2\text{O}$  from the ordinary to the boundary layer state. E. S. H.

**Mol. wt. of gelatin.** W. R. ATKIN (J. Soc. Leather Trades Chem., 1933, 17, 575—582).—The min. mol. wt. of gelatin (I) calc. on the assumption that the (I) mol. contains two histidine mols. is 34,500, which is  $>$  that obtained by Lloyd (B., 1922, 224, 907). There are 360  $\text{NH}_2$ -acid groups in the (I) mol. and 80% have been allocated to individual  $\text{NH}_2$ -acids. The remaining 20% have a higher O content and must contain OH groups. The mean mol. wt. of a (I)  $\text{NH}_2$ -acid is 114, which agrees with X-ray data. D. W.

**Electric conductivity of gelatin.** (MLE.) S. VEIL (Compt. rend., 1933, 197, 1044—1046; cf. A., 1932, 226). The current-time curve of a gelatin film shows a sharp rise to a max. in the first 0.5 hr., followed by a sharp fall in the next 1.5 hr., and then a slow decline to zero. The current-voltage curve accords initially with Ohm's law, but there is a subsequent steady decrease in the current/voltage ratio, resulting finally in a const. "saturation" current. Agar agar behaves similarly though less clearly so. C. A. S.

**Protein systems. II. Rate of freezing and shape of particle in protein solutions.** H. H. WEBER and C. PULLEN (Biochem. Z., 1933, 266, 153—161).—The rate of freezing of supercooled (down to  $-8^\circ$ ) protein solutions is retarded by 10—20% when the colloidal particles are spherical (ovalbumin, myosin), but is unaffected when they are rod-shaped (ovoglobulin, Edsall's myosin). The retardation is independent of  $[\text{H}^+]$  ( $p_H$  4.9—9.4), of the extent of supercooling, and of the presence or absence of electrolytes. W. McC.

**Activity coefficient of ovalbumin in presence of ammonium sulphate.** C. F. FAIRLEY (J. Phys.



ical Chem., 1933, 37, 1075—1082).—The log of the activity coeff. of ovalbumin in presence of  $(\text{NH}_4)_2\text{SO}_4$  deduced from osmotic data is a linear function of the salt concn. The activity coeffs. agree with solubility measurements when the composition of the solid phase is taken into account. H. S. P.

**Temperature coefficients of viscosity of liquids in relation to the structure of caoutchouc in solution.** W. F. BUSSE and E. KARRER (Kolloid-Z., 1933, 65, 211—223).—The relation  $1/\eta = KS^{-1}e^{-q/kT}$ , where  $\eta$  is the viscosity,  $S$  the shearing force,  $r$  the particle radius,  $T$  the abs. temp.,  $K$  and  $k$  are consts., and  $q$  is an energy factor, is derived theoretically and confirmed for solutions of caoutchouc in various org. solvents over a range of systems in which  $\eta$  varied in the ratio 1:10<sup>6</sup>. The relation is not valid when irreversible changes occur in the solution or for solutions in  $\text{Et}_2\text{O}$  near the setting point; mastication, heating, and irradiation produce irreversible changes which displace  $q$  and  $K$  in the direction of lower concn. The results suggest that there is no temp.-variable equilibrium between higher and lower polymerides. The high viscosity cannot be attributed solely to solvation, but is mainly due to the mechanical inclusion of considerable amounts of solvent in the network of the disperse phase. E. S. H.

**Properties of liquid silk.** D. ONGARO (Giorn. Chim. Ind. Appl., 1933, 15, 506—510).—Silk has been obtained in the liquid state direct from the sericogenic glands of the silkworm, without the aid of chemical agents. The silk solution is in unstable equilibrium and its hardening is a true coagulation, even when caused by mechanical agencies. Silk solutions from races or crosses of silkworms with coloured cocoons may sometimes ppt. their pigment some time prior to setting, the coagulum then having a white colour identical with that of coagula from races with white cocoons. The Au index and the protective power of the Au solution are almost const. for solutions from the different races. Under the ultra-microscope the fibroin solution exhibits active Brownian movement, which is much slower than that of the Au solutions. Unlike the coagula obtained by mechanical action, those formed spontaneously from the silk solution are optically inactive. In 1% solution, fibroin has  $[\alpha]_D$  —39.0°. T. H. P.

**Fine structure of silk.** V. Swelling phenomena in fibroin threads. K. OHARA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 22, 216—232).—Swelling of fibroin produced by conc. neutral salt solutions etc. is related to micellar structure. The velocity of swelling of the central zone is < that of the outer layer, resulting in the production of spherical and fan-like forms. The external membrane is semipermeable. R. S.

**Displacement of equilibrium.** R. ÉTIENNE (Compt. rend., 1933, 197, 1117; cf. A., 1933, 1118).—The error suggested by Verschaffelt is non-existent. C. A. S.

**Le Chatelier's principle.** J. M. BIJVOET (Chem. Weekblad, 1933, 30, 742—747).—The apparently anomalous behaviour of the  $\text{N}_2\text{—H}_2$  system on addition

of  $\text{N}_2$  at const. pressure is explicable in terms of the le Chatelier theorem as developed by Wagner.

H. F. G.

**Amino-sulphonic acids. III. Dissociation constants of taurine derivatives.** B. JOSEPHSON (Biochem. Z., 1933, 266, 9—17; cf. A., 1933, 1012).—In taurine, its *N*-alkylated derivatives ( $\text{Me}$ ,  $\text{Me}_2$ ,  $\text{Pr}^n$ , heptyl,  $\text{Ph}$ ,  $\text{CH}_2\text{Ph}$ ) and  $\text{CO}_2\text{H—C}_6\text{H}_4\text{—NH—[CH}_2\text{]}_2\text{—SO}_3\text{H}$  (I) the  $\text{—SO}_3\text{H}$  has a very high dissociation const. (II) which varies with the nature and no. of the substituents. A similar variation occurs in the (always very low) (II) of the substituted  $\text{—NH}_2$ . (I) distinctly exhibits two (II), but taurodeoxycholic acid, probably because its  $\text{—CO}_2\text{H}$  is not free, exhibits only one.

W. McC.

**Dissociation of water in lithium bromide solutions at 25°.** J. E. VANCE (J. Amer. Chem. Soc., 1933, 55, 4518—4521).—The dissociation const. of  $\text{H}_2\text{O}$  in aq.  $\text{LiBr}$  has been calc. from e.m.f. measurements of the cells  $\text{H}_2|\text{LiOH}(m_1), \text{LiBr}(m_2)|\text{AgBr}|\text{Ag}$  and  $\text{H}_2|\text{LiBr}(m), \text{HBr}(0.01)|\text{AgBr}|\text{Ag}$  and from determinations of the activity coeff. of 0.01*M*- $\text{HBr}$ . E. S. H.

**Thermodynamics of ionised water in potassium and sodium bromide solutions.** H. S. HARNED and W. J. HAMER (J. Amer. Chem. Soc., 1933, 55, 4496—4507).—The dissociation const. of  $\text{H}_2\text{O}$  has been derived from measurements of e.m.f. of the cells  $\text{H}_2|\text{K}(\text{Na})\text{OH}(0.01), \text{K}(\text{Na})\text{Br}|\text{AgBr}|\text{Ag}$  and  $\text{H}_2|\text{HBr}(0.01), \text{K}(\text{Na})\text{Br}|\text{AgBr}|\text{Ag}$  in aq. solution at 0—60°. The vals. of the normal potential of the  $\text{Ag}|\text{AgBr}$  electrode are given with an accuracy of  $\pm 0.01$  mv. by  $E_0 = 0.07169 - 5.259 \times 10^{-4}(t - 25) - 3.022 \times 10^{-6}(t - 25)^2$ . The total heat of dissociation of  $\text{H}_2\text{O}$  and the relative partial mol. heat content of  $\text{H}^+$  and  $\text{OH}^-$  in aq.  $\text{KCl}$ ,  $\text{KBr}$ , and  $\text{NaBr}$  solutions at 0—60° have been calc. The results agree with data obtained from determinations of heats of neutralisation at 20°. E. S. H.

**Calculation of the equilibria in keto-enol tautomerism.** G. W. WHELAND (J. Chem. Physics, 1933, 1, 731—736).—Linking and resonance energies deduced from empirical data have been applied to calculate keto-enol equilibria. The method has been used for  $\text{PhOH}$ , resorcinol, phloroglucinol,  $\text{CH}_2\text{Ac}_2$ , hydroxymethylene ketones,  $\text{Et}$  acetoacetate, acetylmalonate, and malonate,  $\text{CHAc}_3$ ,  $\text{CH}(\text{CO}_2\text{Et})_3$ , 1:2-cyclohexadione,  $\text{Ac}_2$ . The results are in qual. agreement with experiment. H. S. P.

**Influence of strength of base on formation of aluminotartaric complexes.** PARISELLE (Compt. rend., 1933, 197, 1214—1216; cf. A., 1926, 957; 1927, 856).— $\text{KOH}$  behaves similarly to  $\text{NaOH}$ , but with  $\text{NH}_3$ , aq. the change in rotation indicates that  $(\text{NH}_4)_2(\text{AlO})\text{C}_4\text{H}_3\text{O}_6$  is only partly formed even with large excess of  $\text{NH}_3$ . Piperidine behaves similarly. With  $\text{C}_3\text{H}_5\text{N}$  and quinoline no aluminotartarate is formed; excess of base produces negative rotation and these bases apparently act merely as solvents.

C. A. S.

**Equilibrium constants in terms of activities derived from cryoscopic data. II. Dissociation of pyridine *o*-chlorophenoxide in *p*-dichlorobenzene.** H. M. GLASS and W. M. MADGIN (J.C.S., 1933, 1431—1435).—The equilibrium const., calc. on an activity basis, is 34.78 at the f.p. of the solution.



This, combined with the previous data in  $C_6H_6$  at its f.p. (A., 1933, 350), gives 6800 g.-cal. for the mol. heat of formation in solution, ignoring any slight variation in  $K$  due to the change of solvent. D. R. D.

**Activity of ammonia in ammonium chloride solutions.** H. E. MATTHEWS and C. W. DAVIES (J.C.S., 1933, 1435—1439).—The distribution of  $NH_3$  between  $CHCl_3$  and  $H_2O$  has been measured at 25° over the range 0—3*M* in the  $H_2O$  layer, and with concns. of  $NH_4Cl$  in the  $H_2O$  up to 0.2*M*. The calc. activities suggest that the salt exerts three superposed effects. D. R. D.

**Application of solubility data to determination of activity coefficients of acid molecules in solutions of sodium and potassium chloride.** E. LARSSON (Svensk Kem. Tidskr., 1933, 45, 236—245).—A review of the author's work. R. P. B.

**Limitations of solubility method for determining dissociation constant.** W. V. BHAGWAT and S. S. DOOSAJ (J. Indian Chem. Soc., 1933, 10, 477—490).—The dissociation consts. of formic, acetic, salicylic, and citric acids have been determined, using the formula  $K_2 = K_1 - a(c - b + a)/(b - a)^2$  (cf. Dhar, A., 1913, ii, 565). The vals. obtained increase with increasing concn. of the acid used. The effect of dilution depends on which of two opposite factors predominates—hydrolysis of the salt and degree of dissociation. E. S. H.

**"Salting-out" and "salting-in" of weak acids.** I. Activity coefficients of the molecules of *o*-, *m*-, and *p*-chlorobenzoic acids in aqueous salt solutions. II. Activity coefficients of the molecules of *o*-, *m*-, and *p*-hydroxybenzoic acids in aqueous salt solutions. A. OSOR and M. KILPATRICK (J. Amer. Chem. Soc., 1933, 55, 4430—4440, 4440—4444).—I. From determinations of the solubilities of  $C_6H_4Cl \cdot CO_2H$  in aq. solutions of alkali salts the mol. solubilities and activity coeffs. have been calc. Both "salting-out" and "salting-in" are observed with the same weak acid. Activity coeffs. of the mols. of  $C_6H_4Cl \cdot CO_2H$  and of  $BzOH$  have the same vals. at corresponding concns.

II. Similar data are given for  $OH \cdot C_6H_4 \cdot CO_2H$ . "Salting-out" consts. in  $KCl$  solutions decrease with transfer of  $OH$  to the *m*- and *p*-positions, respectively. E. S. H.

**Activity coefficient of thallos chloride in protein systems.** J. C. H. STONE and C. F. FAILEY (J. Physical Chem., 1933, 37, 935—949; cf. A., 1932, 802).—Activity coeffs. of  $TlCl$  in solutions of ovalbumin, edestin, excelsin, and hæmoglobin have been calc. from solubility measurements. The changes in solubility are related to the calc. ionic strength of the solutions. F. L. U.

**Binary systems in two phases.** I.  $HCl$ - $Kr$ . II.  $HCl$ - $C_3H_8$ . G. GLOCKER, D. L. FULLER, and C. P. ROE (J. Chem. Physics, 1933, 1, 714—716).—The *p*-*T*-*x* relations of the mixtures  $HCl$ - $Kr$  and  $HCl$ - $C_3H_8$  have been measured. No mixture showed > one liquid phase and retrograde condensation was observed in all cases. H. S. P.

**System lead acetate-acetic acid.** A. W. DAVIDSON and W. CHAPPELL (J. Amer. Chem. Soc., 1933,

55, 4524—4525).— $Pb(OAc)_2 \cdot 0.5AcOH$  is the stable solid phase below 56° over a wide concn. range, although this phase does not appear to separate without inoculation. Above 56°  $Pb(OAc)_2$  is formed. E. S. H.

**System  $Hg_2O$ - $N_2O_5$ - $H_2O$ .** H. G. DENHAM and C. V. FIFE (J.C.S., 1933, 1416—1419).—Schreinemakers' residue method has been applied to the system at 25°. In stable equilibrium with solution there exist  $2Hg_2O \cdot N_2O_5 \cdot H_2O$ ,  $5Hg_2O \cdot 3N_2O_5 \cdot 3H_2O$ , and  $4Hg_2O \cdot 3N_2O_5 \cdot H_2O$ .  $Hg_2(NO_3)_2 \cdot 2H_2O$  exists in two orthorhombic modifications, but the existence of other hydrates of the normal salt could not be confirmed. H. F. G.

**Equilibria in the system ammonium nitrate-sodium nitrate-water.** E. A. NIKITINA (J. Gen. Chem. Russ., 1933, 3, 513—518).—The equilibrium relations have been studied at 0°, 15°, 20°, 30°, 40°, 60°, 80°, and 98°. R. T.

**System cadmium sulphate-sulphuric acid-water.** R. ARDITTI (Compt. rend., 1933, 197, 1209—1211).—On pouring  $H_2SO_4$  into saturated aq.  $CdSO_4$  the ppt. always consists first of  $CdSO_4 \cdot H_2O$  which is stable within certain limits of concn. of  $H_2SO_4$  (varying with temp.), below which it passes slowly into  $3CdSO_4 \cdot 8H_2O$ , and above into  $CdSO_4 \cdot H_2SO_4$ . Solubility curves for 0°, 16°, 21°, and 33.5° are given. Density, refraction, conductivity, and viscosity-wt.-%  $H_2SO_4$  curves for similar solutions show max. (or min.) at the transition point  $3CdSO_4 \cdot 8H_2O \rightarrow CdSO_4 \cdot H_2O$  (cf. A., 1897, ii, 316). C. A. S.

**System  $Na_2S_2O_3$ - $Ag_2S_2O_3$ - $H_2O$  at 25°.** H. BASSETT and J. T. LEMON (J.C.S., 1933, 1423—1427).— $Na_2Ag(S_2O_3)_2 \cdot 2H_2O$ ,  $Na_5Ag_3(S_2O_3)_4 \cdot 2H_2O$ ,  $NaAgS_2O_3 \cdot H_2O$ , and  $NaAg_3(S_2O_3)_2 \cdot H_2O$  are formed. No isomerism is observed; the yellow forms reported (A., 1907, ii, 347; 1922, ii, 57) are probably partly decomposed materials. D. R. D.

**Ternary system diphenyl-diphenylamine-benzophenone.** H. H. LEE and J. C. WARNER (J. Amer. Chem. Soc., 1933, 55, 4474—4477; cf. A., 1933, 228).—Two stable ternary eutectics occur. One at 18.8° contains  $Ph_2$  30.5 mol.-% and  $NHPh_2$  49.0 mol.-%. The other at 16.5° contains  $Ph_2$  30.0 mol.-% and  $COPh_2$  52 mol.-%. Evidence for the existence of two metastable ternary eutectics is given. E. S. H.

**System allyl alcohol-iodine-di-iodopropyl alcohol.** F. G. CAUGHLEY and P. W. ROBERTSON (J.C.S., 1933, 1323—1326).—The dissociation of di-iodopropyl alcohol (I) in  $CCl_4$  solution into I and allyl alcohol (II) corresponds with a gas reaction of the second type; the degree of dissociation at 25° is 28% at dilution 20 and 58% at dilution 160, and 51% at 50° and dilution 20. Light accelerates the forward and reverse reactions, without altering the equilibrium, which is almost independent also of the solvent ( $C_6H_6$ ,  $PhMe$ ,  $C_6H_{14}$ ). The dissociation is unimol. and the reverse reaction bimol., and both are but slightly influenced by catalysts. The calc. heat of formation of (I) from I and (II) is 12.3 kg.-cal. H. F. G.

**Phosphoric acid and the phosphates.** III. Equilibria between phosphoric acid and the



hydrates of calcium sulphate. A. SANFOURCHE and A. KRAPIVINE (Bull. Soc. chim., 1933, [iv], 53, 970—973).—The solubility of  $\text{CaSO}_4$  shows a max. when the solution contains 200—300 g.  $\text{P}_2\text{O}_5$  per litre. The composition of the solid phase is given.

R. S.

Reciprocal salt-pair  $\text{Ca}(\text{NO}_3)_2 + 2\text{KCl}$  at  $-10^\circ$ . I. KRITSCHESKI and R. K. IZKOVITSCH (Z. anorg. Chem., 1933, 215, 103—104).—Compositions of solid and liquid phases for the system  $\text{Ca}(\text{NO}_3)_2\text{—KCl—H}_2\text{O}$  at  $-10^\circ$  have been determined. The industrial production of  $\text{KNO}_3$  at this temp. is not considered practicable.

F. L. U.

Third law of thermodynamics. V. NJEGOVAN (Coll. Czech. Chem. Comm., 1933, 5, 415—423; cf. A., 1933, 351).

D. R. D.

Attempt to express the chemical constant thermodynamically. V. NJEGOVAN (Coll. Czech. Chem. Comm., 1933, 5, 424—426).—The author's conception of "internal effect" (A., 1933, 351) is applied to calculation of the chemical const.

D. R. D.

Free energy of ozone. L. S. KASSEL (J. Chem. Physics, 1933, 1, 414—417).—The three fundamental frequencies deduced by Gerhard (A., 1933, 208) for the  $\text{O}_3$  mol. are not in perfect agreement with experiment. From these vals., however, the free energy is calc. as  $S_{298.1} = 57.0$ , compared with  $S_{273} = 86.5$  from e.m.f. measurements. The max. partial pressure of  $\text{O}_3$  in equilibrium with  $\text{O}_2$  and  $\text{O}$  at 1 atm. is  $1.0 \times 10^{-6}$  atm. at  $3400^\circ$  abs. The 1%  $\text{O}_3$  obtained by heating filaments at  $2300^\circ$  abs. in liquid  $\text{O}_2$  must be formed from at.  $\text{O}$  in the cold regions.

J. W. S.

Thermal dissociation of cyanogen into cyanide radicals. G. B. KISTIAKOWSKY and H. GERSHINOWITZ (J. Chem. Physics, 1933, 1, 432—439; cf. A., 1932, 684).—From measurement of the pressures at which absorption bands due to  $\text{CN}$  produced in the dissociation of  $\text{C}_2\text{N}_2$  at different temp. near  $1200^\circ$  have equal intensities, the heat of dissociation is calc. to be  $77 \pm 4$  kg.-cal. By using existing thermochemical data this is shown to be also the most probable energy of the C—C linking. Similarly calc. vals. for  $\text{HCN} \rightarrow \text{H} + \text{CN}$  and the energy of the C—H linking are  $94.5 \pm 4$  kg.-cal. The heat of sublimation of  $\text{C}$  (graphite) is 154 kg.-cal.

F. L. U.

Heat of dissociation of the carbon-carbon linking. J. B. CONANT (J. Chem. Physics, 1933, 1, 427—431).—Heats and free energies of dissociation of the C—C linking in a series of disubstituted dioxanths and tetraphenylethanes have been calc. on the basis of Ziegler's data for  $\text{C}_2\text{H}_6$  (A., 1929, 1010). The effect of different substituent groups on the heat of dissociation of  $\text{C}_2\text{H}_6$  has been estimated.

F. L. U.

Energy of dissociation of water by symmetrical vibrations and products of this dissociation. M. MAGAT (Compt. rend., 1933, 197, 1216—1218).—A revised and more accurate method of calculating the vibration frequencies of  $\text{H}_2\text{O}$  gives its energy of dissociation as  $269 \pm 3$  kg.-cal. (cf. A., 1933, 552). The difference between this and  $218 \pm 1$  kg.-cal., deduced from thermochemical and spectro-

scopic data, corresponds closely with the energy of activation of the  $\text{O}$  atom ( $45.2$  kg.-cal.). Thus  $\text{H}_2\text{O}$  is dissociated into  $2\text{H}$  and activated  $\text{O}$  (cf. A., 1929, 11; 1931, 1109).

C. A. S.

Thermodynamic properties of the  $\text{H}^1\text{H}^2$ ,  $\text{H}^2\text{H}^2$  molecules and compounds containing the  $\text{H}^2$  atom. H. C. UREY and D. RITTENBERG (J. Chem. Physics, 1933, 1, 137—143).—Calc. vals. for the summation of state and free energies of the mols.  $\text{H}^1_2$ ,  $\text{H}^2_2$ , and  $\text{H}^1\text{H}^2$  are tabulated for the temp. range  $20.4\text{—}700^\circ$  abs., and their dependence on the spin and statistics of  $\text{H}^2$  is discussed. The influence of the  $\text{H}$  isotope on equilibrium const. is illustrated for the reactions  $\text{H}_2 + \text{H}_2^* = 2\text{H}^1\text{H}^2$ ,  $\text{H}_2 + 2\text{H}^2\text{Cl} = \text{H}_2^* + 2\text{H}^1\text{Cl}$ , and  $\text{H}_2 + 2\text{H}^2\text{I} \rightarrow \text{H}_2^* + 2\text{H}^1\text{I}$ .

N. M. B.

Free energy of steam and carbon dioxide. A. R. GORDON (J. Chem. Physics, 1933, 1, 308—312).—Calc. equilibrium consts. for the water-gas equilibrium agree well with experimental vals. over the range  $700\text{—}1259^\circ$  abs. For the producer-gas equilibrium, theory predicts greater dissociation of  $\text{CO}$  into  $\text{CO}_2$  and graphite than is found in practice. This may be explained if graphite has zero point entropy  $>$  that given by the third law of thermodynamics. Equilibrium consts. for the reaction  $2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2 + \text{O}_2$  are tabulated.

D. R. D.

Entropy of nitrous oxide and carbon dioxide. W. H. RODEBUSH (Physical Rev., 1932, [ii], 40, 113).—The calc. entropy of  $\text{N}_2\text{O}$ , based on the views of Plyler and Barker (A., 1932, 108), is  $52.4$  entropy units at  $298^\circ$  abs.; that of  $\text{CO}_2$ , based on the data of Martin and Barker (*ibid.*, 982), is  $51.0$  units at  $298^\circ$  abs.

L. S. T.

Thermodynamic constants of iodine monochloride, iodine monobromide, and bromine monochloride in carbon tetrachloride solutions. C. M. BLAIR, jun., and D. M. YOST (J. Amer. Chem. Soc., 1933, 55, 4489—4496).—From the v.p. of  $\text{ICl}$  and  $\text{Cl}_2$ , heats of dissolution of  $\text{I}$  and  $\text{Br}$ , and heats of formation of  $\text{ICl}$ ,  $\text{IBr}$ , and  $\text{BrCl}$ , the following data have been obtained: free energy  $\text{I } 2660$ ,  $\text{Br } 389$ ,  $\text{Cl}_2$   $1110$ ,  $\text{ICl } -2133$ ,  $\text{IBr } -153$ ,  $\text{BrCl } 393$ ; heat content  $\text{I } 5990$ ,  $\text{Br } 712$ ,  $\text{Cl}_2$   $-3720$ ,  $\text{ICl } -2835$ ,  $\text{IBr } 1721$ ,  $\text{BrCl } -1882$ ; entropy  $\text{I } 39.1$ ,  $\text{Br } 36.8$ ,  $\text{Cl}_2$   $37.1$ ,  $\text{ICl } 38.3$ ,  $\text{IBr } 38.5$ ,  $\text{BrCl } 36.9$ . Reaction between  $\text{Br}$  and  $\text{Cl}_2$  in  $\text{CCl}_4$  solution is appreciably slower than between  $\text{I}$  and  $\text{Cl}_2$  or  $\text{I}$  and  $\text{Br}$ .

E. S. H.

Free energy, entropy, and heat capacity of bromine and hydrogen bromide from spectroscopic data. A. R. GORDON and C. BARNES (J. Chem. Physics, 1933, 1, 692—695).—The equilibrium consts. for the reaction  $\text{Br}_2 \rightleftharpoons 2\text{Br}$  calc. from spectroscopic data differ from Bodenstein's experimental vals. Similar calculations on the dissociation of  $\text{HBr}$  give results which agree with the e.m.f. measurements of Bodenstein and Geiger, but disagree with Falckenstein's data.

H. S. P.

Heat capacities of gaseous mono- and dimethylamine. W. A. FELSING and F. W. JESSEN (J. Amer. Chem. Soc., 1933, 55, 4418—4422).—The mol. heat capacities between  $0^\circ$  and  $50^\circ$  are given by  $9.530 + 0.1108T - 1.212 \times 10^{-4}T^2$  and  $5.595 - 0.1148T + 2.750 \times 10^{-4}T^2$  for  $\text{NH}_2\text{Me}$  and  $\text{NHMe}_2$ , respectively.



The corresponding vals. of  $\gamma$  are 1.202 and 1.149, respectively. E. S. H.

**Evaluation of the series which arise in the calculation of thermodynamic quantities from spectroscopic data.** A. R. GORDON and C. BARNES (J. Chem. Physics, 1933, 1, 297—307).—Tables are given for obtaining the free energy, entropy, and heat capacity at high temp. from the mol. spectrum of a gas, and simplified methods of calculation are given for conditions outside the range of the tables. The procedure is illustrated by calculations for  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{HCl}$ ,  $\text{CO}$ ,  $\text{O}_2$ , and  $\text{NO}$ . D. R. D.

**Mathematical methods for computing thermodynamic functions from spectroscopic data.** L. S. KASSEL (J. Chem. Physics, 1933, 1, 576—585).—Theoretical. Vals. for the entropy, heat content, and heat capacity of  $\text{CO}$  from  $50^\circ$  to  $1400^\circ$  abs. are recorded. H. J. E.

**Heat capacity and entropy of silver sulphate from  $14^\circ$  to  $300^\circ$  abs. Entropy of the sulphate ion.** W. M. LATIMER, J. F. G. HICKS, jun., and P. W. SCHUTZ (J. Chem. Physics, 1933, 1, 424—425).—The heat capacity of  $\text{Ag}_2\text{SO}_4$  has been measured from  $14^\circ$  to  $300^\circ$  abs. and the entropy determined graphically as  $S_{298.1} = 47.76$  e.u. Coupling this val. with the entropy of solution and the entropy of the  $\text{Ag}^+$  ion leads to a val. 2.8 e.u. for the entropy of the  $\text{SO}_4^{--}$  ion at  $298.1^\circ$  abs. J. W. S.

**Heat capacities and entropies of calcium and barium sulphates from  $15^\circ$  to  $300^\circ$  abs. Entropy and free energy of the sulphate ion.** W. M. LATIMER, J. F. G. HICKS, jun., and P. W. SCHUTZ (J. Chem. Physics, 1933, 1, 620—624; cf. A., 1933, 466).—The heat capacities of  $\text{BaSO}_4$  and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  have been measured from  $15^\circ$  to  $300^\circ$  abs. Vals. for  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  vary slightly with crystal size. The entropies at  $298.1^\circ$  abs. are 31.51 and 46.36 e.u., respectively. The entropy and free energy of formation of  $\text{SO}_4^{--}$  are 3.5 e.u. and  $-175,300$  g.-cal., respectively. H. J. E.

**Partial and integral heats of dilution of cadmium sulphate solutions from electromotive force measurements.** V. K. LA MER and W. G. PARKS (J. Amer. Chem. Soc., 1933, 55, 4343—4355; cf. A., 1931, 912).—The e.m.f. of the cell  $\text{Cd}(\text{saturated amalgam})|\text{CdSO}_4, \text{PbSO}_4|\text{Pb}$  (saturated amalgam) has been determined at  $0^\circ$ ,  $10^\circ$ ,  $20^\circ$ , and  $30^\circ$  for concns. of  $\text{CdSO}_4$  between 0.0005 and 0.02*M*. Activity coeffs. are given and previous work is confirmed. The following thermodynamic vals. have been determined for the reaction:  $E^\circ 0.00905V$ ,  $(\partial E^\circ/\partial T)_p - 6.60 \times 10^{-4}$ ,  $(\partial^2 E^\circ/\partial T^2)_p - 1.73 \times 10^{-5}$ ,  $\Delta F^\circ 417.6$  g.-cal.,  $\Delta H^\circ - 9198$  g.-cal.,  $C_p^\circ - 229$  g.-cal. per degree. The calc. partial mol. heat capacity of  $\text{CdSO}_4$  is approx.  $-200$  g.-cal. per degree per mol. at  $15^\circ$ . E. S. H.

**Entropy of a crystalline solution of silver bromide and silver chloride in relation to the third law of thermodynamics.** E. D. EASTMAN and R. T. MILNER (J. Chem. Physics, 1933, 1, 444—456).—The free energy of formation of mixed crystals of  $\text{AgCl}$  and  $\text{AgBr}$  from the pure components has been determined by e.m.f. measurements, and the change in heat content by dissolution of the mixed crystals

and the components respectively in aq.  $\text{Na}_2\text{S}_2\text{O}_3$ . The entropy change obtained from these results is about 1.1 g.-cal. per degree. Sp. heat measurements over the range  $15$ — $298^\circ$  abs. show that at no point does the change in heat capacity differ from 0. Assuming that this remains true below  $15^\circ$  abs., it follows that the entropy change at  $0^\circ$  abs. is the same as at  $298^\circ$  abs. The result is discussed theoretically and a restricted formulation of the third law is suggested. F. L. U.

**New chemical theory: its origin and significance.** A. GOSSELIN (Bull. Soc. chim., 1933, [iv], 53, 923—945).—Theoretical. An extension of Werner's theory with reference to thermochemical properties. R. S.

**Electrolytic conduction in aqueous solutions.** A. C. D. RIVETT (Rept. Austral. Assoc. Adv. Sci., 1933, 21, 420—431).—Liversidge Lecture. An historical review of electrolytic conduction and outline of newer conception developed by Masson. R. S.

**Conductivity of mixtures of electrolytes. II.** V. K. SEMENTSCHENKO and V. V. SERPINSKI (J. Gen. Chem. Russ., 1933, 3, 470—477).—The conductivities of the following aq. solutions at  $25^\circ$ : 0.000125—0.2*N*- $\text{KCl}$ ; 0.001—1.0*N*- $\text{NaN}_3$ ; 0.000125—0.005*N*- $\text{NaBr}$ ; 0.000166—2*N*- $\text{MgSO}_4$ ; 3:1, 1:1, and 1:3 mixtures of  $\text{KCl}$  and  $\text{NaN}_3$  (total concn. 0.001*N* and 0.1*N*), and of  $\text{KCl}$  and  $\text{MgSO}_4$  (total concn. 0.001—2*N*); 1:1:1 and 1:1:2 mixtures of  $\text{KCl}$ ,  $\text{NaBr}$ , and  $\text{MgSO}_4$  (total concn. 0.0005*N* and 0.005*N*) are in closer agreement with Onsager's formula than are the vals. obtained by previous authors. The vals. for mixtures are additive; this is ascribed to the reduced mobility of more, and the enhanced mobility of less, mobile ions. R. T.

**Conductivity measurements of thorium and other jelly-forming systems.** S. PRAKASH (J. Physical Chem., 1933, 37, 907—916; cf. A., 1932, 1202).—The electrical conductivity of systems forming jellies of  $\text{Th}$  phosphate, arsenate, and molybdate, and of  $\text{Fe}^{\text{III}}$  arsenate and  $\text{Al}(\text{OH})_3$  remains const. during setting, and increases after several days. The temp. coeff. is const. between  $35^\circ$  and  $60^\circ$ . F. L. U.

**Conductance of bases in liquid ammonia.** W. W. HAWKES (J. Amer. Chem. Soc., 1933, 55, 4422—4430).—Data are recorded for solutions of  $\text{KNH}_2$  and  $\text{NaNH}_2$  up to dilutions of 52,000 and 36,000 litres, respectively. An upper limit for the dissociation const. of  $\text{NaNH}_2$  is  $2.65 \times 10^{-5}$ . The data deviate from the theory of Fuoss and Kraus (A., 1933, 464) and from the mass action law. E. S. H.

**Electro-endosmosis and electrolytic water transport. III. Solutions of copper salts.** H. C. HEPBURN (Proc. Physical Soc., 1933, 45, 755—764; cf. A., 1931, 1236; 1932, 698).—Measurements have been made of the liquid transport produced by the passage of an electric current through aq.  $\text{CuCl}_2$  and  $\text{Cu}(\text{NO}_3)_2$  by the parchment-paper membrane method, the results being compared with data for  $\text{CuSO}_4$ . The electro-endosmotic effect of the diaphragm is discussed in terms of the influence of the electrical charge of the diaphragm and of the thickness of the double layer formed at the diaphragm-solution



interface. For  $\text{CuCl}_2$  the direction of liquid transport is reversed above 0.1*N*, this reversal being attributed to the effect of the electrolytic  $\text{H}_2\text{O}$  transport.

J. W. S.

**Ionising powers of solvents.** A. H. W. ATEN and L. BOERLAGE (*Rec. trav. chim.*, 1933, 52, 1046—1051).—Theoretically, the presence of positive and negative partial moments in a mixture of solvents should tend to increase the ionising power. This is confirmed by measurements of the conductivities of solutions of  $\text{NH}_4\text{EtCl}$ ,  $\text{NH}_4\text{Et}_2\text{Cl}$ ,  $\text{NH}_4\text{Et}_3\text{Cl}$ , and  $\text{NEt}_4\text{Cl}$  in mixtures of  $\text{NH}_4\text{Ph}$  with  $\text{PhNO}_2$ , and with  $\text{PhCN}$ , but does not hold for mixtures of  $\text{NH}_4\text{Ph}$  and  $\text{PhBr}$ .

H. F. G.

**Electrodes of third kind.** M. LE BLANC and O. HARNAPP (*Z. physikal. Chem.*, 1933, 166, 321—342).—For the satisfactory working of such an electrode, an equilibrium must be established between two sparingly sol. salts and a solution. If the solution is dil. and there is a large difference in solubility between the solid phases, operation of the electrode is possible when the solution dissolves both solid phases. The solubility product of the solid phase having the same cation as the metal electrode must, however, be several powers of 10 < that of the other solid phase, and the ratio of the solubility of the latter to the concn. of the ion to be determined must be as small as possible. Solubilities at 18° of  $\text{CaWO}_4$ ,  $\text{Hg}_2\text{WO}_4$ , and  $\text{Hg}_2\text{C}_2\text{O}_4$  have been determined. The electrodes  $\text{Hg}|\text{Hg}_2\text{WO}_4-\text{CaWO}_4-\text{Ca}^{++}$  and  $\text{Hg}|\text{Hg}_2\text{C}_2\text{O}_4-\text{CaC}_2\text{O}_4-\text{Ca}^{++}$  have been studied, the second proving serviceable. In solutions containing  $\text{Cl}^-$ ,  $\text{Hg}^+$  electrodes are useless owing to separation of  $\text{Hg}_2\text{Cl}_2$  and pptn. of the cation to be determined. The electrode  $\text{Cd}|\text{Cd stearate}-\text{Ca stearate}-\text{Ca}^{++}$  is free from this objection but does not respond to changes in  $[\text{Ca}^{++}]$ .

R. C.

**Cells with liquid ammonia or an ammoniacal solution as solvent.** G. I. COSTEANU (*Compt. rend.*, 1933, 197, 1113—1114; cf. A., 1933, 29).—The e.m.f. of the cells  $\text{Cd}|\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}|\text{NH}_4\text{NO}_3|\text{AgNO}_3|\text{Ag}$  and  $\text{Zn}|\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}|\text{NH}_4\text{NO}_3|\text{AgNO}_3|\text{Ag}$  in liquid  $\text{NH}_3$  containing different amounts of  $\text{H}_2\text{O}$  and at different temp. vary only a few % when the % of  $\text{H}_2\text{O}$  varies from 0 to 80, and temp. from -75° to 18°.

C. A. S.

**Polarographic studies with the dropping mercury cathode.** XXXIV. Suppressive effect of certain alkaloids on the maximum current due to electro-reduction of oxygen. E. HAMAMOTO (*Coll. Czech. Chem. Comm.*, 1933, 5, 427—435).—The adsorbability of five alkaloids at the  $\text{Hg}$ -aq.  $\text{KCl}$  interface is of the same order as that of org. dyes (cf. A., 1931, 914).

D. R. D.

**Electromotive force due to the movement of electrodes in different solutions.** Variation of the phenomenon with concentration, time, and pressure of the dissolved gas. V. G. GEORGHU (*Ann. Sci. Univ. Jassy*, 1933, 18, 335—384).—The e.m.f. has been measured with electrodes of various metals in  $\text{H}_2\text{O}$  and in solutions of acids, bases, and salts. The e.m.f. may be positive or negative and may increase or decrease with time. It depends also on the nature and pressure of the gas above the liquid.

H. S. P.

**Effect of the solvent on the potential of the chloranil electrode.** B. O. HESTON and N. F. HALL (*J. Amer. Chem. Soc.*, 1933, 55, 4729—4730).—The accepted val. (+0.664 volt) for the potential of the saturated chloranil electrode against the  $\text{H}_2$  electrode has been confirmed for 50% aq.  $\text{EtOH}$ , but +0.680 and +0.715 volt have been obtained in  $\text{AcOH}$  and 50% aq. dioxan, respectively. The potential may be assumed independent of the solvent only if the electrode materials remain unsolvated.

E. S. H.

**Hydrolysis and the oxidation-reduction potential of the system  $\text{Fe}^{+++}-\text{Fe}^{++}$ .** P. A. KRIUKOV and G. P. AVSEJEVITSCH (*Z. Elektrochem.*, 1933, 39, 884—891; cf. A., 1933, 909).—The oxidation-reduction potential of  $\text{Fe}$  solutions is correlated with the  $p_{\text{H}}$  of the solution, measured with a glass electrode, for  $p_{\text{H}}$  3.5—6. From the results, and from titration curves, vals. derived for the solubility product of  $\text{Fe}(\text{OH})_2$  and  $\text{Fe}(\text{OH})_3$  are  $3.2-9.3 \times 10^{-14}$  and  $0.1 \times 10^{-36}$  to  $3.45 \times 10^{-35}$ , respectively.

H. J. E.

**Oxidation-reduction potential of system hypoxanthine  $\rightleftharpoons$  uric acid.** (MLLE.) S. FILITTI (*Compt. rend.*, 1933, 197, 1212—1213).—Three different methods give the normal oxidation-reduction potential of this system [in presence of diastase, with 1 : 1'-dimethyl-4 : 4'-dipyridylum chloride (cf. A., 1932, 1102) as indicator, and  $p_{\text{H}}$  7.24—7.34] at 38° as  $0.031 \pm 0.002$  volt, whence  $\Delta F = +2861 \pm 180$  g.-cal. The heat of reaction at const. pressure is -1700 g.-cal.

C. A. S.

**Buffer intensities of milk and milk constituents.**—See A., 1933, 1319.

**Overvoltage of metals.** N. THON (*Compt. rend.*, 1933, 197, 1312—1314).—Deductions made from the view that the relation between current and overvoltage is linear (cf. A., 1932, 700) are not in accord with experiment. The hypothesis of energies of activation (cf. A., 1928, 1088) applied to cryst. metal deposits, e.g.,  $\text{Pb}$ ,  $\text{Zn}$ ,  $\text{Cd}$ ,  $\text{Bi}$ ,  $\text{Cu}$ , and  $\text{Ag}$ , leads to unsatisfactory conclusions; that of active centres (cf. A., 1930, 1376) affords a better explanation. The reverse holds for  $\text{Fe}$ ,  $\text{Co}$ , and  $\text{Ni}$ , and complex salts of other metals (cf. A., 1913, ii, 287). In a gaseous cathode (see below) the absence of active centres explains the high overvoltage.

C. A. S.

**Electrolysis of metallic salt solutions with rarefied gas cathode.** N. THON (*Compt. rend.*, 1933, 197, 1114—1117).—The (metal) cathode is separated from the surface of the electrolyte by a variable distance  $d$ , the space containing only vapour from the solution. With a.c. the system electrolyte|rarefied gas|Pt has a rectifying effect, a positive current passing from liquid to metal. With d.c. at 1000 volts metal is deposited on the surface of the solution only when this contains a salt of a noble metal, e.g.,  $\text{Ag}$ ,  $\text{Au}$ ,  $\text{Pt}$ . In all other cases, including  $\text{Hg}$  and  $\text{Cu}$ ,  $\text{H}_2$  is evolved. Corbino's contrary observation (cf. A., 1927, 523) appears to have been due to the close proximity of the electrode to the surface of the electrolyte, or to the wall of the containing vessel. The facts support Volmer's theory (cf. A., 1932, 24).

C. A. S.



**Electrolytic growth of metallic crystals.** T. ERDEY-GRUZ (*Naturwiss.*, 1933, 21, 799—800).—The growth of single crystals of Ag by electrolysis of solutions of various Ag salts has been examined. The development lacks uniformity in solutions of  $\text{AgNO}_3$ ,  $\text{AgClO}_4$ ,  $\text{AgF}$ , or  $\text{KAg}(\text{NO}_2)_2 + \text{KNO}_2$ . In these cases development occurs at selected points on the cryst. surface, whilst the greater part of the surface appears to be passive. Uniformity is favoured by solutions of  $\text{KAg}(\text{CN})_2 + \text{KCN}$ ,  $\text{AgI} + \text{KI}$ ,  $\text{Ag}_2\text{O} + \text{NH}_3$ ,  $\text{AgCl} + \text{NH}_3$ ,  $\text{AgBr} + \text{NH}_3$ . Complex salts give the best results because the great adsorption of their anions tends to cover the regions of high energy development (sharp points etc.) on the surface.

A. J. M.

**Electrochemistry of chromium. IV.** O. S. FEDEROVA (*J. Gen. Chem. Russ.*, 1933, 3, 636—640).—Theoretical.

R. T.

**Theory of passivity phenomena. XIX. Destruction of natural oxide film of iron on rusting.** W. J. MÜLLER and W. MACHU (*Z. physikal. Chem.*, 1933, 166, 357—364; cf. A., 1933, 787).—In the removal of the oxide film in the rusting of a protected Fe electrode the amount of surface bare at any particular moment can be determined directly from the difference in optical behaviour between the bare surface and the surface still covered. The results agree with those obtained indirectly from the  $i_0 t_p$  curve. The rate of disappearance of the film is at any moment proportional to the amount of surface still covered at that moment.

R. C.

**Theory of passivity. XX. Passivity of nickel.** W. J. MÜLLER and E. LÖW (*Z. Elektrochem.*, 1933, 39, 872—879).—Criticisms of the film theory (Georgi, A., 1932, 1093) are answered. Photomicrographs are given showing oxide films on a passive Ni anode.

H. J. E.

**Theory of passivity. XXI.** W. J. MÜLLER (*Z. Elektrochem.*, 1933, 39, 880—883).—Polemical against E. Müller and Schwabe (cf. A., 1933, 785). The film theory of passivity is supported.

H. J. E.

**Theory of passivity.** E. MÜLLER and K. SCHWABE (*Z. Elektrochem.*, 1933, 39, 884; cf. preceding abstract).—A reply.

H. J. E.

**Anodal passivation of lead.** P. PORFIROV (*J. Gen. Chem. Russ.*, 1933, 3, 590—595).—Passivation of Pb anodes in aq.  $\text{H}_2\text{SO}_4$  is due to deposition of a  $\text{PbSO}_4$  film (I) on the surface, with consequent increase in c.d. on the free areas; this leads to the formation of colloidal  $\text{PbSO}_4$ , involving increased resistance to the passage of current, and resulting in still greater increase in c.d. at the anode to a crit. val. above which (I) is converted into  $\text{PbO}_2$ , corresponding with complete passivation of the anode. In anhyd.  $\text{H}_2\text{SO}_4$  passivation is due to (I) alone.

R. T.

**Thermodynamics and kinetics of gaseous reactions.** W. H. RODEBUSH (*J. Chem. Physics*, 1933, 1, 440—443).—Theoretical.

F. L. U.

**Calculation of reaction velocity as a function of temperature.** A. SKRABAL (*Monatsh.*, 1933, 63, 23—38).—Theoretical. Mathematical methods for the rapid evaluation of the various consts. in the

formulae of (1) Arrhenius, (2) Harcourt and Esson, (3) Berthelot, (4) van 't Hoff, (5) Kooij, and (6) Bodenstein, relating velocity coeffs. with temp., are deduced and the formulae tested. Two-const. formulae (1)—(3) are unsatisfactory, but the three-const. formulae (4) and (5) are satisfactory as extrapolation formulae, and the magnitudes of the extrapolation errors are determined.

J. W. B.

**Relation between molecular activation energy and isokinetic temperature.** H. DAMIANOVICH (*An. Inst. Invest. cient. tecnol.*, 1930, 1, No. 3, 15—29; *Chem. Zentr.*, 1933, ii, 818).—In absence of accelerating factors, and when the van 't Hoff-Arrhenius equation is applicable, the mol. activation energy (I) is approx. proportional to the abs. temp. In isothermal changes (I) behaves like  $\log 1/\text{velocity coeff.}$ , and in unimol. reactions is proportional to the mean life of the mol.

A. A. E.

**Limits of inflammation of mixture  $2\text{H}_2 + \text{O}_2$ .** P. TAUZEN (*Compt. rend.*, 1933, 197, 1046—1049).—The lower (a) and upper (b) limits of temp. of inflammation at varying pressures (0—120 mm. Hg) have been plotted as pressure-temp. curves, (a) by allowing the mixture contained in a vessel outside the furnace to expand into one inside it and at the desired temp.; (b) by passing into this second vessel the desired amount of the mixture at a low temp., and then heating rapidly. For (a) pressure is almost const. from  $420^\circ$  to  $520^\circ$ ; for (b) the curve rises with increasing rapidity until it becomes asymptotic to the ordinate of temp. =  $560^\circ$  approx. The min. temp. of inflammation in a heating tube  $2.5 \times 10$  cm. ( $424^\circ$ ) was < in one  $5 \times 20$  cm. ( $450^\circ$ ), but the curves intersect at about  $520^\circ$ ; in the former temp. of inflammation was lowered, in the latter raised a few degrees, by heating the mixture for some time at a temp.  $15$ — $35^\circ$  below that of inflammation when directly heated thereto.

C. A. S.

**Mechanism of the reaction of hydrogen atoms with oxygen.** J. R. BATES (*J. Chem. Physics*, 1933, 1, 457—465; cf. A., 1933, 358).—Theoretical. The mechanism previously suggested (*ibid.*, 236) affords a satisfactory interpretation of observations on velocity-concn. relations, quantum yield, and temp. coeff.

F. L. U.

**Kinetics of the reaction between hydrogen and nitrous oxide.** I. H. W. MELVILLE (*Proc. Roy. Soc.*, 1933, A, 142, 524—545).—The kinetics of the reaction between  $\text{H}_2$  and  $\text{N}_2\text{O}$  have been studied at 50—400 mm. and  $550$ — $700^\circ$  in  $\text{SiO}_2$  bulbs. The final products are mainly  $\text{N}_2$  and  $\text{H}_2\text{O}$ . The rate is directly proportional to the pressure of  $\text{N}_2\text{O}$  and nearly independent of that of  $\text{H}_2$ , except when the  $\text{N}_2\text{O}$  pressure is high.  $\text{N}_2$  and A have no effect. The apparent energy of activation is 32 kg.-cal. Explosions may occur on raising the pressure and temp. The suggested mechanism of the reaction is as follows: the reaction is of the chain type, initiated by O atoms derived from the thermal dissociation of  $\text{N}_2\text{O}$  mol. and propagated by H atoms and OH radicals. Termination occurs mainly in the gas by combination of H atoms, but some may take place on the walls.

L. L. B.



**Mechanism of explosive combustion of gaseous hydrocarbons.** A. W. FRANCIS (Chem. and Ind., 1933, 926—927).—The nature of the products of explosive combustion is determined primarily by the flame temp. Probably free C results from thermal decomp. of part of the original hydrocarbon rather than by hydroxylation. R. S.

[Mechanism of combustion.] W. A. BONE (Chem. and Ind., 1933, 928—929; cf. preceding abstract).—A criticism. R. S.

**Rate of dissociation of nitrogen tetroxide.** C. E. TEETER, jun. (J. Chem. Physics, 1933, 1, 251—265; cf. A., 1932, 1209).—No measurable dispersion of sound has been found in  $N_2O_4$  up to 53.8 kc. At higher frequencies no evidence of transmission could be observed up to 860 kc., this absorption indicating dispersion. It was not possible, however, to determine whether dissociation, time lag, or a combination of both was responsible. Thus the sonic method for measuring rates of dissociation of gases appears to fail. M. S. B.

**Oxidation of nitric oxide to nitric anhydride by ozone, and under the influence of the silent electrical discharge.** N. KOBOZEV, M. TEMKIN, and S. FRAIBERG (J. Gen. Chem. Russ., 1933, 3, 534—539).—NO reacts with  $O_3$  as follows:  $NO + O_3 \rightarrow NO_2 + O_2$ ;  $2NO_2 + O_3 \rightarrow N_2O_5 + O_2$ . The velocity of reaction is considerably > that of  $O_2$  with NO, and the smallest traces of  $O_3$  are removed from air by NO. The above reactions do not take place if mixtures of air and NO are passed through an ozoniser, as the  $O_2$  necessary for  $O_3$  formation is combined as  $NO_2$ .  $O_3$  has no action on  $N_2O$ . R. T.

**Ignition temperatures of mixtures of hydrogen sulphide, carbon disulphide, and air.** F. D. LEICESTER (J.S.C.I., 1933, 52, 341—346T).—Ignition temp. have been determined up to 500°. A 60%  $H_2S$ -air mixture ignites at 487°. From this point the ignition temp. falls to a min. at 12—13%  $H_2S$ , and then rises again with falling  $H_2S$  content. A 32%  $CS_2$ -air mixture ignites at 332°; the ignition temp. falls smoothly with decreasing  $CS_2$  content, a mixture containing 0.5%  $CS_2$  having an ignition temp. of 81°. The results for  $H_2S$ - $CS_2$ -air mixtures are complex, but addition of  $H_2S$  to  $CS_2$ -air mixtures always causes, at first, a rise in the ignition temp. The whole field of mixtures up to 32%  $CS_2$  and 60%  $H_2S$ , having ignition temp. up to 500°, has been explored.

**Kinetics of the thermal decomposition of methyl ethyl ether.** E. W. R. STEACIE (J. Chem. Physics, 1933, 1, 618—619).—The heat of activation is  $54,500 \pm 1500$  g.-cal, which harmonises with vals. for other ethers, and is > Hinshelwood and Glass' val. (A., 1929, 1148). H. J. E.

**Factor independent of temperature in unimolecular reactions.** G. SALOMON (Helv. Chim. Acta, 1933, 16, 1354—1360).—From available data it is shown that in the Arrhenius equation for reactions of the first order,  $K = Z \cdot e^{-E/RT}$ , Polanyi and Wigner's theoretical conclusion (A., 1929, 404) that  $Z = 10^{14}$  approx. is valid where the mol. contains only atoms of approx. equal wt., there is no steric interference,

and any solvent required has no influence. Where, however, the velocity of reaction varies with the solvent any val. may be found for  $Z$  and for the heat of activation  $E$ . M. S. B.

**Facility of ring-formation in cyclic imino-compounds.** G. SALOMON (Helv. Chim. Acta, 1933, 16, 1361—1373).—From known data for the velocity of ring closure of the halogenoalkylamines to cyclic imines at different temp. the heat of activation  $E$  and factor  $Z$  (cf. preceding abstract) have been calc. The reaction can take place only if an activated mol. happens to be in the "ring position" and the statistical equilibrium, ring position  $\rightleftharpoons$  chain position, influences the val. of  $Z$ . The length of the chain and hence the deviation of valency linkings in forming the ring influences the velocity of ring formation. 3- and 4-membered rings require a higher heat of activation than 5- and 6-membered rings. On the other hand, the 7-membered ring also requires a large heat of activation, possibly because the space arrangement of the solute mol. in the solvent favourable to reaction depends on the length of the chain. The influence of substituents is discussed and illustrated by the behaviour of the Ph- and Me-substituted chloro- and bromo-ethylamines. The influence of the solvent on the ring and chain equilibrium is discussed and it is shown that the ring position of the solute mol. probably predominates when the solvent differs most, physically, from the solute. This is in agreement with the behaviour of  $\epsilon$ -chloroamylamine and of  $CH_2Br \cdot CH_2 \cdot NH_2$  in  $H_2O$  and in org. solvents, since  $Z$  in the former solvent may be as much as  $10^{5-6}$  times > in the latter. The effect is balanced to some extent by the fact that  $E$  is about 5 kg.-cal. lower in the org. solvents than in  $H_2O$ . There is no simple connexion between the dipole moment of the solvent and reaction velocity. M. S. B.

**Effect of ethyl radicals on the thermal decomposition of azomethane. Kinetics of the thermal decomposition of lead tetraethyl. Ethyl radicals and hydrogen.** J. A. LEERMAKERS (J. Amer. Chem. Soc., 1933, 55, 4508—4517).—The thermal decomp. of  $PbEt_4$  at 245—275° and initial pressures of 13—52 mm. is unimol. and 96—97% homogeneous. The rate coeffs. are given by  $k_1 = 1.2 \times 10^{12} e^{-36,900/RT}$  sec.<sup>-1</sup> Experiments on the decomp. of  $PbEt_4$  in presence of azomethane (I) show that the Et radical does not react with (I) at about 275°. Et radicals do not react appreciably with  $H_2$  at 275°. The calc. activation energies of bimol. reactions of Et radicals with  $H_2$  or (I) are > 15 kg.-cal. E. S. H.

**Thermal decomposition of ethylene iodide.** L. B. ARNOLD, jun., and G. B. KISTIAKOWSKY (J. Chem. Physics, 1933, 1, 166—169; 287, errata).—Investigation of the homogeneous gaseous decomp. in the temp. range 205—230° indicates two simultaneous reactions giving the same final products,  $C_2H_4$  and  $I_2$ . One is a reaction, similar to that in solution, catalysed by I atoms; the other is a unimol. decomp. Activation energies are 30,200 and 36,600 g.-cal., respectively. Results for the catalysed reaction in solution and in the gas phase are in agreement, indicating negligible solvent influence. N. M. B.



Cross-activation in the unimolecular decomposition of mixtures of gaseous methyl and ethyl ether. E. W. R. STEACIE (J. Chem. Physics, 1933, 1, 313—316).—Repetition of previous work (A., 1932, 576) with more accurate temp. control indicates that the cross-activation efficiency of collisions between  $\text{Me}_2\text{O}$  and  $\text{Et}_2\text{O}$  mols. is 40—60%, confirming Kassel's result (*ibid.*, 1209) qualitatively but not quantitatively. D. R. D.

Quantum mechanics of chemical reactions involving conjugate double linkings. H. EYRING, A. SHERMAN, and G. E. KIMBALL (J. Chem. Physics, 1933, 1, 586—592).—Theoretical. The addition of Br to butadiene occurs most readily in the  $\alpha\delta$  position, and when the additive mol. approaches in the plane of the C atoms. The activation energy is 30—60 kg.-cal., and the homogeneous reaction would be very slow at room temp. Actually it is fairly rapid, and the addition reaction must therefore occur at a surface. The surface reaction mechanism is discussed.

H. J. E.

Influence of substituents on heat of activation of a simple addition reaction. E. HERTEL and J. DRESSEL (Z. physikal. Chem., 1933, B, 23, 281—290).—The velocity of addition of  $\text{NPhMe}_2$  and its derivatives to trinitroanisole and its derivatives has been determined at various temp. These reactions follow the bimol. law and involve the transfer of the Me group of the anisole to the  $\text{NH}_2$ -group of the aniline. In respect of their effect on the heat of activation,  $Q$ , substituents follow the same order as for their effect on basicity and their auxochromic action.  $Q$  is an additive property which is influenced by a fixed amount by a given substitution. R. C.

Mechanism of substitution reactions. A. R. OLSON (J. Chem. Physics, 1933, 1, 418—423).—For many reactions of the type  $AB+C \rightarrow AC+B$ , the strength of the linking between A and B is too great to account for the rate of reaction, so addition or simultaneous additions and dissociations must occur. From the quantum mechanical conception of linkings a spatial inversion of A must occur for every such substitution. The theory is applied to the Walden inversion, and a correlation is obtained between the rotational and configurative changes. Its application to the Beckmann rearrangement and to *cis-trans*-isomerism is also indicated. J. W. S.

Thermal decomposition of ethyl mercaptan and ethyl sulphide.—See this vol., 56.

Rate of bromate formation in aqueous solutions containing hypobromous acid and its anion. H. A. LIEBHAFSKY and B. MAKOWER (J. Physical Chem., 1933, 37, 1037—1046).—At low  $[\text{Br}^-]$ , solutions of  $\text{HOBr}$  are more stable than accords with the rate of the reaction  $5\text{HOBr} = \text{BrO}_3' + 2\text{Br}_2 + \text{H}^+ + 2\text{H}_2\text{O}$ . The rate-determining step appears to be  $2\text{HOBr} + \text{OBr}^- \rightarrow \text{BrO}_3' + 2\text{Br}^- + 2\text{H}^+$ . The reaction probably does not result from triple collisions, but the mechanism is not understood. The reactions for  $\text{ClO}_3'$ ,  $\text{BrO}_3'$ , and  $\text{IO}_3'$  formation are analogous.

H. S. P.

Temperature coefficient of the decomposition of hydrogen peroxide in presence of potassium

iodide. W. C. K. HENDER and R. A. ROBINSON (Trans. Faraday Soc., 1933, 29, 1300—1305).—The reaction at 15—45° in 0.01—0.06*N*-aq. KI is unimol. with respect to  $\text{H}_2\text{O}_2$ , and proportional to  $[\text{KI}]$ . The observed rate is accounted for by a triple collision mechanism involving the  $\text{H}_2\text{O}$  mol. Similar results are found in  $\text{MeOH}$  and  $(\text{CH}_2\text{OH})_2$  as solvent. In  $\text{EtOH}$  bimol. collisions between  $\text{H}_2\text{O}_2$  and KI will account for the observed rate. Neutral salts influence the temp. coeff. slightly in aq. KI. H. J. E.

Velocity of esterification of alcohols in acetic acid. II. A. KAILAN and S. SCHWEBEL (Monatsh., 1933, 63, 52—78; cf. A., 1932, 1210).—The velocity of esterification ( $v$ ) of  $\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}$  (I),  $\text{CH}_2\text{Ph}(\text{OH})$ ,  $\text{CH}_2\text{Ph}(\text{CH}_2\text{OH})$ ,  $\text{CH}_2\text{Ph}(\text{CH}_2\text{CH}_2\text{OH})$ , and *o*-, *m*-, and *p*-nitrobenzyl alcohols in  $\text{AcOH}$  containing initially 0.128 or 1.068 mol.  $\text{H}_2\text{O}$  per kg. 100% acid ( $w_0$ ) has been determined by the f.-p. method (A., 1929, 605) ( $w = 0.2460\Delta + 0.02512\Delta^2 - 0.001061\Delta^3$ ). Esterification is complete in all cases. In the absence of  $\text{HCl}$   $w_0$  has little influence on  $v$ , the ratio of the unimol.  $k_0$  for  $w_0 = 0.128$  and 1.068 varying between 0.72 and 1.20 according to the alcohol. With  $\text{HCl}$  catalysis ( $k_c$  for  $\text{HCl}$  concn.  $c$ ) increase in  $w_0$  accelerates esterification, ( $k_c - k_0$ )/ $c$  being increased by 16—49% as  $w_0$  increases from 0.128 to 1.068:  $v$  is approx. proportional to  $c$  and with 1 mol.  $\text{HCl}$  per kg. 100%  $\text{AcOH}$  is 4000—6000 times  $>$  its val. for the uncatalysed reaction under otherwise similar conditions. In these primary alcohols a double linking has a retarding effect,  $v$  for (I) being only about 54% of its val. for  $\text{Pr}^n\text{OH}$ . Substitution of H by Ph in the  $\alpha$ ,  $\beta$ , and  $\gamma$  positions to the OH reduces  $v$  to, respectively, 31, 69, and 59% of its original val., whereas the ratio of  $v$  for  $\text{CH}_2\text{Ph}(\text{OH})$  and its *o*-, *m*-, and *p*- $\text{NO}_2$ -derivatives is 1:0.32:0.58:0.48. These results are compared with the effect of similar substitution in the corresponding acids. J. W. B.

Velocity of hydrolysis of simple ethers. A. SKRABAL and A. ZAHORKA (Monatsh., 1933, 63, 1—22).—By determination of the alcohols formed, on hydrolysis, by the method of Fischer and Schmidt (A., 1926, 632; apparatus modified), the velocity coeffs. for the acid hydrolysis ( $p\text{-C}_6\text{H}_4\text{Me}(\text{SO}_3\text{H})$  as catalyst) of highly purified samples of  $\text{Et}_2\text{O}$  ( $k_1$ ),  $\text{Pr}^n\text{O}$  ( $k_2$ ), and  $\text{Pr}^n\text{OEt}$  ( $k_m$ ) in  $\text{H}_2\text{O}$  at 55°, 65°, 75°, 85°, and 95°, are found to be, respectively;  $k_1$  —, 0.0435, 0.200, 0.776, 2.63;  $k_2$  0.312, 1.605, 7.10, 26.16, —;  $k_m$  0.0725, 0.385, 1.821, 7.11, —,  $\times 10^{-6}$ . The effect of temp. is given by:  $\log k_1 = -14535/T - 0.057476T + 55.069$ ;  $\log k_2 = -14592/T - 0.060150T + 57.711$ , and  $\log k_m = -13445.6/T - 0.048120T + 49.6355$ , whence extrapolated vals. of  $k$  at 25° and 125° are obtained. The half-val. period for  $\text{Et}_2\text{O}$  in *N*-acid solution at 25° is  $4.75 \times 10^{10}$  min. The ratio  $k_1:k_m:k_2$  = approx. 1:10:33. The val. of  $k_m$  lies between  $\sqrt{(k_1k_2)}$  and  $\frac{1}{2}(k_1+k_2)$ , being nearer to the geometric mean at lower temp. and to the arithmetic mean at higher temp. Hence the presence of each group modifies the contribution of the other towards the velocity of hydrolysis. Cases where  $k_{RR'}$  is  $<$  or  $< \frac{1}{2}(k_{2R} + k_{2R'})$  are discussed on a theoretical basis for ethers  $\text{ROR}'$  when R and R' are both alkyl, both



acyl, or mixed alkyl and acyl groups, and examples of each type are cited.

J. W. B.

**Velocity of decomposition of diazo-compounds in water.** XII. E. YAMAMOTO, R. GOSHIMA, and J. HASHIMA (J. Soc. Chem. Ind. Japan, 1933, 36, 609—613B).—The decomp. velocities, between 0° and 80°, of 1:4- and 1:5-NH<sub>2</sub>-C<sub>10</sub>H<sub>6</sub>-SO<sub>3</sub>H and Cleve's acid are recorded.

R. S.

**Velocity of diazotisation of aromatic amines.** S. UENO and T. SUZUKI (J. Soc. Chem. Ind. Japan, 1933, 36, 615—619B).—With 47 aromatic amines the velocity of diazotisation is increased by increasing the HCl concn. (0.05—4*N*), by the presence of NaCl or KCl, and by negative substituents in the order Cl < CO<sub>2</sub>H < SO<sub>3</sub>H < NO<sub>2</sub>, and at 10° is 3—4 times > at 0°. In the NH<sub>2</sub>Ph series it is greater with *o*- than with *p*- or *m*-substituted derivatives (except that strongly negative substituents, e.g., SO<sub>3</sub>H or NO<sub>2</sub>, are equally effective in the *o*- and *p*-position), is scarcely affected by alkyl and decreased by alkoxy-groups. In the C<sub>10</sub>H<sub>7</sub>-NH<sub>2</sub> series the effects of substitution are irregular. Diazotisation is very much more rapid in HBr, but slow in HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, or 1:5-C<sub>10</sub>H<sub>6</sub>(SO<sub>3</sub>H)<sub>2</sub>.

R. S. C.

**Hydrolysis of ethylene bromide with alcoholic alkali hydroxide.** A. L. BERNOUILLE and W. KAMBLI (Helv. Chim. Acta, 1933, 16, 1187—1200).—By hydrolysis of C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub> with aq. K<sub>2</sub>CO<sub>3</sub> a yield of > 90% (·CH<sub>2</sub>·OH)<sub>2</sub> may be obtained. With K<sub>2</sub>CO<sub>3</sub> in H<sub>2</sub>O-EtOH mixtures the chief product is CH<sub>3</sub>:CHBr. With EtOH-NaOH the only product is CH<sub>3</sub>:CHBr and the reaction has been followed kinetically at 21—31°. The reaction is bimol. and the reaction velocity is much reduced by the addition of H<sub>2</sub>O. The dependence of the velocity coeff. on temp. follows the same exponential law whether H<sub>2</sub>O is present or not.

M. S. B.

**Kinetics of reaction of alkaline-earth metals with nitrogen and other gases.** II. Kinetics of reaction of alkaline-earth metals with nitrogen. III. Action of sodium and other substances as "exciters" of reaction between calcium and nitrogen. A. VON ANTROPOFF and K. H. KRÜGER. IV. Kinetics of reaction between calcium and nitrogen in presence of argon. A. VON ANTROPOFF and H. KLINGEBIEL (Z. physikal. Chem., 1933, 167, 49—53, 54—61, 62—70; cf. A., 1929, 34).—II. Sr and Ba are considerably more active towards N<sub>2</sub> than is Ca, and are never passive, i.e., nitride formation occurs throughout the mass of the metal instead of being confined to a surface film. Reaction begins with Sr at 350° and with Ba at 200°; in each case the velocity rises continually with temp. With Sr, but not with Ba, the reaction is accelerated by Na or NaOH.

III. At 700° the passivity of Ca is not eliminated by Na. At lower temp. Na initiates the reaction between Ca and N<sub>2</sub>, but the reaction once started proceeds more rapidly if the Na, which has a retarding action similar to that of an indifferent gas, is removed. Li, K, NaOH, Na<sub>2</sub>O, Na<sub>2</sub>O<sub>2</sub>, and NH<sub>4</sub>NO<sub>3</sub> also serve as "exciters," the action of the Na compounds possibly depending on the formation of Na by reaction with

the Ca. Na can effect activation independently of the presence of NaOH.

IV. The rate of reaction with a mixture of N<sub>2</sub> and A of a Ca rod the end face of which is activated with a grain of Na first rises rapidly as reaction proceeds, owing to increase in the reacting surface area, then falls rapidly, on account of accumulation of A in the porous nitride layer, and finally decreases slowly and linearly after attainment of a stationary state in which the velocity is determined by the rate of diffusion of N<sub>2</sub> through the nitride layer. In the removal of N<sub>2</sub> from A by means of hot Ca turnings the Ca should be activated with NaOH. The reaction velocity is greatly enhanced and spectrally-pure A is readily obtained.

R. C.

**Influence of fluid velocity on heterogeneous reactions.** II. Dissolution velocity of metallic copper in ammoniacal cupric solutions. S. UCHIDA and I. NAKAYAMA (J. Soc. Chem. Ind. Japan, 1933, 36, 635—642B).—Cu<sup>II</sup>-NH<sub>3</sub> solution, saturated with O<sub>2</sub>, and circulated through Cu tubes of various diameters, dissolves Cu in accordance with the theory of heterogeneous reactions involving fluid films (cf. A., 1933, 911). The variation is analogous to the case of heat transfer.

R. S.

**Dissolution of magnesium in aqueous salt solutions.** III. L. WHITBY (Trans. Faraday Soc., 1933, 29, 1318—1331; cf. A., 1933, 1017).—The initial rates of dissolution of Mg in aq. KCl, KBr, KI, and K<sub>2</sub>SO<sub>4</sub> (*N* and 0.001*N*), in saturated aq. Mg(OH)<sub>2</sub>, and in 0.001*N*-aq. KOH were of the same order, irrespective of the solute or its dilution. Smaller Mg surfaces give a disproportionately high rate in relation to larger surfaces. Results support the theory of primary preferential OH discharge. The solubility of Mg(OH)<sub>2</sub> in the *N*-salt solutions, in 0.001*N*-KOH, and in H<sub>2</sub>O has been measured.

H. J. E.

**Validity of the mass-action law in the reaction of proteins with acids and bases.** G. ETTISCH and G. V. SCHULZ (Biochem. Z., 1933, 265, 338—369).—The combination of serum-globulin and -albumin with bases can be divided into two reactions, one primary and immediate, the other secondary and requiring several hr. With acids the secondary reaction is insignificant. The primary reaction is purely ionic, and follows the zwitterion scheme; the equilibrium between bound and free H<sup>+</sup> and OH<sup>+</sup> obeys the mass law. Three alkali- and two acid-binding groups may be distinguished in terms of their dissociation consts. and the amounts of each are determined. The isoelectric point of albumin is calc. from the dissociation consts.

P. W. C.

**Homogeneous catalysis of stereoisomeric change in oximes.** T. W. J. TAYLOR and D. C. V. ROBERTS [with P. JULIFF and (Miss) M. S. MARKS] (J.C.S., 1933, 1439—1444).—The determination of the rate of transformation,  $\alpha$ , at 55°, of 0.04—0.054*M*- $\alpha$ - to  $\beta$ -benzilmonoxime in EtOH is based on the observation that whereas the  $\beta$ -oxime reacts only very slowly with Cu(OAc)<sub>2</sub> the  $\alpha$  isomeride rapidly forms an insol. Cu complex in EtOH.  $\alpha$  is unimol. with respect to  $\alpha$ -oxime and is strongly catalysed by LiCl (I) and NMe<sub>4</sub>Cl but not by KOAc (II) and KEtSO<sub>4</sub>.



Catalysis by HCl is greatly diminished by  $\text{H}_2\text{O}$ . Analogous qual. results are recorded for the effects of (I) and (II) on the transformation of  $\beta$ - into  $\alpha$ -benzaloxime. It is probable that the catalysis involves an interaction between the electronic systems of the ion-pair (or undissociated mol.) of the electrolyte and the C:N linking of the oxime. J. G. A. G.

**Kinetics of reaction between potassium persulphate and potassium ferrocyanide in neutral solution.** J. HOLLUTA and W. HERRMANN (Z. physikal. Chem., 1933, 166, 453—467).—The reaction has been studied at  $15^\circ$ . All the classical methods of determining the order fail. The second-order velocity coeff. remains const. throughout a given experiment but varies with the initial concn., whilst the third-order coeff. rises as reaction proceeds. These anomalies are due to the presence of a powerful electrostatic ionic field, and to  $\text{K}^+$  having a strong sp. accelerating action. In conc. aq.  $\text{K}_2\text{SO}_4$  the second-order velocity coeff. ceases to vary with the initial concn. and the reaction becomes a normal second-order reaction. Diffused daylight does not affect the reaction. A possible reaction mechanism is outlined. R. C.

**Chemical kinetics. Temperature dependence of energy of activation. Entropy and free energy of activation.** V. K. LA MER (J. Chem. Physics, 1933, 1, 289—296).—Published data for the decomp. of  $\text{CO}(\text{CH}_2\text{CO}_2\text{H})_2$  by  $\text{H}_2\text{O}$ , the reaction between NaOPh and various alkyl iodides, and the decomp. of diacetone alcohol by aq. and aq.-MeOH solutions of NaOH indicate that the energy of activation, as calc. from the temp. coeff. of the reaction velocity, varies with temp. The theoretical foundation of the Arrhenius and Brønsted equations is discussed, and it is deduced that the Hinshelwood-Moelwyn-Hughes collision theory can be true only in the improbable event of the entropy of activation being zero. D. R. D.

**Catalytic oxidations. II. Oxidation of benzaldehyde. III. Oxidation of pyruvic acid.** K. MEYER (J. Biol. Chem., 1933, 103, 25—37, 39—49).—II. PhCHO, when purified by distillation and fractional crystallisation, is not autoxidised in  $\text{C}_6\text{H}_6$ , but in the presence of small amounts of Fe it absorbs O readily without an induction period. As catalyst pyridine-hæmochromogen is more effective than  $\text{Fe}^{++}$ , and  $\text{Fe}^{++}$  than  $\text{Fe}^{+++}$ . If purified by distillation alone, PhCHO appears to be accompanied by substances which inhibit activation by a heavy metal such as Fe, Cu, or Ni. PhOH inhibits the catalytic activity of 10 times its equiv. of Fe. A greater effect is achieved by adding the PhOH before the Fe rather than after. In presence or absence of PhCHO,  $\text{BzO}_2\text{H}$  is immediately decomposed in acid solution with liberation of  $\text{O}_2$ , but with PhCHO in non-aq. solution the per-acid is stable even in the presence of hæmin.

III. The autoxidation of  $\text{AcCO}_2\text{H}$  in alkaline solution is catalysed by hæmin and, to a much greater extent, by certain fluorescent dyes, the latter requiring the presence of light. It is probably the enolic form of the acid which is oxidised and the principal product is  $\text{H}_2\text{C}_2\text{O}_4$ . The speed of the photochemical reaction is proportional to the concn. of  $\text{AcCO}_2\text{H}$  and to the

log. of the concn. of fluorescent dye. Fluorescence seems a necessary property of the photosensitiser, but chemical constitution is evidently important also. The reaction is not inhibited by PhOH. M. S. B.

**Pseudo-atoms and isosteric compounds. III. Comparative studies with benzene, thiophen, and furan.** H. ERLÉNMEYER and M. LEO (Helv. Chim. Acta, 1933, 16, 1381—1389).—The catalytic action of  $\text{C}_6\text{H}_6$ ,  $\text{C}_4\text{H}_4\text{S}$ , and  $\text{C}_4\text{H}_4\text{O}$  on the reaction  $\text{EtI} + \text{NEt}_3 = \text{NEt}_4\text{I}$  has been compared. The velocity coeff. for  $\text{C}_4\text{H}_4\text{S}$  is much  $>$  for either of the other two. This has led to a comparison of all the known physical data for the three compounds and their derivatives. There is a remarkable similarity between the physical data for  $\text{C}_6\text{H}_6$  and  $\text{C}_4\text{H}_4\text{S}$ , but  $\text{C}_4\text{H}_4\text{O}$  shows considerable deviations. This is attributed to a similarity between the outer electron systems of S and the group  $\cdot\text{CH}:\text{CH}\cdot$  so that the latter group behaves as a pseudo-S atom. It is also significant that the resonance potentials of S and  $\text{C}_6\text{H}_2$  are the same, 6.5 volts, whilst that of O is 9.1 volts. It thus appears that  $\text{C}_6\text{H}_6$  and  $\text{C}_4\text{H}_4\text{S}$  have a similar mol. field, and this similarity is not shared by  $\text{C}_4\text{H}_4\text{O}$ . M. S. B.

**Catalysed reaction of hydrogen with water.** J. HORIUTI and M. POLANYI (Nature, 1933, 132, 819).—The exchange of atoms between  $\text{H}_2$  and  $\text{H}_2\text{O}$  previously observed (A., 1933, 1233) is catalysed by Pt black. This may be due to the ionisation of  $\text{H}_2$  corresponding with the electromotive process of the  $\text{H}_2$  electrode, and if the  $\text{H}_2$  contains heavy  $\text{H}_2$  (I) leads to the replacement of (I) by H. The slow at. exchange between H and  $\text{H}_2\text{O}$  previously observed may be due to some catalyst, possibly the walls of the vessel, acting in a similar way.  $\text{H}_2\text{O}$  containing (I) reacts with Fe more slowly than ordinary  $\text{H}_2\text{O}$ . L. S. T.

**Effect of salts on the catalytic decomposition of hydrogen peroxide by colloidal platinum.** M. A. HEATH and J. H. WALTON (J. Physical Chem., 1933, 37, 977—990).—The decomp. of  $\text{H}_2\text{O}_2$  by colloidal Pt at  $25^\circ$  in presence of various concns. of NaCl,  $\text{BaCl}_2$ ,  $\text{AlCl}_3$ ,  $\text{ThCl}_4$ ,  $\text{NaNO}_3$ ,  $\text{Al}(\text{NO}_3)_3$ , and  $\text{Th}(\text{NO}_3)_4$  has been investigated. A relation exists between the rate of decomp. and the rate of migration of the Pt particles in an electric field, but this is less marked with Th salts. Anions except  $\text{NO}_3^-$  affect the decomp., due possibly to substitution of OH groups in  $\text{Pt}(\text{OH})_6^{--}$  (I). A possible mechanism for the decomp. of  $\text{H}_2\text{O}_2$  due to (I) is given. H. S. P.

**Kinetics of contact oxidation of  $\text{SO}_2$ .** G. K. BORESKOV and V. P. PLIGUNOV (J. Appl. Chem. Russ., 1933, 6, 785—796).—Taylor and Lenher's formula (A., 1931, 1246) is applicable to the reaction  $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$  catalysed by a V catalyst (I) of the approx. composition  $8\text{SiO}_2 \cdot 2\text{SnO}_2 \cdot \text{V}_2\text{O}_5 \cdot \text{K}_2\text{O} \cdot \text{BaO}$ . The apparent heat of activation is 55 kg.-cal. at  $< 440^\circ$ , and 20 kg.-cal. at  $> 440^\circ$ ; in the latter case identical results are obtained using Pt catalyst. At  $< 440^\circ$ , the velocity of reaction is proportional to that of elimination of  $\text{SO}_3$  from the active surface of (I). Formulæ are given connecting yield of  $\text{SO}_3$  with temp., velocity of flow, and concn. of substrates. R. T.

**Dissolution of metals in acids.** M. SCHUNKERT (Z. physikal. Chem., 1933, 167, 19—28; cf. A., 1931,



576).—Such substances as albumin, dextrin, gelatin, and saponin reduce the rate of dissolution of Fe and Zn in dil. and conc. aq.  $\text{H}_2\text{SO}_4$ , the retarding action running parallel with the adsorbability as measured by the Au no. Me-violet and methylene-blue retard the dissolution of Fe in conc.  $\text{H}_2\text{SO}_4$  and accelerate the dissolution of Zn in dil.  $\text{H}_2\text{SO}_4$ . Salts may have either a retarding or an accelerating action. The above foreign substances are effective only if they are deposited on the metal itself, and have no effect if they are deposited on the impurities responsible for local action. The variable effect of salts is attributed to changes in the degree of dissociation on addition to the acid. R. C.

**Catalytic polymerisation of propylene.**—See B., 1933, 997.

**Catalytic high-pressure hydrogenation of aromatic hydrocarbons.**—See B., 1933, 1046.

**Influence of traces of oxygen on decomposition of acetaldehyde by heat.** LETORT (Compt. rend., 1933, 197, 1042—1044).—The decomp. of  $\text{MeCHO}$  at 477° and 225 mm. Hg pressure was examined in a  $\text{SiO}_2$  vessel so designed as to exclude all trace of  $\text{O}_2$  in excess of  $10^{-4}$  mm. Hg, alone, and with addition of definite amounts of  $\text{O}_2$   $\times$  0.034 mm. Hg. In absence of  $\text{O}_2$  the reaction is of order 2.2; in presence thereof (e.g., 0.0135 mm. Hg pressure) the reaction occurred as in its absence after 17.8% of the  $\text{MeCHO}$  had been decomposed, by which time 6 vols. of  $\text{O}_2$  had caused decomp. of an additional 9800 vols. of  $\text{MeCHO}$ . The irregularities previously noted (cf. A., 1926, 804; 1931, 1001; 1933, 910) are due to the presence of traces of  $\text{O}_2$ . C. A. S.

**Catalytic activity of liquid and solid surfaces. Decomposition of methyl alcohol on solid and liquid zinc.** E. W. R. STEACIE and E. M. ELKIN (Proc. Roy. Soc., 1933, A, 142, 457—465).—There is no discontinuity at the m.p. of Zn when the metal is used as a catalyst for the thermal decomp. of gaseous  $\text{MeOH}$  between 360° and 440°. It is concluded that the whole surface of the metal is uniformly active, and that the catalytic activity of a solid cannot be limited to a part of the surface. L. L. B.

**Concentration of deuterium by electrolysis.** D. H. RANK (J. Chem. Physics, 1933, 1, 750).—The low concn. of "deuterium" [ $\text{H}^2$ ] in commercial electrolytic cells run hot is due to losses of  $\text{H}_2\text{O}$  vapour with the electrolytic gases and to evaporation. H. S. P.

**Current distribution at the anode in the electrolytic formation of sodium persulphate.** O. ESSIN and E. ALFIMOWA (Z. Elektrochem., 1933, 39, 891—894; cf. A., 1933, 34, 468).—The previous equation for the division of current between the various anode processes is applicable to the electrolytic formation of  $\text{Na}_2\text{S}_2\text{O}_8$  when changes are made in the type of cathode and in the e.d. The addition of HF is also without influence. H. J. E.

**Polarographic studies with the dropping mercury cathode.** XXXV. **Electrolysis of aqueous solutions of beryllium salts.** W. KEMULA and M. MICHALSKI (Coll. Czech. Chem. Comm., 1933, 5,

436—442).—The deposition of Be at the dropping Hg cathode is preceded by  $\text{H}_2$  evolution, the effect being reduced by higher Be concns. The close similarity between the deposition potentials of Be and Al makes it impossible to separate these metals. D. R. D.

**Anodic dissolution of copper-tin alloys.**—See B., 1933, 1013.

**Anodic behaviour of copper in alkali chloride and hydrogen chloride solutions.** Z. SZABO (Magyar Chem. Fol., 1933, 39, 1—19; Chem. Zentr., 1933, ii, 345).—In 1—6M solutions in  $\text{H}_2$  the Cu dissolves as  $\text{Cu}^+$  and forms  $\text{CuCl}_3^-$ . The potential of the Cu electrode depends on  $[\text{Cu}]$  and  $[\text{Cl}^-]$  of the solution. Lewis' law holds for complex anions. Activity coeff. and equilibrium const. for  $\text{CuCl}_3^-$  are calc.; the latter is  $0.145 \times 10^{-5}$ . A. A. E.

**Electrolysis of acetates in absolute alcohol.** F. FICHTER and R. E. MEYER (Helv. Chim. Acta, 1933, 16, 1408—1412).—The electrolysis of  $\text{NaOAc}$  and  $\text{AcOH}$  in  $\text{MeOH}$  and in  $\text{H}_2\text{O}$ , respectively, has been carried out under exactly similar conditions in order to investigate the character of the Kolbe hydrocarbon synthesis. The output of  $\text{CO}_2$  and  $\text{C}_2\text{H}_6$  in  $\text{MeOH}$  is slightly  $>$  in  $\text{H}_2\text{O}$ , whilst  $\text{H}_2$  is somewhat less. A little  $\text{C}_2\text{H}_4$  is always present in the anode gases, but in larger amount from the  $\text{H}_2\text{O}$  solution, and a very little  $\text{O}_2$  in both cases. The results are considered to favour the view that  $\text{Ac}_2\text{O}_2$  is an intermediate product in the Kolbe hydrocarbon synthesis and that  $\text{O}_2$  itself takes part in the electrochemical oxidation. Experiments show that  $\text{Mg}(\text{OAc})_2$  in  $\text{MeOH}$  is of little use for the Kolbe synthesis, for, although a considerable quantity of  $\text{C}_2\text{H}_6$  is obtained from the  $\text{H}_2\text{O}$  together with some  $\text{C}_2\text{H}_4$ ,  $\text{O}_2$ , and  $\text{CO}_2$ , the  $\text{MeOH}$  solution gives very little gas at the anode and no  $\text{C}_2\text{H}_6$  at either electrode, pure  $\text{H}_2$  only being formed at the cathode. Variation of the  $\text{NaOAc}$  or  $\text{KOAc}$  concn. whilst the  $\text{AcOH}$  concn. remains const. at 20% gives a max. yield of  $\text{C}_2\text{H}_6$  at an intermediate concn. of salt. The max. for  $\text{KOAc}$  is at 1.44N. M. S. B.

**Electrolytic oxidation of anthracene to anthraquinone.** N. S. DROZDOV and S. S. DROZDOV (J. Appl. Chem. Russ., 1933, 6, 897—902).—Anthracene (I) in  $\text{COMe}_2$ - $\text{H}_2\text{SO}_4$  solution combines directly with  $\text{O}$  at the anode to yield anthraquinone (II); this does not take place with suspensions of (I) in  $\text{H}_2\text{SO}_4$ , when the agency of a catalyst is necessary for the transference of  $\text{O}$ . The velocity of oxidation using  $\text{Ce}_2(\text{SO}_4)_3$  catalyst is  $>$  with  $\text{K}_2\text{Cr}_2\text{O}_7$ , but the product is considerably more contaminated with products of further oxidation of (II). The nature of the above reactions is not affected by varying c.d. at the anode. Anthraquinol is not an intermediate product in the above processes. R. T.

**Recombination of atomic hydrogen in the tungsten arc.** F. J. HAVLICEK (Helv. phys. Acta, 1933, 6, 165—197; Chem. Zentr., 1933, ii, 832).—Recombination is unimol., and an intermediate state is probably involved. The temp. coeff. of the velocity coeff. is given by  $189e^{-2040/K^7}$ . Hence the higher is the temp., the greater is the velocity of recombina-



ation. At room temp. the half-val. period is approx. 0.175 sec. A. A. E.

**Electrolysis in the glow discharge. IV.** A. KLEMENC and H. F. HOHN (Z. physikal. Chem., 1933, 166, 343—356; cf. A., 1931, 805).—The products in this electrolysis are qualitatively independent of the polarity of the discharge vessel. The current yield,  $A$ , is greater in the cathode than in the anode fall. In the reduction of  $\text{HClO}_3$  and  $\text{HClO}_4$ ,  $A$  is much  $>$  corresponds with Faraday's law. It is concluded that in electrolysis in the glow discharge "active" uncharged substances participate in the electrochemical processes. These include such substances as at. H and also substances formed in ordinary electrolysis on discharge of the ions. The production of  $\text{H}_2\text{S}_2\text{O}_8$  in the electrolysis of aq.  $\text{H}_2\text{SO}_4$  shows that the mechanism of formation cannot be  $2\text{HSO}_4' + 2\oplus \rightarrow \text{H}_2\text{S}_2\text{O}_8$ ; possibly it is  $2\text{HSO}_4' + \text{O} + \text{H}_2\text{O} = \text{H}_2\text{S}_2\text{O}_8 + 2\text{OH}'$ . R. C.

**Reactions of the hydroxyl radical in the electrodeless discharge in water vapour.** W. H. RODEBUSH and M. H. WAHL (J. Chem. Physics, 1933, 1, 696—702).—When the electrodeless discharge is produced in a stream of  $\text{H}_2\text{O}$  vapour at 0.1—0.2 mm. pressure, about 50% of the  $\text{H}_2\text{O}$  is converted into  $\text{H}_2\text{O}_2$  which may be frozen out. The formation of  $\text{H}_2\text{O}_2$  is attributed to dissociation of  $\text{H}_2\text{O}$  into  $\text{H}'$  and  $\text{OH}'$  followed by  $2\text{OH} = \text{H}_2\text{O}_2$ .  $\text{H}_2\text{O}_2$  is not obtained in tubes with electrodes owing to the catalytic action of the spluttered metal. Spectroscopic examination showed two new bands with heads at 3564 and 3326 Å. which are attributed to  $\text{OH}'$ . H. S. P.

**Chemical action of the [electric] spark on gases at low pressure.** H. LEFÈVRE (Chim. et Ind., 1933, 29, Spec. No., 427—431).—Pure  $\text{CO}_2$ , at pressures of 0.1—18 mm. of Hg, was subjected to electric discharges (I) from condensers; the effect of varying the initial pressure of the gas, the energy of (I), and the no. of sparks, on the reaction  $2\text{CO}_2 = 2\text{CO} + \text{O}_2$  is described. "Asymmetric" (I) of low energy, having the nature of Geissler tube discharges, produced very little, and (I) of higher energy ("symmetrical"), relatively great (e.g., 15%), decomp. of  $\text{CO}_2$ . The decomp. of  $\text{CH}_4$  by (I), mainly into  $\text{C}_2\text{H}_2$  and  $\text{H}_2$ , is discussed, and is concluded to be too small to be of industrial interest. A. L. R.

**Heterogeneous chemical reactions in the silent electric discharge. VI.** S. MIYAMOTO (J. Sci. Hiroshima Univ., 1933, A, 3, 347—366; cf. A., 1933, 33, 682).—The following salts are reduced by gaseous  $\text{H}_2$  in the silent discharge;  $\text{Co}(\text{NO}_3)_2$ ,  $\text{Ni}(\text{NO}_3)_2$ ,  $\text{KNO}_3$ ,  $\text{KNO}_2$ ,  $\text{AgNO}_2$ ,  $\text{Mn}(\text{NO}_3)_2$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{Zn}(\text{NO}_3)_2$ , and  $\text{Cd}(\text{NO}_3)_2$ . Details of the reaction products are given; in no case did they include azides, hyponitrites, or  $\text{NH}_2\text{OH}$ . J. W. S.

**Inertness and chemical activity of the rare gases.** H. DAMIANOVICH (An. Inst. Invest. cient. tecnol., 1930, 1, No. 3, 30—44; Chem. Zentr., 1933, ii, 847).—When a discharge is passed in He between Pt electrodes the product contains 15% of a substance insol. in  $\text{HCl-HNO}_3$  and considered to be a compound. Products obtained in He,  $\text{O}_2$ ,  $\text{N}_2$ , and  $\text{H}_2$  are compared. A. A. E.

**Density of the product of the action of helium on platinum.** H. DAMIANOVICH and J. PIAZZA (An. Inst. Invest. cient. tecnol., 1930, 1, No. 3, 45—48; Chem. Zentr., 1933, ii, 847).—The product has  $d$  15, or after 3 months in He 16.8. A. A. E.

**Action of nitrogen at low pressure on platinum under the influence of the electric discharge.** H. DAMIANOVICH and G. BERRAZ (An. Inst. Invest. cient. tecnol., 1930, 1, No. 3, 53—63; Chem. Zentr., 1933, ii, 848).—A dark grey substance,  $d$  18.3, having a metallic lustre is obtained; 7.7% is sol. in dil.  $\text{HCl-HNO}_3$ . A. A. E.

**Action of oxygen at low pressure on platinum under the influence of the electric discharge.** H. DAMIANOVICH and J. PIAZZA (An. Inst. Invest. cient. tecnol., 1930, 1, No. 3, 49—53; Chem. Zentr., 1933, ii, 847).—The product obtained from  $\text{O}_2$  at 2—0.08 mm. and 380—1500 volts has  $d$  15.4. 32.6% is sol. in  $\text{HCl-HNO}_3$ . The composition corresponds with the formula  $\text{Pt}_2\text{O}_3$ . A. A. E.

**Action of hydrogen at low pressure on platinum under the influence of the electric discharge.** H. DAMIANOVICH and C. CHRISTEN (An. Inst. Invest. cient. tecnol., 1930, 1, No. 3, 54—57; Chem. Zentr., 1933, ii, 847).—With pure Pt and  $\text{H}_2$  at 0.1—4 mm. and 500—550 volts slow absorption of  $\text{H}_2$  and sputtering of Pt occur. A. A. E.

**Effect of electric discharges on hydrocarbons at low pressure.** C. C. CHRISTEN (An. Inst. Invest. cient. tecnol., 1930, 1, No. 3, 71—81; Chem. Zentr., 1933, ii, 850).—With  $\text{C}_7\text{H}_{16}$ , using Ni electrodes and 300—600 volts, partial condensation, independent of temp., occurs. The product is a non-volatile yellowish-brown mass; the portion insol. in light petroleum and sol. in  $\text{Et}_2\text{O}$  is attacked by conc.  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , and Br. The product slowly absorbs atm.  $\text{O}_2$ . A. A. E.

**Weigert effect. (Effect of dye concentration on photodichroism.)** W. KEMULA (Z. physikal. Chem., 1933, B, 23, 305—314).—The variation with the type of gelatin and colour of light of the Weigert effect in gelatin films coloured with various dyes and exposed to white and monochromatic linearly polarised light has been studied. With increasing dilution of dye the photodichroic sensitivity shifts more and more from the subsidiary max. towards the principal max. of extinction at longer wave-lengths, whilst the short-wave subsidiary max. diminishes and the long-wave principal max. is scarcely affected. It is suggested that the dye occurs in two photosensitive forms having different extinction curves, and that with decreasing dye concn. the concn. of the form with the short-wave extinction max. decreases more rapidly than the concn. of the form with the long-wave max. The gelatin film also exerts a filter action. The phenomena of photoanisotropy are due to photochemical changes in the particles of binding medium, the fibres being coloured dichroically by adsorption of dye. R. C.

**Physico-chemical study of the function of sodium sulphite in photographic developers.** K. M. PANDALAI and G. G. RAO (Z. anorg. Chem., 1933, 215, 23—32).—From experiments on the



reduction of AgCl by quinol and metol developers, it is concluded that normal development is an induced reaction in which Ag halide is the actor, the org. reducing agent the inductor, and  $\text{Na}_2\text{SO}_3$  the acceptor. Quinol reacts primarily with AgCl, and the quinone formed is then reduced by the  $\text{Na}_2\text{SO}_3$ . Photographic plates treated with a mixture of  $\text{Na}_2\text{SO}_3$  and quinone or quinhidrone undergo slow but otherwise normal development. F. L. U.

**Actinometry with uranyl oxalate at  $\lambda$  278, 253, and 208 m $\mu$ , including a comparison of periodically intermittent and continuous radiation.** F. P. BRACKETT, jun., and G. S. FORBES (J. Amer. Chem. Soc., 1933, 55, 4459—4466).—The gross quantum yield, in mols. of  $\text{H}_2\text{C}_2\text{O}_4$  per quantum, in the photolysis of solutions containing 0.05M- $\text{H}_2\text{C}_2\text{O}_4$  and 0.01M- $\text{UO}_2\text{SO}_4$  is  $0.48 \pm 0.01$  when  $\lambda$  is 208 m $\mu$ ,  $0.63 \pm 0.03$  for 253 m $\mu$ , and  $0.59 \pm 0.01$  for 278 m $\mu$ . The light source was a Zn spark of high constancy. The absorption coeffs. involved are given. Periodically intermittent and const. radiation are photochemically equiv. E. S. H.

**Photochemical studies. XVI. Chlorination of benzene.** H. P. SMITH, W. A. NOYES, jun., and E. J. HART (J. Amer. Chem. Soc., 1933, 55, 4444—4459; cf. A., 1932, 349).—The reaction in the gaseous phase proceeds by a short chain reaction. At the beginning of the reaction the rate of change of pressure is proportional to the square root of the light intensity, the pressure of the  $\text{Cl}_2$ , and the pressure of the  $\text{C}_6\text{H}_6$ . The main initial reaction is addition, but substitution also occurs. The mechanism is discussed. E. S. H.

**Reaction mechanism of photochemical conversion of *o*-nitrobenzaldehyde into *o*-nitrosobenzoic acid in ultra-violet light.** K. G. ZIMMER (Z. physikal. Chem., 1933, B, 23, 239—255).—The infra-red absorption of  $\text{o-NO}_2\text{C}_6\text{H}_4\text{CHO}$  (I) at various temp. gives no indication that (I) is a mixture of tautomerides. Observations on the dichroism of crystals for wave-lengths 436 and 405 m $\mu$  give a possible explanation of the dependence of the yield in the cryst. state on the plane of polarisation of the incident light. There is no appreciable photo-electric effect or fluorescence. The primary process in the photochemical reaction is dissociation of (I) into  $\text{o-NO-C}_6\text{H}_4\text{CHO}$  and O. These products by re-combination may either form  $\text{o-NO-C}_6\text{H}_4\text{CO}_2\text{H}$  acid or re-form (I), which explains the low quantum yield, although other causes, particularly energy dissipation, may contribute. The temp. coeff. between 45° and 70° is  $< 1$ . R. C.

**Solarisation of glass by soft X-rays.** H. KERSTEN and C. H. DWIGHT (J. Chem. Physics, 1933, 1, 627—629).—The intensity of the brown coloration and the rate of fading have been investigated under various conditions of temp., tube current, etc. D. R. D.

**Decomposition of sodium azide by controlled electron bombardment and by ultra-violet light.** R. H. MÜLLER and G. C. BROUS (J. Chem. Physics, 1933, 1, 482—491).—Cryst.  $\text{NaN}_3$  is decomposed by electrons possessing energies  $> 11.5$  volts. The reaction velocity has been studied in relation to the

voltage. The threshold wave-length for photochemical decomp. is about 405 m $\mu$ , and the rate  $\propto$  light intensity. There is no apparent relation between the energies needed for the two types of decomp. F. L. U.

**Effect of a wave-capturing oscillating circuit on chemical reactions.** A. DE P. FORJAZ (Compt. rend., 1933, 197, 1124—1125).—Exposure to a Lakhovsky oscillating circuit ( $\lambda = 1.256$  m.) catalyses certain reactions, e.g., it accelerates the interaction of EtOH and AcOH, the ageing of wine, ionisation, and allotropic change, and lowers the acidity of an oil or of vinegar. C. A. S.

**Decomposition of chloroform by radiations from radon.** G. HARKER (J. Proc. Roy. Soc. New South Wales, 1933, 67, 96—117).— $\text{CHCl}_3$  is decomposed by  $\gamma$ -radiation to give  $\text{Cl}_2$  and, by subsequent reaction,  $\text{CCl}_4$  and HCl. The effect of various metal filters has been measured. Minute traces of impurities affect the amount of decomp.; the presence or accumulation of the reaction products decreases the amount of decomp. Secondary radiation has no effect. 29.8 and 251.3 g.-cal. of X- and  $\gamma$ -radiation, respectively, are needed for decomp. of 1 mol. of  $\text{CHCl}_3$ . R. S. C.

**Physiological effects of radio waves.** J. L. DONNELLY (Science, 1933, 78, 290).—The heating effect of short radio waves on solutions of various electrolytes previously observed (A., 1930, 1376) has been confirmed. Dil. solutions of purified glucose and a solution of HCl in  $\text{C}_6\text{H}_6$  are not heated by high-frequency currents (I). PhOH was partly liquefied, but no temp. change was observed. The system  $\text{H}_2\text{O}$ -PhOH shows no temp. increase on irradiation. The therapeutic use and physiological effect of (I) are discussed in the light of the above results. L. S. T.

**Use of liquid air for the purification of radium emanation.** N. MORTARA (Atti R. Accad. Lincei, 1933, [vi], 17, 1069—1072).—The use of freshly prepared liquid air or liquid  $\text{N}_2$  is recommended for the condensation of Rn owing to the lower temp. obtainable. With liquid  $\text{O}_2$  the loss of Rn is considerable. O. J. W.

**Heavy water.** K. F. BONHOEFFER (Angew. Chem., 1933, 46, 776—779).—A lecture.

**Concentration of  $\text{H}^2$  isotope.** G. N. LEWIS and R. T. MACDONALD (J. Chem. Physics, 1933, 1, 341—344; cf. A., 1933, 442).—By electrolysing 20 litres of  $\text{H}_2\text{O}$  from an old commercial electrolytic cell in four stages until only 0.5 c.c. remained,  $\text{H}_2\text{O}$  of  $d$  1.073 was obtained. No large accumulations of heavy O isotopes occurred and, assuming the  $d$  to vary linearly with the fraction of  $\text{H}^2$ , 2/3 of the H in this  $\text{H}_2\text{O}$  was  $\text{H}^2$ . Further reduction of the vol. to 0.25 would give 99%  $\text{H}^2$ . In electrolysis the % loss of  $\text{H}^1$ : % loss of  $\text{H}^2 = 5 : 1$ . Provisionally it is found that the concn. of  $\text{H}^2$  in ordinary  $\text{H}_2\text{O}$  is 1 in 6500. J. W. S.

**Isotopic fractionation of water.** E. W. WASHBURN, E. R. SMITH, and M. FRANDSEN (J. Chem. Physics, 1933, 1, 288).—By the isotopic fractionation of  $\text{H}_2\text{O}$  electrolytically (A., 1932, 894) the  $d$ , f.p., and



b.p. of the residual  $H_2O$  rise continuously as electrolysis proceeds, whilst  $n$  decreases. By successive recombination of the electrolytically obtained O and H and re-electrolysis it should be possible to obtain isotopically pure  $H_2O$  of composition  $H^{16}O$ .

M. S. B.

**Isotopic fractionation of water by distillation and by adsorption.** E. W. WASHBURN and E. R. SMITH (J. Chem. Physics, 1933, 1, 426; cf. preceding abstract; A., 1932, 793).—A difference of 64.9 p.p.m. was found between the  $d$  of the initial distillate and final residue on distillation of 10 litres of  $H_2O$  through a 35-ft. fractionating column, the residue having increased by 53.3 p.p.m. After 300 g. of charcoal had been immersed in 500 g.  $H_2O$  for 3 weeks the  $d$  of the supernatant  $H_2O$  had decreased by 6.5 p.p.m. and that of the absorbed water increased by 6.7 p.p.m. Fractionation of  $H_2O$  can therefore be carried out both by distillation and by adsorption.

J. W. S.

**Decomposition of water by metalloids [and non-metals].** J. CAMPARDOU (Bull. Soc. chim., 1933, [iv], 53, 986—992).—A preliminary discussion.

R. S.

**Complex periodides.** G. SPACU and P. SPACU (Bul. Soc. Stiinte Cluj, 1932, 7, 154—159; Chem. Zentr., 1933, ii, 686).—The following compounds have been prepared:  $[Cu en_2]I_2 \cdot 2I_2$ ,  $[Cd en_2]I_2 \cdot I_2$ ,  $[Zn en_2]I_2 \cdot I_2$ ,  $[Ni en_2]I_2 \cdot I_2$ ,  $[Cu pn_2]I_2 \cdot I_2$ . Attachment of  $I_2$  prevents dissociation of  $[M en_2]$ .

A. A. E.

**Complex thiocyanate amines. II, III.** G. SPACU and G. GRECU (Bul. Soc. Stiinte Cluj, 1931, 6, 238—254, 1932, 7, 13—24; Chem. Zentr., 1933, ii, 685).—II. The following compounds have been prepared:

$[Ag(SCN)_4][Co en_3]$ ,  $[Ag(SCN)_4][Cr en_3]$ ,  $[Ag(SCN)_3][Cr(NH_3)_6]Cl$ ,  $[Zn(SCN)_4][Co en_3]SCN$ ,  $[Hg(SCN)_4]_3[Cr en_3]_2$ ,  $[Hg(SCN)_4]_3[Co(NH_3)_6]_2$ ,  $[Hg(SCN)_2]Cl[Co en_2Cl_2](1:6)$ ,  $[Cr(SCN)_6]_2[Zn en_2]_3$ ,  $[Cr(SCN)_6][Co en_3]$ ,  $[Cr(SCN)_6]_3[Co en_2Cl_2]_3(1:6)$ ,  $[Cr(SCN)_4(NH_3)_2]_2[Cu en_2]$ .

$[Cr(SCN)_4(NH_3)_2]_2[Ni en_2] \cdot 2H_2O$ ,  $[Cr(SCN)_4(NH_3)_2][Cd en_2]$ ,  $[Cr(SCN)_4(NH_3)_2][Co en_3]$ ,  $[Cr(SCN)_4(NH_3)_2][Co en_2Cl_2](1:6)$ ,  $[Cr(SCN)_4(NH_3)_2][Co en_2Cl_2](1:2)$ .

$[Cr(SCN)_4(NH_3)_2]_3[Cr en_3]$ ,  $[Mn(SCN)_4][Cu en_2]$ ,  $[Mn(SCN)_4][Cd en_2] \cdot 2H_2O$ ,  $[Mn(SCN)_6][Ni en_2]_2$ .

III.  $[Bi(SCN)_6][Co en_3]$ ,  $[Bi(SCN)_6][Cr en_3]$ ,  $[Cr(SCN)_6][Co(NH_3)_6] \cdot 2H_2O$ ,  $[Cr(SCN)_6][Co en_2(SCN)_2](1:6)$  and  $(1:2)_3 \cdot 2H_2O$ ,  $[Cr(SCN)_6][Co en_2Br_2](1:6)_3$ .

$[Cr(SCN)_6][Co en_2(NO_2)_2](1:6)$  and  $(1:2)_3$ ,  $[Cr(SCN)_4(NH_3)_2][Co en_2(SCN)_2](1:6)$  and  $(1:2)_2$ ,  $[Cr(SCN)_4(NH_3)_2][Co en_2Br_2](1:6)$ ,  $[Cr(SCN)_4(NH_3)_2][Co en_2(NO_2)_2](1:6)$  and  $(1:2)_2$ .

A. A. E.

**Homogeneous and heterogeneous complex salts in solution.** V. G. SPACU and P. SPACU (Bul. Soc. Stiinte Cluj, 1932, 7, 95—103; Chem. Zentr., 1933, ii, 685—686).—The following compounds have been prepared (pn=propylenediamine):  $[HgI_4][Cu pn_2]$ ,  $[AgI_2][Cu pn_2]$  (suitable for gravimetric determination of Ag in presence of Cu),  $[Ni en_3]S_2O_3$  (suitable for determination of  $S_2O_3^{2-}$  in presence of  $SO_4^{2-}$ ,  $SO_3^{2-}$ ,  $S^{2-}$ ,  $SCN^-$ , and  $S_4O_6^{2-}$ ).

$[HgI_3][Co en_2(SCN)_2] \cdot 4H_2O$ ,  $[PbI_4][Co en_2(SCN)_2]_2$ ,  $[AgI_2][Co en_2Cl_2](1:2)$  and  $(1:6)$ .

A. A. E.

**Hydrated calcium aluminates.** J. LEFOL (Compt. rend., 1933, 197, 919—921).—Curves relating the no. of mols. of  $H_2O$  remaining to the temp., obtained by Guichard's method (cf. A., 1926, 1021), for (1)  $Al_2O_3 \cdot 4CaO \cdot 12H_2O$ , (2)  $Al_2O_3 \cdot 3CaO \cdot 21H_2O$  (needles), (3)  $Al_2O_3 \cdot 3CaO \cdot 6H_2O$  (cubic), and (4)  $Al_2O_3 \cdot 2CaO \cdot 7H_2O$  (cf. A., 1930, 162, 436, 872) indicate the formation of the following hydrates from (1) with 10.5—11  $H_2O$  at 95°, and 6  $H_2O$  at 175°; (2) with 8—8.5  $H_2O$  at 135°; (3) with 1.5  $H_2O$  at 260—310°, (3) itself being stable to about 250°; and (4) with 5  $H_2O$  at 150°, dehydration beginning at 65°, up to which temp. 0.5—1 mol.  $H_2O$  had been absorbed.

C. A. S.

**Purification of mercury.**—See B., 1933, 1062.

**Purification of mercury by an electrolytic method.** M. E. HANKE and M. JOHNSON (Science, 1933, 78, 414—415).—The Hg is made the positive pole of a 110-volt d.c., first in presence of 10%  $H_2SO_4$  (I), and then in presence of 5% NaCl. Finally, it is made negative in presence of (I). Scum is removed by filtration between the steps. 500 c.c. of Hg can be purified in 1.5 hr.

L. S. T.

**Decomposition of mercurous iodide into mercury and mercuric iodide. Equilibrium states. Crystallisation of the compound.** M. FRANÇOIS (Ann. Chim., 1933, [x], 20, 285—303).—A full account of work previously published (A., 1896, i, 22, ii, 248, 301, 363; 1897, ii, 492; 1898, ii, 334).

F. L. U.

**Crystal analysis of unstable precipitates.** P. JOLIBOIS and G. FOURETIER (Compt. rend., 1933, 197, 1322—1323).—An X-ray photograph taken within 0.02 sec. of the mixing of streams of aq.  $HgCl_2$  and aq. KI (cf. A., 1920, ii, 112) showed the structure of the yellow  $HgI_2$  thus pptd. to be identical with that of yellow  $HgI_2$  obtained at 140°.

C. A. S.

**Reduction of alumina by carbon.** W. D. TREADWELL and A. GYGER (Helv. Chim. Acta, 1933, 16, 1214—1225).— $Al_2O_3$  is reduced by C in a circulating stream of A. The resulting CO content of the A atm. is determined by measuring the heat conductivity of the gas by the changes in resistance of a heated Pt wire in the gas mixture. By rapid heating to 2000° abs. the equilibrium is represented by the equation  $Al_2O_3 + 3C \rightleftharpoons 2Al + 3CO$ .  $Al_4C_3$  is probably formed either by the reaction  $3CO + 6Al \rightleftharpoons Al_4C_3 + Al_2O_3$  or  $2Al_2O_3 + 9C \rightleftharpoons Al_4C_3 + 6CO$  and the equilibrium condition is not reached in the apparatus. The CO pressure appears to remain const. as long as metallic Al is present. Micro-analytical methods are described for the determination of Al and  $Al_4C_3$  in the reaction mixture, Al by reduction of  $FeCl_3$  to  $FeCl_2$  and  $Al_4C_3$  by treatment with dil. HCl and combustion over CuO of the  $H_2$  and  $CH_4$  produced.

M. S. B.

**Luminescent aluminium oxides and their crystallochemical relationships to the natural and synthetic precious stones of the corundum type and their colorations.** E. TIEDE and H.



LÜDERS (Ber., 1933, 66, [B], 1681—1689; cf. A., 1931, 1253).—Conditions are described which permit the sesquioxides of Cr, Rh, Ti, V, Fe, and Ga which crystallise in the corundum lattice to be mixed with  $\text{Al}_2\text{O}_3$  to form a series of mixed crystals on a basis of isomorphism. Only those sesquioxides which are involved in the corundum lattice are capable of luminescence and all yield fluorescent systems. The fundamental crystallographic conditions of fluorophors are therefore markedly more simple than those of phosphors. The colour and luminescent powers of the mixtures melted in the  $\text{H}_2\text{--O}_2$  flame or cathode-ray furnace are compared with those of natural precious stones. H. W.

**Artificial transformation of felspar into kaolin.** R. SCHWARZ and G. TRAGESER (Z. anorg. Chem., 1933, 215, 190—200).—If felspar (I) is heated with pure  $\text{H}_2\text{O}$  the latter becomes increasingly alkaline through hydrolysis of (I). By a preliminary heating at  $850^\circ$  the rate of attack is reduced, owing to diminution of surface exposed by aggregation of particles. Superheated steam at  $500^\circ$  or  $1000^\circ$ , either alone or mixed with  $\text{SO}_2$ ,  $\text{NH}_3$ , or  $\text{HCl}$ , has the same effect. By treatment with  $N\text{--HCl}$  at  $330^\circ$  for 250 hr. under pressure in a steel bomb ( $320^\circ$  gives approx. 110 atm.  $\text{H}_2\text{O}$  vapour), (I) is partly transformed into kaolin (II), as shown by the dehydration curve of the product and X-ray diagram. A similar result is obtained with  $0.5N\text{--HCl}$  at  $320^\circ$  for 115 hr., but not at  $180^\circ$  and  $250^\circ$ . Instead, a residue rich in  $\text{SiO}_2$  is left ( $\text{Al}_2\text{O}_3:\text{SiO}_2 = 1:7\text{--}8.6$ ). No (II) formation has been observed with  $\text{H}_2\text{SO}_4$  or  $\text{HF}$ .  $\text{CO}_2$  at 190 atm. and  $320^\circ$  for 250 hr. produced no marked change. (II) is decomposed at  $220^\circ$  by  $0.5N\text{--HCl}$ , owing to the much greater solubility of  $\text{Al}_2\text{O}_3$  compared with  $\text{SiO}_2$ . At  $320^\circ$  the greatly increased solubility of  $\text{SiO}_2$  results in a saturated solution in which (II) is stable and from which it can separate. Hence under these conditions any suitable silicate such as orthoclase, leucite, or anorthite will form (II).

M. S. B.

**Formation of silicon carbide.** K. ARNDT and E. HAUSMANN (Z. anorg. Chem., 1933, 215, 66—74; cf. B., 1932, 134).—Reduction of  $\text{SiO}_2$  by C begins at about  $1600^\circ$ . At  $2250^\circ$   $\text{SiC}$  is decomposed, the resulting graphite retaining the form of the original crystals. No difference in behaviour was observed when using anthracite, wood C, or petrol C with quartz sand as starting material. So-called "siloxicon," reported to be formed at  $1600^\circ$ , is  $\text{SiC}$  in a microcryst. condition. F. L. U.

**Germanium.** XL. Action of ammonia on monochloromonogermane and dichloromonogermane. Action of water on monochloromonogermane. L. M. DENNIS and R. W. WORK. XLI. New salts of fluogermanic acid. L. M. DENNIS and B. J. STANESLOW [with W. D. FORGENG] (J. Amer. Chem. Soc., 1933, 55, 4486—4489, 4392—4396).—XL. The reactions of  $\text{GeH}_3\text{Cl}$  and  $\text{GeH}_2\text{Cl}_2$  with excess of liquid  $\text{NH}_3$  are represented by  $3x\text{GeH}_3\text{Cl} + 3x\text{NH}_3 = 3x\text{NH}_4\text{Cl} + x\text{GeH}_4 + 2(\text{GeH})_2$  and  $\text{GeH}_2\text{Cl}_2 + 2\text{NH}_3 = \text{Ge} + 2\text{NH}_4\text{Cl}$ . When excess of  $\text{H}_2\text{O}$  acts on  $\text{GeH}_3\text{Cl}$  neither  $\text{H}_2$  nor the hypothetical  $(\text{GeH}_3)_3\text{O}$  is produced.

XLI. The prep., optical properties (including  $n$ ),  $d$ , and solubilities in  $\text{H}_2\text{O}$ ,  $\text{MeOH}$ , and  $\text{EtOH}$  of the following are described:

$(\text{NH}_4)_2\text{GeF}_6$ ;  $(\text{NH}_4\text{OH})_2\text{H}_2\text{GeF}_6$ ;  $(\text{N}_2\text{H}_4)_2\text{H}_2\text{GeF}_6$ ;  $(\text{NH}_2\text{Ph})_2\text{H}_2\text{GeF}_6$ ;  $(\text{NHPhMe})_2\text{H}_2\text{GeF}_6$ ;  $(\text{NPhMe}_2)_2\text{H}_2\text{GeF}_6$ . All the salts are sol. in  $\text{H}_2\text{O}$ , but are hydrolysed with separation of  $\text{GeO}_2$ .  $(\text{NH}_2\text{OH})_2\text{H}_2\text{GeF}_6$  forms a dihydrate. E. S. H.

**Rapid heating of lead azide in a vacuum.** W. SCHUMACHER (Compt. rend., 1933, 197, 917—918).— $\text{PbN}_6$  or Ag fulminate detonates on heating in vac. in the same way as in air, thus differing from Hg fulminate. C. A. S.

**Nitric oxide-sulphurous acid.** I, II. E. WEITZ and F. ACHTERBERG (Ber., 1933, 66, [B], 1718—1727, 1728—1733).—I. As working hypothesis, the constitution  $\left[ \begin{smallmatrix} \text{O}:\text{S}:\text{O} \\ \text{O}:(\text{NO})_2 \end{smallmatrix} \right]_{\text{H}}$  is assigned to nitric oxide-sulphurous acid. The formation of the salts is to some extent reversible, since the alkali salts when heated decompose (sometimes "spontaneously") into  $\text{SO}_4''$  and  $\text{N}_2\text{O}$  (70—80%) and  $\text{SO}_3''$  and  $\text{NO}$ . In  $\text{H}_2\text{O}$ , the K salt (I) decomposes almost quantitatively into  $\text{SO}_4''$  and  $\text{NO}$ , whilst in presence of alkali  $\text{SO}_3''$  and  $\text{N}_2\text{O}$  appear; the Na salt (II) decomposes more readily. (II) reduces Fehling's solution more readily than does (I) in accordance with the usual greater stability of the complex salts of K. In alkaline solution the salts are slowly but quantitatively oxidised by  $\text{KMnO}_4$  to  $\text{SO}_4''$  and  $\text{NO}_2'$  and further in acid solution to  $\text{NO}_3'$ :  $\text{K}_2\text{SO}_3 \cdot 2\text{NO} + 4\text{O} + \text{H}_2\text{O} = \text{K}_2\text{SO}_4 + 2\text{HNO}_3$ . Absorption of  $\text{NO}$  by aq.  $\text{K}_2\text{SO}_3$  occurs most rapidly in presence of 0.1—0.2 mol. of  $\text{KOH}$ . Neutral solutions of (I) and (II) slowly become alkaline,  $\text{K}_2\text{SO}_3 \cdot 2\text{NO} + \text{K}_2\text{SO}_3 + \text{H}_2\text{O} = \text{K}_2\text{S}_2\text{O}_6 + \text{N}_2\text{O} + 2\text{KOH}$ , the change being ultimately inhibited by the  $\text{KOH}$  produced. A similar but very slow change which is finally inhibited by alkali takes place between (I) and alkali thiosulphate. The reaction  $\text{K}_2\text{SO}_3 \cdot 2\text{NO} + \text{EtOH} = \text{KEtSO}_4 + \text{N}_2\text{O} + \text{KOH}$  is also arrested by the liberated alkali. Unexpectedly, these "sulphonating" actions occur more rapidly in slightly acidic than in neutral or alkaline solution. (I) and  $\text{K}_2\text{SO}_3$  appear to react in the solid phase. Atm. oxidation of (I) occurs in presence of traces of acid ( $\text{HCl}$  or  $\text{KHSO}_4$ ),  $2\text{K}_2\text{SO}_3 \cdot 2\text{NO} + \text{O}_2 = 2\text{K}_2\text{SO}_4 + 4\text{NO}$ . K tetroxalate is without action, whereas  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  causes development of heat and production of  $\text{K}_2\text{SO}_3$  in addition to  $\text{K}_2\text{SO}_4$ .

II. Treatment of (I) with  $\text{FeSO}_4$  yields the unstable salt  $\text{K}_4\text{Fe}(\text{SO}_3 \cdot 2\text{NO})_3$  which decomposes in presence of its mother-liquor into  $\text{K}_2\text{SO}_4$ ,  $\text{FeSO}_4$ ,  $\text{N}_2\text{O}$ , and a little  $\text{Fe}(\text{OH})_3$  and basic  $\text{Fe}'''$  salt. Under similar conditions (II) gives an intense red solution (III). Solutions of (I),  $\text{FeSO}_4$ , and  $\text{NH}_3$  salts give essentially the same product as without  $\text{NH}_3$ , but it appears more stable and less definite in composition. (III) does not add  $\text{NO}$ . Rapid absorption occurs when  $\text{NO}$  is passed into  $\text{FeSO}_3$  suspended in  $\text{Na}_2\text{SO}_3$ ;  $\text{Fe}'''$  and  $\text{NH}_4\text{OH}$  result. (I) and  $\text{FeSO}_3$  yield the salt  $\text{KFe}_4\text{S}_3(\text{NO})_{11} \cdot \text{H}_2\text{O}$ ,  $\text{NO}$  appearing to be lost as such from (I).  $\text{Co}'''$  salts and (I) in neutral solution apparently afford mixtures of  $\text{K}_4\text{Co}(\text{SO}_3 \cdot 2\text{NO})_3$  and  $\text{K}_2\text{Co}(\text{SO}_3 \cdot 2\text{NO})_2$ ; in presence of  $\text{NH}_3$  a red solution



results which rapidly evolves gas and deposits ill-defined ppts. Zn and Mn solutions give the salts  $K_4Zn(SO_3,2NO)_3$  and  $K_4Mn(SO_3,2NO)_3$ , respectively. (II) does not yield ppts. under like conditions, but characteristic colours are developed in the solutions. (I) and La salts appear to yield a series of colourless double salts. (II) and  $TiNO_3$  or  $BaCl_2$  yield the respective compounds  $Ti_2SO_3,2NO$  and  $BaSO_3,2NO,2H_2O$ . With  $[Co(NH_3)_6]Cl_3$  the substance  $[Co(NH_3)_6]Cl(SO_3,2NO),H_2O$  results. H. W.

**Phosphoric acid and the phosphates. I. Formation of the basic alkaline-earth phosphates.** A. SANFOURCHE. **II. Volumetric titration of phosphoric acid and the phosphates. IV. Action of water on monocalcium phosphate.** A. SANFOURCHE and B. FOCET (Bull. Soc. chim., 1933, [iv], 53, 951—963, 963—969, 974—980).—I. The composition of the ppts. formed by addition of  $Ba(OH)_2$ ,  $Sr(OH)_2$ , and  $Ca(OH)_2$  to  $H_3PO_4$  solutions has been examined. At 100° the end products are respectively a tribasic phosphate, a hydroxyapatite (I), and a mixture of (I) and tetrabasic phosphate. The tri- and tetra-basic phosphates are regarded as salts of the acid  $H_8P_2O_9$ .

II. (a) Titration with 0.1N-NaOH in presence of  $CaCl_2$  ( $CaCl_2 : P_2O_5$ , 5—10) is recommended. Addition of excess alkali and back titration introduces errors due to formation of (I) (cf. above). (b) The solution, containing < 0.2 g.  $H_3PO_4$ , is neutralised against Me-orange. 20 c.c. of 5% aq.  $AgNO_3$  are added and the  $HNO_3$  liberated is titrated with 0.1N-NaOH against Me-red. Near the end-point, the ppt. is allowed to settle and more indicator added. The method is not suitable for solutions containing Fe or Al.

IV. The amount of  $CaHPO_4$  formed at various concns. of  $CaH_4(PO_4)_2$  salt is given. No decomp. occurs in solutions containing < 1.3%. The reverse reaction between  $CaHPO_4,2H_2O$  and  $H_3PO_4$  attains the same equilibrium at once, but when the anhyd. salt is used false equilibria occur. R. S.

**Oxidation of hypophosphoric acid by bromine.** B. BLASER and P. HALPERN (Z. anorg. Chem., 1933, 215, 33—43).—Contradictory statements in the literature regarding the oxidation of  $H_4P_2O_6$  by Br are attributed to the fact, now observed, that the reaction is strongly influenced by the  $p_H$  of the mixture. At  $p_H$  8  $H_4P_2O_6$  is formed rapidly and quantitatively, whilst outside the limits 5—11 the reaction is scarcely detectable. In the alkaline range the oxidation is powerfully catalysed by  $Cu^{II}$ . The constitution of  $H_4P_2O_6$  is discussed. F. L. U.

**Ammoniates of vanadium halides.** F. EPHRAIM and E. AMMANN (Helv. Chim. Acta, 1933, 16, 1273—1287).—The compound  $VBr_2$  has been obtained as a light reddish-brown cryst. substance by the reduction of  $VBr_3$  with  $H_2$ . The action of liquid  $NH_3$  at or below room temp. on this and other V halides has been investigated.  $VCl_2$ ,  $VCl_3$ ,  $VBr_2$ , and  $VBr_3$  form amines, but not  $VCl_4$ , although it combines readily with  $NH_3$ . Decomp. curves are given for the various amines. Except  $VBr_2$  they all take up rather > 6 $NH_3$ , probably as the result of absorption, and on raising the temp. this is gradually given up until the pentammine is formed. For this there is a well-

defined decomp. temp. at which the triammine is obtained:  $VCl_2$ , 171—178°,  $VCl_3$ , 178—179°, and  $VBr_2$ , 210—214°. The decomp. of  $VBr_3,5NH_3$  takes place above 240°, but is less clearly defined and does not go quite so far as the triammine. The amines are all readily attacked by atm.  $O_2$  and by  $H_2O$ . This contrasts with the behaviour of the corresponding  $Cr^{III}$  and  $Co^{III}$  compounds, although, from the fact that  $V^{III}$  has the same no. of electrons in the outside shell as  $Cr^{III}$ , it might have been expected that the corresponding amines would display a similar behaviour. Densities have been determined for the different halides and amines and the % contraction on the formation of the  $V^{II}$  is compared with those for the halides and amines of bivalent Cr, Mn, Fe, Co, and Ni and shown to be similar. M. S. B.

**Heteroplex compounds containing antimony tribromide.** A. C. VOURNASOS (Praktika, 1932, 7, 227—232; Chem. Zentr., 1933, ii, 522).—The following compounds are described:  $K_2Sb_3Br_9I_2$ ,  $HgSb_6Br_{18}I_2$ ,  $K_2Sb_3Br_9F_2$ ,  $SrSb_3Br_9Cl_2,6H_2O$ ,  $K_2Sb_3Br_9(SCN)_2$ ,  $K_2Sb_3Br_9(NO_3)_2$ ,  $NaSb_3Br_9N_3$ . A. A. E.

**Complex bromo-compounds of antimony.** W. PETZOLD (Z. anorg. Chem., 1933, 215, 92—102; cf. A., 1933, 1258).—The following compounds are described:  $(NMe_4)_3Sb_2Br_{11}$ ,  $(C_5H_5N)_3Sb_2Br_{12}$ ,  $RSbBr_6$  ( $NH_2Me_2$ ,  $NH_2Et_3$ ,  $NEt_4$ , guanidinium, 2:4:6-collidinium, 5:7-dibromohydroxyquinolinium),  $(NHMe_3)_2SbBr_8$ ,  $RSbBr_7$ , and  $R_3Sb_2Br_{15}$  (2:4:6-collidinium),  $R_2SbBr_9$  ( $\alpha$ - and  $\beta$ -picolinium, 2:4-lutidinium). F. L. U.

**Sulphur monoxides. III. Formation of sulphur monoxide in some chemical decompositions.** P. W. SCHENK and H. PLATZ (Z. anorg. Chem., 1933, 215, 113—128).—In the decomp. of  $SOCl_2$  vapour by heating with metals a large yield of SO is obtained with Ag, Sb, Na, and Sn, for which the heat of formation of the chlorides is > that of the oxides, but little or none with Mg, Al, and Zn, for which the contrary is the case. The amount of SO present in the vapour can be determined spectroscopically. SO cannot be separated from  $SOCl_2$  by cooling to -60°, since it dissolves in the latter with decomp. into S and  $SO_2$ . No SO is obtained by the thermal decomp. of  $SOCl_2$  alone, nor by that of  $H_2S_2O_3$  and  $H_2S_2O_4$  or their Na salts. SO is not an intermediate product in the reaction between  $H_2S$  and  $SO_2$  in presence of  $H_2O$  to form  $H_2S_2O_6$ . At room temp.  $S_2O_3$  gives the orange substance regarded as  $S_2O_2$ , the anhydride of  $H_2S_2O_3$ , but no SO is found in the vapour (cf. Wöhler and Wegwitz, A., 1933, 919). No SO is formed by the thermal dissociation of  $SO_2$ , but it is formed on combustion of S vapour present in excess. M. S. B.

**Oxidation of chromic oxide in aqueous solution by atmospheric oxygen under pressure.** V. V. IPATIEV, jun., and V. G. TRONEV (J. Appl. Chem. Russ., 1933, 6, 832—838).—Conversion of  $Cr(OH)_3$  into  $CrO_3$  does not occur in media of  $p_H$  < 3, under pressures of 75—100 atm.; in 4N- $Na_2CO_3$  100% conversion is attained. Aq.  $CrO_3$  is quantitatively reduced to  $Cr(OH)_3$  when heated with > N-acids, at 1—100 atm. R. T.



**Reduction of chromic oxide to chromium.**—See B., 1933, 1014.

**Fluorine.** O. RUFF (Angew. Chem., 1933, 46, 739—742).—Published data on the fluorides of Cl, Br, I, O, S, N, and C are reviewed. The prep. and properties of the following are described:  $ReF_6$  [m.p.  $18.8^\circ$ , b.p.  $47.6^\circ$ ,  $d$  (liquid) 3.61],  $ReOF_4$  [m.p.  $39.7^\circ$ , b.p.  $62.7^\circ$ ,  $d$  (liquid) 3.72],  $O_2F_2$  (m.p.  $-160^\circ$ , b.p.  $-57^\circ$ ,  $d$  1.45). E. S. H.

**Fluorine polyhalides of organic amines.** H. S. BOOTH, W. C. MORRIS, and G. D. SWARTZEL (J. Amer. Chem. Soc., 1933, 55, 4466—4468).—The prep. and properties of the following are described:  $NH_3MeF, ICl_3$ , m.p.  $35-40^\circ$ ;  $NH_3Et_2F, ICl_3$ , m.p.  $60-63^\circ$ ;  $NHMe_2F, ICl_3$ , m.p.  $121-145^\circ$ ;  $NMe_3F, ICl_3$ , m.p.  $267-270^\circ$ ;  $C_5H_5NHF, ICl_3$ , m.p.  $187-190^\circ$ . Thermal dissociation occurs on heating. The stability increases with the no. of Me groups. E. S. H.

**Rhenium tribromide.** H. HAGEN and A. SIEVERTS (Z. anorg. Chem., 1933, 215, 111—112).— $ReBr_3$  is formed as a greenish-black sublimate when Re is heated at  $500^\circ$  in Br vapour. In presence of  $O_2$  a dark blue distillate, probably containing oxybromide, is formed at  $400^\circ$ . F. L. U.

**Oxygen and halogen compounds of rhenium.** I. NODDACK and W. NODDACK (Z. anorg. Chem., 1933, 215, 129—184).—*Na rhenite*,  $Na_2ReO_3$ , is a brown powder insol. in  $H_2O$  and aq. NaOH but slowly attacked by acids with separation of  $ReO_2$  in  $H_2SO_4$  and green  $H_2ReCl_6$  in conc. HCl.  $K_2ReO_3$  is similar.  $BaReO_3$  can only be obtained mixed with  $Na_2ReO_3$ . Rhenites behave similarly to manganites. By the fusion of NaOH with  $NaReO_4$  under suitable conditions *Na hyporhenate*, probably either as the pyro-salt,  $Na_4Re_2O_7 \cdot H_2O$ , or the ortho-salt  $Na_3HReO_4$ , is obtained in light, sand-yellow, hexagonal plates or prisms stable under aq. or EtOH-NaOH, in which it is almost insol. The K salt has not been obtained in the solid state, but probably as a deep yellow solution. The Ba salt has been obtained mixed with Na salt. *Ba rhenate*,  $BaReO_4$ , an unstable leaf-green salt formed by the fusion of  $ReO_2$  with  $Ba(ReO_4)_2$  and NaOH, cannot be freed from  $Ba(ReO_4)_2$ . The corresponding Na compound, also impure, is readily attacked by  $H_2O$ . By fusion of colourless  $NaReO_4$  with NaOH in air the product is red when hot and yellow when cold, and the *Ba mesoperrhenate*,  $Ba_3(ReO_5)_2$ , is similarly obtained, and can also be prepared by pptn. of  $Ba(OH)_2$  by  $NaReO_4$  in aq. NaOH. It is citron-yellow when cold, but red at  $800^\circ$ , and is decomposed by  $H_2O$  into  $Ba(ReO_4)_2$  and  $Ba(OH)_2$ .  $K_4Re_2OCl_{10}$  forms mixed crystals with the corresponding Ru compound,  $K_4Ru_2OCl_{10}$ . No evidence of salts of the composition  $X_2Re(OH)Cl_5$  or  $X_2Re(OH)Br_5$  has been obtained. From the deep green solution of  $H_2ReCl_6$  salts of K, Rb, Cs, Tl, Ag,  $Hg^I$ ,  $NH_4$ , MeN (?), and of  $C_5H_5N$ , quinoline, and nitron, are pptd. The double chlorides of the alkali metals form deep green solutions which are fairly stable. Solubility data are given for  $K_2ReCl_6$ ,  $Cs_2ReCl_6$ , and  $K_4Re_2O_4Cl_{10}$  in HCl and  $H_2SO_4$ , and comparative electrical conductivities for  $K_2PtCl_6$ ,  $K_2ReCl_6$ , and  $K_4Re_2O_4Cl_{10}$ .  $H_2ReCl_6$  is a very weak acid.  $H_2ReBr_6$  forms a deep yellow solu-

tion by boiling  $ReO_2$  with conc. HBr and gives cryst. ppts. of  $X_2ReBr_6$  with K, Rb, and Cs salts, and  $C_5H_5N$  and nitron. These are stable in solutions containing  $> 15\%$  HBr. The properties of  $ReCl_3$  have been more extensively studied, and a *double salt*,  $C_5H_5N \cdot HCl \cdot ReCl_3$ , has been obtained.  $ReBr_3$  has also been prepared as black crystals and the *double salt*  $C_5H_5N \cdot HBr \cdot ReBr_3$ . In alkaline solutions any compound containing Re of intermediate valency tends to split up, giving compounds of Re in different stages of oxidation, the proportion of each depending on conditions. By this means a strongly reducing solution containing  $Re^{II}$  has been prepared. It gives a brown ppt. on dilution with  $H_2O$  or treatment with bases and a black sulphide with  $H_2S$ . By reduction of an ice-cold acid solution of  $ReCl_3$  with Zn or Na amalgam the solution becomes red and then bluish-violet, with strong reducing properties, and apparently contains  $Re^I$ . A brown cryst. ppt. of  $K_2ReOCl_6$  can be obtained, but it is very unstable, like the original  $ReOCl_4$ . Another compound of  $Re^{VI}$ , of the probable composition  $C_5H_5N \cdot HCNS \cdot ReO(CNS)_4$ , has also been obtained. A method is described for determining the valency of Re in its different compounds by oxidising to  $Re^{VII}$  with chromate and determining gravimetrically the  $Cr_2O_3$  formed. M. S. B.

**Mesoperrhenates.** B. SCHARNOW (Z. anorg. Chem. 1933, 215, 185—189; cf. preceding abstract).—The conditions of formation of  $Ba_3(ReO_5)_2$  by evaporation of aq.  $Ba(ReO_4)_2$  with excess of aq.  $Ba(OH)_2$  and with exclusion of atm.  $CO_2$  have been investigated. The formation takes place at a lower  $Ba(OH)_2$  concn. the higher is the concn. of  $Ba(ReO_4)_2$ , but there must always be a considerable excess of  $Ba(OH)_2$ . It forms small yellow hexagonal prisms and is readily decomposed in the moist state by  $CO_2$  forming  $Ba(ReO_4)_2$  and  $BaCO_3$ . The corresponding Sr compound is not formed because the solubility of  $Sr(OH)_2$  is not sufficiently high. Conductivity data are given for perrhenic acid.  $\lambda$  diminishes rapidly with increasing concn. M. S. B.

**Corrosion of iron.** E. TOPORESCU (Compt. rend., 1933, 197, 1040—1041).—Corrosion, ordinarily attributed to "differential aeration," is due to the depolymerisation and consequent increased chemical activity caused by surface tension on liquids (e.g.,  $H_2O$  or 6% aq. NaCl) drawn up by such tension, e.g., between two plates of Fe placed at an angle of  $7^\circ$ . The corrosion product shows rhythmic growth similar to Liesegang rings. C. A. S.

**Complex platinum compounds with ter- and quinque-valent platinum.** VI. P. C. RAY and N. N. GHOSH (Z. anorg. Chem., 1933, 215, 201—204).—By the action of bases on  $PtBrEt_3S_2$  (cf. A., 1933, 476) a series of compounds has been built up in which there are always 2 atoms of Br and the no. of Pt atoms is 2 or a multiple of 2. These are:  $Pt_2Br_2Et_2S_2 \cdot 2C_5H_5N$ , m.p.  $205^\circ$ ;  $Pt_2Br_2Et_2S_2 \cdot 2C_6H_7N$ , m.p.  $240^\circ$  (decomp.);  $Pt_4Br_2(Et_2S_2)_3 \cdot NH_4Et$ ;  $Pt_6Br_2(Et_2S_2)_5 \cdot 2CH_3Ph \cdot NH_2$ ;  $Pt_{10}Br_2(Et_2S_2)_9 \cdot 2NHPh \cdot NH_2$ ;  $Pt_{10}Br_2(Et_2S_2)_9 \cdot NPr_3$ . M. S. B.

**Electrometric studies of the precipitation of hydroxides.** XII. Reaction of sodium hydroxide on platinic chloride in solution. Reaction



of potassium cyanide on platinic chloride. H. T. S. BRITTON and E. N. DODD (J.C.S., 1933, 1429—1431).— $\text{PtCl}_4$  hydrolyses slowly in aq. solution, thus:  $\text{PtCl}_4 + x\text{H}_2\text{O} = \text{Pt}(\text{OH})_x\text{Cl}_{4-x} + x\text{HCl}$ . In presence of  $\text{NaOH}$ ,  $x$  may be as high as 3, and the resultant complex has no conductivity, but combines with  $\text{NaCl}$  forming a feebly conducting complex containing Pt in the anion. Aq.  $\text{PtCl}_4$  reacts with  $\text{KCN}$ , liberating  $\text{HCN}$  by virtue of the acid formed by hydrolysis. The  $\text{Pt}(\text{OH})_3\text{Cl}$  is not decomposed by excess of  $\text{KCN}$  and no platinicyanide is formed. D. R. D.

Sulphides, selenides, and tellurides of the six platinum metals. L. WÖHLER, K. EWALD, and H. G. KRALL (Ber., 1933, 66, [B], 1638—1652).—The metal chloride is intimately mixed with excess of metalloid and heated in a porcelain boat in  $\text{CO}_2$  until reaction commences. The cold mass is powdered and transferred to a hard glass tube, which is evacuated, sealed, and heated until reaction is complete. Excess of S, Se, or Te is removed by treating the product with  $\text{CS}_2$  followed by boiling 5%  $\text{Na}_2\text{S}$ , hot 0.5*N*- $\text{KCN}$ , and boiling 2*N*- $\text{HNO}_3$  followed by dil.  $\text{KOH}$ , respectively. The products obtained are such as contain the highest % of metalloid possible under the conditions. The existence of lower compounds is investigated by their isothermal decomp. at lower temp. in  $\text{H}_2$  or, preferably  $\text{N}_2$ . Several sulphides are prepared from the metallic chloride and  $\text{H}_2\text{S}$  (free from  $\text{H}_2$ ) at high temp. The following are described:  $\text{IrS}_3$  and  $\text{IrS}_2$  degraded to  $\text{IrS}$ ;  $\text{IrSe}_2$  whence  $\text{IrSe}$ ;  $\text{IrTe}_3$  whence  $\text{IrTe}_2$ ;  $\text{Rh}_2\text{S}_5$ ,  $\text{Rh}_2\text{Se}_5$ , and  $\text{RhTe}_2$ ;  $\text{RuS}_2$ ,  $\text{RuSe}_2$ , and  $\text{RuTe}_2$ ;  $\text{OsS}_2$ ,  $\text{OsSe}_2$ , and  $\text{OsTe}_2$ ;  $\text{PdS}_2$ ,  $\text{PdS}$ ,  $\text{PdSe}_2$ ,  $\text{PdTe}_2$ ;  $\text{PtS}_2$ ,  $\text{PtS}$ ,  $\text{PtSe}_2$ ,  $\text{PtTe}_2$ . A stable intermediate between  $\text{OsS}_2$  and  $\text{Os}$  or between  $\text{RuS}_2$  and  $\text{Ru}$  probably does not exist. The stability of the compounds towards chemical reagents diminishes with increasing at. wt. of the metalloid. H. W.

[Indirect volumetric determinations.] C. V. BORDEIANU (Arch. Pharm., 1933, 271, 514).—A reply to Eisenbrand (A., 1933, 686). R. S. C.

Determination of moisture.—See B., 1933, 1039.

Detection of chloride in presence of other halides. W. BRASH (Analyst, 1933, 58, 686).—The mixed halides are pptd. with  $\text{AgNO}_3$ ; the ppt. is suspended in  $\text{H}_2\text{O}$ , and treated with  $\text{K}_3\text{Fe}(\text{CN})_6$  and a few drops of dil. aq.  $\text{NH}_3$ . A brown ppt. of  $\text{Ag}_3\text{Fe}(\text{CN})_6$  indicates  $\text{Cl}'$ . E. C. S.

Determination of available chlorine in bleach liquor.—See B., 1933, 1008.

Determination of bromide by conversion into cyanogen bromide. S. I. SCHODTSEV (J. Appl. Chem. Russ., 1933, 6, 991—994).—Aq.  $\text{Cl}_2$  is added to 50—100 c.c. of solution containing  $\leq 2$  mg.  $\text{Br}'$ , 10 c.c. of *N*- $\text{KCN}$  are added, excess of  $\text{Cl}_2$  is removed by aspiration, 2 g. of  $\text{KI}$  are added, and liberated  $\text{I}$  is titrated with aq.  $\text{Na}_2\text{S}_2\text{O}_3$ . The advantages of the use of  $\text{Cl}_2$  as oxidant rather than  $\text{KMnO}_4$ ,  $\text{KIO}_3$ , or  $\text{KBrO}_3$  consist in the facility of removal of excess of oxidant, and in that the method is applicable in presence of org. impurities. R. T.

Determination of small amounts of iodine and bromine in presence of chlorine, especially in

mineral waters. G. LOCKEMANN and T. KUNZMANN (Z. anal. Chem., 1933, 94, 385—396).—(a)  $\text{I}'$ , liberated by  $\text{FeCl}_3$ , is determined colorimetrically. (b) The total halogen is determined by titration with  $\text{AgNO}_3$ . (c) Addition of a known, insufficient vol. of *N*- $\text{AgNO}_3$  ppts.  $\text{AgI} + \text{AgBr} + \text{some AgCl}$ . From the wt. of this, with (a), the amount of  $\text{Br}$  is calc. The amount of  $\text{Cl}$  is evaluated from (a), (b), and (c).

J. S. A.

Argentometric determination of iodides using cinchonine and bismuth nitrates as indicator. R. UZEL (Coll. Czech. Chem. Comm., 1933, 5, 383—395).—A mixture of cinchonine nitrate and  $\text{Bi}(\text{NO}_3)_3$  may be used as internal indicator in the titration of  $\text{I}'$  with  $\text{AgNO}_3$  in presence of  $\text{HNO}_3$ . The orange-red compound  $\text{C}_{19}\text{H}_{22}\text{ON}_2 \cdot \text{HBIl}_4$  (I) is formed and is decomposed by  $\text{AgNO}_3$ . The results are 0.5% low. Most common ions do not interfere. If  $\text{PO}_4'''$  or  $\text{AsO}_4'''$  is present, excess of the  $\text{Bi}$  reagent must be added to ppt. these. The titration may be performed in presence of  $\text{Cl}'$  and  $\text{Br}'$ . If  $[\text{Br}'] > 4[\text{I}']$ , an equal vol. of  $\text{Pr}^0\text{OH}$  should be added to suppress the ionisation of the bromide and lower the solubility of (I). If  $[\text{Cl}'] > 20[\text{I}']$  or  $[\text{CNS}'] > [\text{I}']$ , the  $\text{I}'$  must be pptd. as  $\text{AgI}$  from  $\text{NH}_3$  solution, reduced by  $\text{Zn}$  and acid, and then titrated as described above. In presence of  $\text{CN}'$  the titration must be carried out in strongly acid solution.  $\text{Fe}(\text{CN})_6'''$  and  $\text{Co}(\text{CN})_6'''$ , if present in considerable quantity, should first be pptd. by means of  $\text{Zn}(\text{NO}_3)_2$ . The method may also be employed for the determination of  $\text{Ag}'$  by titration with  $\text{KI}$ . D. R. D.

Volumetric determination of small quantities of inorganic iodine. J. F. SADUSK, jun., and E. G. BALL (Ind. Eng. Chem. [Anal.], 1933, 5, 386—389).—Under the prescribed conditions, Winkler's method gives trustworthy results for  $< 1$  mg.  $\text{I}$ .  $\text{Cl}'$  and  $\text{SO}_4''$  do not interfere, unless present in high concn.,  $[\text{Br}']$  should not exceed  $20 \times [\text{I}']$ ,  $\text{NO}_2'$  should be absent, and  $[\text{Fe}''']$  should be  $< 0.1 \times [\text{I}']$ . E. S. H.

Determination of small quantities of fluorine. Steiger-Merwin reaction. I. Optimum conditions and interference. II. Procedure. H. J. WICHMANN and D. DAHLE (J. Assoc. Off. Agric. Chem., 1933, 16, 612—619, 619—624).—(1) The yellow colour of  $\text{H}_2\text{O}_2$ -peroxidised  $\text{Ti}$  develops only at  $p_{\text{H}} > 4$  and the bleaching action of  $\text{F}$ , which is the basis of the above determination, increases with increasing  $p_{\text{H}}$  to a max. at approx. 1.5 and then decreases almost to zero at 2.5. The bleaching per unit of  $\text{F}$  increases with increase in concn. of  $\text{F}$  and decrease in  $\text{Ti}$ , the sensitiveness being greatest for 0.02—0.01 mg.  $\text{F}$ , which is the lower limit of the reaction if a polarising photometer is used. Curves show the effects on the reaction of various quantities of inorg. substances (especially  $\text{Al}$ ,  $\text{SO}_3$ ,  $\text{P}_2\text{O}_5$ ), org. matter from apple skins, and colouring matters of fruits, and indicate that complexes are formed which invalidate the reaction because the effects on the  $\text{Ti}$  of the foreign substance and the  $\text{F}$  are not additive.

II. A procedure based on the above data is described in which the equiv. of 0.01—0.05 mg. of  $\text{F}$  is used and the  $p_{\text{H}}$  adjusted to  $1.50 \pm 0.02$  by 1:10  $\text{HCl}$ ; a mixture of 2 c.c. of 20%  $\text{TiCl}_3$  and



20 c.c. of HCl is diluted to 1 litre and 2 c.c. are used. The max. errors for samples of apple peelings, cabbages, and rat-feeds containing 0.0006—0.1% NaF and 0—0.5 mg. F were  $-0.01\%$  and  $-0.03$  mg., respectively. F occurs as a natural ingredient of drinking- $H_2O$  (0.45—3.9 p.p.m.); in manufactured phosphates as a remnant of that originally present in the rock (256—307 p.p.m.); in spray residues of apples and vegetables (1.7—135.3 p.p.m.); and in strawberry juice used as preservative (141 p.p.m.). J. G.

**Determination of fluorides.** I. M. KORENMAN (J. Appl. Chem. Russ., 1933, 6, 986—987).—Small quantities of F are determined with an error of  $\pm 6\%$  by comparing the coloration given by the solution with 5 c.c. of 0.045%  $Ti(SO_4)_2$ , 3 c.c. of 3%  $H_2O_2$ , and  $H_2O$  to 25 c.c. with that given by a standard solution.  $< 0.002$  mg. HF per litre of air can be detected by the change in colour from violet to yellow of a test-paper dipped in Zr alizarin lake and HCl. R. T.

**Fluorometry.** I. I. TANANAEV (J. Appl. Chem. Russ., 1933, 6, 939—944).—Excess of  $SiO_2$  is added to 10 c.c. of aq. NaF, the solution is made acid to Me-orange with conc. HCl, and then neutral with 0.5N-KOH (I), when 10 c.c. of 4N- $CaCl_2$  are added, and the solution is titrated with (I) (phenolphthalein); 1 equiv. of (I) is used per equiv. of F. Directions are given for the fluorometric titration of Ca, Al, Fe, and  $SiO_2$ ; these determinations can be performed in 30 min., and are as accurate as the usual methods. R. T.

**Determination of fluorine in insoluble fluorides.** A. A. BORKOVSKI and N. A. PORFIREV (J. Appl. Chem. Russ., 1933, 6, 984—985).—F in fluor-spar or cryolite is determined with an error of  $\pm 1\%$  by the following modification of Tananaev's method: 0.2—0.5 g. of substance is ground with 1 g. of  $SiO_2$  and added to 40 c.c. of 25%  $H_2SO_4$ ,  $H_2SiF_6$  is distilled off into  $H_2O$ , the distillate is made neutral with 0.25N-NaOH, and F' is determined titrimetrically according to I. Tananaev (cf. preceding abstract). R. T.

**Titration of sodium sulphide with potassium ferricyanide.** A. A. VASSILIEV and M. E. SCHUB (J. Appl. Chem. Russ., 1933, 6, 988—990).—20 c.c. of aq.  $Na_2S$  (I) are titrated with 0.1N- $K_3Fe(CN)_6$  (II) to the appearance of a red coloration with 0.4% Na nitroprusside (III). 20 c.c. of (I), 10 c.c. of 0.5N-NaOH, 5 c.c. of (III), and 50 c.c. of  $H_2O$  are then added to the vol. of (II) used in the first titration, and the mixture is titrated further with (II), adding  $\leq 1$  drop every 10 sec. The  $Na_2S$  content so found is  $>$  that by direct titration, during which part of the  $Na_2S$  undergoes oxidation, and is practically identical with that found iodometrically. R. T.

**Flask oxidation in determination of sulphurous acid by distillation.** P. F. NICHOLS and H. M. REED (Ind. Eng. Chem. [Anal.], 1933, 5, 398—399).—No means of entirely preventing oxidation in the distillation flask was discovered. E. S. H.

**Inhibiting effect of certain substances on oxidation of sulphurous acid.** J. S. MITCHELL, G. A. PITMAN, and P. F. NICHOLS (Ind. Eng. Chem. [Anal.],

1933, 5, 415—416).—Numerous substances, known to inhibit the oxidation of  $Na_2SO_3$  and  $NaHSO_3$  solutions, are found to inhibit the oxidation of  $H_2SO_3$ . None of these was found effective in increasing the yield of  $H_2SO_3$  distilled from dried fruits. E. S. H.

**Direct titration of sulphate.** Tetrahydroxyquinone as an internal indicator. W. C. SCHROEDER (Ind. Eng. Chem. [Anal.], 1933, 5, 403—406).— $SO_4^{--}$  (2—20 mg. in 25 c.c.) is determined by direct titration with aq.  $BaCl_2$ , with tetrahydroxyquinone as indicator. The error is  $\pm 0.2$  mg.  $SO_4^{--}$ . The max. amounts of other ions permissible in the solution are:  $CO_3^{--}$  7.5,  $Al^{+++}$  5,  $SiO_3^{--}$  25,  $Mg^{++}$  15,  $Fe^{++}$  0.1 mg.;  $Ca^{++}$ ,  $OH^+$ , and  $Cl^-$  have no effect. E. S. H.

**Sodium rhodizonate as an indicator for determination of sulphate ions in acid mixtures.** M. N. MARUSCHKIN (J. Appl. Chem. Russ., 1933, 6, 951—962).—The results obtained by Strebinger and Zombory's method (A., 1930, 53) are high, owing to adsorption of Ba and  $H_2SO_4$  salts from the solution. In determination of pure  $H_2SO_4$ ,  $BaSO_4$  adsorbs exclusively  $BaCl_2$ , in presence of  $HNO_3$   $Ba(NO_3)_2$  is very strongly adsorbed, and in presence of alkali sulphates  $K_2SO_4$  is adsorbed  $>$  is  $Na_2SO_4$ . R. T.

**Determination of small amounts of selenium in pyrites.**—See B., 1933, 1055.

**Determination of nitrogen by burning in the flaming arc.** W. D. TREADWELL and T. ZURRER (Helv. Chim. Acta, 1933, 16, 1180—1187).—The gas, containing  $\approx$  a few %  $N_2$  and a large and therefore practically const. proportion of  $O_2$ , is allowed to flow, at about 1 litre per min., through a flaming arc, requiring about 20 watts, between Pt electrodes. The gases are absorbed in aq. NaOH at a rate proportional to their concn. and the amount of NaOH neutralised is determined by conductometric titration. A formula from which the concn. of  $N_2$  may be determined is deduced. The results are in good agreement with those obtained by other methods. M. S. B.

**Titration of ammonia in presence of boric acid.** Macro- and micro-Kjeldahl procedures. E. W. MEEKER and E. C. WAGNER (Ind. Eng. Chem. [Anal.], 1933, 5, 396—398).—The end-point is determined by colour matching with Me-red. E. S. H.

**Accurate semimicro-Kjeldahl determination.** D. I. HITCHCOCK and R. C. BELDEN (Ind. Eng. Chem. [Anal.], 1933, 5, 402).—Northrop's method (A., 1933, 94) is modified by using Hg and Se simultaneously as catalysts; the mean error is 0.2%. E. S. H.

**Determination of small quantities of nitrous acid by the esterification method.** I. J. SCHAFERSCHTEIN (J. Appl. Chem. Russ., 1933, 6, 995—997).—Fischer and Schmidt's method (A., 1929, 667) serves for determining 0.025—5 mg. of  $NaNO_2$ , with certain modifications, viz., air is substituted for  $CO_2$  for aspiration of  $MeNO_2$ , and Bernoulli's reagent for KI in determining  $MeNO_2$ . If EtOH is used in place of MeOH, the results should be multiplied by 1.075. The results are 40% low if impure MeOH is used. R. T.

**Determination of nitrates in water.**—See B., 1933, 1088.



**Mould-growth test for minute amounts of arsenic.** H. R. SMITH and E. J. CAMERON (Ind. Eng. Chem. [Anal.], 1933, 5, 400—401).—The sample is added with *Scopulariopsis brevicaulis* (Sacc.), Bainier, to a synthetic medium of Czapek's solution and agar. Small amounts of As (1 p.p.m. in a 1-g. sample) are detected by the odour of  $\text{AsMe}_3$ , which develops within 2—5 hr. E. S. H.

**Determination of traces of arsenic by Cribier's method.** I. Mechanism of the method. H. GRIFFON and M. BUISSON (J. Pharm. Chim., 1933, [viii], 18, 422—437).—The method (cf. A., 1921, ii, 653) is extremely sensitive, but is essentially comparative, so that the experimental details must be followed exactly and fresh standard stains made for new reagents. With  $10^{-4}$  to  $10^{-7}$  g. As, the stain reaches its max. length in 20 min., when the rate of  $\text{AsH}_3$  formation is at a max. The max. rate at which  $\text{H}_2$  is evolved is proportional to the amount of As present. Only about 30% of the As is liberated as  $\text{AsH}_3$ , which produces the stain. The success of the method in analysis depends entirely on the prep. of the standard stains. S. C.

**Determination of silicon in sea-water.** T. G. THOMPSON and H. G. HOULTON (Ind. Eng. Chem. [Anal.], 1933, 5, 417—418).— $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4$  are added to the sample and the colour is compared with a picric acid standard. E. S. H.

**Colorimetric determination of carbon dioxide in gas mixtures.** P. W. WILSON (Science, 1933, 78, 462—463).—The method previously described (A., 1932, 1222) is modified for routine analyses so that  $p_{\text{H}}$  is determined colorimetrically. L. S. T.

**Distillation of hydrocyanic acid from sulphuric acid solutions.** **Determination [of cyanides].** S. MORRIS and V. G. LILLY (Ind. Eng. Chem. [Anal.], 1933, 5, 407—408).—The presence of Cl' does not adversely affect the distillation. Rubber stoppers and corks absorb HCN and should be protected by Sn foil. In absence of  $\text{Fe}(\text{CN})_6^{4-}$  and taking the prescribed precautions the method of Pagel and Carlson (A., 1933, 137) is accurate to 0.05%. E. S. H.

**Determination of alkalis as silicofluorides.** W. D. TREADWELL and W. KÖNIG (Helv. Chim. Acta, 1933, 16, 1201—1208).—If hydrated  $\text{SiO}_2$  containing NaCl is evaporated to dryness on the  $\text{H}_2\text{O}$ -bath with HF, Na passes quantitatively into  $\text{Na}_2\text{SiF}_6$  and can thus be accurately determined.  $\text{Na}_2\text{SiF}_6$  gives an acid reaction in solution, owing to the formation of HF, and the result obtained gravimetrically may be checked by treating the solution of  $\text{Na}_2\text{SiF}_6$  with  $\text{CaCl}_2$ .  $\text{CaF}_2$ , hydrated  $\text{SiO}_2$ , and free acid are formed, and the acid may be titrated electrometrically or by using an indicator such as bromocresol-purple, since there is a sharp end-point at  $p_{\text{H}}$  5.7. By combining the gravimetric and electrometric methods, binary mixtures of the alkalis may be determined. If Mg is present it is first removed by pptn. with hydroxyquinoline. The method is also suitable for micro-determinations. M. S. B.

**Separation of alkalis in silicate analysis and the titrimetric determination of potassium.** P. N. GRIGORIEV (Sprechsaal Keram., 1933, 66, 162—

163; Chem. Zentr., 1933, i, 3766).—After opening up with  $\text{HF} + \text{H}_2\text{SO}_4$  the excess of acid is removed by gentle ignition until fumes of  $\text{SO}_3$  are no longer evolved.  $\text{Ba}(\text{OH})_2$  is added instead of  $\text{BaCl}_2$  and the excess, together with basic constituents other than alkalis, removed with  $(\text{NH}_4)_2\text{CO}_3$  and aq.  $\text{NH}_3$ , or by passing  $\text{CO}_2$  into the alkaline solution. K is determined by a modification of the cobaltinitrite method. A. A. E.

**Titrimetric determination of perchlorates: microanalysis of potassium.** A. BOLLIGER (Z. anal. Chem., 1933, 94, 403—408).—The perchlorate (I) and picrate of methylene-blue (II) are sol. in  $\text{CHCl}_3$ . To the solution of the perchlorate to be determined is added 0.001N-(II) in slight excess,  $+\text{NaH}_2\text{PO}_4$  as buffer  $+\text{CHCl}_3$  to extract (I). Excess of (II) is determined by titration with 0.001N-picric acid, the picrate being extracted with  $\text{CHCl}_3$  from the  $\text{H}_2\text{O}$  layer until colourless. When  $> 1$  mg.  $\text{ClO}_4^-$  is present, (I) may be removed by centrifuging before extraction. 0.025 mg.  $\text{KClO}_4$  may be determined to within 5% in presence of  $\text{SO}_4^{2-}$  or  $\text{PO}_4^{3-}$ . J. S. A.

**Comparison of colorimetric methods for determining potassium.** F. ALTEN, H. WEILAND, and K. KURMIES (Z. Pflanz. Düng., 1933, 32, A, 171—182).—The cobaltinitrite ppt. obtained by the methods of Wrangell (B., 1933, 162), of Herzner (A., 1931, 1259), and of Fischer (*ibid.*) contains more Na than is required by  $\text{K}_2\text{Na}[\text{Co}(\text{NO}_2)_6]$ . By pptn. in presence of saturated NaCl solution,  $\text{K}_3[\text{Co}(\text{NO}_2)_6] \cdot \text{Na}_3[\text{Co}(\text{NO}_2)_6]$  (I) is invariably produced. In the Wrangell colorimetric method the colour intensity is proportional to the concn. only in the range  $(10—300) \times 10^{-6}$  g.  $\text{N}_2\text{O}_3$  in 100 c.c. Moreover, the nitrosoindole solution is unstable. Riegler's naphthol reagent is suitable for concns.  $> 15 \times 10^{-6}$  g.  $\text{N}_2\text{O}_3$  in 100 c.c. The colour obtained by Griess' reagent is suitably permanent and is applicable over wide ranges of  $[\text{NO}_2^-]$ . Details are given of a modified method involving pptn. of K as (I). A. G. P.

**Determination of sodium as sodium triuranyl magnesium acetate.** F. ALTEN, H. WEILAND, and E. HILLE (Z. Pflanz. Düng., 1933, 32, A, 129—140).—The methods of Blanchetière (A., 1923, ii, 579) (1), of Weiland (A., 1928, 383) (2), and of Kahane (A., 1930, 726, 880) (3) are compared. In (1) and (2), the use of  $\text{BaCl}_2$  instead of  $\text{Ca}(\text{OH})_2$  and uranyl acetate is recommended for the removal of  $\text{PO}_4^{3-}$  prior to the pptn. of the Na salt. Excessive amounts of K are pptd. by tartaric acid instead of EtOH. In (3) the inclusion of EtOH in the reagent solution is impracticable in the presence of  $\text{K}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{NH}_4^+$ , or  $\text{CaSO}_4$ . Details are given for the analysis of fertiliser materials, plant ash, and soil extracts, and for the recovery of U from wash liquors etc. A. G. P.

**Direct determination of sodium in presence of large amounts of calcium, magnesium, and ammonium.** T. NODA (J. Soc. Chem. Ind. Japan, 1933, 36, 635B).—The uranyl Mg acetate method (cf. A., 1930, 726) gave an accuracy of 1% in the determination of Na (1—2 mg. NaCl) in presence of  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ , or  $\text{NH}_4\text{Cl}$  (2.0 g.) at the dilutions (per c.c.) 0.1 g. Ca, 0.07 g. Mg, or 0.04 g.  $\text{NH}_4$ . R. S.



**Microchemical detection of rubidium in presence and absence of caesium.** N. A. TANANAIEV, A. G. KANKANJAN, and M. V. DARBINJAN (*J. Appl. Chem. Russ.*, 1933, 6, 980—983).—The min. concn. in which Rb can be detected as  $\text{Rb}_2\text{AuPdCl}_7$  (I) is 0.3 mg. per c.c. in absence, and 0.2 mg. in presence, of Cs and other cations; Cs can similarly be detected as  $\text{Cs}_2\text{AuPdCl}_7$  (II) in  $< 0.0004N$  solutions. The crystals of (I) and (II) are octahedral when pptd. from 0.1N and cruciform when pptd. from  $< 0.1N$  solutions. Rb cannot be detected by the above method in solutions in which  $[\text{Rb}]:[\text{Cs}] > 1:4$ . Cs may be separated by pptn. as  $\text{CsBiF}_4$  (A., 1932, 1010).

R. T.

**Iodometric determination of silver.** (MILE.) M. L. JOSTEN (*Compt. rend.*, 1933, 197, 1324—1326; cf. A., 1928, 1391; 1931, 1023).—The reactions consequent on mixing an I-iodide solution with one of  $\text{AgNO}_3$  are: (a)  $\text{KI} + \text{AgNO}_3 = \text{AgI} + \text{KNO}_3$ ; (b)  $\text{I}_2 + \text{H}_2\text{O} + \text{AgNO}_3 = \text{AgI} + \text{HOI} + \text{HNO}_3$ ; (c)  $\text{HOI} + \text{KI} = \text{I}_2 + \text{KOH}$ ; and (d)  $3\text{HOI} + 3\text{AgNO}_3 = 2\text{AgI} + 3\text{HNO}_3 + \text{AgIO}_3$  (pptd.); the pptn. of  $\text{AgIO}_3$  vitiates the result. The change of tint (starch being present) occurs when the no. of mols. of  $\text{AgNO}_3$  added equals that of mols. of  $\text{KI}$  + half the no. of atoms of I [(a) and (b) above]. For accurate work aq.  $\text{AgNO}_3$  should be poured into aq.  $\text{KI}$  with addition of only one drop of  $\text{EtOH}$ —I, thus avoiding the difficulty resulting from (d). C. A. S.

**Silver electrodes "of the second kind" as comparison and indicator electrodes.** W. HILTNER (*Z. anal. Chem.*, 1933, 95, 37—43; cf. A., 1933, 1027).— $\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{AgI}$ , or  $\text{Ag}_2\text{S}$  electrodes, stabilised by addition of aq.  $\text{NaCl}$ ,  $\text{AgNO}_3$ , or  $\text{Ag}_2\text{SO}_4$ , may be used as comparison electrodes, or as indicator electrodes in determining Ag in presence of oxidising agents, or for the respective anions. The halides may be fused on to a Pt wire. They are unsuitable for pptn. reactions with  $\text{PO}_4'''$ ,  $\text{CrO}_4''$ , or  $\text{C}_2\text{O}_4''$ . The  $\text{Ag}_2\text{S}$  electrode may be used in cyanometric Ni determinations.

H. J. E.

**Analytical and quantitative lines of silver, arsenic, bismuth, cadmium, copper, mercury, lead, antimony, and tin in the arc spectrum, between 2330 Å. and 3400 Å.** S. PIÑA DE RUBIES and M. A. BARGUES (*Z. anorg. Chem.*, 1933, 215, 205—210).—The substance to be examined is diluted with  $\text{NaCl}$  to concns. from 1% to 0.0001%, and 0.05 g. of the mixture is used. It also contains 0.5% Mo as reference element. Intensities obtained from spectrographs of three different resolving powers are recorded. Analytical lines are those for the 1% mixture. They are always the same if the same quantity of substance is vaporised. Quant. lines are those analytical lines the intensities of which are not changed by the electrical conditions of the arc within certain limits.

M. S. B.

**Magneto-optic Nicol rotation method for quantitative analysis of calcium.** E. R. BISHOP, C. B. DOLLINS, and I. G. OTTO (*J. Amer. Chem. Soc.*, 1933, 55, 4365—4370).—The procedure described is suitable for  $[\text{Ca}']$  between  $3.74 \times 10^{-12}$  and  $1 \times 10^{-3}$  g. per c.c. More conc. solutions are diluted. The results are not influenced by the presence of  $\text{Mg}''$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{H}^+$ ,  $\text{SO}_4''$ ,  $\text{NO}_3'$ , or  $\text{PO}_4'''$ . The error in duplicate deter-

minations or in comparison with  $\text{KMnO}_4$  titrations is about 10%. E. S. H.

**Volumetric determination of the hardness of water.**—See B., 1933, 1038.

**Determination of calcium in lead-calcium alloys.**—See B., 1933, 1062.

**Determination of magnesium by the drop method.** N. A. TANANAIEV and P. S. SAVTSCHENKO (*J. Appl. Chem. Russ.*, 1933, 6, 970—975).—1—1.5 c.c. of 2N- $\text{NH}_4\text{Cl}$ , excess of N- $\text{Na}_2\text{CO}_3$ , and 2—3 drops of aq.  $\text{H}_2\text{O}_2$  are added to 2—3 c.c. of solution (I), which is then boiled and filtered. A few drops of aq.  $\text{NH}_3$  and of aq.  $\text{Na}_3\text{PO}_4$  are added to the filtrate (II), when a ppt. of  $\text{Mg}_2\text{P}_2\text{O}_7$  (III) indicates the presence of  $< 0.02$  mg. of Mg per c.c. of (I). The presence of other cations does not interfere, but  $\text{AsO}_4'''$  and  $\text{PO}_4'''$  should previously be removed. Mg may be determined as (III) gravimetrically or nephelometrically, or by removing  $\text{NH}_4^+$  from (II) by aq.  $\text{CH}_2\text{O}$ , pptg. Mg as  $\text{Mg}(\text{OH})_2$  by aq. alkali, and weighing the  $\text{MgO}$  obtained by igniting  $\text{Mg}(\text{OH})_2$ . R. T.

**Qualitative analysis of the hydrogen sulphide group without ammonium polysulphide.** R. W. HUFFERD (*Ind. Eng. Chem. [Anal.]*, 1933, 5, 422).—The solution is boiled with aq. Br, excess of Br is driven off,  $\text{H}_2\text{S}$  is passed, and the ppt. is treated with freshly prepared  $\text{NH}_4\text{HS}$ . E. S. H.

**Qualitative analysis of small amounts of minerals. II. Detection of small amounts of zinc with dithizone.** G. RIENACKER and W. SCHIEFER (*Z. anal. Chem.*, 1933, 94, 409—415; cf. A., 1932, 588).—A  $\text{CCl}_4$  solution of dithizone gives with alkaline Zn solutions a red coloration in the  $\text{H}_2\text{O}$  layer which is sp. (limit  $5 \times 10^{-6}$  g.). Cd, Cu, and Hg interfere and must first be removed by  $\text{H}_2\text{S}$ . J. S. A.

**Precipitation conditions of zinc sulphide and aluminium hydroxide, and the gravimetric separation of zinc from aluminium.** J. N. FRERES (*Z. anal. Chem.*, 1933, 95, 1—36).— $(\text{NH}_4)_2\text{SO}_4$  is added to the solution containing Zn, preferably as  $\text{ZnSO}_4$  and with little  $\text{Cl}'$ , and  $\text{H}_2\text{SO}_4$  added until it is just acid to Me-orange. Zn is pptd. in hot solution as  $\text{ZnS}$  by  $\text{H}_2\text{S}$ , finely-divided filter-paper being present. The ppt. is ignited in  $\text{H}_2\text{S}$  and weighed as  $\text{ZnS}$ . Factors affecting the separation and pptn. are discussed. The potentiometric determination of Zn in presence of  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{CNS}$ , and  $(\text{NH}_4)_2\text{SO}_4$  indicates complex ion formation. H. J. E.

**Determination of lead as carbonate and its separation from silver by means of carbonic acid in dilute pyridine solution.** A. JÍLEK and J. KOŤA (*Coll. Czech. Chem. Comm.*, 1933, 5, 396—410).—The neutral solution, containing  $> 0.2$  g. of Pb and  $> 0.2$  g. of Ag, is diluted to 80 c.c., 5 c.c. of  $\text{EtOH}$  and 15 c.c. of 10% aq.  $\text{C}_5\text{H}_5\text{N}$  are added, and  $\text{CO}_2$  is passed for 45 min. After 2—3 hr.,  $\text{CO}_2$  is passed again for 5 min., and the ppt. is collected and washed with  $\text{H}_2\text{O}$  saturated with  $\text{CO}_2$  and containing 4%  $\text{EtOH}$  and 0.4%  $\text{C}_5\text{H}_5\text{N}$ . The ppt. may be dried at  $120^\circ$  and weighed as  $\text{PbCO}_3$ , or ignited and weighed as  $\text{PbO}$ . The Ag may be pptd. from the filtrate by means of  $\text{HCl}$ . D. R. D.



**Spectrographic adsorption measurements with metal ion solutions at powder surfaces.** E. BERL and B. SCHMITT (Kolloid-Z., 1933, 65, 264—267).—Analysis of ultimate rays allows the detection of 0.001% of Cu, Pb, Zn, or Cd in mineral powders.

E. S. H.

**Use of amyl alcohol in the sodium diethyldithiocarbamate method for determination of copper.** R. W. THATCHER (J. Amer. Chem. Soc., 1933, 55, 4524).—*iso*Amyl alcohol, redistilled at 129—131°, is preferred to *n*-amyl alcohol.

E. S. H.

**Application of diphenylcarbazine and diphenylcarbazone to mercurimetric microtitration.** J. V. DUBSKÝ and J. TRTÍLEK (Chem. Listy, 1933, 27, 385—388).—Diphenyl-carbazide and -carbazone give intense violet colorations in presence of  $\text{Hg}^{++}$ . Accurate results are obtained using these indicators in titration of  $\text{Cl}^-$  by 0.01*N*- $\text{Hg}(\text{NO}_3)_2$ ;  $\text{Cu}^{++}$ ,  $\text{Cd}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Fe}^{++}$ ,  $\text{Ca}^{++}$ , and  $\text{Ba}^{++}$  do not interfere. The solution titrated should contain a small excess of  $\text{HNO}_3$ .

R. T.

**Detection of europium, and three lines of extreme sensitivity.** G. PICCARDI (Atti R. Accad. Lincei, 1933, [vi], 17, 1092—1094).—The three lines 4661, 4627, and 4594 Å. of Eu are shown very persistently in the flame spectrum of that element even when only a trace of it is mixed with Nd-Sa-Gd mixtures, and they may serve to detect Eu in such mixtures.

O. J. W.

**Drop reaction for aluminium.** S. N. POTCHNIKOV (J. Appl. Chem. Russ., 1933, 6, 948—950).—Al is detected in presence of other cations by adding excess of  $(\text{NH}_4)_2\text{S}$ , acidifying with 2*N*-HCl, boiling, and filtering. 0.05% Na alizarinsulphonate and an equal vol. of 5%  $\text{Na}_2\text{S}_2\text{O}_3$  are added to the filtrate, and the solution is boiled during 1 min.; if < 0.04 mg. Al is present the ppt. of S is coloured rose to orange-red.

R. T.

**Micro-analysis of aluminium. I. Determination of iron, copper, and manganese.**—See B., 1933, 1062.

**Tervalent manganese. VIII. Determination of  $\text{MnO}_2$  in pyrolusite by thermal degradation to  $\text{Mn}_2\text{O}_3$ .** W. FRANKE and A. FREITAG (Z. anorg. Chem., 1933, 215, 105—110; cf. A., 1930, 179).—The thermal deoxygenation of  $\text{MnO}_2$  in artificial "pyrolusites" is influenced by the nature of the other substances present, and no definite temp. can be prescribed for the change  $\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3$ . Determinations based on extraction with dil.  $\text{H}_2\text{SO}_4$  are also unsatisfactory.

F. L. U.

**Colorimetric determination of iron with sulphosalicylic acid.** F. ALTEN, H. WEILAND, and E. HILFE (Z. anorg. Chem., 1933, 215, 81—91).—Extinction coeffs. of mixtures of sulphosalicylic acid with acid and alkaline Fe solutions in presence of various foreign substances (B., 1932, 50) have been measured. The colour is influenced by  $[\text{H}^+]$ ,  $\text{PO}_4^{+++}$ ,  $\text{Mn}^{++}$ , and org. substances. Procedure is described, involving the use of citrate buffers and colour filters, whereby disturbances due to the factors named, other than  $\text{Mn}^{++}$ , may be eliminated.

F. L. U.

**Antimony as an indicator electrode in potentiometric titration of iron and aluminium.** E. W. KANNING and F. H. KRATLI (Ind. Eng. Chem. [Anal.], 1933, 5, 381—383).—Sb is a suitable indicator electrode for the pptn. of  $\text{Fe}^{+++}$  and Al from neutral solutions of their chlorides by adding NaOH. Mixtures of  $\text{FeCl}_3$  and  $\text{AlCl}_3$  can be determined approx., especially when present in equal proportions.

E. S. H.

**Increased sensitivity of a microchemical reaction for  $\text{Co}^{++}$  and  $\text{Cu}^{++}$ , and the induced reaction of  $\text{Fe}^{++}$ ,  $\text{Fe}^{+++}$ , and  $\text{Ni}^{++}$ .** I. M. KORENMAN (Z. anal. Chem., 1933, 95, 44—48).—Co-pptn. of  $\text{Co}[\text{Hg}(\text{CNS})_4]$  (blue), or  $\text{Cu}[\text{Hg}(\text{CNS})_4] \cdot \text{H}_2\text{O}$  (yellowish-green), with  $\text{Zn}[\text{Hg}(\text{CNS})_4]$  (white) by  $(\text{NH}_4)_2[\text{Hg}(\text{CNS})_4]$  increases the sensitivity for  $\text{Co}^{++}$  and  $\text{Cu}^{++}$  25- and 16-fold to  $1:10^5$  and  $1:1.3 \times 10^5$ , respectively. Salts of  $\text{Fe}^{++}$ ,  $\text{Fe}^{+++}$ , and  $\text{Ni}^{++}$  give no ppt. with  $(\text{NH}_4)_2[\text{Hg}(\text{CNS})_4]$  alone, but form characteristic mixed crystals in presence of  $\text{Zn}^{++}$ .

H. J. E.

**Determination of small quantities of nickel in rock analysis.** H. F. HARWOOD and L. S. THEOBALD (Analyst, 1933, 58, 673—682).—In ordinary routine analysis Ni is partly co-pptd. with the  $\text{R}_2\text{O}_3$  oxides, but not completely, even in the presence of Br and  $\text{NH}_3$ . A correction must be applied to the  $\text{Al}_2\text{O}_3$  for the Ni co-pptd. Ni is not co-pptd. with  $\text{SiO}_2$ , CaO, or MgO. Ni is determined directly, on a separate sample of rock, in presence of Fe, Al, Ca, Mg, and alkalis (citric acid being added to prevent pptn. of the  $\text{R}_2\text{O}_3$  oxides) by pptn. with dimethylglyoxime (I).  $\alpha$ -Furildioxime can replace (I) and is preferable when < 0.02% of Ni is present. 0.0025% of NiO can be detected in 2 g. of rock.

E. C. S.

**Determination of nickel and small quantities of aluminium in heat-resistant alloys.**—See B., 1933, 1014.

**Electrolytic determination of chromium with rotating mercury electrode.** P. S. TUTUNDŽIĆ (Z. anorg. Chem., 1933, 215, 19—22; cf. A., 1932, 243).—By using a rotating Hg cathode the time required for electrolytic determination of 0.1—0.2 g. of Cr may be reduced to 120 min.

F. L. U.

**Application of the potential-forming system metal/metal anion to potentiometric titrations. I. Precipitation titration of chromate, molybdate, and tungstate, and of some metal ions, using chromium, molybdenum, and tungsten indicator electrodes.** H. BRINTZINGER and E. JAHN (Z. anal. Chem., 1933, 94, 396—403).— $\text{CrO}_4^{--}$ ,  $\text{MoO}_4^{--}$ , and  $\text{WO}_4^{--}$  may be titrated potentiometrically, preferably at 95°, against 0.1*N*- $\text{BaCl}_2$ , using Cr-plated stainless steel, Mo or W wire, respectively, as electrode. Ba, Sr, Pb, Cu, Cd, and Mn may be determined similarly by titration with  $\text{Na}_2\text{MoO}_4$ . For Sr and Mn, 30—40 vol.-% of EtOH should be added.  $\text{Na}_2\text{CrO}_4$  and  $\text{Na}_2\text{WO}_4$  may also be used.

J. S. A.

**Electro-analytic determination of chromium at a rotating mercury electrode.** P. S. TUTUNDŽIĆ (Bull. Soc. Chim. Yougoslav., 1933, 4, 101—105).—The method previously described (A., 1932, 243) gives good results for the determination of Cr.

R. T.



**Determination of titanium in steel.**—See B., 1933, 1060.

**Determination of zirconium in steel.**—See B., 1933, 1060.

**Qualitative analysis of small amounts of minerals. III. Detection of tantalum and niobium.** G. RIENACKER and W. SCHIFF (Z. anal. Chem., 1933, 94, 415—422; cf. this vol., 48).—Ta is detected by the pptn. of tantalic acid from acid solution. The mineral is fused with  $\text{NaHSO}_4$ , dissolved in dil.  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$ , and  $\text{H}_2\text{SO}_3$  added. The solution is boiled,  $\text{H}_2\text{SO}_3$  being slowly added to replace evaporated  $\text{H}_2\text{O}$ . Pptn. of Ta, but not Nb if alone, occurs in 10—15 min. Yellow  $\text{WO}_3$ , sol. in  $\text{NaOH}$ , is also pptd.  $\text{H}_3\text{PO}_4$  or a large excess of  $\text{SiO}_2$  interferes. Nb in 0.5 c.c. of the dil.  $\text{H}_2\text{SO}_4$  solution from a  $\text{NaHSO}_4$  fusion is reduced to  $\text{Nb}^{\text{III}}$  by Zn, 0.5 c.c. of alizarin in EtOH added, then 0.4 c.c. of 10%  $\text{H}_2\text{SO}_4$  + 1 drop of saturated aq. Na tartrate + 1 drop of saturated aq. NaOAc. In presence of Nb, a red Nb-alizarin lake of indefinite composition is pptd.

J. S. A.

**Spectro-analytic investigation of purest platinum.** W. GERLACH (Physikal. Z., 1933, 34, 846; cf. A., 1933, 800).—The following specifications are given: technically pure Pt, 99.5%; chemically pure, impurity 0.01—0.1%; physically pure, 0.001—0.01%; spectroscopically pure, < 0.001%.

A. J. M.

**Sources of error in liquid thermometers due to the behaviour of the indicator.** W. GRUNDMANN (Z. Physik, 1933, 86, 550—554).—The effect of compressibility, gas absorption, distillation, and contraction of the liquid on the accuracy of these thermometers is discussed.

A. B. D. C.

**Modified design for mercury bulb of thermostat.** G. B. HEISIG and A. E. CAMERON (Ind. Eng. Chem. [Anal.], 1933, 5, 420—421).—The bulb is filled with Hg, has a large surface, but uses a small amount of Hg. The device enables a 25-litre thermostat to be kept at  $25 \pm 0.002^\circ$ .

E. S. H.

**Automatic cryostat.** A. E. CAMERON (Rev. Sci. Instr., 1933, [ii], 4, 610—611).—An apparatus for the range  $0^\circ$  to  $-70^\circ$ , with a max. variation of  $\pm 0.1^\circ$ , to operate for 12—24 hr., is described. Cooling liquid is forced from a reservoir, an equal vol. of liquid being automatically siphoned back from the bath.

N. M. B.

**Determination of heat of dissolution.** M. M. POPOV, K. G. CHOMJAKOV, N. N. FEODOSSJEV, and P. K. SCHIROKICH (Z. physikal. Chem., 1933, 167, 29—34).—With calorimeters so constructed as to permit thorough mixing of the contents and consisting solely of metal parts not projecting far out of the liquid the adiabatic method of operation and the usual method give the same result. The mol. heat of dissolution of KCl in 200 mols. of  $\text{H}_2\text{O}$  at  $20^\circ$  is  $-4.376 \pm 0.1\%$  kg.-cal.<sub>15</sub>

R. C.

**Vacuum annealing furnace.** E. F. LOWRY (Rev. Sci. Instr., 1933, [ii], 4, 606—609).—The furnace tube and heater elements are constructed of 80:20 Cr-Ni; rubber gaskets are replaced by picein wax joints.

N. M. B.

**Wide-angle magnetic spectrometer.** C. D. BOCK (Rev. Sci. Instr., 1933, [ii], 4, 575—580).—An instrument for focussing widely divergent ions is described. By a suitable variation in the intensity of the deflecting magnetic field, a second-order focus is obtained.

N. M. B.

**Use of thermionic valves and undamped high-frequency oscillations in quantitative spectrum analysis.** G. POTAPENKO (Z. anorg. Chem., 1933, 215, 44—48).—An arrangement for generating a.c. at 80—100 kv. and  $>10^6$  cycles for the production of spark spectra is described. The spark is very const. and analytical results are reproducible. The spectra are practically free from air lines.

F. L. U.

**Production of astigmatism in spectrographs by inclining lenses.** A. COUDER (Compt. rend., 1933, 197, 1199—1201).—A method for enlarging the image of a spectral line as it falls on a photographic plate, by means of astigmatism caused by inclining the lenses by rotating them around an axis parallel to the edges of the prism, is described.

C. A. S.

**Röntgengoniometer.** E. SCHIEBOLD (Z. Krist., 1933, 86, 370—383).—The instrument ("rotation röntgengoniometer") resembles in principle that of Sauter (cf. A., 1933, 451, 480); anticipation is claimed.

C. A. S.

**Measurement of vibration ellipse by means of elliptically polarised light of great ellipticity.** C. MÜNSTER (Z. Krist., 1933, 86, 325—334).

C. A. S.

**Complementary colour relations.** E. GENBERG (Proc. Physical Soc., 1933, 45, 836—840).—Pairs of wave-lengths have been determined which are complementary with respect to equi-energy radiation taken as white. The energy and luminosity of one of the complementaries for unit luminosity of the white are given.

J. W. S.

**Nephelometry.**—See B., 1933, 991.

**Fluorescence testing.**—See B., 1933, 1067.

**Unidirectional photo-cells.** F. ROTHER and H. BOMKE (Physikal. Z., 1933, 34, 865—870).—Methods are described for the improvement of the efficiency of unidirectional  $\text{Cu}_2\text{O}$  cells. A thin layer of  $\text{Cu}_2\text{O}$  is best, but there is a practical limit to this. The efficiency can be increased by preparing the  $\text{Cu}_2\text{O}$  layer in an atm. of  $\text{H}_2\text{O}$  vapour. The addition of a foreign metal to the Cu on which the  $\text{Cu}_2\text{O}$  is formed may alter the properties of the latter, owing to the presence of the foreign metal in the diffusion layer. If the Cu is alloyed with a metal which is permeable to, or dissolves,  $\text{O}_2$ , e.g., Ag, the  $\text{Cu}_2\text{O}$  may be formed between a zone of Cu and one of the added metal. Cells with this arrangement are more efficient.

A. J. M.

**Light beam of uniform intensity of cross-section.** J. T. LAY and I. C. CORNOG (Rev. Sci. Instr., 1933, [ii], 4, 600—602).—For the measurement of the intensity of a beam of light at any point in its cross-section a photo-electric method is described, leading to the production of a beam varying in intensity by  $<0.3\%$  over an area of 30 sq. cm.

N. M. B.



**Reduction of grain effects in microphotometer readings.** S. HARRIS (Rev. Sci. Instr., 1933, [ii], 4, 598—599; cf. Richtmyer, A., 1933, 800).—Grain effect is reduced by the use of a slit of adjustable width and length. N. M. B.

**Microphotometer.** J. WEIGLE (Rev. Sci. Instr., 1933, [ii], 4, 595—597).—The instrument embodies a simple device for controlling the movement of the photographic plate and the device for recording the galvanometer deflexions. N. M. B.

**Improved design of the mechanical interval sorter and its application to the analysis of complex spectra.** G. R. HARRISON (Rev. Sci. Instr., 1933, [ii], 4, 581—586).—The machine previously described (cf. A., 1933, 247) is improved to record groups of lines containing a no. of lines given by their frequency density. Motor drive is employed; the tape will record in either direction, and improved calibration of the tape eliminates errors due to stretch. Intervals up to 10,000 wave nos., accurate to  $\pm 0.02$  wave no., can be recorded. Applications to the spectra of Os, Ir, and Ce are given. N. M. B.

**Apparatus for determination of  $p_H$ .** W. HÜTINGER (Woch. Brau., 1933, 50, 338—339).—The circuit consists of the solution of unknown  $p_H$  connected to a standard acid solution by a KCl—agar bridge and a capillary electrometer. After addition of a little quinhydrone to each cell alkali is run into the acid until a null point is reached, and the  $p_H$  calc. from the titration val. The method is rapid and accurate. R. H. H.

**Stabilising of cold-cathode X-ray tubes.** I. FANKUCHEN (Rev. Sci. Instr., 1933, [ii], 4, 593—594).—Instability due to irregular gas emission from parts of the tube subjected to electrical discharges is eliminated by confining the intense electrical fields in the tube to regions where the length of the lines of force is  $<$  the mean free path of the ions at the existing gas pressure. N. M. B.

**Variation of electrical conductivity of dielectrics with temperature in a range from  $20^\circ$  to  $-110^\circ$ .** S. SHIMIZU (Sci. Rep. Tôhoku, 1933, 22, 662—686).—In general, a linear relation between the log of the conductivity and  $1/T$  exists for quartz, cristobalite, kaolin, filter-paper, selenite, volcanic glass, ebonite, and mica, but with most of these, sharp changes of slope occur at sp. temp. In some cases, these anomalies are correlated with the presence of  $H_2O$ . J. G. A. G.

**Simple high [electrical] resistance.** I. C. JONES (Nature, 1933, 132, 823; cf. A., 1933, 1265). L. S. T.

**Amplification and recording of rapid Geiger-Müller counter impulses.** G. L. LOCHER (J. Franklin Inst., 1933, 216, 553—558).—A circuit which is of high sensitivity and can record up to 1400 impulses per sec. is described. The true no. of impulses is  $Nx/(1 - e^{-x})$ , where  $N$  is the observed no., and  $x$  is the average no. of impulses occurring in the resolving time of the apparatus. Photo-electric processes play an important part in the recovery time of counters. A. G.

**Demonstration experiment. Barkhausen effect up to the Curie point.** O. TESCHE (Physikal. Z., 1933, 34, 879).—A ferromagnetic wire, heated by a.c., is surrounded symmetrically by a ring-coil. The Barkhausen effect can be shown to disappear on passing through the Curie point. A. J. M.

**Absolute measurement of magnetic fields.** H. AUER (Ann. Physik, 1933, [v], 18, 613—624).—A method is described for measuring intense magnetic fields (about 8000 gauss) with an accuracy of  $\pm 0.026\%$ . J. W. S.

**Use of glass filter apparatus in the determination of the adsorptive or catalytic activity of technical adsorbents.** F. KRCZIL (Chem.-Ztg., 1933, 57, 803—805).—Porous glass plates (I) are useful for removing suspended solids from gas streams, for efficient scrubbing of gases by liquids, for saturating gases with the vapours of liquids, and for removing suspended liquid particles from saturated gases. (I) can also be used for absorbing indicators for detecting the presence of certain constituents in gas currents. Various types of apparatus containing (I) in different forms for the above and other purposes are illustrated. A. R. P.

**Filtering device.** E. B. KESTER (Ind. Eng. Chem. [Anal.], 1933, 5, 422). E. S. H.

**Automatic pipette washer.** E. HOWELL and F. M. FRANK (Amer. J. Public Health, 1933, 23, 1186). E. C. S.

**Burette fitted with reservoir.** M. CHATRON (Bull. Soc. Chim. biol., 1933, 15, 1154—1155). H. D.

**Weighing burette.** J. CORNOG and R. CORNOG (Ind. Eng. Chem. [Anal.], 1933, 5, 408). E. S. H.

**Apparatus for microanalysis of gas.** J. S. SWEARINGEN, O. GERBES, and E. W. ELLIS (Ind. Eng. Chem. [Anal.], 1933, 5, 369—370).—Blacet and Leighton's method is modified. E. S. H.

**New apparatus for gas analysis.** A. G. SUVOROV (J. Appl. Chem. Russ., 1933, 6, 1005—1009).—Apparatus for analysis of gases containing  $CO_2$ ,  $O_2$ ,  $CH_4$ ,  $C_2H_6$  and higher hydrocarbons,  $H_2$ ,  $N_2$ ,  $H_2S$ ,  $NO$ , and  $NO_2$  is described. R. T.

**Stirring rod with fritted glass disc.** J. E. S. HAN (Ind. Eng. Chem. [Anal.], 1933, 5, 421). E. S. H.

**Apparatus for the determination of m.p., b.p., transition points, ignition temperatures, etc., specially for use with a small quantity of sample.** S. WATANABE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 22, 264—268).—The material is placed in a cup surrounding one of two Cu—constantan junctions connected to a recording galvanometer. The temp. of the enclosing vessel is indicated thermoelectrically and a record of the thermal changes in the material is obtained. R. S.

**Instrument for rapid determination of moisture.**—See B., 1933, 991.

**Simplified micro-comparator.** W. STIRLING (Analyst, 1933, 58, 684—686).—Apparatus for simultaneous examination of objects at distances up to 30 cm. apart is described. E. C. S.



**Laboratory drain-tray.** J. L. WILSON (Ind. Eng. Chem., 1933, 25, 1216).—A portable enamelled tray is illustrated. C. I.

**Determination of surface and interfacial tensions.** J. C. SPEAKMAN (J.C.S., 1933, 1449—1453).—The difference between the pressures required to depress to the same horizontal level the menisci in two capillary tubes of different diameter is an exact measure of the surface or interfacial tension. Data for  $C_6H_6$ ,  $H_2O$ ,  $C_6H_6-H_2O$ ,  $Et_2O-H_2O$ , and  $CHCl_3-H_2O$  are recorded and the special advantages of the method are emphasised. J. G. A. G.

**Recovery of iodine from metallic iodides by oxidation with technical nitric acid.** R. F. McCLEARY and E. F. DEGERING (Ind. Eng. Chem. [Anal.], 1933, 5, 420).—A suitable apparatus is described. E. S. H.

**Bumping prevention.** J. E. S. HAN (Ind. Eng. Chem. [Anal.], 1933, 5, 362).—A sieve plate of Ag or Pt is recommended. E. S. H.

**Continuous liquid extractor.** A. MAZUR, R. ROSENTHAL, and B. HARROW (Ind. Eng. Chem. [Anal.], 1933, 5, 419). E. S. H.

**Apparatus for filling large closed-end manometers.** A. E. CAMERON (Ind. Eng. Chem. [Anal.], 1933, 5, 419). E. S. H.

**Concentration gradient in the ultra-centrifuge cell.** O. LAMM (Nature, 1933, 132, 820—821).—A new refraction method for determining the concentration gradient in a sedimentation equilibrium is described. L. S. T.

**Ultracentrifuge.** J. W. BEAMS, A. J. WEED, and E. G. PICKELS (Science, 1933, 78, 338—340).—Details of a high-speed, air-driven centrifuge are given. L. S. T.

**Paper hygrometers.** G. R. R. BRAY (Nature, 1933, 132, 857). L. S. T.

**Paper hygrometers.** P. H. PRIOR (Nature, 1933, 132, 857).—In comparatively still air the rate of change of stretch may, after an initial period, become so small that a condition resembling equilibrium is reached. Air velocity is thus an important factor. L. S. T.

**Cellophane in the determination of humidity.** E. SCHWEITZER (Naturwiss., 1933, 21, 784—787).—Cellophane (I) is very permeable to  $H_2O$  vapour, and could be used to cover hygrometers (II) to prevent access of dust and corroding fumes. It is also hygroscopic, and (II) could be constructed based on the gain in wt. The degree of humidity can also be found by impregnating (I) with  $CoCl_2$  and noting the colour change, preferably by finding the absorption

limit in the ultra-violet. The extension which (I) undergoes on taking up  $H_2O$  can be made the basis of portable (II). The absorption of  $H_2O$  also alters the strength of (I), and the R.H. can be determined by finding the pressure required to burst a membrane of (I), and its curvature. (I) can be used in standardising hygrometers by placing a mass of (I) which has taken up  $H_2O$  in the instrument. A. J. M.

**Continuously operating laboratory apparatus for high-pressure reactions.** L. VON SZESZICH and H. VOLLBRECHT (Chem. Fabr., 1933, 6, 469—471).—The reaction vessel (a 25-c.c. steel tube) is connected to a pump and a compressor for introducing liquid and gas, respectively, a condenser, a separator, and a pressure gauge, and is surrounded by an electrically heated furnace. The apparatus is specially designed for small-scale studies of gas- and liquid-phase reactions of all kinds. H. F. G.

**Solubility of sulphur dioxide in tap lubricants.** M. FRANCIS (Rev. Sci. Instr., 1933, [ii], 4, 615—619).—Pressure-solubility curves are given for lanoline, Ramsay Fett, beeswax-vaseline grease,  $H_3PO_4$ , Apiczon, picein, and white sealing-wax. N. M. B.

**Simple agitation device.** G. W. MARKS (Science, 1933, 78, 483).—An oil-can, suitably cut and suspended, is oscillated by a stream of compressed air. L. S. T.

**Griffiths' sensitive manometer.** P. C. VINCENT (Proc. Physical Soc., 1933, 45, 808—832).—The instrument is analogous to the  $H_2O$  U-tube manometer, but with an aq. solution of uranine in place of  $H_2O$ , and pure air-free  $H_2O$  in place of air. The accuracy is  $\pm 1\%$  over the pressure range 2—20 dynes per sq. cm. J. W. S.

**Griffiths' method for determining a small change in the density of a liquid.** P. C. VINCENT (Proc. Physical Soc., 1933, 45, 833—835).—The dissolution of glass by  $H_2O$  and the resulting increase in  $d$  of the latter have been followed by means of the special manometer (cf. preceding abstract). The  $d$  of  $H_2O$  does not change appreciably during weeks of contact with  $SiO_2$ . J. W. S.

**Gasometric determination of density of solids.** J. PIAZZA (An. Inst. Invest. cient. tecnol., 1930, 1, No. 3, 64—70; Chem. Zentr., 1933, ii, 911).—The substance is placed in one of two horizontal single-bulbed capillary tubes in which the movement of a Hg meniscus caused by changes of pressure is observed. The vol. or  $d$  is determined with the aid of a graph. A. A. E.

**Century of progress in chemistry.** A. B. LAMB (Science, 1933, 78, 371—376).—An address. L. S. T.

## Geochemistry.

**Ultra- $\gamma$ -radiation.** E. A. SMITH and F. M. SMITH (Bul. Soc. Stiinte Cluj, 1932, 7, 104—112; Chem. Zentr., 1933, ii, 175).—Results of measurements of ultra- $\gamma$ -radiation in Australia, Canada, Greenland, Spitzbergen, and India are reported. A. A. E.

**Absorption of ultra-violet radiation in the lower atmosphere.** L. HERMAN (Compt. rend., 1933, 197, 1342—1344).—Ten absorption bands, degraded towards the red, have been observed between  $\lambda$  2400 and 2800; 8 have been measured. All are



triple, the other constituents being much fainter, and resembling those of  $O_2$  under pressure (cf. A., 1932, 891; 1933, 759). C. A. S.

**Origin of atmospheric ozone.** A. DAUVILLIER (Compt. rend., 1933, 197, 1339—1341).—The  $O_3$  content at ground level at Scoresby Sound (Greenland) was determined during each day from Nov. 1932 to Aug. 1933. The max., 57 mg. per cu. m., occurred at the end of Dec. The amount varied with the wind, being lowered by a N.E. wind to about 4–6 mg., rising when the wind dropped by 10–15 mg. per day. It was much lower (average only 6 mg.) in spring and summer. The amount also varied with the prevalence of aurora with a lag indicating that the aurora is accompanied by formation of  $O_3$  in the upper air, whence it takes about a month to descend to ground level. Its presence in the air was further proved by the ultra-violet spectrum in the twilight of the polar night. C. A. S.

**Formaldehyde in the upper atmosphere.** N. R. DHAR and A. RAM (Nature, 1933, 132, 819–820).—All samples of rain- $H_2O$  contain 0.00015–0.0012 g. of  $CH_2O$  (I) per litre, the amount being greater when the rainfall is preceded by clear sunny days. (I) may thus be the result of photo-formation from  $CO_2$  and  $H_2O$  in the atm., at a height < that of the formation of  $O_3$ . The absorption of solar radiations shorter than 2900 Å. may be partly due to the (I) present in the atm. L. S. T.

**Calcium carbonate and carbonic acid content of sea-water according to the scientific results of the "Meteor" expedition.** V. M. GOLDSCHMIDT (Naturwiss., 1933, 21, 811–817).—A report of the chemical work of the German "Meteor" Atlantic expedition, 1925–1927. The results of the determination of the solubility of  $CaCO_3$  in sea- $H_2O$  are given. The connexion between the  $CO_2$  pressure and  $[H^+]$ , and the causes of  $H_2CO_3$  distribution, are discussed. A. J. M.

**Heavy metals in natural mineral waters.** S. S. MIHOLIC (Bull. Soc. Chim. Yougoslav., 1933, 4, 107–120).—European mineral  $H_2O$  can be classified into three groups, according to their heavy metal content. Those containing predominately Ni and Co correspond with the Archean folding, Sn with the Hercynian, and Pb and Zn with the Alpine folding. Data for the Caledonian folding are not available. R. T.

**Bacterial activity in the thermal springs of Aix and Aix-Burtscheid.** A. BRUSSOFF, F. REINARTZ, and A. SCHLOEMER (Z. Unters. Lebensm., 1933, 66, 446–453).—The stony and sandy lime deposits in the thermal  $H_2O$  at Aix-Burtscheid are formed by the activity of  $SiO_2$ , Fe, and CaO bacteria. E. C. S.

**Radioactivity of springs on the massif of the Ballon d'Alsace.** R. DELABY, R. CHARONNAT, and M. JANOT (Compt. rend., 1933, 197, 1140–1142; cf. A., 1933, 251).—The most radioactive springs (93.1–106.3 m $\mu$ c.) are at the source of the Savoureuse river, and derived from granite, but the variation with rainfall is the reverse of that previously stated (cf. A., 1920, ii, 727). Radioactivity of the  $H_2O$  rapidly decreases along this river, being practically zero 3 km.

from its source. Observations on the Ballon de Servance (max. 38 m $\mu$ c.) confirm the close connexion of radioactivity with the granite. C. A. S.

**Beryllium and helium. I. Helium contained in beryls of varied geological age.** (LORD) RAYLEIGH (Proc. Roy. Soc., 1933, A, 142, 370–381; cf. A., 1933, 692).—The He content of more than 60 specimens of beryl has been determined. Large He content is limited to specimens of great geological age. L. L. B.

**Geochemistry of the alkali metals.** V. M. GOLDSCHMIDT, H. BERMAN, H. HAUPTMANN, and C. PETERS (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., 1933, 235–244; Chem. Zentr., 1933, i, 3911–3912).—Arc spectrographic analytical methods are described. Average vals. for terrestrial rocks are:  $Li_2O$  0.1,  $Rb_2O$  0.03,  $Cs_2O$  0.001%; Li:Na (atoms) 1:150. The behaviour of alkali metals in magmatic and magmatic-pneumatolytic rocks is discussed. Rb is always accompanied in minerals by much K; Cs accumulates in the sublimation products of effusive rocks. The effect of weakening and sedimentation on the distribution of alkali metals is also discussed. A. A. E.

**Geochemistry of selenium.** V. M. GOLDSCHMIDT and O. HEFTER (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., 1933, 245–252; Chem. Zentr., 1933, i, 3912).—The geochemical separation of Se from S is discussed in relation to their similar ionic dimensions and to the conditions of oxidation. The determination of Se in sulphate minerals is described. A. A. E.

**Geochemistry of germanium.** V. M. GOLDSCHMIDT and C. PETERS (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., 1933, 141–166; Chem. Zentr., 1933, i, 3912–3913).—Results of arc or X-ray spectroscopic determinations in many rocks and minerals are reported. A method for detecting 0.0001% is described. Ge was detected in almost all magmatic rocks and minerals except dunite; its associations are recorded. The distribution of Ge in sedimentary rocks is discussed. In meteorites Ge accumulates in the Ni-Fe rather than in the troilite. The average Ge content of silicate rocks is about 0.0006%  $GeO_2$ . A. A. E.

**Presence of gallium in sulphide ores.** A. GRÜNBERG, A. FILIPPOV, and I. JASVONSKIJ (Compt. rend. Acad. Sci. U.S.S.R., 1933, 2, 69–74).—Minerals and ores from Altai have been investigated for Ga, which appears most richly in Ridder Zn blende. A. B. D. C.

**Apatite and nepheline from Chibinogorsk, Kola Peninsula.** F. VOGEL (Metall u. Erz, 1933, 30, 191–193; Chem. Zentr., 1933, ii, 758).

**Variation in electrical conductivity of hydrous minerals with temperature.** S. SHIMIZU (Sci. Rep. Tôhoku, 1933, 22, 633–661).—In general, the conductivities,  $k$ , of minerals of the type  $xAl_2O_3 \cdot ySiO_2 \cdot zH_2O$  (I),  $Al_2O_3 \cdot xH_2O$ , and  $K_2O \cdot xAl_2O_3 \cdot ySiO_2 \cdot zH_2O$  increase with rise of temp. and the anomalous variations are correlated with discontinuous vol. changes and the heat effects revealed by thermal analysis. With (I), max. vals. of  $k$  at 100–200° and 450–650° correspond with the absorption of heat due to elimination of  $H_2O$ , whilst the abrupt decrease of  $k$  at 900—



1000° is correlated with evolution of heat. The dehydration of diasporite proceeds stepwise.

J. G. A. G.

**Age of Fitchburg granite.** A. C. LANE (Science, 1933, 78, 435).—Microchemical analysis indicates an age of  $36 \times 10^7$  years for the Fitchburg granite.

L. S. T.

**Alkaline granite from Magasbukk, Ditrau.** V. IANOVICI (Ann. Sci. Univ. Jassy, 1933, 18, 113—117).—A chemical analysis and a petrographical description are given.

H. S. P.

**Talc-serpentine-chlorite rocks of south Mewar and Dungarpur.** B. K. GHOSH (Rec. Geol. Surv. India, 1933, 66, 449—460).—A series of talc-serpentine-chlorite rocks occurring in Dungarpur and Mewar (Udaipur), Rajputana, is derived from intrusive peridotites or pyroxenites by the action of  $H_2O$  and  $CO_2$  aided by faulting and folding on the magnesian minerals:  $4MgSiO_3$  (enstatite) +  $H_2O$  +  $CO_2 = Mg_3H_2(SiO_3)_4$  (talc) +  $MgCO_3$ ;  $CaMg_3(SiO_3)_4$  (tremolite) +  $H_2O$  +  $CO_2 = Mg_3H_2(SiO_3)_4$  +  $CaCO_3$ ; and  $4Mg_2SiO_4$  (olivine) +  $H_2O$  +  $5CO_2 = Mg_3H_2(SiO_3)_4$  +  $5MgCO_3$ . Calcite and magnesite both occur in the deposits, together with magnetite, rutile, ilmenite, chromite, etc.

C. A. S.

**Olivine-gabbro from the Jocotca region, Ditrau.** V. IANOVICI (Ann. Sci. Univ. Jassy, 1933, 18, 107—112).—A petrographical description and a chemical analysis of a new olivine-gabbro are given.

H. S. P.

**Composition of matlockite.** W. NIEUWENKAMP (Z. Krist., 1933, 86, 470—471).—The powder diagram of  $PbFCl$  (cf. A., 1932, 450) is identical with that of matlockite, showing that the latter has the same composition, and not  $Pb_2OCl_2$ . Analysis gave 6.5% F (calc. for  $PbFCl$  7.3%).

C. A. S.

**New minerals.** H. UNGEMACH (Compt. rend., 1933, 197, 1132—1134).—Revised measurements of the following minerals from Tierra Amarilla (Chili) are given (cf. Z. Krist., 1889, 15, 1): copiapite, triclinic,  $a:b:c=0.4134:1:1.3280$ ,  $\alpha$   $100^\circ 12'$ ,  $\beta$   $86^\circ 47'$ ,  $\gamma$   $90^\circ 32'$ ; quenstedtite, triclinic,  $a:b:c=0.2621:1:0.2776$ ,  $\alpha$   $94^\circ 10'$ ,  $\beta$   $101^\circ 44.5'$ ,  $\gamma$   $96^\circ 18.5'$ ; the coquimbite includes two distinct species, of the same composition, and often occurring together, coquimbite proper, hexagonal,  $a:c=1:1.5643$ ; and a new rhombohedral variety, *paracoquimbite*,  $a:c=1:2.3464$ , pale violet. The following from the same locality are new: *amarillite*,  $NaFe(SO_4)_2 \cdot 6H_2O$ , pale yellow, monoclinic,  $a:b:c=0.7757:1:1.1482$ ,  $\beta$   $84^\circ 23'$ ; *lapparentite*,  $[AlFe]_2O_3 \cdot 2SO_3 \cdot 10H_2O$ , monoclinic,  $a:b:c=0.2919:1:0.24155$ ,  $\beta$   $85^\circ 10'$ ; and *leucoglaucite*,  $Fe_2O_3 \cdot 4SO_3 \cdot 5H_2O$ , resembling, but with less  $H_2O$  than, rhomboclase, pale greenish-blue, hexa-

gonal,  $a:c=1:0.5589$ . Associated with the foregoing are S, chalcantite, natrojarosite, roemerite, fibroferite, and halotrichite.

C. A. S.

**Barytes in granulite sand of Alençon (Orne).** L. BERTHOIS (Compt. rend., 1933, 197, 1051—1052).—Barytes forms 0.017—0.086 (average 0.038)% of the sand bordering the granulite intrusion at Alençon, and is so distributed as to indicate its derivation from the granulite, probably by fumarole action. It also occurs in larger amounts (30—60 times) in the arkose of the Inferior Oolite in this neighbourhood, but is of similar origin, a larger proportion of the other material having been removed.

C. A. S.

**Evolution of heat on contact of dry earth with water.** P. HAGENE (Compt. rend., 1933, 197, 935—937; cf. A., 1933, 590).—The heat evolved on moistening dried and comminuted samples of humus from pollarded hollow willows and an ash is 18.65—23.60 g.-cal. per kg., the content of org. matter being 47.4—87.4%. That evolved by surface soils from the neighbourhood of Dijon and containing little organic matter, after similar treatment, is 4.02—8.04 g.-cal. per kg. The proportion of the evolved heat due to the mineral content of humus and of soil is about the same.

C. A. S.

**Bitumen deposits and lignite field of Chalaïnov, Heilungkiang Province [China].** T. F. HOU (Bull. Geol. Survey China, 1932, 19, 51—76).—Bitumen occurring in cavities or pores in trachyte (3 specimens, 2.2, 12.8, 3.4%) contained, respectively, fixed C 42.6, 34.2, 11.4; ash 15.2, 4.4, 28.2; volatile matter 42.2, 61.4, 60.4%, and had  $d$  1.53, 1.16, 1.16, and m.p.  $70^\circ$ ,  $55^\circ$ ,  $100^\circ$ . Bituminous matter is regarded as one of the end phases of volcanic activity and to have been deposited simultaneously with agate. Lignites from the same area contained  $H_2O$  34.80—49.92, volatile matter 16.54—30.04, fixed C 27.22—32.26, ash 4.66—8.00, S 0.25—0.59%, and had calorific val. 3580—4784.

CH. ABS.

**Vanadium in mineralised bitumens.** N. A. ORLOV and V. A. USPENSKI (J. Appl. Chem. Russ., 1933, 6, 1010—1022).—A review of lit.

R. T.

**Troilite nodules of meteorites. Geochemistry of chromium, nickel, and tin.** V. M. GOLDSCHMIDT and C. PETERS (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., 1933, 278—287; Chem. Zentr., 1933, ii, 849).—Ni, Cr, Sn, and Ge in troilites of meteorites have been determined by X-ray or are spectrography, and their chemical relationships in troilites are discussed.

A. A. E.

[Young's modulus and Poisson's ratio with reference to geophysical applications.] W. A. ZISMAN (Proc. Nat. Acad. Sci., 1933, 19, 989—990).—Errata are given (cf. A., 1933, 1028, 1029).

## Organic Chemistry.

**$\alpha\delta$ -Addition and subtraction reactions in hydrocarbon chemistry.** L. S. KASSEL (J. Chem. Physics, 1933, 1, 749—750).—The mechanism of the hydrogenation and dehydrogenation of hydrocarbons is discussed.

H. S. P.

**Mechanism of explosive combustion of gaseous hydrocarbons.**—See this vol., 34.

**Preparation and reactions of  $\delta\delta$ -dimethyl- $\Delta^4$ -pentene (neopentylethylene).** F. C. WHITMORE



and A. H. HOMER (J. Amer. Chem. Soc., 1933, 55, 4555—4559).— $\text{MgBr}\cdot\text{Cl}$  and allyl bromide give a good yield of  $\delta\delta$ -dimethyl- $\Delta^2$ -pentene (I), b.p. 72.35°/760 mm., purified through its dibromide, b.p. 77—78°/9 mm. (I) and dry  $\text{HBr}$  at 0° afford  $\delta\delta$ -dimethyl- $n$ -amyl bromide, b.p. 70—71°/35 mm., 154°/730 mm.; the Grignard reagent and  $\text{O}_2$  give  $\delta\delta$ -dimethyl- $n$ -amyl alcohol, b.p. 96°/62 mm., 158°/737 mm. ( $\alpha$ -naphthylurethane, m.p. 80.5—81°). (I) does not react with dry  $\text{HI}$  at 0—5°. (I) and  $\text{AcOH}$ -conc.  $\text{H}_2\text{SO}_4$  give the acetate, b.p. 92—93°/10 mm., of  $\delta\delta$ -dimethylpentan- $\beta$ -ol ( $\alpha$ -naphthylurethane, m.p. 86.5—87°), and a mixture, b.p. 72—82°/740 mm., of olefines. (I) is polymerised by 85%  $\text{H}_2\text{SO}_4$  at 5—20° to a mixture of products; 100%  $\text{H}_2\text{SO}_4$  has little action.

H. B.

**Preparation of  $\beta\zeta$ -dimethylheptadiene.** H. I. WATERMAN and W. J. C. DE KOK (Rec. trav. chim., 1933, 52, 1007—1012).—Methylheptenone, prepared from citral and 10%  $\text{K}_2\text{CO}_3$ , is condensed with  $\text{MgMeI}$ , and the resulting  $\beta\zeta$ -dimethylheptenol, b.p. 80—80.5°/14 mm., dehydrated with  $\alpha$ - $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$  at 145°.  $\beta\zeta$ -Dimethylheptadiene, b.p. 143.7±0.2°/762 mm. (purified over  $\text{Na}$ ), which is probably a mixture of isomerides, absorbs the calc. vol. of  $\text{H}_2$  with formation of  $\beta\zeta$ -dimethyl- $n$ -heptane. Determination of the Br val. (McIlhiney) is no criterion of its purity.

H. A. P.

**Preparation of vinylacetylene by Willstätter and Wirth's method.** E. A. SHILOV, A. N. MAKASHINA, A. I. SMIRNOVA, and G. I. YAKIMOV (Sintet. Kauchuk, 1933, No. 1, 4—12).—(1)  $\alpha\delta$ -Butylene dibromide is obtained directly from technical butadiene by Thiele's method. (2)  $\text{NMe}_3$  is used instead of  $\text{NHMe}_2$ :  $(\text{CH}_2\text{Br}\cdot\text{CH})_2 + 2\text{NMe}_3$  (in dry  $\text{MeOH}$ ) =  $[\text{CH}_2(\text{NMe}_3\text{Br})\cdot\text{CH}]_2$ . The dibromide is shaken with  $\text{H}_2\text{O}$  and pptd.  $\text{Ag}_2\text{O}$  to give  $[\text{CH}_2(\text{NMe}_3\cdot\text{OH})\cdot\text{CH}]_2$ , which on distillation affords  $\text{CH}_2\cdot\text{CH}\cdot\text{C}\cdot\text{CH}$ .

CH. ABS.

**Acetylene polymerides and their derivatives.** XVII. Mercury derivatives of vinylacetylene. W. H. CAROTHERS, R. A. JACOBSON, and G. J. BERCHET (J. Amer. Chem. Soc., 1933, 55, 4665—4667).— $\text{CH}_2\cdot\text{CH}\cdot\text{C}\cdot\text{CH}$  (I) and  $\text{EtOH}\cdot\text{K}_2\text{HgI}_4$  or cold  $\text{AcOH}\cdot\text{Hg}(\text{OAc})_2$  give *Hg divinylacetylde* (II), m.p. 144—145°, which absorbs  $\text{O}_2$  when kept in air to give an explosive compound, reacts with  $\text{Br}(\text{I})$  in  $\text{CHCl}_3$  to form  $\text{CH}_2\cdot\text{CH}\cdot\text{C}\cdot\text{CHBr}(\text{I})$ , and with  $\text{Na}$  in  $\text{C}_6\text{H}_6$  affording  $\text{CH}_2\cdot\text{CH}\cdot\text{C}\cdot\text{CHNa}$ . (I) or (II) with  $\text{AcOH}\cdot\text{Hg}(\text{OAc})_2$  at 60—70° gives  $\alpha\alpha$ -di(acetoxymercuri)- $\beta$ -acetoxymercurio- $\Delta^2$ -butadiene (III),  $\text{CH}_2\cdot\text{CH}\cdot\text{C}(\text{O}\cdot\text{HgOAc})\cdot\text{C}(\text{HgOAc})_2$  [corresponding tri-chloro-, -bromo-, and -iodo-mercuri-derivatives, prepared from (III) and  $\text{KHal}$  in 50%  $\text{AcOH}$ ], hydrolysed (dil.  $\text{HCl}$ ) to *Me vinyl ketone*. (III) and  $\text{Br}$  in  $\text{CHCl}_3$  give *tribromomethyl vinyl ketone*, b.p. 128—130°/0.04 mm., m.p. 73—75°.

H. B.

**Acetylene polymerides and their derivatives.** XVIII.  $\alpha$ -Halogeno- $\beta$ -vinylacetylenes. R. A. JACOBSON and W. H. CAROTHERS (J. Amer. Chem. Soc., 1933, 55, 4667—4669).— $\alpha$ -Chloro-, b.p. 55—57°/760 mm.,  $\alpha$ -bromo-, b.p. 52—53°/217 mm., and  $\alpha$ -iodo- (I), b.p. 78°/125 mm.,  $\beta$ -vinylacetylenes are prepared from  $\text{CH}_2\cdot\text{CH}\cdot\text{C}\cdot\text{CH}$  and aq.  $\text{NaOHal}$  in  $\text{N}_2$ ; they

often explode in air and polymerise to explosive black solids. (I), also prepared from  $\text{CH}_2\cdot\text{CH}\cdot\text{C}\cdot\text{CH}\cdot\text{MgBr}$  and I, with  $\text{EtOH}\cdot\text{HCl}$ ,  $\text{CuCl}$ , and  $\text{NH}_4\text{Cl}$  gives a compound,  $\text{C}_4\text{H}_4\text{ClI}$ , b.p. 73.5—74.5°/35 mm., which polymerises to a black tar.

H. B.

**Decomposition of chloroform by radiations from radon.**—See this vol., 40.

**Hydrolysis of ethylene bromide with alcoholic alkali hydroxide.**—See this vol., 36.

**Preparation of trimethylene chlorobromide.** I. STRUKOV (Khim. Farm. Prom., 1933, 2, 66—68).—In Bruylants' method the allyl chloride is saturated with  $\text{HBr}$  in sunlight; the yield is 95—97%. CH. ABS.

**$\alpha\epsilon$ -Dibromopentane.** J. D. A. JOHNSON (J.C.S., 1933, 1531—1532).— $\alpha\epsilon$ -Dibromopentane (I), prepared from 1-benzoylpiperidine and  $\text{PBr}_5$  by (essentially) von Braun's method (A., 1904, i, 841; 1905, i, 596), contains 15—16% of  $\text{PhCN}$ . Pure (I), b.p. 95.5°/10 mm., m.p. —29.5° (lit. —35 to —34°), is obtained by dissolution of the mixture (b.p. up to 105°/10 mm.) in light petroleum (b.p. 40°) and extraction with seven successive amounts of conc.  $\text{H}_2\text{SO}_4$ . The parachor of (I) is anomalous.

H. B.

**Molecular rotations in members of homologous series.** P. A. LEVENE and R. E. MARKER (J. Biol. Chem., 1933, 103, 299—309).—The max.  $[\text{M}]_D^{25}$  for numerous members of the series  $\text{CHMeR}\cdot[\text{CH}_2]_n\text{X}$ ; where R is Et,  $\text{Pr}^a$ ,  $\text{Bu}^a$ ,  $n$ -amyl, and  $n$ -heptyl, X is Br, OH, Me,  $\text{CO}_2\text{H}$ , and  $\text{CO}_2\text{Et}$ , and  $n=0-5$ , are compared. The contribution of the  $\cdot\text{CH}_2\cdot\text{OH}$  group approaches closely to that of Me after a certain distance from the asymmetric centre is reached (provided R contains  $> 2$  C atoms) but never equals it.

The Grignard reagent from  $\gamma$ -methylhexyl bromide,  $[\text{M}]_D^{25}$  —7.6° (all vals. are homogeneous), and  $\text{CH}_2\text{O}$  give  $\delta$ -methylheptyl alcohol, b.p. 81°/18 mm.,  $[\text{M}]_D^{25}$  0° [bromide, b.p. 80°/15 mm.,  $[\text{M}]_D^{25}$  —5.2° (—14.5°)]. The *d-Et* ester, b.p. 95°/25 mm.,  $[\text{M}]_D^{25}$  +4.18° (+12.84°), of  $\delta$ -methylhepticoic acid,  $[\text{M}]_D^{25}$  +3.56°, is reduced (Na,  $\text{EtOH}$ ,  $\text{PhMe}$ ) to *d- $\epsilon$ -methylheptyl alcohol*, b.p. 87°/20 mm.,  $[\text{M}]_D^{25}$  +3.9° (+12°) [bromide, b.p. 86°/14 mm.,  $[\text{M}]_D^{25}$  +4.81° (+14.92°)]. The *d-Et* ester, b.p. 110°/25 mm.,  $[\text{M}]_D^{25}$  +4.4° (+13.66°), of  $\epsilon$ -methyl-octicoic acid,  $[\text{M}]_D^{25}$  +3.93°, is similarly reduced to *d- $\zeta$ -methyl-octyl alcohol*, b.p. 100°/20 mm.,  $[\text{M}]_D^{25}$  +4° (+12.5°) [bromide, b.p. 101°/14 mm.,  $[\text{M}]_D^{25}$  +4.48° (+13.96°)], whilst the *l-Et* ester, b.p. 112°/30 mm.,  $[\text{M}]_D^{25}$  —1.21° (—5.9°), of  $\delta$ -propylhexoic acid,  $[\text{M}]_D^{25}$  —0.76°, gives *l- $\epsilon$ -propylhexyl alcohol*, b.p. 110°/25 mm.,  $[\text{M}]_D^{25}$  —0.37° (—1.72°) [bromide, b.p. 95°/12 mm.,  $[\text{M}]_D^{25}$  —1.53° (—7.78°)]. The *l-Et* ester, b.p. 125°/25 mm.,  $[\text{M}]_D^{25}$  —1.45° (—2.84°), of  $\delta$ -butylhexoic acid,  $[\text{M}]_D^{25}$  —0.86°, similarly affords  $\epsilon$ -butylhexyl alcohol, b.p. 125°/25 mm.,  $[\text{M}]_D^{25}$  0° [bromide, b.p. 112°/12 mm.,  $[\text{M}]_D^{25}$  —2.69° (—5.29°)], whilst the *l-Et* ester, b.p. 140°/25 mm.,  $[\text{M}]_D^{25}$  —0.92° (—1.69°), of  $\delta$ -amylhexoic acid,  $[\text{M}]_D^{25}$  —0.33°, gives *d- $\epsilon$ -amylhexyl alcohol*, b.p. 140°/25 mm.,  $[\text{M}]_D^{25}$  +1.03° (+1.85°) [bromide, b.p. 124°/12 mm.,  $[\text{M}]_D^{25}$  —1.89° (—4.02°)]. The vals. quoted in parentheses are calc. max.

H. B.

**Detection of sorbitol in the presence of dulcin and saccharin.** G. REIF (Z. Unters. Lebensm., 1933, 66, 408—412).—Dulcin (I),  $\text{PhCHO}$ , and  $\text{H}_2\text{SO}_4$  give



*benzylidenedulcin*, m.p. 205—206°, which gives an orange-yellow colour with  $\text{COMe}_2$  and  $\text{H}_2\text{SO}_4$  and thus interferes with the detection of sorbitol (II). (I) also forms a cryst. acetate which interferes with the identification of sorbitol hexa-acetate. Both (I) and saccharin (III) are removed by animal C when Werder's technique (B., 1929, 619) is employed. (III) does not, however, give a  $\text{:CHPh}$  compound, so does not interfere with the colour and Ac tests for (II).

E. C. S.

**Preparation and significance of glyceromono-phosphoric acid.** C. NEUBERG and M. KOBEL (Angew. Chem., 1933, 46, 711—713).—Hexoso diphosphate (I) solution from the fermentation of glucose, sucrose, fructose, mannose, galactose, or maltose with yeast (fresh, dry, or extract) in presence of excess of phosphate is dismutated with NaF and MeCHO (or *iso*-valeraldehyde) for 3.5 hr., yielding *l*-glycerophosphoric acid (II), which is isolated as the Ba H salt ( $+2\text{H}_2\text{O}$ ). Phosphate goes into org. combination in both stages. With dil. yeast extract, or with lower (I) concn., the yield is less, whilst more NaF is required. (I) is also obtained from Na glyceraldehyde phosphate using extract free from carbohydrates under similar conditions, the yield being approx. halved in absence of MeCHO. The significance of (II) and its aldehyde as intermediates in the process of fermentation is discussed.

A. A. L.

**Thermal decomposition of ethyl mercaptan and ethyl sulphide.** W. M. MALISOFF and E. M. MARKS (J. Chem. Physics, 1933, 1, 284—284; cf. A., 1931, 1393).—Polemic. Trenner and Taylor (A., 1933, 374) carried out their investigations under conditions different from those employed by the authors.

M. S. B.

**Thermal decomposition of ethyl mercaptan and ethyl sulphide.** N. R. TRENNER and H. A. TAYLOR (J. Chem. Physics, 1933, 1, 286; cf. preceding abstract).—Polemic. There is no reason to suppose that mercaptan decomp. in hydrocarbon solvents will be different from that in the pure state.

M. S. B.

**Composition of fatty acid mixtures. I. Relation of composition to Dalican's curve.** R. N. WENZEL (Ind. Eng. Chem. [Anal.], 1933, 5, 393—396).—Limitations of the use of the curve are emphasised and illustrated.

R. S. C.

**Ethyl and methyl fluoroformates.** H. C. GOSWAMI and P. B. SARKAR (J. Indian Chem. Soc., 1933, 10, 537—539).—*Me*, b.p. 40°, and *Et*, b.p. 57°, *fluoroformates* are prepared from  $\text{ClCO}_2\text{Alk}$  and anhyd. TlF.

H. B.

**Preparation of derivatives of vinylacetic acid.** L. FALAISE and R. FROGNIER (Bull. Soc. chim. Belg., 1933, 42, 427—441).—Vinylacetonitrile (I) is obtained in good yield by Breckpot's method (A., 1931, 194); allyl formate or a mixture of allyl alcohol and formate can also be used. (I) is hydrolysed rapidly by conc. HCl to vinylacetic acid (II); small amounts of  $\beta$ -chloro- $\alpha$ -butyronitrile and crotonic acid are also formed. (II) is unaffected by dry HCl; esterification ( $\text{EtOH-HCl}$ ) gives 70% of *Et* vinylacetate, b.p. 124.2—124.4°/761.5 mm., which is also unaffected by dry HCl.

H. B.

**Determination of the double linking [in derivatives of the butenoic acids].** R. FROGNIER and F. VAN GOETSENHOVEN (Bull. Soc. chim. Belg., 1933, 42, 391—409).—The rate of addition of Br (in  $\text{CCl}_4$ ) to the following substances (in  $\text{CCl}_4$ ) at room temp. in the dark is vinylacetic acid  $\gg$  *Et* vinylacetate (I)  $\gg$  vinylacetonitrile (II)  $>$  crotonic acid (III)  $>$  *trans*-crotononitrile (IV)  $>$  *cis*-crotononitrile (V). A method [based on that of Heim (A., 1931, 205)] in which the substance (in  $\text{CCl}_4$ ) is treated with  $\text{KBr-KBrO}_3$  and 10%  $\text{H}_2\text{SO}_4$  is described; the no. of mols. of Br added are: (II) 0.99, (I) 0.99, (IV) 0.016, (V) 0.006, *Et* crotonate 0.02. In presence of sunlight, similar addition of Br to all the nitriles is rapid. (II) does not add I in  $\text{CCl}_4$ ; reaction is rapid with ICl, but occurs more slowly with IBr (in  $\text{CHCl}_3$  and the dark). Addition of 1 mol. of Br to most of the above compounds occurs much more rapidly in presence of  $\text{H}_2\text{O}$ . Treatment of (II) with  $\text{Br-H}_2\text{O}$  gives 93.3 mol.-% of H' per mol. of Br added; addition of KBr, KCl, and  $\text{KNO}_3$  decreases the amount of H' in the order quoted. Addition of HOBr (prepared using  $\text{HgO}$ ) to (II) occurs to the extent of 97.5%; (IV) similarly adds 1% (in presence of 10%  $\text{H}_2\text{SO}_4$ , almost quant. addition is accomplished; similar quant. addition is found with HOBr from  $\text{Br-H}_2\text{O}$  and  $\text{Ag}_2\text{SO}_4$ ). The question of lactone formation and the secondary reactions occurring during the decomp. of excess of Br by KI are discussed.

H. B.

**Electrolytic oxidation of glycollic acid in alkaline solution.** E. TOMMILA (Suomen Kem., 1933, 6B, 70).—Electrolytic oxidation of  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (Fe, Ni, or Cu anode) affords  $\text{CHO}\cdot\text{CO}_2\text{H}$ ,  $\text{H}_2\text{C}_2\text{O}_4$ , and  $\text{HCO}_2\text{H}$ . With a Pt anode,  $\text{CH}_2\text{O}$  is the main product; some  $\text{H}_2$  is also liberated.

J. L. D.

**Apparatus for determination of lactic acid.** H. J. FUCHS (Z. physiol. Chem., 1933, 221, 271—277).—A current of air introduces the  $\text{KMnO}_4$  below the surface of the boiling reaction mixture and carries over the MeCHO through a reflux condenser into an improved absorption apparatus containing  $\text{NaHSO}_3$ .

J. H. B.

**Benzyl laevulate.** P. P. T. SAH, H. H. LEI, and H. M. FANG (J. Amer. Chem. Soc., 1933, 55, 4727—4728).—Laevulic acid (52 g.),  $\text{CH}_2\text{Ph}\cdot\text{OH}$  (160 g.), HCl (7 g.), and PhMe (440 g.) are boiled for 24 hr.; subsequent distillation gives *benzyl laevulate* (65 g.), b.p. 181—183°/17 mm. (*phenyl*-, m.p. 91—92°, *p*-tolyl-, m.p. 99—100°, *p*-chlorophenyl-, m.p. 106—107°, and *p*-bromophenyl-, m.p. 103°, *hydrzones*).

H. B.

**Polymerisation and ring formation. XVIII. Polyesters from  $\alpha$ -hydroxydecoic acid.** W. H. CAROTHERS and F. J. VAN NATTA (J. Amer. Chem. Soc., 1933, 55, 4714—4719).—A series of polyesters ( $M$  780—25,200) of the type  $\text{OH}\cdot[(\text{CH}_2)_9\cdot\text{CO}\cdot\text{O}]_n\cdot[\text{CH}_2]_9\cdot\text{CO}_2\text{H}$  are prepared from  $\alpha$ -hydroxydecoic acid (I) by heating under various conditions;  $M$  is determined by titration with  $\text{EtOH-KOH}$  in  $\text{EtOH-CHCl}_3$  and the esters are hydrolysed ( $\text{EtOH-NaOH}$ ) to (I). A small amount of the dimeric lactone of (I) (cf. Lycan and Adams, A., 1930, 65) is always formed in the above preps. Numerous physical data are given; strong oriented fibres (cf. A.,



1932, 601) are obtained only from the esters of  $M > 9330$ .

H. B.

**Ether-like compounds. XI. Ether-lactone with seven-membered ring.** M. H. PALOMAA and U. TOUKOLA (Ber., 1933, 66, [B], 1629—1632; cf. A., 1933, 697).— $\gamma$ -Methoxypropoxyacetic acid, b.p. 140—140.5°/7 mm., is demethylated with difficulty to a Br-free product by HBr.  $\gamma$ -Hydroxypropoxyacetic acid, prepared from  $\text{ONa} \cdot [\text{CH}_2]_3 \cdot \text{OH}$  and  $\text{CH}_2\text{Cl} \cdot \text{CO}_2\text{Na}$ , passes at 200—220°/0.1—1 mm. into the corresponding lactone,  $\text{O} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{C} \cdot \text{O} \cdot \text{O} \end{smallmatrix}$ , m.p. 135.5°, which does not tend to polymerise and in  $\text{COMe}_2 \cdot \text{H}_2\text{O}$  is hydrolysed by acid about 1/90 as fast as  $\text{O} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{C} \cdot \text{O} \end{smallmatrix} \text{O}$ .

H. W.

**Reactivity of atoms and groups in organic compounds. XIV. Influence of substituents on thermal stability of derivatives of malonic acid.** J. F. NORRIS and H. F. TUCKER (J. Amer. Chem. Soc., 1933, 55, 4697—4704).—The m.p. (tube), m.p. (Dennis bar), and decomp. temp. (average val.) [determined by a modification of the method previously used (A., 1931, 197)], respectively, are given after the malonic acids,  $\text{CRR}'(\text{CO}_2\text{H})_2$ : R, R' =  $\text{H}_2$ , 129—131°, 134°, 129°; H, Pr $^\beta$ , 87—91°, 88°, 103°; H, CHMe:CH $_2$ , 97—101°, 95°, 99°; H, sec.-Bu, 75—76°, 76°, 98°; H, isoamyl, 95—96°, 96°, 101°; H, Ph, 139—141°, 169°, 123°; H, *o*-C $_6$ H $_4$ Cl, 128—130°, 133°, 101°; H, CH $_2$ Ph, 119—120°, 120°, 116°; Me $_2$ , 193—194°, 195°, 150°; Et $_2$ , 126—127°, 126° 126°; Me, Et, 121—122°, 121°, 123°; Me, Pr $^\alpha$ , 102—106°, 105°, 98°; Me, Pr $^\beta$ , 120—124°, 126°, 110°; Me, CHMe:CH $_2$ , 89—91°, 85°, 96°; Me, Bu $^\alpha$ , 98—99°, 98°, 109°; Ph, Et, 153—155°, 182°, 117°; Cl, Et, 110.2°, —, 96°; Cl, Pr $^\alpha$ , 98.8—99.3°, —, 76°; Cl, Bu $^\alpha$ , 90.7—91.8°, —, 83°. The use of a method involving the detection of the CO $_2$  liberated gives vals. 1—3° higher. The decomp. temp. of  $\text{CHR}(\text{CO}_2\text{H})_2$  is < that of  $\text{CH}_2(\text{CO}_2\text{H})_2$ . The relationship between the decomp. temp. and structure of substituents is discussed.  $\text{CH}_2(\text{CO}_2\text{H})_2$  decomposes at 115—116° in presence of H $_2$ O, AcOH, KHSO $_4$ , Mg, Al, and ZnCl $_2$  at varying rates.

H. B.

**Specific oxidising action of selenium dioxide.** R. MÜLLER (Ber., 1933, 66, [B], 1668—1670).—SeO $_2$  oxidises  $\text{CH}_2(\text{CO}_2\text{Et})_2$  in xylene at 130° to Et $_2$  ketomalonate, which partly decomposes into Et $_2$ C $_2$ O $_4$  and CO; the liberated H $_2$ O causes partial hydrolysis to Et H mesoxalate. Similarly,  $\text{CH}_2\text{Ac} \cdot \text{CO}_2\text{Et}$  affords Et  $\alpha$ -diketobutyrate (disemicarbazone, m.p. 270°); a secondary formation of AcCHO is not observed.

H. W.

**Ethylene [glycol] glutarate.** Y. TSUZUKI (Bull. Chem. Soc. Japan, 1933, 8, 313—316).— $(\text{CH}_2 \cdot \text{OH})_2$ , glutaric acid, and ZnCl $_2$  (0.5 mol.) at 135—140° give a gummy H ester,  $\text{OH} \cdot [\text{CH}_2]_2 \cdot \text{O} \cdot [\text{CO} \cdot (\text{CH}_2)_3 \cdot \text{CO}_2 \cdot (\text{CH}_2)_2 \cdot \text{O}]_3 \cdot \text{CO} \cdot [\text{CH}_2]_3 \cdot \text{CO}_2\text{H}$ . The degree of polymerisation of this ester being < that in the succinic acid series, and that in the maleic < that in the fumaric acid series, is in agreement with stereochemical considerations.

R. S. C.

**Chain abbreviation and ring formation during thermal degradation of natural polyene dyes.** R. KUHN and A. WINTERSTEIN (Ber., 1933, 66, [B],

1733—1741; cf. A., 1933, 145).—Fresh analyses of the product (I), m.p. 135°, obtained in 10—12% yield by the thermal decomp. of crocetin Me $_2$  ester (II) (*loc. cit.*) indicate the formula C $_{15}$ H $_{20}$ O $_4$  instead of C $_{16}$ H $_{22}$ O $_4$ . (I) is transformed by HI or KOH-EtOH into the dicarboxylic acid (III) C $_{13}$ H $_{16}$ O $_4$ , m.p. 296° (corr.; Berl), re-transformed into (I) by CH $_2$ N $_2$ . (III) absorbs 4 H $_2$  and yields approx. 3 mols. of AcOH when oxidised by CrO $_3$ . The absorption spectrum of (I) in *n*-C $_6$ H $_{14}$  indicates that all the double linkings are conjugated among themselves and with the carboxyls. Since the difference between the mols. of (I) and (II) is C $_7$ H $_8$  (corresponding with PhMe lost during degradation) (I) is Me $_2$   $\alpha\delta$ -trimethyl- $\Delta^{2,7,9}$ -octatetraene- $\alpha\delta$ -dicarboxylate. (I) does not exist preformed in natural (II); chromatographic separation of mixtures of (I) and (II) is easy. Small amounts of triacylcrocetin (IV) are obtained by thermal decomp. of (II) hydrolysed to the dicarboxylic acid C $_{20}$ H $_{24}$ O $_4$ , m.p. 263—264° (corr.; Berl), which absorbs only 4 H $_2$ , and hence contains three rings. The absorption spectrum shows > two conjugated linkings. During the degradation of (II), 12% of (I), 1% of (IV), 10% of PhMe + *m*-xylene, and 2% of (II) are obtained.

H. W.

**Vitamin-C.** P. KARRER, K. SCHÖPP, and F. ZEHNDER (Helv. Chem. Acta, 1933, 16, 1161—1163).—The action of MgMeI on dimethylisopropylidene-ascorbic acid leads to the development of 2OH without loss of OMe, thus confirming the lactone formula of Hirst *et al.* (A., 1933, 594) in contrast with the Me ester structure. Oxidation of ascorbic to dehydro-ascorbic acid (I) corresponds exactly with that of dialuric acid to alloxan (II). The possibility of a peroxide constitution of (I) [and also (II)] is indicated by the oxidising action and absence of colour.

H. W.

**Thioketonic esters. IV.** S. K. MITRA (J. Indian Chem. Soc., 1933, 10, 491—495; cf. A., 1933, 698).—CH $_2$ EtAc  $\cdot$  CO $_2$ Et and H $_2$ S in EtOH-HCl at 0° give Et  $\alpha$ -ethylthioacetoacetate (I), b.p. 85°/14 mm., hydrolysed (10% H $_2$ SO $_4$ ) to COMePr. (I) and NHPH-NH $_2$  afford 1-phenyl-3-methyl-4-ethyl-5-pyrazolone (II), m.p. 108°. The Na derivative of (I) in C $_6$ H $_6$  with EtBr, Bu $^\beta$ I, AcCl, and BzCl gives Et  $\beta$ -ethyl-, b.p. 95°/14 mm.,  $\beta$ -isobutyl-, b.p. 100°/15 mm.,  $\beta$ -acetyl- (III), b.p. 105°/12 mm., and  $\beta$ -benzoyl-, b.p. 185°/18 mm., -thiol- $\alpha$ -ethylcrotonate, respectively, all of which with NHPH-NH $_2$  afford (II). MgEtBr and (III) give COMeEt and (I).

H. B.

**Influence of traces of oxygen on decomposition by heat of acetaldehyde.**—See this vol., 38.

**Unsaturated aldehydes. IV. Dicrotonaldehyde and octatrienal from crotonaldehyde.** K. BERNHAUER and R. DROBNICK (Biochem. Z., 1933, 266, 197—201; cf. A., 1932, 834).—The acid C $_8$ H $_{12}$ O $_4$ , obtained by oxidation of condensation products (I) of CHMe:CH-CHO, is dicrotonic acid. Oxidation of the fraction of (I) of b.p. 96—102°/12 mm. gives octatrienoic acid. Hence (I) probably contain dicrotonaldehyde and octatrienal.

W. McC.

**Semi-acetals.** SCHIMMEL & Co. (Report, 1933, 78—81; Chem. Zentr., 1933, ii, 1008—1009).—When the aldehyde has :CH $_2$  adjacent to :CO, what-



ever the constitution of the alcohol, semi-acetal formation is indicated by increase in  $d$  and  $n$  of the product. The reaction is exothermic. Citronellal and citronellol react, but not citral and geraniol. Aromatic aldehydes behave analogously. For optically active substances  $[\alpha]$  is practically additive.  $n$ -Decaldehyde and decyl alcohol give a compound,  $C_{20}H_{22}O_2$ ,  $M[\alpha]$  97.9° (semi-acetal, calc. 97.72°; mixture 98.29°), relatively stable towards alkali. M.p.,  $d$ ,  $n_D^{20}$ , and  $n_D$  for semi-acetals from aliphatic and aromatic (including optically active) aldehydes,  $R \cdot CH_2 \cdot CHO$  or  $R \cdot CHO$ , and alcohols are tabulated.

A. A. E.

**Determination of small quantities of acetone in presence of other substances.** I. N. KORENMAN (J. Appl. Chem. Russ., 1933, 6, 1002—1004).— $COMe_2$  (0.00025—0.001 mg. per 100 c.c.) is determined colorimetrically by the Frommer-Emilowicz reaction (salicylaldehyde and NaOH). A no. of org. solvents do not interfere.

R. T.

**Hydrogenolysis of sugars.** W. H. ZARTMAN and H. ADKINS (J. Amer. Chem. Soc., 1933, 55, 4559—4563).—Hydrogenation [ $H_2$  (300 atm.), Cu—Cr oxide catalyst, EtOH at 250°] of glucose, sorbitol, mannitol, sucrose, lactose, maltose,  $\alpha$ -methyl- $d$ -glucoside, glucose penta-acetate, and gluconolactone (I) gives varying amounts of MeOH, EtOH,  $OH \cdot CHMe \cdot CH_2 \cdot OH$ , and (probably) 4-hydroxy-2- $\alpha$ -hydroxyethylfuran, b.p. 118—125°/1 mm.,  $\alpha\beta\gamma$ -trihydroxyhexane, b.p. 142—144°/1 mm., and  $\alpha\beta\gamma\delta$ -tetrahydroxyhexane, b.p. 214—215°/1 mm. Some  $(\cdot CH_2 \cdot OH)_2$  is produced from (I).

H. B.

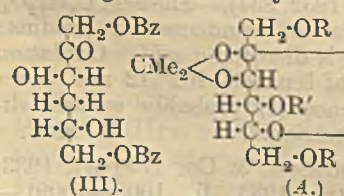
**Shaffer and Hartmann combined carbonate-citrate method for determination of glucose.** J. O. HALVERSON and F. W. SHERWOOD (Ind. Eng. Chem. [Anal.], 1933, 5, 418—419).—The method is accurate if the error incidental to the standard conditions used is determined.

R. S. C.

**Acceleration by boric acid of the mutarotation of glucose.** G. AURIACCIO (L'Ind. Chimica, 1933, 8, 1369—1370).— $H_3BO_3$  accelerates the mutarotation. 0.5—3% solutions do not influence the equilibrium rotation.

H. F. G.

**Derivatives of  $\gamma$ -fructose. New isopropylidene-fructose.** L. ZERVAS and P. SESSLER (Ber., 1933, 66, [B], 1698—1703).—Fructose cyanohydrin, m.p. 114—115° (improved prep.) ( $Ac_6$  derivative, m.p. 80—82°), is converted by  $BzCl$  in anhyd.  $C_5H_5N$  into the unstable *dibenzoylfructose cyanohydrin* (I), m.p. about 150° [additive compounds with  $C_5H_5N$  (II), m.p. 128° (corr.),  $[\alpha]_D^{20}$   $-13.3^\circ$  in  $C_5H_5N$ , and with  $AcOH$ , m.p. 140° (corr.)]. Inability of (I) to react with  $CPh_3Cl$  is evidence of the location of the  $Bz$  groups at 1 and 6. (II) is transformed by  $Ag_2CO_3$  in boiling  $EtOAc$  into *fructose 1:6-dibenzoate* (III),



little conc.  $H_2SO_4$  afford 2:3-isopropylidene- $\alpha$ - $d$ -fructo-

*furanose 1:6-dibenzoate*. (IV;  $A$ ;  $R=Bz$ ;  $R'=H$ ), m.p. 118° (corr.),  $[\alpha]_D^{20} +13.5^\circ$  in EtOH,  $+12.7^\circ$  in  $COMe_2$ , transformed by  $BzCl$  in  $C_5H_5N$  into the *tribenzoate* (V) ( $A$ ;  $R=R'=Bz$ ), m.p. 137° (corr.),  $[\alpha]_D^{20} -9^\circ$  in  $COMe_2$ . (IV) is hydrolysed by  $Ba(OH)_2$  to 2:3-isopropylidene- $\alpha$ - $d$ -fructofuranose (VI) [ $A$ ;  $R=R'=H$ ], m.p. 80°,  $[\alpha]_D^{20} +18.9^\circ$  in  $H_2O$ ,  $[\alpha]_D^{20} +14.1^\circ$  in  $COMe_2$ , which does not reduce Fehling's solution, is not oxidised by  $Pb(OAc)_4$  (Criegee), and does not react with  $COMe_2$  and  $H_2SO_4$ . Benzoylation transforms (VI) into (V), whilst  $Ac_2O$  in  $C_5H_5N$  yields the *triacetate*, m.p. 55°,  $[\alpha]_D^{20} -8^\circ$  in EtOH, and  $CPh_3Cl$  affords *ditriphenylmethylisopropylidene-fructose*, m.p. 155° (corr.),  $[\alpha]_D^{20} -5.2^\circ$  in  $C_5H_5N$ . H. W.

**Action of nitric acid on sugars.** S. VON MONASTERSKI (Z. ges. Schiess- u. Sprengstoffw., 1933, 28, 349—350).—*Sucrose octanitrate*, m.p. 80—82°, explodes at 169—170°, is prepared by adding  $HNO_3$  ( $d$  1.498), dropwise, and then oleum (17%  $SO_3$ ) to a mixture of sucrose and carbamide nitrate and pouring the solution into cold  $H_2O$ ; alternatively a mixture of sugar and pinene hydrochloride is nitrated at 0° with mixed acid ( $H_2SO_4$  50,  $HNO_3$  38,  $SO_3$  5,  $H_2O$  7%), the mixture heated to 80°, and poured into cold  $H_2O$ . *Maltose octanitrate* (I), m.p. 135°, explodes at 171—180°, is prepared by heating maltose and carbamide nitrate with  $HNO_3$  and oleum at 80°, evolution of  $N$  oxides being avoided. "Maltobenzite," explodes at 200°, is prepared by heating a mixture of (I),  $m\text{-}C_6H_4(NO_2)_2$ , and  $C_6H_6$  to 70°, kneading to a plastic mass, heating to 95°, again kneading, and cooling. Heats of explosion, fall-hammer and Pb-block tests are recorded. W. J. W.

**Material synthesis of wood substance from the wood-forming plant saps. Fructose as the primitive substance in the synthesis of "lignin."** H. WISLICENUS and H. HEMPEL [with (in part) K. UEBEL, H. FRIEDERICI, and H. VON ZEHMEN] (Cellulosechem., 1933, 14, 149—168).—Largely a more detailed account of work previously reviewed (A., 1930, 824; 1933, 989). Fructose (I) is readily autoxidised (sterile air), particularly in dil. alkaline solution, to colloidal products which are adsorbed by  $Al(OH)_3$ . Similar products are formed from (I) (much more readily and to a larger extent than from glucose) by dehydration (heat;  $H_2SO_4$ ;  $Ac_2O$ — $ZnCl_2$ ). These products resemble the "primitive lignin" of the cambial sap, suggesting that lignin may arise from (I). H. B.

**Glycerolysis of sucrose.** H. VOGEL (Ber., 1933, 66, [B], 1670—1672).—When heated with glycerol at 130°/11 mm., sucrose yields a syrup from which abs. EtOH causes separation of a solid giving phenylglucosazone, m.p. 204°,  $[\alpha]_D^{20} +52.01^\circ$  in  $H_2O$ , when treated with  $NHPh \cdot NH_2$  at 100° and  $\beta$ -glucose penta-acetate, m.p. 132°, when boiled with  $Ac_2O$  and  $NaOAc$ . The non-cryst. portion yields glycerylfructoside, slowly converted by  $NHPh \cdot NH_2$  in boiling  $H_2O$  into glucosazone.  $\alpha$ -Galactosan (I), rhamnosan, and arabinosan with glycerol at 120°/12 mm. yield bitter syrups which do not reduce Fehling's solution.  $\alpha$ -Glucosan and (I) are transformed by MeOH at 120° into  $\alpha$ -methyl-glucoside and -galactoside, respectively. H. W.



Glucosides of *p*-nitro- and *p*-amino-phenol and their fermentative scission.—See A., 1933, 1286.

Glucosidic azo-dyes.—See A., 1933, 1286.

Heart glucosides. IV. Deacetyldigilanids A, B, and C. A. STOLL and W. KREIS (Helv. Chim. Acta, 1933, 66, 1390—1407; cf. A., 1933, 1146).—Digilanid A in MeOH is transformed by aq. Ca(OH)<sub>2</sub> at room temp. into deacetyldigilanid A (I), C<sub>47</sub>H<sub>74</sub>O<sub>18</sub>, m.p. 258° (decomp.) after softening at 255° (corr.), [α]<sub>D</sub><sup>20</sup> +10.4° in 75% EtOH, probably identical with purpleagluconide A. Treatment in 95% EtOH with 2N-H<sub>2</sub>SO<sub>4</sub> at 40° converts (I) into digitoxigenin, digitoxose (II), and digilanidobiose (III): C<sub>47</sub>H<sub>74</sub>O<sub>18</sub> + 3H<sub>2</sub>O = C<sub>23</sub>H<sub>34</sub>O<sub>4</sub> + 2C<sub>6</sub>H<sub>12</sub>O<sub>4</sub> + C<sub>12</sub>H<sub>22</sub>O<sub>9</sub>. Hydrolysis with an enzyme prep. (IV) from the leaves of *Digitalis purpurea* leads to digitoxin. Deacetyldigilanid B, m.p. 240° (corr., decomp.), [α]<sub>D</sub><sup>20</sup> +20.4° in 75% EtOH, obtained in the same manner as (I), is hydrolysed by acid to gitoxigenin, (II), and (III): C<sub>47</sub>H<sub>74</sub>O<sub>19</sub> + 3H<sub>2</sub>O = C<sub>23</sub>H<sub>34</sub>O<sub>5</sub> + 2C<sub>6</sub>H<sub>12</sub>O<sub>4</sub> + C<sub>12</sub>H<sub>22</sub>O<sub>9</sub>, and by (IV) to gitoxin (V). Cryst. deacetyldigilanid C, m.p. 265—268° (decomp.) after darkening at 235° (corr.) and softening at 255° (corr.), derived similarly from digilanid C, is hydrolysed by acid to digoxigenin, (II), and (III): C<sub>47</sub>H<sub>74</sub>O<sub>19</sub> + 3H<sub>2</sub>O = C<sub>23</sub>H<sub>34</sub>O<sub>5</sub> + 2C<sub>6</sub>H<sub>12</sub>O<sub>4</sub> + C<sub>12</sub>H<sub>22</sub>O<sub>9</sub>, and by (IV) to (V). The physiological activity of the digilanids is retained in their deacetyl derivatives. H. W.

Emulsin. XIII. Preparation and enzymic fission of glucosides of *N*-acetylglucosamine and 2-deoxyglucose. B. HELFERICH and A. ILOFF (Z. physiol. Chem., 1933, 221, 252—258; cf. this vol., 109).—Alkaline hydrolysis of tetra-acetylphenyl-β-d-glucosaminide, m.p. 201.5—202° (corr.), decomp. from 185°, [α]<sub>D</sub><sup>18</sup> -10° in CHCl<sub>3</sub>, gave *N*-acetylphenyl-β-d-glucosaminide (I), m.p. 238° (decomp.), [α]<sub>D</sub><sup>20</sup> -5.4° in H<sub>2</sub>O. There is no parallelism between the hydrolysis of (I), phenyl-β-glucoside and -α-d-mannoside, indicating that the enzymes concerned differ. Bromination of triacetylglucal, elimination of Br with AgOAc, and fusion with PhOH gave triacetylphenyl-α-d-glucoside 2-bromohydrin, m.p. 104—106° (corr.), [α]<sub>D</sub><sup>21</sup> +60.7° in CHCl<sub>3</sub>, converted by NaOMe in MeOH into phenyl-α-d-glucoside 2-bromohydrin (II), m.p. 122—124° (corr.), [α]<sub>D</sub><sup>20</sup> +88.2° in H<sub>2</sub>O, which, with Na-Hg, gave phenyl-2-deoxy-α-d-glucoside (III), m.p. 162—163° (corr.), [α]<sub>D</sub><sup>18</sup> +159° in H<sub>2</sub>O. Acetylation of 2-deoxyglucose and fusion with PhOH of the tetra-acetate, m.p. 109—110°, [α]<sub>D</sub><sup>21</sup> +109°, and hydrolysis of the Ac groups of the resulting tetra-acetylphenyl-2-deoxyglucoside, m.p. 87—88° (corr.), [α]<sub>D</sub><sup>21</sup> +146°, also gave (III). (II) is not hydrolysed by emulsin. The hydrolysis of (III) is paralleled by α-mannosidase, but not by β-glucosidase, fission.

J. H. B.

Phosphorus of potato starch. T. POSTERNAK (Compt. rend., 1933, 197, 1157—1158).—Hydrolysis of potato starch (I) with ox pancreas or malt extract and treatment of the filtrate with Pb subacetate (II) and 10% aq. NH<sub>3</sub> gives a ppt. containing about 80% of the original P. Dissolution of the dry ppt. in AcOH, neutralisation with aq. NH<sub>3</sub>, and addition of EtOH affords a viscous product which gives a further ppt. with (II) in AcOH. Decomp. of this with H<sub>2</sub>SO<sub>4</sub>

and neutralisation with Ba(OH)<sub>2</sub> gives (by pptn. with EtOH) (probably) a Ba hexaoxide monophosphate, which reduces Fehling's solution and contains one reducing group (determined by NaOI) per atom of P. It is hydrolysed (2% H<sub>2</sub>SO<sub>4</sub>) to glucose and (probably) Ba maltose monophosphate, which is fairly resistant to hydrolysis. A biose monophosphate acid has also been isolated from the hydrolysate of (I) with 2% H<sub>2</sub>SO<sub>4</sub>. (I) consists of long chains of glucose residues linked through the α-position; the P is attached (as phosphate) to one of the residues. H. B.

Determination of glycogen. M. SAHYUN (J. Biol. Chem., 1933, 103, 203—208).—The use of > 50 mg. of activated C (I) or norit in the method previously described (A., 1932, 77) does not prevent hydrolysis of glycogen (II) by N-H<sub>2</sub>SO<sub>4</sub>; with larger amounts (100—200 mg.), results similar to those of Bancroft and Fry (A., 1933, 457) and Good *et al.* (*ibid.*, 625) are obtained. (I) adsorbs very little H<sub>2</sub>SO<sub>4</sub>. The pptd. (II) (cf. *loc. cit.*) is completely hydrolysed by 5N-H<sub>2</sub>SO<sub>4</sub> (as little as possible to be used) at 100° in 15—20 min. H. B.

Oxycellulose. K. H. BERGMANN (Angew. Chem., 1933, 46, 713—716).—The applicability of the KMnO<sub>4</sub> no. method is confirmed for carbohydrates and related compounds, but requires modification when applied to oxycellulose (I) (improved prep.). (I) is extracted from the fibre by repeated treatment with hot NaOH and titrated with KMnO<sub>4</sub>, the KMnO<sub>4</sub> no. being calc. by an approx. formula. The results agree with those obtained from the loss in wt. of the fibre to within 1%. The acidified (CO<sub>2</sub> or AcOH) extract gives a substance (C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>)<sub>n</sub>, also obtained from (I) prepared by different methods. It is not glycuronolactone. Fibres containing (I) produced by different methods with cold KOH yield the K salt (sinters and reddens 135°, suddenly sinters, decomp., and partly melts 163°, sinters 183°, strong decomp. 186°) of polyglycuronic acid. The fall in strength of fibre is proportional to the increase in (I) content. A. A. L.

Chemical nature of hypochlorite oxycelluloses. R. HALLER and F. LORENZ (Helv. Chim. Acta, 1933, 16, 1165—1180).—American cotton is purified by treatment with "degomma" at 40°, followed by twice boiling with 2% NaOH in absence of air under slightly increased pressure for 8 hr. and subsequent washing with running H<sub>2</sub>O, treatment with 0.5% H<sub>2</sub>SO<sub>4</sub>, and final washing. The product is soaked in NaOCl containing little NaOH, thoroughly squeezed, exposed to CO<sub>2</sub> for 12 hr., soured with 0.5% HCl, washed with H<sub>2</sub>O, and dried at 50°. Extraction with H<sub>2</sub>O (Soxhlet) shows that the degradation products of oxy- (I) are much more firmly retained than those of hydro-cellulose. Extraction with wet steam is much more effective than with H<sub>2</sub>O. The extractions show that a portion of the reducing degradation products in (I) can be removed, and that these are in adsorptive union with (I). Fibrous structure is apparently retained by the residue, which, however, crumbles readily and is shown by acid val. and [α] to retain degradation products not removable by H<sub>2</sub>O. Treatment of the relatively very small extract with neutral and basic Pb acetate leads to the identification of



*d*-saccharic acid and acids derived from higher carbohydrates which yield *d*-glucose when hydrolysed. The bulk of the residue is a neutral material which strongly reduces Fehling's solution, does not react with  $\text{NHPh}\cdot\text{NH}_2$ ,  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$ ,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ , or  $\text{NH}_2\cdot\text{CS}\cdot\text{NH}\cdot\text{NH}_2$ ; it yields a freely-sol. Ac derivative and is hydrolysed to *d*-glucose. It is considered that the oxidation of cellulose by  $\text{NaOCl}$  is initiated by hydrolytic fission of the highly-polymerised mol.

H. W.

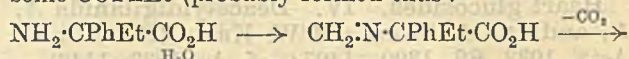
**Behaviour of hydrochlorides of organic bases towards chloroauric acid. Constitution of the abnormal auric chloride complexes.** D. C. SEN (J. Indian Chem. Soc., 1933, 10, 497—501).—Complexes of the type  $\text{BH}[\text{AuCl}_4]$  (I) (m.p. quoted in parentheses), where B is 1 mol. of base, are prepared by Fenner and Tafel's method (A., 1900, i, 111) from base hydrochloride and  $\text{HAuCl}_4$  in  $\text{H}_2\text{O}$ ; in  $\text{EtOH}\text{-HCl}$  (cf. *loc. cit.*), the complexes  $\text{BH}[\text{AuCl}_4]\cdot\text{B}\cdot\text{HCl}$  (II) (the constitutions are assigned from determinations of sp. resistance and mol. vol.) are often formed. (II) decompose in  $\text{H}_2\text{O}$ ,  $\text{COMe}_3$ , or hot  $\text{EtOH}$  to (I) and  $\text{B}\cdot\text{HCl}$ . The following are described: (I), where B is quinoline (238°), piperidine (206°),  $\text{NH}_2\text{Et}$  (195°),  $\text{CH}_2\text{Ph}\cdot\text{NH}_2$  (168°), and  $\text{NMe}_3$  (220°); (II), where B is quinoline (180°), piperidine (183°) (lit. 170°), and  $\text{NH}_2\text{Et}$  (70°).

H. B.

**Action of formaldehyde on amines and amino-acids.** H. T. CLARKE, H. B. GILLESPIE, and S. Z. WEISSHAUS (J. Amer. Chem. Soc., 1933, 55, 4571—4587).— $\text{NH}_2\text{Alk}$  and  $\text{NHAlk}_2$  are methylated by  $\text{CH}_2\text{O}$  (1.1 mol. per Me group introduced) in warm  $\text{HCO}_2\text{H}$  to  $\text{NMe}_2\text{Alk}$  and  $\text{NMeAlk}_2$ , respectively; the H involved in the reduction is supplied (mainly) by the  $\text{HCO}_2\text{H}$ :  $\text{NHR}_2 + \text{CH}_2\text{O} + \text{HCO}_2\text{H} \rightarrow \text{NMeR}_2 + \text{CO}_2 + \text{H}_2\text{O}$ .  $\text{NH}_2\text{Bu}$ ,  $\text{CH}_2\text{Ph}\cdot\text{NH}_2$ , piperidine (I),  $(\text{-CH}_2\cdot\text{CH}_2\cdot\text{NH}_2)_2$ , and 2:4:6- $\text{C}_6\text{H}_3\text{Br}_3\cdot\text{NH}_2$  are thus converted into  $\text{NMe}_2\text{Bu}$ ,  $\text{CH}_2\text{Ph}\cdot\text{NMe}_2$  (II), 1-methylpiperidine (III),  $(\text{-CH}_2\cdot\text{CH}_2\cdot\text{NMe}_2)_2$ , and 2:4:6- $\text{C}_6\text{H}_3\text{Br}_3\cdot\text{NMe}_2$ , respectively;  $\text{NH}_2\text{Ph}$  gives a viscous product and the reaction fails with amides,  $\text{CO}(\text{NH}_2)_2$ , guanidine, and  $\text{NH}_2\text{OH}$ .  $\text{NH}(\text{CH}_2\text{Ph})_2$  (IV) similarly affords  $\text{NMe}(\text{CH}_2\text{Ph})_2$  (V) (main product),  $\text{PhCHO}$ , and (probably) (II).  $\text{CH}_2[\text{N}(\text{CH}_2\text{Ph})_2]_2$  is converted by warm  $\text{HCO}_2\text{H}$  into (IV) and (V);  $\text{CHPh}\cdot\text{N}\cdot\text{CH}_2\text{Ph}$  is not an intermediate, since this is readily hydrolysed by  $\text{HCO}_2\text{H}$ . Methylenedipiperidine and  $\text{HCO}_2\text{H}$  similarly afford (I) and (III); in these cases, the change  $\text{CH}_2(\text{NR}_2)_2 \rightarrow \text{NHR}_2 + \text{OH}\cdot\text{CH}_2\cdot\text{NR}_2$  (which is subsequently reduced) probably occurs.  $(\text{C}_2\text{H}_5)_3\text{N}_4$  (VI) and warm  $\text{HCO}_2\text{H}$  give (mainly)  $\text{NH}_3$  and  $\text{NMe}_3$  together with small amounts of  $\text{NH}_2\text{Me}$  and  $\text{NHMe}_2$ ; about 75% of the C of (VI) is found as Me. In all the above reactions, some of the H (for reduction) is supplied by  $\text{CH}_2\text{O}$ .  $\text{MeCHO}$ ,  $\text{HCO}_2\text{NH}_4$ , and  $\text{HCO}_2\text{H}$  give 2-methyl-5-ethylpyridine;  $\text{CO}_2$  is not produced (cf. above).

Methylation of various  $\text{NH}_2$ -acids is accomplished under similar conditions. Thus,  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  gives 60—70% of  $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (hydrochloride, m.p. 189—190°), and a little  $\text{NMe}_3$ ;  $\alpha$ -aminoisobutyric acid affords 80% of  $\alpha$ -dimethylaminoisobutyric acid [hydrochloride, m.p. 264° (decomp.); Me ester, b.p. 154—155°];  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  yields 38% of

$\text{NMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (hydrochloride, m.p. 188—191°);  $\alpha$ -amino- $\alpha$ -phenylbutyric acid furnishes  $\alpha$ -dimethylamino- $\alpha$ -phenylbutyric acid, m.p. 220° (decomp.), and some  $\text{COPhEt}$  (probably formed thus:



$\text{NH}_2\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$  similarly affords some  $\text{PhCHO}$ . Alanine, leucine, and  $\alpha$ -amino-octioic and glutamic acids do not give the  $\text{NMe}_2$ -derivatives; volatile bases are produced. *dl*-Phenylalanine (VII),  $\text{CH}_2\text{O}$ , and  $\text{HCO}_2\text{H}$  (or  $\text{AcOH}$ ) give (mainly)  $\text{NH}_2\text{Me}$  and (probably)  $\beta$ -phenyl- $\alpha$ -2:3-diketo-4-phenyl-1-pyrrolidylpropionic acid (VIII), m.p. 245—246° [*Ba* salt (+3 $\text{H}_2\text{O}$ ); Me ester, m.p. 118°; *anil* anilide, m.p. 215°; Me ether, m.p. 75—90° (*Ba* salt; Me ester, m.p. 78°; *anilide*, m.p. 208°)]; *l*-phenylalanine affords a similar compound, m.p. 250—251°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -37.6° in *N*- $\text{NaOH}$ . (VIII) is also obtained from (VII),  $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CO}_2\text{H}$  (IX) (which is undoubtedly an intermediate in the above reaction), and  $\text{CH}_2\text{O}$  in  $\text{AcOH}$ . *l*-*p*-Methoxyphenylalanine (X) and (IX) similarly afford (probably)  $\beta$ -anisyl- $\alpha$ -2:3-diketo-4-phenyl-1-pyrrolidylpropionic acid, m.p. 239—240°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -135.5° in *N*- $\text{NaOH}$ ; with  $\text{CH}_2\text{O}$  and  $\text{HCO}_2\text{H}$ , (X) yields (probably)  $\beta$ -anisyl- $\alpha$ -2:3-diketo-4-anisyl-1-pyrrolidylpropionic acid, m.p. 231° (decomp.), [ $\alpha$ ]<sub>D</sub><sup>20</sup> -31° in *N*- $\text{NaOH}$ . (VIII) is oxidised by alkaline  $\text{KMnO}_4$  to  $\text{BzOH}$  and (probably) a little (IX) and by  $\text{Ag}_2\text{O}$  to  $\text{PhCHO}$ . (VIII) and  $\text{Ac}_2\text{O}$  give a compound,  $\text{C}_{21}\text{H}_{17}\text{O}_4\text{N}$ , m.p. 192—194°, whilst with  $\text{BzCl}$  and aq.  $\text{NaOH}$  a compound,  $\text{C}_{26}\text{H}_{23}\text{O}_6\text{N}$ , m.p. 60° (previous softening), results; these are hydrolysed to (VIII). (VIII) and  $\text{NH}_2\text{OH}$  afford a compound,  $\text{C}_{19}\text{H}_{18}\text{O}_4\text{N}_2$ , m.p. 185—186° (decomp.) (yellow > 160°), also hydrolysed to (VIII).

H. B.

**Mechanism of action of carbon disulphide on primary and sec. amines.** H. S. FRY and W. V. CULP (Rec. trav. chim., 1933, 52, 1061—1066).—Interaction of sec. (aralkyl-)amines with excess of  $\text{CS}_2$  in presence of I (1 equiv.) and  $\text{C}_5\text{H}_5\text{N}$  (excess) gives only thiuram disulphides (44—89% of theory). Since primary amines under these conditions give only thiocarbamides (A., 1913, i, 1174), it is concluded that this latter reaction occurs in accordance with the equation  $\text{NHR}\cdot\text{CS}\cdot\text{SH} + \text{NH}_2\text{R} \rightarrow \text{H}_2\text{S} + \text{NHR}\cdot\text{C}(\text{NH})\cdot\text{SH} \rightarrow \text{CS}(\text{NHR})_2$ . *Bis*- $\alpha$ -naphthylethyl-, m.p. 166.7°, and  $\beta$ -naphthylethyl-thiuram disulphide, m.p. 158—159°, are described. H. A. P.

**Fluorine polyhalides of organic amines.**—See this vol., 44.

**Action of trimethylamine on  $\alpha\gamma$ -tetramethyldiamino- $\beta\gamma$ -hydroxypropane dimethiodide.** L. GORINI (Gazzetta, 1933, 63, 751—756).—If in the prep. of  $\text{OH}\cdot\text{CH}(\text{CH}_2\cdot\text{NMe}_3)_2$  from  $\text{OH}\cdot\text{CH}(\text{CH}_2\text{I})_2$  and  $\text{NMe}_3$  an autoclave is used, with excess of  $\text{NMe}_3$ , the product contains increasing quantities of  $\text{OH}\cdot\text{CH}(\text{CH}_2\cdot\text{NMe}_2)_2$  (I) and  $\text{NMe}_2\text{I}$  as the concn. of  $\text{NMe}_3$  and the hydrolytic power of the solvent increase. (I), new b.p. 46°/2 mm., forms a di-iodide (II), m.p. 225°, and a dihydrochloride (III), m.p. 256°, which are also prepared from the iodo- and chloro-hydrins and  $\text{NHMe}_2$ ; with  $\text{Ac}_2\text{O}$  (III) forms tetramethyldiaminoisopropyl acetate dihydrochloride, m.p. 247°. E. W. W.



**Amidoxime salts. I. Hippuramidoxime.**

J. V. DUBSKÝ and J. TRTÍLEK (Coll. Czech. Chem. Comm., 1933, 5, 310—316).—Addition of  $\text{NH}_4\text{OH}$  in 96%  $\text{EtOH}$  to a warm solution of  $\text{NHBz}\cdot\text{CH}_2\cdot\text{CN}$  in  $\text{EtOH}$  affords *hippuramidoxime* (I)

$\text{NHBz}\cdot\text{CH}_2\cdot\text{C}(\text{NOH})\cdot\text{NH}_2$  (tautomeric), m.p. 123—126°, the  $\text{Cu}$ ,  $\text{RCu}\cdot 2\text{H}_2\text{O}$  ( $\text{R} = [\text{NHBz}\cdot\text{CH}_2\cdot\text{C}(\text{NH}_2)\cdot\text{NO}]$ ), losing 1  $\text{H}_2\text{O}$  at 100° to give  $\text{RCuOH}\cdot\text{H}_2\text{O}$ , and  $\text{Ni}$ ,  $\text{R}_2\text{NiOH}$  (II) [from (I),  $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ , and  $\text{H}_2\text{O}_2$  in  $\text{NH}_3$  solution], decomp. in boiling  $\text{H}_2\text{O}$ , compounds of which are described and their constitutions discussed. According to conditions mixtures of (II) and compounds of type  $\text{R}_2\text{Ni}$  may be obtained.

J. W. B.

**Diamino-acid, canavanin. III. Constitution of canalin.** M. KITAGAWA and S. MONOBE (J. Biochem. Japan, 1933, 18, 333—343).—Canalin (A., 1933, 382) (*sulphate*; *Bz*, *lactam*, m.p. 163—164°; *Et* ester *hydrochloride*) is reduced by  $\text{H}_2$ —Pt-black to  $\alpha$ -amino- $\gamma$ -hydroxybutyric acid and  $\text{NH}_3$ . The structure  $\text{CH}_2(\text{ONH}_2)\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$  is proposed.

F. O. H.

**Additive compounds of cystine and picric acid.** G. TOENNIES (Z. physiol. Chem., 1933, 222, 1—2).—Picric acid (A) and *l*-cystine (B) form complexes  $\text{AB}_3$  (from  $\text{H}_2\text{O}$ ) and  $\text{AB}_6$  (from  $\text{MeOH}$ ). In  $\text{MeOH}$  in presence of A the  $[\alpha]$  of B is 25% > the normal val.

J. H. B.

**Production of cysteine from cystine by irradiation.** P. SZENDRŐ, U. LAMPERT, and F. WREDE (Z. physiol. Chem., 1933, 222, 16—20).—*l*-Cysteine is formed in 5% yield by irradiation of cystine with ultra-violet light.

J. H. B.

**Action of carbon monoxide on iron and cobalt complexes of cysteine.** M. P. SCHUBERT (J. Amer. Chem. Soc., 1933, 55, 4563—4570).—Cysteine hydrochloride (I),  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ , and  $\text{KOH}$  in  $\text{H}_2\text{O}$  and  $\text{CO}$  give after acidification ( $\text{HCl}$ ) the complex (II),  $\text{Fe}[\text{S}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}]_2\cdot 2\text{CO}\cdot\text{H}_2\text{O}$  ( $\text{Na}_2$  salt +  $2\text{H}_2\text{O}$ ), which is stable in air but decomposes (into its components) in warm aq. solution.  $\text{K}_2$  cobaltobiscysteinate (A., 1933, 1039) does not give a complex analogous to (II); 1 mol. of  $\text{CO}$  is absorbed in solution and  $\text{K}_3$  cobalttricycysteinate (III) (*loc. cit.*) and the acid  $\text{H}[\text{Co}(\text{CO})_4]$  (IV) [ $\text{Ag}$  (+0.5 and  $2\text{H}_2\text{O}$ ), blackens at about 90°, and *Hg*, m.p. 82° (decomp.), salts] are produced. (III) and  $\text{CO}$  in aq.  $\text{KOH}$  give  $\text{K}_2\text{CO}_3$  and (IV). Acidification ( $\text{HCl}$ ) of solutions containing (IV) affords *Co tetracarbonyl* (+0.5  $\text{H}_2\text{O}$ ), decomp. 48—50°, which with (I) and aq.  $\text{KOH}$  gives (III) and (IV).

H. B.

**Basis for the physiological activity of -onium compounds. XIII. Betaine-amides.** R. R. RENSHAW and H. T. HOTCHKISS, jun. XIV. Aryl ethers of choline. I. R. R. RENSHAW and W. D. ARMSTRONG (J. Biol. Chem., 1933, 103, 183—186, 187—189).—XIII. (cf. A., 1926, 1232). *Betaine-amides*,  $\text{NHR}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NMe}_3\text{Cl}$ , where *R* is *Me* (I), m.p. 171—172° (all m.p. are corr.); *Et*, m.p. 203—204°; *Pr*, m.p. 165°; *Bu*, m.p. 177°; *Ph* (II), m.p. 223° (corresponding *bromide*, m.p. 215°); *p*-tolyl, m.p. 235° (decomp.); *p*-hydroxyphenyl, m.p. 198°; *o*-, m.p. 195°, and *p*-, m.p. 218°, -anisyl; *o*-, m.p. 160°, and *p*-, m.p. 215°, -phenetyl; *p*-nitrophenyl, m.p. 143—144°

(corresponding *bromide*, m.p. 235—236°);  $\alpha$ - $\text{C}_{10}\text{H}_7$ , m.p. 165.5°;  $\beta$ - $\text{C}_{10}\text{H}_7$ , m.p. 188°, and  $\text{NHR} = 1$ -piperidyl, m.p. 129°, are prepared from  $\text{NMe}_3$  and  $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NHR}$  usually in  $\text{PhMe}$ . Of the alkyl-amides, (I) possesses the max. muscarine-like action (III). With the arylamides, no (III) is observed; (I) gives a strong stimulating nicotine action.

XIV (cf. A., 1932, 622).  $\beta$ -Phenoxyethyl- (IV), m.p. 167°, and  $\gamma$ -phenoxypropyl-, m.p. 156°, -trimethylammonium bromides are described. (IV) produces a marked stimulation of blood pressure and respiration.

H. B.

**Ethylenic nitriles.  $\alpha$ -Methyl- $\Delta^a$ -hexenonitriles and  $\alpha$ -butylacrylonitrile.** A. CRAEN (Bull. Soc. chim. Belg., 1933, 42, 410—418).—Successive treatment of  $\alpha$ -hydroxy- $\alpha$ -methylhexonitrile with  $\text{SOCl}_2$  and dry  $\text{HCl}$  gives  $\alpha$ -chloro- $\alpha$ -methyl- (I), b.p. 62—63°/10 mm.,  $\beta$ -chloro- $\alpha$ -methyl- (II), b.p. 84—84.2°/10 mm., and  $\alpha$ -chloromethyl- (III), b.p. 94—94.6°/10 mm., -hexonitriles. (II) and  $\text{C}_5\text{H}_5\text{N}$  at 150° afford *cis*- (IV), b.p. 46—47°/10 mm., and *trans*-, b.p. 59.4—59.6°/10 mm.,  $\alpha$ -methyl- $\Delta^a$ -hexenonitriles, whilst (III) similarly gives  $\alpha$ -butylacrylonitrile (V), b.p. 45.8—46°/10 mm. (I) similarly yields a mixture of (IV) and (V). The above unsaturated nitriles are hydrolysed to the unsaturated amides, m.p. 74—74.2°, 54.8—55.7°, and 75—76°, respectively.

H. B.

**Effect of ethyl radicals on the thermal decomposition of azomethane. Kinetics of thermal decomposition of lead tetraethyl. Ethyl radicals and hydrogen.**—See this vol., 34.

**Esters of tetrathio-orthogermanic acid.** H. J. BACKER and F. STIENSTRA (Rec. trav. chim., 1933, 52, 1033—1038).—The following are prepared by interaction of the appropriate Na mercaptide with  $\text{GeCl}_4$  in  $\text{C}_6\text{H}_6$  or (better) from the thiol,  $\text{NaOEt}$ , and  $\text{GeCl}_4$  in  $\text{EtOH}$ : *Me*, m.p. -3°, b.p. 138—140°/4 mm.; *Et*, b.p. 164.5—165.5°/5 mm.; *Pr*, b.p. 191—192°/4—5 mm.; *Pr*, m.p. 15°, b.p. 162—164°/4 mm.; *Bu*, b.p. 222—223°/4—5 mm.; *sec*-, b.p. 200—201°/5 mm., *iso*-, b.p. 199—200°/4—5 mm., and *tert*-.butyl, m.p. 172—173°; *Ph*, m.p. 101.5°; *p*-tolyl, m.p. 110—111° [with  $\text{Br}$  in  $\text{CHCl}_3$  gives  $(\text{C}_6\text{H}_4\text{Me})_2\text{S}_2$ ], and (*p*- $\text{C}_6\text{H}_4\text{Br}$ )<sub>4</sub> tetrathio-orthogermanate, b.p. 196—196.5°. Interaction of  $(\text{CH}_2\text{Cl}\cdot\text{CH}_2)_2\text{O}$  with  $\text{CS}(\text{NH}_2)_2$  gives the corresponding isothiocarbamide derivative, converted by warm  $\text{NaOH}$  into  $\beta\beta'$ -dithioldiethyl ether, b.p. 217°; this with  $\text{GeCl}_4$  and  $\text{NaOEt}$  gives the corresponding spiro-ester,  $\text{Ge}\left[\begin{smallmatrix} \text{S}\cdot\text{CH}_2\cdot\text{CH}_2 \\ \text{S}\cdot\text{CH}_2\cdot\text{CH}_2 \end{smallmatrix}\right]_2$ , m.p. 159—159.5°.

H. A. P.

**Organo-metallic compounds. II. Reaction between aliphatic organic compounds of tin and tin tetrahalides.** K. A. KOZESCHKOV (Ber., 1933, 66, [B], 1661—1665; cf. A., 1929, 712).—The reactions  $3\text{SnR}_4 + \text{SnX}_4 = 4\text{SnR}_3\text{X}$ ;  $2\text{SnR}_4 + \text{SnRX}_3 = 3\text{SnR}_3\text{X}$ ;  $\text{SnR}_4 + \text{SnR}_2\text{X}_2 = 2\text{SnR}_3\text{X}$ ;  $\text{SnR}_4 + \text{SnX}_4 = 2\text{SnR}_2\text{X}_2$ ;  $\text{SnR}_4 + 2\text{SnRX}_3 = 3\text{SnR}_2\text{X}_2$ ;  $2\text{SnR}_3\text{X} + \text{SnX}_4 = 3\text{SnR}_2\text{X}_2$ , and  $\text{SnR}_3\text{X} + \text{SnRX}_3 = 2\text{SnR}_2\text{X}_2$  ( $\text{R} = \text{Me}$ ,  $\text{Et}$ , or  $\text{Pr}$ ;  $\text{X} = \text{Cl}$ ,  $\text{Br}$ ) occur readily and with good yields, so that they can be used for the prep. of  $\text{SnR}_2\text{X}_2$  and  $\text{SnR}_3\text{X}$  without useless elimination of alkyl halide. The use of sealed tubes is unnecessary. The possible reaction  $\text{SnR}_4 + 3\text{SnX}_4 = 4\text{SnRX}_3$  leads



only to production of  $\text{SnR}_2\text{X}_2$ . Aryl groups are less firmly bound than alkyl radicals to Sn and the first two alkyl groups are more readily lost than the remaining pair. *Sn Me<sub>2</sub> sulphide*, m.p. 148°, appears new. H. W.

**Nitrosites and nitrosates. III.** (SIGNA.) L. MONTI and F. BUCCI (*Gazzetta*, 1933, 63, 708—712; cf. A., 1931, 194; 1932, 943).—Methylcyclohexene nitrosate when heated in an inert gas evolves  $\text{N}_2$ , NO, and  $\text{CO}_2$ ; stilbene  $\psi$ -nitrosite gives  $\text{N}_2$  and NO, with traces only of  $\text{CO}_2$ .  $(\text{NO}_2 \cdot \text{CHPh})_2$  sublimes unchanged at 150°; when heated quickly at 240° it partly sublimes and partly decomposes, evolving mainly NO. E. W. W.

[Photo-]chlorination of benzene.—See this vol., 40.

**Catalytic oxidation of ethylbenzene in the liquid phase.** C. E. SENSEMAN and J. J. STUBBS (*Ind. Eng. Chem.*, 1933, 25, 1286—1287).—Oxidation of PhEt containing  $\text{MnO}_2$  by air at 120° yields  $\text{CHPhMe} \cdot \text{OH}$  (I) (12.8% of the unrecovered PhEt),  $\text{COPhMe}$  (II) (26%),  $\text{BzOH}$  (III) (36.5%), and  $\text{CH}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ . The yields vary considerably with variation of temp. between 110° and 130°. Traces only of (III) are formed at temp. <115°. The yield of (I) tends to an approx. const. val. after 6 hr., whilst that of (II) tends to fall. H. F. G.

**Action of fluorine on aromatic compounds under various conditions. I.** L. A. BIGELOW, J. H. PEARSON, L. B. COOK, and W. T. MILLER, jun. (*J. Amer. Chem. Soc.*, 1933, 55, 4614—4620).—When  $\text{F}_2$  (prep. by electrolysis of  $\text{KHF}_2$  described) is passed into a solution of  $\text{C}_{10}\text{H}_8$  in  $\text{CCl}_4$  at 0° [contrary to Ruff and Keim (A., 1932, 142),  $\text{Cl}_2$  is liberated from the  $\text{CCl}_4$ ], a product (I), decomp. 148—155°, containing 52.4% F is ultimately obtained. (I) is decomposed by aq.  $\text{Na}_2\text{CO}_3$  in  $\text{Et}_2\text{O}$ , is converted by fuming  $\text{HNO}_3$  into a similar product (57.4% F), is not oxidised by  $\text{CrO}_3$ - $\text{AcOH}$  at 70°, and is not reduced ( $\text{H}_2$ , Pt); oxidation ( $\text{KMnO}_4$ ) results in almost complete destruction. Similar products (% F quoted after substance used), all decomp. 90—110°, are obtained from 1- $\text{C}_{10}\text{H}_7\text{Me}$  30.7, 2- $\text{C}_{10}\text{H}_7\text{Me}$  27.2,  $\alpha$ - $\text{C}_{10}\text{H}_7\text{OMe}$  33.3,  $\beta$ - $\text{C}_{10}\text{H}_7\text{OMe}$  30.4,  $\alpha$ - $\text{C}_{10}\text{H}_7\text{OH}$  30.4,  $\beta$ - $\text{C}_{10}\text{H}_7\text{OH}$  29.8, 1- $\text{C}_{10}\text{H}_7\text{NO}_2$  34.4, 1- $\text{C}_{10}\text{H}_7\text{Br}$  35.9, and tetrahydronaphthalene 26.4; decahydronaphthalene does not give a derivative of this type. Under comparable conditions, the  $\alpha$ - gives a higher yield than the  $\beta$ -isomeride. Similar compounds, decomp. 115—150°, containing 25.6—31.2% F and 1.3—8.6% Cl are formed similarly from benzoin, deoxybenzoin,  $\text{CH}_2\text{Bz}_2$ , and  $\text{Bz}_2$ ; the Cl content increases with the power of enolisation of the original compound. PhMe and  $\text{F}_2$  in  $\text{CCl}_4$  containing a little I at 0° react more slowly;  $\text{C}_6\text{Cl}_6$ ,  $p$ - $\text{C}_6\text{H}_4\text{MeCl}$ , and fractions containing 33.5—52.7% Cl and 7.8—14% F are isolable. Explosions do not occur when the reactions are carried out in absence of any significant vapour phase. A Cu reaction vessel is described. H. B.

**Decomposition of iodobenzene dichloride. IX.** Mol. wt. and electrical conductivity of solutions. X. Discussion of salt structure proposed for iododichlorides, iodine trichloride, and phos-

phorus pentachloride. E. V. ZAPPI and J. CORTELEZZI (*Anal. Asoc. Quím. Argentina*, 1933, 21, 71—99; cf. A., 1933, 385, 942).—Stable  $\text{PhICl}_2$  is prepared in purified  $\text{CHCl}_3$ , and with precautions against formation of HCl. The mol. wt. in  $\text{PhNO}_2$  or  $\text{POCl}_3$  indicates dissociation, but vals. of  $\lambda_\infty$  in  $\text{C}_5\text{H}_5\text{N}$  or  $\text{PhNO}_2$  are low, and solutions in  $\text{POCl}_3$ ,  $\text{AsCl}_3$ , or  $\text{CHCl}_3$  are non-conducting. It is concluded that such dissociation as occurs is mol., viz.,  $\text{PhICl}_2 \rightleftharpoons \text{PhI} + \text{Cl}_2$ . The dissociation of  $\text{ICl}_3$ ,  $\text{C}_5\text{H}_5\text{NCl}$ , and  $\text{PCl}_5$  is probably analogous. Conductivity in  $\text{PhNO}_2$  or  $\text{POCl}_3$  is due to formation of complexes. Ionic formulæ, e.g.,  $[\text{PhICl}]\text{Cl}$ , are to be discarded. R. K. C.

**Styrene and metastyrene.** S. NATELSON (*Ind. Eng. Chem.*, 1933, 25, 1391—1394).—The combination of  $\text{C}_2\text{H}_4$  with  $\text{C}_6\text{H}_6$  to PhEt in presence of  $\text{AlCl}_3$  is accelerated by relatively small increases in pressure (about 6 cm.), and by initial addition of HCl with the  $\text{C}_2\text{H}_4$ , which leads to formation of an additive compound of  $\text{AlCl}_3$  with EtCl which appears to be the active catalyst. Vigorous agitation suppresses the formation of  $\text{C}_6\text{H}_4\text{Et}_2$ ,  $\text{C}_6\text{H}_3\text{Et}_3$ , etc. The best procedure for conversion into  $\text{CHPh} \cdot \text{CH}_2$  is to chlorinate until 60% of the calc. quantity for  $\text{CHClPhMe}$  is absorbed (variation in temp. is without marked effect on the final result) and heat the product with Ag-Hg. Metastyrene is conveniently formed by polymerisation with 2% PhCHO and 0.6%  $\text{O}_2$  in an autoclave at 150°/10—15 lb. per sq. in. H. A. P.

**Highly arylated derivatives of benzene. I.** W. DILTHEY, W. SCHOMMER, and O. TRÖSKEN (*Ber.*, 1933, 66, [B], 1627—1628).—Tetraphenylcyclopentadienone (I) and maleic anhydride afford endocarbonyltetraphenyl-dihydrophthalic anhydride, m.p. 223° (decomp.) [corresponding acid], which passes when heated into CO and tetraphenyl-dihydrophthalic anhydride, m.p. 243° (varying with rate of heating), converted at about 200° in presence or absence of dehydrogenating agents into tetraphenylphthalic anhydride (II), m.p. 286°. (I) affords the following compounds: from  $\text{C}_2\text{H}_2$ , 1:2:3:4-tetraphenylbenzene, m.p. 190—191°, obtained also by decarboxylation of (II); from  $\text{CPh} \cdot \text{CH}$ , pentaphenylbenzene, m.p. 246—247°; from toluene or stilbene,  $\text{C}_6\text{Ph}_6$ , m.p. 421—422° [Durand et al. (A., 1931, 207) give m.p. 266°]; from phenylpropionic acid, pentaphenylbenzoic acid, m.p. 345°; from phenylpropionitrile, pentaphenylbenzonitrile, m.p. 271—272°; from phenylpropionaldehyde, pentaphenylbenzaldehyde. H. W.

**Diphenyls. XII.** Nitration of halogenated diphenyls. XIII. Attempts to obtain  $\sigma$ -diphenylene. L. MASCARELLI and D. GATTI (*Gazzetta*, 1933, 63, 654—660, 661—665).—XII. 2-Chlorodiphenyl with  $\text{HNO}_3$ - $\text{H}_2\text{SO}_4$  yields 2-chloro-4'-nitro- (I), m.p. 73—74°, and 2-chloro-3':4'-dinitro-diphenyl (II), m.p. 158—159°, identified by conversion into  $p$ -nitro- and 3:4-dinitro-benzoic acids. (II) is reduced to 2-chloro-3':4'-diaminodiphenyl (dihydrochloride, decomp. 233—300°), from which 2:3':4'-trichlorodiphenyl, m.p. 65—66°, is prepared. Nitration of 2:2'-dichlorodiphenyl (cf. A., 1932, 729) gives a  $(\text{NO}_2)_2$ -compound, m.p. 205°. 4-Bromodiphenyl yields two isomeric  $(\text{NO}_2)_2$ -compounds, m.p. 205—206° and



147—148°. The results of Shaw and Turner with 4:4'-dibromodiphenyl (*ibid.*, 259) are confirmed. 3-Chlorodiphenyl forms a  $(NO_2)_2$ -derivative, m.p. 202—203°.

XIII. 2:2'-Dibromodiphenyl is unaffected by Na in  $Et_2O$ ; the prep. of *o*-diphenylene by Dobbie *et al.* (J.C.S., 1911, 99, 683) may have been due to catalysis by impurities. 2:2'-Diiododiphenyl is also recovered, with a halogen compound, m.p. 54°. 2:2'-Dichlorodiphenyl gives  $Ph_2$ , *o*- $C_6H_4BrI$  and Cu (+CuO) at 230—240° yield diphenylene oxide.

E. W. W.

Analogues of resolvable diphenyls. M. E. MACLEAN and R. ADAMS (J. Amer. Chem. Soc., 1933, 55, 4683—4688).—Di-2:4:6-trimethylphenyl sulphone, m.p. 202—204° (all m.p. are corr.) (lit. 195°) (from 2:4:6- $C_6H_2Me_3SO_2Cl$ , *s*- $C_6H_3Me_3$ , and  $AlCl_3$  in  $CS_2$ ), and  $HNO_3$  (d 1.42) at 100° (bath) give the 3:3'-( $NO_2$ )<sub>2</sub>-derivative, m.p. 172—174°, reduced (Zn, dil. HCl, AcOH) to di-3-amino-2:4:6-trimethylphenyl sulphone (I), m.p. 217.5—218.5° (camphor- and bromocamphor-sulphonates). The 3:3'-( $NO_2$ )<sub>2</sub>-derivative, m.p. 171.5—172.5°, of 2:4:6:2':4':6'-hexamethylbenzophenone is similarly reduced to 3:3'-diamino-2:4:6:2':4':6'-hexamethylbenzophenone (II), m.p. 163—164.5° [camphor- (+2H<sub>2</sub>O) and bromocamphor- (+2H<sub>2</sub>O)-sulphonates], which is reduced (Clemmensen) to 3:3'-diamino-2:4:6:2':4':6'-hexamethyldiphenylmethane (III), m.p. 160—160.5° (dihydrochloride, decomp. 220—290°; camphor- and bromocamphor-sulphonates). (I), (II), and (III) could not be resolved; their salts do not exhibit mutarotation at 0°. The possibility of stereoisomerism in such compounds is discussed. 3:5-Dinitro-2:4:6:2':4':6'-hexamethylbenzophenone, m.p. 199—200°, is prepared from 3:5-dinitro-2:4:6-trimethylbenzoyl chloride, *s*- $C_6H_3Me_3$ , and  $AlCl_3$ .

H. B.

Stereochemistry of diphenyls. XXXIV. Preparation and properties of 2:4:5:6:2':4':5':6'-octamethyldiphenyl- and diphenyl-3:3'-disulphonic acids. A. E. KNAUF and R. ADAMS (J. Amer. Chem. Soc., 1933, 55, 4704—4709).—2:3:4:6- $C_6HMe_4MgBr$  and anhyd.  $CuCl_2$  in  $Et_2O$  give 2:4:5:6:2':4':5':6'-octamethyldiphenyl (diisoduryl), m.p. 121—122° [3:3'- $Ac_2$ , m.p. 184°, and 3:3'-di(chloroacetyl), m.p. 183—184°, derivatives], which with  $ClSO_3H$  at 0° affords diisoduryl-3:3'-disulphonyl chloride, m.p. 159—160°. Na diisoduryl-3:3'-disulphonate and strychnine hydrochloride in  $H_2O$  give a distrychnine salt, m.p. 252—255° (decomp.),  $[\alpha]_D^{20}$  -14° in 80% MeOH, separable by EtOH into more sol., m.p. 248—251° (decomp.),  $[\alpha]_D^{20}$  -10.3° in 80% MeOH, and less sol., m.p. 252—255° (decomp.),  $[\alpha]_D^{20}$  -21.6° in 80% MeOH, salts. These are decomposed by aq.  $NH_3$  to d-,  $[\alpha]_D^{20}$  +11.2° in  $H_2O$ , and l-,  $[\alpha]_D^{20}$  -11.4° in  $H_2O$ ,  $-NH_4$  diisoduryl-3:3'-disulphonate, respectively. Diphenyl-3:3'-disulphonic acid [brucine, m.p. 268—270° (softens at 244°), and strychnine salts], prepared from benzidine-3:3'-disulphonic acid, could not be resolved.

H. B.

Di-*p*-substituted derivatives of diphenylmethane and diphenylethane. T. REICHSTEIN and R. OPPENAUER (Helv. Chim. Acta, 1933, 16, 1373—

1380; cf. Connerade, A., 1932, 1122).— $CH_2PhCl$ , polyoxymethylene, and 84%  $H_2SO_4$  at  $\geq 20^\circ$  yield 4:4'-di(chloromethyl)diphenylmethane (I), m.p. 110° (corr.), b.p. 180°/0.2 mm. (slight decomp.), the constitution of which is established by its conversion into *pp'*-ditolylmethane. (I) is transformed by KOAc in AcOH into 4:4'-di(acetoxymethyl)diphenylmethane, m.p. 50°, whence 4:4'-di(hydroxymethyl)diphenylmethane, m.p. 123° (corr.), oxidised ( $N_2O_4$  in  $CHCl_3$ ) to diphenylmethane-4:4'-dialdehyde, m.p. 85.5—86° (corr.) [dioxime, m.p. 184° (corr.), dehydrated to 4:4'-di(cyanomethyl)diphenylmethane, m.p. 167° (corr.)]. Dibenzyl (improved prep. from  $CH_2PhCl$  and Mg activated by I in  $Et_2O$ ) is converted by polyoxymethylene, anhyd.  $ZnCl_2$ , and HCl at  $\geq 50^\circ$  into 4:4'-di(chloromethyl)diphenylethane (II), m.p. 97°, b.p. 190°/0.2 mm., also obtained by aid of "dichloro-ether" (from 40%  $CH_2O$  and HCl) and transformed by Zn dust and AcOH into  $\alpha$ -*β*-di-*p*-tolylethane (III), m.p. 82°. 4:4'-Di(acetoxymethyl)-, m.p. 123° (corr.), and 4:4'-di(hydroxymethyl)-, m.p. 161° (corr.), b.p. about 195°/0.2 mm., -diphenylethane are described. Diphenylethane-4:4'-dialdehyde, has m.p. 126° (vac.). 4:4'-Di(cyanomethyl)diphenylethane, m.p. 130° (corr.), is obtained from (II) and NaCN in  $H_2O$ ; it is hydrolysed to the corresponding acid, the *Ce* salt of which when heated at 450°/vac. is transformed mainly into (III) with a little 4:4'-dimethylstilbene unaccompanied by cyclic ketone.

H. W.

Electrolytic oxidation of anthracene to anthraquinone.—See this vol., 38.

Rearrangements of polyinenes. VI. Tetradiphenylditert.-butylethynylethane. J. C. Y. TSAO and C. S. MARVEL (J. Amer. Chem. Soc., 1933, 55, 4709—4713).—Di-*p*-diphenyl ketone (I) and  $CBu^tC:MgBr$  give di-*p*-diphenylditert.-butylethynylcarb-inol (II), m.p. 172—173° (tube), 180—181° (Maquenne block), converted by conc.  $H_2SO_4$ -AcOH into *Bu^t*  $\beta$ -di-*p*-diphenyldivinyl ketone, m.p. 144—145°, and by  $PBr_3$  in  $Et_2O$  at 0° into the corresponding bromide (III), m.p. 135—136°. (III) and "mol." Ag in  $Et_2O$  give a hydrocarbon (IV),  $C_{62}H_{54}$ , m.p. (block) 166°, also formed from (II) and  $TiCl_3$  in EtOH. (III) and 40% Na-Hg in  $Et_2O$  and  $N_2$  afford Na di-*p*-diphenylditert.-butylethynylmethyl, converted by *s*- $C_2Me_4Br_2$  at 0° into (IV) and at -80° into the very unstable *s*-tetra-*p*-diphenylditert.-butylethynylethane (V). A solution of (V) in PhMe absorbs  $O_2$  readily at -80° and gives (I); when kept at 0°, (IV) is produced. (IV) is oxidised ( $O_2$ ) in boiling xylene to about 50% of (I); absorption of  $O_2$  does not occur at room temp.

H. B.

Sensitiveness to light of aromatic nitro-compounds. II. *peri*-Derivatives of 1-nitronaphthalene. R. E. STEIGER (Helv. Chim. Acta, 1933, 16, 1315—1323).—Nitronaphthalenesulphonyl chlorides are hydrolysed with unexpected ease by moist  $C_5H_5N$ . 1-Nitronaphthalene-5-sulphonyl chloride and technical  $C_5H_5N$  give pyridinium 1-nitronaphthalene-5-sulphonate, m.p. 194—195° (corr.); the prep. of the corresponding K salt is described. Pyridinium 1-nitronaphthalene-8-sulphonate, m.p. 165—167° (corr.), is obtained by heating the sulphonyl chloride



with NaOH followed by HCl and  $C_5H_5N$ . *Methylpyridinium 1-nitronaphthalene-8-sulphonate*, m.p. 162—164° (corr.), after softening, is derived from the Me ester and  $C_5H_5N$  in  $C_6H_6$ . *K 1-nitronaphthalene-8-sulphonate* is described. H. W.

**Dissociable organic oxides : second isomeride of oxytetraphenylrubene (rubrene oxide).** L. ENDERLIN (Compt. rend., 1933, 197, 691—693).—Conc. acids convert rubrene oxide (I), in  $C_6H_6$ , into an *isomeride* (II),  $C_{42}H_{28}O_2(+C_6H_6)$ , m.p. 205° (decomp.), containing one reactive H. Like (I), (II) is unstable to light and heat, but its thermal decomp. does not yield O. Unlike the isomeride previously described (A., 1930, 1173), it does not regenerate the rubene on reduction, but with Zn in boiling AcOH yields, almost quantitatively, the hydrocarbon  $C_{42}H_{26}$  (A., 1932, 261). A. C.

**Compounds related to rubenes.** C. DUFRASSE and P. CHOVIN (Compt. rend., 1933, 197, 1127—1129).—Treatment of  $CH_2Bz \cdot CO \cdot CO_2Et$  with  $PCl_5$ , decomp. of the excess of  $PCl_5$  with a ketone, and careful thermal decomp. gives a red compound, probably  $C_{20}H_{12}O_4$ , m.p. 317° (yield about 3%), the absorption spectrum of which is analogous to that of tetraphenylrubene. It does not form a dissociable oxide when irradiated in solution in presence of air. H. B.

**Carbon rings. XXVI. Poly-membered cycloalkylamines.** L. RUZICKA, M. W. GOLDBERG, and M. HURBIN (Helv. Chim. Acta, 1933, 16, 1339—1342; cf. A., 1933, 599).—*cycloOctanoneoxime*, b.p. 128—129°/14 mm., m.p. about 33°, is reduced by Na and boiling EtOH to *cyclooctylamine* (I), b.p. about 80°/10 mm. [hydrochloride, m.p. 244—245° (decomp.); *cyclooctylcarbamide*, m.p. 179—180° (corr.)]. Similarly, *cyclopentadecanoneoxime*, m.p. 75—76°, affords *cyclopentadecylamine* (II) [hydrochloride, partial decomp. about 300°; sulphate; phosphate; nitrate; tartrate; acetate, m.p. 137.5—138° after softening at 135°; citrate; *cyclopentadecylcarbamide*, m.p. 165°]. *cycloTriacontane-1:16-dione* affords (Na and boiling amyl alcohol) 1:16-*diaminocyclotriacontane* (III),

$NH_2 \cdot CH < \begin{smallmatrix} CH_2 \\ | \\ CH_2 \end{smallmatrix} \begin{smallmatrix} 14 \\ | \\ 14 \end{smallmatrix} > CH \cdot NH_2$  (dihydrochloride, decomp. about 240°; diacetate, m.p. 178—179° after marked softening). The physiological action of (I), (II), and (III) is described. H. W.

**Transpositions of anilides. II.** A. GIACALONE (Gazzetta, 1933, 63, 761—763; cf. A., 1932, 1024).— $NHPh \cdot CHO$ ,  $NH_2Ph$ , and  $NH_2Ph \cdot HCl$  with  $ZnCl_2$  at 170° yield *p*-leucaniline and a substance, m.p. 261°.  $NHPhAc$  and  $NHPhBz$  give only the acet- and benzamidines. E. W. W.

**Reductive fission of phenyl-R-anilinomethane.** I. GASPOULOS (Praktika, 1932, 7, 47—50; Chem. Zentr., 1933, ii, 43).—Reductive fission of  $NHPh \cdot CHRPh$  (from  $NPh \cdot CHPh + XMgR \rightarrow MgX \cdot NPh \cdot CHRPh \rightarrow NHPh \cdot CHRPh$ ) with Zn-Hg in hot HCl solution gives  $NH_2Ph$  and  $CH_2RPh$ .  $CH_2Ph_2$  and  $CHPh \cdot C_{10}H_7 \cdot \alpha$  were prepared. A. A. E.

**Optical activity in relation to tautomeric change. I. Conditions underlying the transport of the centre of asymmetry in tautomeric systems.** C. K. INGOLD and C. L. WILSON (J.C.S., 1933, 1493—1505).—Consideration is given to the conditions necessary for the retention or loss of enantiomeric identity during the transformation of a prototropic (or anionotropic) system

$(X \cdot \overset{*}{A}R^1R^2 \cdot B \cdot CR^3R^4 \rightleftharpoons \overset{*}{A}R^1R^2 \cdot B \cdot CR^3R^4 \cdot X)$  such that the single asymmetric centre (\*) is transported, during conversion, from the point of detachment of the mobile group (X) to the point of its reunion. For a large retention of enantiomeric identity, a mechanism inhibiting intramol. rotation during interconversion is necessary; this is illustrated by the conversion of linalyl acetate or formate into the corresponding optically active  $\alpha$ -terpinyl ester, which is a ring-chain, pentad, anionotropic change. The behaviour of a triad, prototropic system (in which there is no such mechanism) is also illustrated; propagation of asymmetry is shown, by examination of (optically active) *p*-chlorobenzhydrylidene- $\alpha$ -phenylethylamine and  $\alpha$ -phenylethylidene-*p*-chlorobenzhydrylamine, to be very small. Exploratory experiments with anionotropic and prototropic systems are first described.

Mesityl oxide and  $MgPhBr$  in  $Et_2O$  at 0° give (probably)  $\alpha$ -phenyl- $\alpha\gamma$ -dimethylcrotyl alcohol (attempted acylation results in loss of  $H_2O$ ), which when distilled affords  $\gamma$ -phenyl- $\alpha$ -methylbutadiene, b.p. 94—96°/16 mm. (ozonolysis products,  $CH_2O$ ,  $BzOH$ , and a neutral substance which gives the  $CHI_3$  reaction); this is probably identical with the  $\alpha$ -phenyl- $\alpha\gamma\gamma$ -trimethylallene of Klages (A., 1904, i, 567).  $\alpha$ -Phenylcrotyl alcohol (I), b.p. 88—90°/1 mm. (Burton, A., 1929, 554), is dehydrated by heating with  $o$ - $C_6H_4(CO)_2O$  alone or in  $C_5H_5N$  to  $\alpha$ -phenylbutadiene and its dimeride. (I) and  $(\cdot CH_2 \cdot CO)_2O$  at 100° give  $\alpha$ -phenylcrotyl succinate, m.p. 72—80° (II) (ozonolysis products,  $BzOH$  and  $MeCHO$ ); in  $C_5H_5N$ , 20% of (II) and 80% of  $\alpha$ -phenylcrotyl *H* succinate, m.p. 76—78°, result. Crotonaldehyde and  $MgMeI$  afford  $\alpha$ -ethylcrotyl alcohol, b.p. 135—142°/770 mm., which, like (I), is probably a mixture of *cis*- and *trans*-forms;  $\alpha$ -ethylcrotyl *p*-nitrobenzoate, m.p. 42—43.5°, and 3:5-dinitrobenzoate, m.p. 47—48°, are prepared from the fraction, b.p. 137.1°/764.8 mm.

$Et \beta$ -hydroxy- $\beta\beta$ -diphenyl- $\alpha$ -methylpropionate and cold conc.  $H_2SO_4$  give 3-phenyl-2-methylindenone (III), m.p. 85° [2:4-dinitrophenylhydrazones, m.p. 259° (decomp.)], reduced ( $H_2$ ,  $PtO_2$ ) to 3-phenyl-2-methylindanone (2:4-dinitrophenylhydrazones, m.p. 176—177°). (III) and  $MgPhBr$  (2.5 mols.) afford 1-hydroxy-1:3-diphenyl-2-methylindene, m.p. 92°; reduction ( $H_2$ ,  $PtO_2$ ) of this and subsequent distillation gives 1:3-diphenyl-2-methylindene, m.p. 108°. Attempts to obtain alcohols from (III) and Grignard reagents containing basic groups in  $C_5H_5N$  were unsuccessful; in one experiment using *p*- $C_6H_4Br \cdot NMe_2$ , a *p*-dimethylaminophenylpyridine, m.p. 228—229°, was obtained.

9-Fluorenylamine (IV) [prepared by reduction (Zn dust, AcOH) of fluorenoneoxime],  $COPhMe$ , and a little EtOH at 100° give an  $\alpha$ -phenylethylidene-9-fluorenylamine (V), m.p. 156.5—157.5°, fluorenylidene-9-fluorenylamine, m.p. 175° (decomp.) [also prepared



from (IV) and fluorenone (VI) at 100°], and unidentified material, m.p. 230—250°. (IV) and C<sub>6</sub>H<sub>5</sub>Me at 140—145° afford difluorenyl, m.p. 239—240°, also formed when (IV) is heated at 180°. Isomerisation of (V) with 1:33*N*-EtOH-NaOEt at 85° and subsequent hydrolysis (20% HCl) gives (IV), (VI), C<sub>6</sub>H<sub>5</sub>Me,  $\alpha$ -phenylethylamine (VII) (benzoate, m.p. 141°), and a red substance (the amount of which increases with time of heating). Fluorenylidene- $\alpha$ -phenylethylamine could not be prepared from (VII) and (VI) or 9:9-dichlorofluorene.

Benzhydrylamine (VIII) is prepared by reduction (Na, EtOH) of C<sub>6</sub>H<sub>5</sub><sub>2</sub>N·OH or by hydrolysis (N<sub>2</sub>H<sub>4</sub>, H<sub>2</sub>O method) of *phthalbenzhydrylimide*, m.p. 149—150° [from CHPh<sub>2</sub>Br and *o*-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>NK or *o*-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>NH·K<sub>2</sub>CO<sub>3</sub> in xylene]. PhCHO and (VIII) give benzylidenebenzhydrylamine (IX), m.p. 101—102° (lit. 98—99°). C<sub>6</sub>H<sub>5</sub>Cl<sub>2</sub> and CH<sub>2</sub>Ph·NH<sub>2</sub> at 100° afford benzhydrylidenebenzylamine (X), m.p. 60—61°. The mobility and equilibrium of the system (IX)  $\rightleftharpoons$  (X) are measured; at equilibrium, the respective % are 43 and 57. *Benzhydrylidenebenzhydrylamine*, m.p. 152° [from (VIII) (3.5 mols.) and C<sub>6</sub>H<sub>5</sub>Cl<sub>2</sub> (1 mol.) at 100° and from (VIII) and C<sub>6</sub>H<sub>5</sub>Me at 180°], and *benzhydrylidene- $\alpha$ -phenylethylamine*, m.p. 52° [from (VII) and C<sub>6</sub>H<sub>5</sub>Cl<sub>2</sub> at 100° or 140°], are described. *p*-Methylbenzhydrylidene- $\alpha$ -phenylethylamine, b.p. 198—201°/0.1 mm., is similarly prepared; this appears to be isomerised slowly by EtOH-NaOEt. *p*-Chlorobenzhydrylidene- $\alpha$ -phenylethylamine, b.p. 195—198°/0.05 mm. [from (VII) and *p*-chlorobenzophenone dichloride (XI), b.p. 160°/1 mm., 207—209°/22 mm., at 100°], undergoes half-conversion to equilibrium with 1:33*N*-EtOH-NaOEt at 85° in about 2 days; the equilibrium mixture contains approx. equal amounts of the two isomerides.

Hydrolysis of the azomethines obtained from (XI) and optically impure *d*- $\alpha$ -phenylethylamine (XII) with 20% HCl gives (XII) of a higher rotatory power than the original base; this is ascribed to the asymmetric influence of an optically active solvent [i.e., excess of (XII) used in the prep.]. The (XII) recovered (as hydrochloride) from the original condensation with (XI) has a corresponding lower rotatory power. The phenomenon is not observed with optically pure *d*-,  $\alpha_{D}^{17.5}$  +22.22° (*l*=50 mm.), and *l*- $\alpha$ -phenylethylamine,  $\alpha_{D}^{16.5}$  -22.92° (*l*=50 mm.) (benzoate, m.p. 163—163.5°). Equilibration of the *p*-chlorobenzhydrylidene- $\alpha$ -phenylethylamines prepared from the pure bases with 1:33*N*-EtOH-NaOEt at 85° and subsequent hydrolysis gives some (XIII) (below) of very small rotatory power.

*p*-Chlorobenzhydrylamine (XIII), b.p. 161°/0.9 mm., 188—189°/13 mm. [hydrochloride, m.p. 304—305° (decomp.); *d*- $\alpha$ -bromocamphor- $\pi$ -sulphonate, m.p. 251°; *Ac* derivative, m.p. 132°], is prepared by reduction (Zn dust, AcOH) of *p*-chlorobenzophenoneoxime and is resolved by *d*-camphor-10-sulphonic acid into the *l*-form,  $\alpha_{D}^{20}$  -2.06° (*l*=50 mm.) (*d*-bromocamphor-10-sulphonate, m.p. 218°), and by *l*-malic acid into *d*-,  $\alpha_{D}^{19}$  +0.43° (*l*=50 mm.) (*l*-malate, m.p. 171°), and *l*-forms,  $\alpha_{D}^{19}$  -0.2° (*l*=50 mm.) [*H* *l*-malate, m.p. 160° (decomp.)]. Impure  $\alpha$ -phenylethylidenep-chlorobenzhydrylamine is obtained from (XIII) and C<sub>6</sub>H<sub>5</sub>Me at 140°; considerable racemisation occurs when optically active (XIII) is used. *Benzhydrylamine- $\alpha$ -methyl* H. B.

### Rearrangement of *o*-acetamido-sulphoxides.

A. LEVI, L. A. WARREN, and S. SMILES (J.C.S., 1933, 1490—1493; cf. A., 1933, 58).—2-Nitro-2'-aminodiphenyl sulphide, m.p. 85° (prep. described), and 4-chloro-2-nitro-2'-aminodiphenyl sulphide, m.p. 130° (*Ac* derivative, m.p. 150°), similarly prepared, when acetylated and treated with H<sub>2</sub>O<sub>2</sub> in AcOH at 100° during 2 hr. afford 2-nitro-2'-acetamidodiphenyl sulphoxide (I), m.p. 160° (oxidised further to the sulphone), and 4-chloro-2-nitro-2'-acetamidodiphenyl sulphoxide (II), m.p. 179—180°, which with 10% H<sub>2</sub>SO<sub>4</sub>-EtOH at 70—80° in 2 hr. affords 4-chloro-2-nitro-2'-aminodiphenyl sulphoxide, m.p. 162°, re-acetylated to (II). (I) in EtOH at 50° with 2 mols. *N*-NaOH and excess of MeI undergoes rearrangement to 2-*o*-nitrophenylaminophenyl Me sulphoxide (III), m.p. 149—151°, but with 1 mol. *N*-NaOH gives 2-*o*-nitrophenylacetamidophenyl Me sulphoxide (IV), m.p. 160—161°, converted by NaOH into (III), thereby showing that rearrangement precedes deacetylation, so that the process must be regarded as the displacement of thionyl by ·NHAc. (III) and (IV) liberate SHMe with warm HI. (III) is oxidised by H<sub>2</sub>O<sub>2</sub> in AcOH at 100° to 2-*o*-nitrophenylaminophenyl Me sulphone, m.p. 130—131°, identical with the methylation product of the corresponding sulphinic acid. (I) readily dissolves in hot *N*-NaOH (3 mols.) to give an impure product containing sulphinic acid which, when reduced with dil. HI and SO<sub>2</sub>, affords bis-2-*o*-nitrophenylaminophenyl disulphide, m.p. 149—151°. (II) with *N*-NaOH (2 mols.) and MeI affords 2-*p*-chloro-*o*-nitrophenylaminophenyl Me sulphoxide, m.p. 152°, oxidised to 2-*p*-chloro-*o*-nitrophenylaminophenyl Me sulphone, m.p. 187°, identical with a sample prepared from the sulphinic acid. The amine from (II) was partly recovered after treatment with 2*N*-NaOH at 90—100° during 2 hr., which indicates that ·NHAc is more active in these rearrangements than ·NH<sub>2</sub>. Interaction of 2-nitrophenyl 4-hydroxy-*m*-tolyl sulphide with H<sub>2</sub>O<sub>2</sub> in AcOH at 100° during 3 hr. affords 2-nitrophenyl 4-hydroxy-*m*-tolyl sulphoxide, m.p. 206—207°, which is recovered (together with some *o*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·OH) after treatment with 2*N*-NaOH at 100° during 15 min. 2-Nitrophenyl 2-acetoxy-1-naphthyl sulphoxide, m.p. 169°, is obtained from the sulphide and H<sub>2</sub>O<sub>2</sub> in AcOH, and is hydrolysed (boiling 2*N*-NaOH) to the hydroxy-sulphoxide, m.p. 144° (decomp.), which undergoes no rearrangement with alkali, indicating that aromatic ·OH is less active in these displacements than ·NHAc or ·NH<sub>2</sub>. J. L. D.

### Reactions of diphenyl-4-carbimide [*p*-xenylcarbimide] with alcohols and amino-compounds.

I. Alcohols and phenols. II. Amines. III. Hydrazines. M. J. VAN GELDEREN (Rec. trav. chim., 1933, 52, 969—975, 976—978, 979—981).—I. 4-C<sub>6</sub>H<sub>4</sub>Ph·NCO (I) is proposed as a reagent for identifying OH-compounds; it is conveniently used in C<sub>6</sub>H<sub>6</sub>+light petroleum. The following are described (in addition to many in A., 1931, 834): *n*-hexyl, m.p. 98°; *n*-heptyl, m.p. 105°; *n*-octyl, m.p. 110°; *n*-nonyl, m.p. 115°; *n*-decyl, m.p. 111°; *n*-undecyl, m.p. 106°; *n*-dodecyl, m.p. 113°; CH<sub>2</sub>Ph·CH<sub>2</sub>, m.p. 151°; CHPh<sub>2</sub>, m.p. 197°; and *l*-menthyl, m.p. 157°, *p*-xenylcarbimides. cycloHexyl *p*-xenylcarbimide.



ate has m.p. 140° (lit. 166°). No reaction was observed with  $\text{C}_6\text{H}_5\text{OH}$ .

II. The following are described: *p*-xenylcarbamide, decomp. 210°; *N*-*p*-xenyl-*N'*-methyl-, decomp. 186°; *N'*-ethyl-, decomp. 210°; *N'*-*n*-propyl-, m.p. 195°; *N'*-*n*-amyl-, m.p. 152°; *N'*-*n*-butyl-, m.p. 153°; *N'*-*n*-heptyl-, m.p. 146°; *N'*- $\alpha$ -naphthyl-, decomp. 238°;  $\beta$ -naphthyl-, decomp. 255°; *p*-piperidyl-, m.p. 185°; *N*-*N'*-dimethyl-, m.p. 175°; *di*-ethyl-, m.p. 136°; *di*-*n*-propyl-, m.p. 124°; *phenylmethyl*-, m.p. 136°; and *diphenylcarbamide*, decomp. 174°; *N*-phenyl-, decomp. 240°; *o*-, decomp. 225°; *m*-, decomp. 212°; and *p*-tolyl-, decomp. 246°; *p*-anisyl-, decomp. 232°; and *m*-nitrophenyl-*N'*-*p*-xenylcarbamide, decomp. 227°; and *s*-di-*p*-xenylcarbamide, decomp. 312°.

III. Interaction of  $\text{NHPh}\cdot\text{NH}_2$  and its derivatives containing a primary  $\text{NH}_2$  with (I) in  $\text{C}_6\text{H}_6$ , PhMe, or light petroleum gives 1:4-disubstituted semicarbazides; the products do not interact with PhCHO. Of these 1-phenyl-, decomp. 218° (*p*-Br-, decomp. 225°, and *p*-NO<sub>2</sub>-compound, decomp. 235°); 1-*o*-, m.p. 186°; *m*-, m.p. 178°, and *p*-tolyl-, m.p. 178°; 1-phenyl-1-methyl-, m.p. 184°, and 1:1-diphenyl-4-*p*-xenyl-semicarbazide, decomp. 236°, are described. By gradual addition of (I) to  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  cooled in ice and salt 4-*p*-xenylsemicarbazide, decomp. 250—260° [*CHPh*·, decomp. 234°, *CMc*·, decomp. 225°, and 1-*Ac* derivative, decomp. 218—220° (no *CHPh*· derivative)], is formed in a yield of 70% of theory; *s*-di-*p*-xenylcarbamyldiazine is also prepared. H. A. P.

[Complex] ammines from cadmium salts and cyclic diamines. R. CERNATESCU and M. PONI (Ann. Sci. Univ. Jassy, 1933, 18, 385—403).—Vals. of the dissociation const. of the phenylenediamines, determined by electrometric titration with HCl, are in the order  $o < m < p$ , and bear no apparent relation to the composition of the complex salts with Ni, Cu, and Co. The following compounds are described [*Bo*, *Bm*, *Bp* are *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ ]: [*CdBo*] $(\text{NO}_3)_2$ ; [*CdBm*] $(\text{NO}_3)_2$ ; [*CdBp*] $(\text{NO}_3)_2$ ; [*CdBo*] $\text{Cl}_2$ ; [*CdBm*] $\text{Cl}_2$ ; [*CdBp*] $\text{Cl}_2$ ; [*CdBo*] $\text{Br}_2$ ; [*CdBm*] $\text{Br}_2$ ; [*CdBp*] $\text{Br}_2$ ; [*CdBo*] $\text{I}_2$ ; [*CdBm*] $\text{I}_2$ ; [*CdBp*] $\text{I}_2$ ; [*CdBo*] $\text{SO}_4$ ; [*CdBp*] $\text{SO}_4$ ; [*Cd*1:8- $\text{C}_{10}\text{H}_6(\text{NH}_2)_2$ ] $\text{Cl}_2$ ; [*Cd*1:8- $\text{C}_{10}\text{H}_6(\text{NH}_2)_2$ ] $\text{Br}_2$ ; [*Cd*1:8- $\text{C}_{10}\text{H}_6(\text{NH}_2)_2$ ] $\text{I}_2$ ; [*Cd*1:5- $\text{C}_{10}\text{H}_6(\text{NH}_2)_2$ ] $\text{Br}_2$ ; and [*Cd*1:5- $\text{C}_{10}\text{H}_6(\text{NH}_2)_2$ ] $\text{I}_2$ . H. A. P.

Ammines from phenylenediamines and metallic salts. R. CERNATESCU and M. PAPAFIL (Ann. Sci. Univ. Jassy, 1933, 18, 404—414; cf. preceding abstract).—The following compounds are described [*Bo*, *Bm*, *Bp* represent *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ ]: [*CuBo*] $\text{SO}_4\cdot\text{H}_2\text{O}$ ; [*CuBo*] $(\text{NO}_3)_2$ ; [*CuBp*] $\text{SO}_4\cdot\text{H}_2\text{O}$ ; [*CoBp*] $\text{Cl}_2$ ; [*CoBo*] $\text{SO}_4$ ; [*CoBm*] $\text{SO}_4$ ; [*CoBp*] $\text{SO}_4$ ; [*CoBp*] $\text{Br}_2$ ; [*NiBo*] $\text{SO}_4$ ; [*NiBp*] $\text{SO}_4$ ; and [*NiBp*] $\text{Br}_2$ . H. A. P.

*p*-Azoxydiphenyl and *p*-azodiphenyl. D. VORLANDER (Ber., 1933, 66, [B], 1666—1667).—*p*-Azoxydiphenyl is an enantiotropic cryst. liquid, the region of existence of the cryst. liquid being about 49° (260—211°), whereas *p*-azodiphenyl is a monotropic cryst. liquid or enantiotropic cryst. liquid with a region of about 1°. H. W.

Azo-dyes and intermediates. XII. Preparation of "homologous" azo-dyes with higher mol. wt. XIII. Influence of molecular size on properties of azo-dyes. P. RUGGLI and O. BRAUN (Helv. Chim. Acta, 1933, 16, 858—873, 873—884; cf. A., 1933, 59).—XII. Series of azo-dyes of regularly increasing mol. wt. are prepared by using *J*-acid (6-amino- $\alpha$ -naphthol-3-sulphonic acid) (I) both as a diazo- and coupling component, halogenated middle or end components being used in order to obtain by elementary analysis an exact measure of mol. size. Gradual addition of Br to an aq. solution of Na naphthionate (II) [1:4- $\text{C}_{10}\text{H}_6(\text{NH}_2)\cdot\text{SO}_3\text{Na}$ ] gives a ppt. of 2-bromonaphthionic acid (III); at higher temp. 2:4-dibromo- $\alpha$ -naphthylamine, m.p. 115° (*Ac* derivative, m.p. 226°), is formed. Similarly bromination of the *Ac* derivative of (II) gives 1:4- $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{NHAc}$ . Bromination of a cold aq. suspension of 1:7- $\text{C}_{10}\text{H}_6(\text{NH}_2)\cdot\text{SO}_3\text{H}$  gives the 2:4-*Br*<sub>2</sub>-derivative (IV) (*K* salt). Diazotised (IV) coupled (alkaline) with (I) gives the monoazo-dye (brownish-red), which after re-diazotisation couples with (I) to the disazo-dye, (IV)  $\rightarrow$  (I)  $\rightarrow$  (I); repetition of the process gives the trisazo-dye, (IV)  $\rightarrow$  (I)  $\rightarrow$  (I)  $\rightarrow$  (I), and finally the tetrakisazo-dye, (IV)  $\rightarrow$  (I)  $\rightarrow$  (I)  $\rightarrow$  (I)  $\rightarrow$  (I), the shades of which deepen through reddish-violet to deep violet. All are isolated as their cryst. Na salts. For comparison the monoazo-dyes, (III)  $\rightarrow$  (I), Cleve's acid [1:6- and 1:7- $\text{C}_{10}\text{H}_6(\text{NH}_2)\cdot\text{SO}_3\text{H}$ ]  $\rightarrow$  (I), and (IV)  $\rightarrow$   $\beta$ - $\text{C}_{10}\text{H}_7\cdot\text{OH}$ , are prepared. Similar series of dyes are prepared from tetrazotised 3:3'-dichloro- (V) and 2:2'-dichloro-4:4'-diaminodiphenyl (VI), and 2,4, and 6 equivs. of (I), but the tetrakisazo-dye from (VI) and the hexakisazo-dye from both (V) and (VI) were made from the dyes, (I)  $\rightarrow$  (I) and (I)  $\rightarrow$  (I)  $\rightarrow$  (I) and the tetrazotised diamines. In the former series all the dyes were violet, but increasing in blueness with increasing mol. wt., and in the latter the first was a clear brownish-red, and the remainder violet. They were isolated by salting out with  $\text{NH}_4$  carbonate or NaOAc (the former causes partial conversion into  $\text{NH}_4$  salt) and removal of the precipitant by heat or with EtOH.

XIII. Determinations of solubility, shade, rate of diffusion, dyeing properties, and behaviour towards electrolytes (and acids) are made in the above series of dyes. In all cases the effect of increasing mol. wt. is bathochromic, but is less marked in the higher members and quantitatively is dependent on constitution. Increase in mol. wt. in the series from (IV) causes decreased affinity for wool both in neutral and acid baths, but leads to a regular increase in affinity for cuprammonium silk, so that the dyes containing 3 or 4 equivs. of (I) form a characteristic test for this fabric. The dyes from (V) decrease in substantivity as the series is ascended, whereas those from (VI) behave in exactly the reverse manner. Substantivity is therefore purely a constitutional function, and is not necessarily conferred by mol. complexity. Adsorption by the fibre if the result of poor  $\text{H}_2\text{O}$ -solubility is reversible, but if due to constitutional substantivity is no longer truly reversible.

H. A. P.  
Interactions of chloro-substituted aldehydes with chloro-substituted arylhydrazines. F. D.



CHATTAWAY and A. ADAIR (J.C.S., 1933, 1488—1490).—Interaction of 2 : 5- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{NH}\cdot\text{NH}_2\cdot\text{HCl}$  (I) and butylchloral hydrate (II) in EtOH at room temp. during 0.5 hr. affords 2 : 5-dichlorobenzeneazo- $\beta$ - $\gamma$ -dichloro- $\Delta^a$ -butylene (crimson) (III), m.p. 101°, converted by HCl in dry  $\text{C}_6\text{H}_6$  into a solution (pale yellow) of butylchloral-2 : 5-dichlorophenylhydrazone which easily loses HCl to give (III). (III) in boiling  $\text{C}_6\text{H}_6$  slowly affords  $\alpha\beta$ -dichlorocrotonaldehyde-2 : 5-dichlorophenylhydrazone (IV), m.p. 90° (Ac derivative, m.p. 150°), another isomeride (V), m.p. 116° (Ac derivative, m.p. 139°), being obtained when the hydrazone is formed in cold AcOH. Either Ac derivative with  $\text{Cl}_2$  in hot  $\text{CHCl}_3$  affords  $\alpha\beta$ -tetrachlorobutaldehyde-2 : 5-dichloro-N-acetylphenylhydrazone, m.p. 154°, which indicates that (IV) and (V) are *cis-trans* forms. 2 : 4 : 5-Trichlorophenylhydrazine hydrochloride and (II) in  $\text{H}_2\text{O}$  at 40—50° afford  $\alpha\beta$ -dichlorocrotonaldehyde-2 : 4 : 5-trichlorophenylhydrazone (VI), m.p. 86° (Ac derivative, m.p. 123°), the intermediate azo-butylene being too unstable to isolate. No second form of (VI) [cf. (IV)] is obtained. When the reaction occurs in boiling EtOH,  $\beta$ -chloro- $\alpha$ -ketobutaldehyde-2 : 4 : 5-trichlorophenylhydrazone (VII), m.p. 162°, is obtained, which when boiled with (I) in EtOH affords the 2 : 4 : 5 : 2' : 5'-pentachlorodiphenylosazone of  $\alpha$ -keto- $\beta$ -methoxybutaldehyde, m.p. 212°. (VII) is cyclised by 1 mol. of hot  $\text{NaOEt}$ -EtOH to 4-hydroxy-1-(2' : 4' : 5'-trichlorophenyl)-5-methylpyrazole. (I) and  $\text{CCl}_3\cdot\text{CHO}$  in  $\text{H}_2\text{O}$  afford 2 : 5-dichlorobenzeneazo- $\beta\beta$ -dichloroethylene, m.p. 93°, unaffected by boiling EtOH in the absence of HCl. When the reaction is carried out in boiling EtOH, *Et glyoxylate*-2 : 5-dichlorophenylhydrazone (VIII), m.p. 90°, is obtained. *Et glyoxylate*-2 : 4 : 5-trichlorophenylhydrazone (IX), similarly prepared, has m.p. 102°. (VIII) or (IX) in warm  $\text{CHCl}_3$  with  $\text{Cl}_2$  affords *Et*  $\omega$ -chloroglyoxylate-2 : 4 : 5-trichlorophenylhydrazone, m.p. 115°, converted into the  $\omega$ - $\text{NH}_2$ -compound, m.p. 140°, with  $\text{NH}_3$  in EtOH- $\text{H}_2\text{O}$ . J. L. D.

**Behaviour of phenylhydrazones with condensing agents.** III. A. GIACALONE (Gazzetta, 1933, 63, 757—760; cf. A., 1932, 1026).— $\text{NHPh}\cdot\text{NH}_2\cdot\text{HCl}$  and aromatic aldehydes in hot EtOH form, through the phenylhydrazones, derivatives of  $\text{CHPh}_3$ , e.g., 4'-hydroxy-4 : 4'-bis-(*p*-hydroxybenzylidenetriphenylmethane, m.p. 192—193°. 4 : 4'-Bis(benzylidenetriphenylmethane, m.p. 200° and about 180°, are similarly obtained; *p*-tolylhydrazine does not yield such derivatives. E. W. W.

**Preparation of *p*-phenylenedihydrazine hydrochloride.** H. A. J. SCHOUTISSEN (J. Amer. Chem. Soc., 1933, 55, 4545—4546).— $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$  is tetrazotised with nitrosylsulphuric acid in  $\text{H}_3\text{PO}_4$  at  $-5^\circ$  and the solution added to  $\text{SnCl}_2$  in conc. HCl at  $-10^\circ$ ; addition of conc. HCl ppts. *p*-phenylenedihydrazine dihydrochloride (I), decomp. when heated. The free base could not be isolated; aq. solutions are unstable. (I) and aq.  $\text{CuSO}_4$  give  $p\text{-C}_6\text{H}_4\text{Cl}_2$ ;  $p\text{-C}_6\text{H}_4\text{I}_2$  is formed using I in aq. KI. (I) and aq.  $\text{KNCO}$  afford *p*-phenylenedisemicarbazide, chars when heated. H. B.

**Diazotisation of weakly basic amines.** H. A. J. SCHOUTISSEN (J. Amer. Chem. Soc., 1933, 55, 4531—

4534).—Successive treatment of  $\text{NH}_2\text{Ph}$  in conc.  $\text{H}_2\text{SO}_4$  with nitrosylsulphuric acid (I) (theoretical quantity) and  $\text{HNO}_3$  (*d* 1.51) (excess) at  $0^\circ$ , addition of the reaction mixture to aq. KOH, and coupling with  $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$  gives (mainly) *m*-nitrobenzeneazo- $\beta$ -naphthol, indicating that diazotisation with (I) occurs slowly or not at all, since the primarily formed diazonium compound will resist nitration (cf. A., 1922, i, 181).  $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  is not diazotised by (I) in conc.  $\text{H}_2\text{SO}_4$  at  $0^\circ$ ; it is recovered by addition of  $\text{PhNO}_2$  after 2 hr. The following weakly basic amines are diazotised by treatment with (I) in an excess of conc.  $\text{H}_2\text{SO}_4$  at  $0^\circ$  and subsequent addition of  $\text{H}_3\text{PO}_4$  (*d* 1.7) [which releases  $\text{HNO}_2$  from (I)], also at  $0^\circ$ : 2 : 4-dinitro-, 2 : 6-dichloro- and -dibromo-4-nitro-, 2 : 4 : 6-trinitro-, and 2 : 4 : 6-trinitro-3-methoxy- and -ethoxyanilines. 3 : 5-Dichloro-, m.p. 153°, and 3 : 5-dibromo-, m.p. 153.5°, -4-iodonitrobenzenes; 2 : 6-dichloro-, m.p.  $> 270^\circ$ , and 2 : 6-dibromo-, m.p. 221—222°, -4-nitrobenzeneazo- $\beta$ -naphthols; 2 : 4 : 6-trinitrobenzeneazo-phenol, m.p. 194°, -anisole, m.p. 148°, and -phenetole, m.p. 171—172°; 2 : 4 : 6-trinitro-3-methoxybenzeneazo-phenol, m.p. 165°, and -anisole, m.p. 118°, and 2 : 4 : 6-trinitro-3-ethoxybenzeneazophenol, m.p. 149°, are thus prepared. H. B.

**Character of the diazonium group.** Tetrazotisation of *p*-phenylenediamines. H. A. J. SCHOUTISSEN (J. Amer. Chem. Soc., 1933, 55, 4535—4541).—Diazotisation normally occurs when various *p*-phenylenediamines are treated with  $\text{HNO}_2$ ; the  $\cdot\text{N}_2\text{X}$  group so formed is strongly negative and thus inhibits salt formation of the second  $\text{NH}_2$  group. The theories of Cain (J.C.S., 1907, 91, 1049) and Morgan (*ibid.*, 1910, 97, 2561) are rejected.  $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$  is tetrazotised quantitatively when a solution of its hydrochloride in  $\text{H}_3\text{PO}_4$  (*d* 1.7) is treated with a solution of  $\text{NaNO}_2$  in conc.  $\text{H}_2\text{SO}_4$  at  $-5^\circ$ ; excess of  $\text{HNO}_2$  is removed with  $\text{CO}(\text{NH}_2)_2$ . Nitro- (I), 2 : 5- and 2 : 6- (II) -dichloro-, 2 : 6-dibromo-, and trichloro-*p*-phenylenediamine [the  $\text{Ac}_2$  derivative of which is prepared from the  $\text{Ac}_2$  derivative of (II) and  $\text{Ca}(\text{OCl})_2$  in AcOH], and *p*-phenylenediaminesulphonic are similarly tetrazotised.  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$  is similarly tetrazotised; treatment with aq. KI gives a poor yield of  $o\text{-C}_6\text{H}_4\text{I}_2$ . 2 : 5-Diiodonitrobenzene, m.p. 109—110°, and 4-iodo-2-nitrophenol, m.p. 81°, are obtained from tetrazotised (I) and aq. KI. 1 : 3-Dibromo-2 : 5-diiodobenzene has m.p. 115°. H. B.

**Character of the diazonium group.** Preparation of mixed disazo-dyes. H. A. J. SCHOUTISSEN (J. Amer. Chem. Soc., 1933, 55, 4541—4545).—Coupling of  $\text{ArN}_2\text{X}$  with  $\text{PhOMe}$  in a medium of conc.  $\text{H}_2\text{SO}_4$  (1 vol.) +  $\text{H}_3\text{PO}_4$  (*d* 1.7) (2 vols.) (diazotisation is effected in this medium) occurs rapidly only when  $\text{NO}_2$ -groups are *o*- and *p*- to  $\cdot\text{N}_2\text{X}$ ; with  $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ , rapid coupling occurs with *p*- $\text{NO}_2$ -derivatives. Tetrazotised  $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$  couples with  $\text{PhOMe}$  and  $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$  as rapidly as 2 : 4-( $\text{NO}_2$ ) $\text{C}_6\text{H}_3\cdot\text{N}_2\text{X}$ , indicating that the  $\cdot\text{N}_2\text{X}$  group has the "negative" character of two (*o*- and *p*-)  $\text{NO}_2$ -groups. Such coupling occurs with 1 mol. only of  $\text{ArOH}$  or  $\text{ArOMe}$ ; the resulting azo-diazonium compound is isolated by dilution of the reaction mixture with  $\text{H}_2\text{O}$  and can then be coupled with a second mol. of  $\text{ArOH}$  (not  $\text{ArOMe}$ ) in alkaline



solution. Disazo-dyes (m.p. given after the second component) are thus prepared from  $p$ -C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> and  $\beta$ -C<sub>10</sub>H<sub>7</sub>·OH +  $\beta$ -C<sub>10</sub>H<sub>7</sub>·OH,  $\beta$ -C<sub>10</sub>H<sub>7</sub>·OH + PhOH (m.p. 231—232°) (the same dye is formed from  $\beta$ -C<sub>10</sub>H<sub>7</sub>·OMe + PhOH; hydrolysis of the ether occurs during the first coupling),  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·OH + PhOH, PhOH + PhOH [m.p. 270° (decomp.)], PhOMe + PhOH (m.p. 206—207°), and PhOEt + PhOH (m.p. 179°). H. B.

**Velocity of diazotisation of aromatic amines.**—See this vol., 36.

[Metallic salts of] diazoamino-compounds. A. MANGINI and I. DEJUDICIBUS (Gazzetta, 1933, 63, 601—612).—These salts are either (I) yellow, non-explosive, regarded as *anti*, e.g.,  $\begin{array}{c} \text{Ph}\cdot\text{N} \\ | \\ \text{N}\cdot\text{NM}\cdot\text{Ph} \end{array}$ , or (II) deeply coloured, explosive, regarded as *syn* and co-ordinated, e.g.,  $\begin{array}{c} \text{N}\cdot\text{Ph} \\ || \\ \text{N}\cdot\text{NM}\cdot\text{Ph} \end{array}$ , or they are chromo-isomeric (I and II) in both forms. The following are prepared: from diazoaminobenzene, in Et<sub>2</sub>O with KOMe, the *K* salt (II); in MeOH with Hg(OAc)<sub>2</sub>, the Hg<sup>II</sup> salt (I and II), and similarly the Cu salt (+MeOH) (II). From *m*-nitrodiazoaminobenzene, Cu (II), Hg<sup>II</sup> (I and II), and Ag (I and II) salts. From *p*-nitrodiazoaminobenzene, K and Na (nitronic?), Ag (I and II), Hg<sup>II</sup> (I and II), and Cu (II) salts. The colours of these and analogous salts are tabulated. E. W. W.

**Reactions of diphenyl thiocarbonate with salts of heavy metals.** G. A. GARKUSCHA (J. Gen. Chem. Russ., 1933, 3, 596—602).—The reaction of Ph<sub>2</sub>thiocarbonate with salts of heavy metals was investigated to ascertain whether, by analogy with the esters of thiophosphoric acid, derivatives were obtained in which S displaced O attached to the org. radical: PS(OR)<sub>3</sub> → PO(OR)<sub>2</sub>·SR. The expected reaction, however, did not take place, but the S was removed as the metal sulphide, being replaced by O with the formation of Ph<sub>2</sub>CO<sub>3</sub>, m.p. 78°. H<sub>2</sub>O takes part in the reaction, since the perfectly dry reagents do not react. The metal salts were AgCl, AgI, HgCl<sub>2</sub>, HgI<sub>2</sub>, AgOAc,  $o$ -C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>Ag)<sub>2</sub>,  $o$ -OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>Ag, Cu(OBz)<sub>2</sub>, Ag<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, Hg(NHBz)<sub>2</sub>, and Hg(NHAc)<sub>2</sub>. M. Z.

**Esters of tetrathio-orthocarbonic acid.** H. J. BACKER and P. L. STEDEHOUDER (Rec. trav. chim., 1933, 52, 1039—1045).—C(SPh)<sub>4</sub> (I) (A., 1913, i, 396) is converted by Br in CHCl<sub>3</sub> into the unstable octa-(II), which on keeping in air gives the *tetra-bromide*, m.p. 179°; this with boiling EtOH gives Ph<sub>2</sub>S<sub>2</sub>, and with 2*N*-NaOH the *disulphoxide*, C(SPh)<sub>2</sub>(SOPh)<sub>2</sub>, m.p. 41—42°, also obtained from (II) and NaOH and by oxidation [of (I)?] with conc. HNO<sub>3</sub>. With HgCl<sub>2</sub> in COMe<sub>2</sub> (I) gives the compound C(SPh)<sub>4</sub>·6HgCl<sub>2</sub>, decomp. 200°. The “salt” of NH<sub>2</sub>·C(NH)·SPh with its (NO<sub>2</sub>)<sub>2</sub>-derivative gives (I) with PhSH and also with CMe<sub>3</sub>·SH in MeOH (instead of the expected mixed ester); with MeOH alone at its b.p. Ph<sub>2</sub>S<sub>2</sub> and a little (I) are formed. *cyclohexylisothiocarbamide hydrobromide*, m.p. 207° [from C<sub>6</sub>H<sub>11</sub>Br and CS(NH<sub>2</sub>)<sub>2</sub>], gives with aq. HNO<sub>3</sub> the “salt”, C<sub>6</sub>H<sub>11</sub>·S·C(N·NO)·N·NOH·NH<sub>2</sub>·C(NH)·S·C<sub>6</sub>H<sub>11</sub>, which explodes at 100—105°, and with *N*-NaOH at 70—75° gives *cyclohexyl tetrathio-orthocarbonate*, m.p. 169° (III).

This forms viscous oils with Br and HgCl<sub>2</sub>, and on oxidation with H<sub>2</sub>O<sub>2</sub> in AcOH gives *cyclohexylsulphonic acid* (*Ba* salt). Crystallographic data of (I) and (III) are given.  $\beta$ -Naphthyl tetrathio-orthocarbonate has m.p. 134—136° (*tetrabromide*, m.p. 120—130°). H. A. P.

**Alkyl derivatives of halogenophenols and their bactericidal action.** II. Bromophenols. E. KLARMANN, L. W. GATES, V. A. SHTERNOV, and P. H. COX, jun. (J. Amer. Chem. Soc., 1933, 55, 4657—4662).—*p*-Bromo-*o*-alkylphenols are prepared generally by rearrangement of *p*-bromophenyl esters with AlCl<sub>3</sub> and subsequent Clemmensen reduction; *o*-bromo-*p*-alkylphenols are obtained from  $p$ -C<sub>6</sub>H<sub>4</sub>Alk·OH and Br. The following are described: *p*-bromophenyl acetate, b.p. 100°/2 mm., *propionate*, b.p. 113°/3 mm., *butyrate*, b.p. 112°/2 mm., *valerate*, b.p. 134—138°/4 mm., and *hexoate*, b.p. 139—140°/2 mm.; 5-bromo-2-hydroxyphenyl Me, m.p. 57·3°, *Et*, m.p. 76°, *Pr*, b.p. 127—132°/3 mm., m.p. 53·6°, *Bu*, b.p. 127—136°/2 mm., and *n*-amyl, m.p. 60·5°, *ketones*; 2-methyl-, b.p. 118—123°/7 mm., m.p. 63·5° (from  $o$ -C<sub>6</sub>H<sub>4</sub>Me·OH and Br), 2-ethyl-, b.p. 110°/3 mm., 2-*n*-propyl-, b.p. 113—117°/3 mm., m.p. 42°, 2-*n*-butyl-, b.p. 125—127°/2 mm., m.p. 43·5°, 2-*n*-amyl-, b.p. 143—145°/3 mm., m.p. 36°, 2-sec.-amyl-, b.p. 134—138°/4 mm. (from  $p$ -C<sub>6</sub>H<sub>4</sub>Br·OH, *n*-amyl alcohol, conc. HCl, and ZnCl<sub>2</sub>), 2-*n*-hexyl-, b.p. 150—152°/4 mm., m.p. 53·6°, and 2-cyclohexyl-, b.p. 167°/5 mm., m.p. 43·8° (from *o*-cyclohexylphenol and Br), 4-bromophenols; 4-tert.-amyl-, b.p. 122°/4 mm., 4-*n*-hexyl-, b.p. 148°/7 mm., and 3:5-dimethyl-4-*n*-propyl-, m.p. 91·3°, 2-bromophenols. The above phenols are strongly germicidal towards *Eberthella typhi*, *Staph. pyogenes aureus*, *Mycobacterium tuberculosis (hominis)*, and *Monilia albicans*; they compare favourably with the Cl-analogues (A., 1933, 817). H. B.

**Chloro-derivatives of benzylphenols.** II. Mono-, di-, and tri-chloro-derivatives of *o*- and *p*-benzylphenols. R. C. HUSTON, R. L. GUILLE, P. S. CHEN, W. N. HEADLEY, G. W. WARREN, L. S. BAUR, and B. O. MATE (J. Amer. Chem. Soc., 1933, 55, 4639—4643).—Cl-derivatives of 2- and 4-hydroxydiphenylmethanes are prepared from chlorobenzyl (and benzyl) chlorides and PhOH (and chlorophenols) by the Claisen method (A., 1925, i, 656) or by condensation with AlCl<sub>3</sub>; in the former method, the yields (from the *m*-substituted CH<sub>2</sub>PhCl) are increased by addition of the corresponding Ph benzyl ether. The presence of Cl in the ring of CH<sub>2</sub>PhCl exerts a retarding influence (*m* > *o* > *p*) on the yield of hydroxydiphenylmethane and phenol ether in the Claisen reaction, and prevents ether formation with AlCl<sub>3</sub>. The following derivatives are described: (a) of 2-hydroxydiphenylmethane: 2'-, b.p. 146—151°/3 mm. (*benzoate*, b.p. 173—176°/2·5 mm.), 3-, m.p. 40·5—41·5° (*benzoate*, m.p. 69—71°; *benzenesulphonate*, m.p. 62—64°; *p*-toluenesulphonate, m.p. 81·5—83·5°), 3'-, b.p. 192—194°/14 mm. (*benzoate*, m.p. 67—67·4°), 5-, m.p. 48—49° (*benzoate*, m.p. 54—55°; *benzenesulphonate*, m.p. 68—69°; *p*-toluenesulphonate, m.p. 75—75·5°), and 4'-, m.p. 60—61°. Cl-derivatives: 5:4'-Cl<sub>2</sub>-derivative, m.p. 44·5—45·5° (*benzoate*, m.p. 84·5—85·5°); 3:5:2'-, m.p. 59·5—60·5° (*benzoate*, m.p. 81—82°),



3:5:3', m.p. 59.4—60° (benzoate, m.p. 63.5—64°; benzenesulphonate, m.p. 114.5—115°; p-toluenesulphonate, m.p. 125.4—126°), and 3:5:4', m.p. 69.5—70.5°, -Cl<sub>3</sub>-derivatives; (b) of 4-hydroxydiphenylmethane: 2', m.p. 68—69° (benzoate, m.p. 64.5—65.5°), 3-, b.p. 145—148°/3 mm. (benzoate, m.p. 71—73°; benzenesulphonate, m.p. 65—68°; p-toluenesulphonate, m.p. 51—53°), 3', b.p. 200—202°/14 mm. (benzoate, m.p. 57.5—58°), and 4', m.p. 87—87.5° (benzoate, m.p. 115—116°), -Cl-derivatives; 3:5:2', m.p. 86.5—87.5° (benzoate, m.p. 86—87°), 3:5:3', m.p. 79—80° (benzoate, m.p. 130—130.4°; p-toluenesulphonate, m.p. 104.5—105°), and 3:5:4', m.p. 61.5—62.5° (benzoate, m.p. 116—117°), -Cl<sub>3</sub>-derivatives. The following ethers are obtained in the Claisen method and are synthesised from the requisite phenol, benzyl chloride, and MeOH-NaOMe: Ph o-, b.p. 140—145°/2.5 mm., m., m.p. 36—36.4°, and p-, m.p. 85.5—86.5°, -chlorobenzyl; p-chlorophenyl p-chlorobenzyl, m.p. 80—81°; o-, b.p. 138—140°/3 mm., and p-, m.p. 70—71°, -chlorophenyl benzyl; 2:4-dichlorophenyl o-, m.p. 61—62°, m., m.p. 42.5°, and p-, m.p. 64.5—65.5°, -chlorobenzyl; 4-chloro-2-benzylphenyl benzyl, m.p. 53—54°. H. B.

**Formaldehyde condensations with phenol and its homologues.** II. G. T. MORGAN and N. J. L. MORGAN (J.S.C.I., 1933, 52, 418—420).—Acidic condensations of m-5- (I) and o-4-xenol (II) with CH<sub>2</sub>O, followed in each case by extraction with hot H<sub>2</sub>O, yielded small amounts of the six theoretically possible dihydroxytetramethyldiphenylmethanes. The isomerides from (I), of undetermined orientation, were: (III) prisms from MeOH, m.p. 274—276° (dibenzoate, m.p. 148°; Br<sub>4</sub>-derivative, m.p. 264°; another Br-derivative, m.p. 164°), (IV) needles from dil. EtOH, m.p. 169.5° (Br-derivative, m.p. 230°), (V) plates from dil. EtOH, m.p. 168° (dibenzoate, m.p. 130°). They were separated through the insolubility of (III) in cold C<sub>6</sub>H<sub>6</sub>, and the greater solubility of (IV) in light petroleum over (V). (III) was synthesised from 4-hydroxy-2:6-dimethylbenzyl alcohol and (I) under acid conditions. Distillation of the resin in vac. gave 25% of volatile material, mainly (I) together with unidentified needles, and left an insol. residue. The isomerides extracted from (II) condensations were: (VI) needle-plates from dil. EtOH, m.p. 163°, (VII) needles from dil. EtOH, m.p. 164.5—166°. Their separation depended on the lower solubility in H<sub>2</sub>O, and greater solubility in petroleum, of (VI) over (VII). The third isomeride (VIII) crystallised from a conc. C<sub>6</sub>H<sub>6</sub> solution of the resin, and gave minute matted needles from C<sub>6</sub>H<sub>6</sub>-petrol, m.p. 212—213°. (VI) and (VIII) were synthesised by acidic condensation of o-4-xenol alcohol and (II). If the constitution of the alcohol be assumed as 2-hydroxy-4:5-dimethylbenzyl alcohol, (VII) is probably 2:2'-dihydroxy-5:6:5':6'-tetramethyldiphenylmethane.

**Thiophenol.** I. Condensation reaction between thiophenols and condensed aldehyde-ammonias. G. DOUGHERTY and W. H. TAYLOR (J. Amer. Chem. Soc., 1933, 55, 4588—4593; cf. A., 1933, 499).—PhSH, p-C<sub>6</sub>H<sub>4</sub>Br·SH, p-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>·SH, p-C<sub>6</sub>H<sub>4</sub>Me·SH, and CH<sub>2</sub>Ph·SH react with hexamethylenetetramine (I) in boiling dioxan to give tri(phenyl-, decomp. on attempted distillation [hydrolysed (AcOH-

HCl) to NH<sub>3</sub>, PhSH, and CH<sub>2</sub>O], tri-(p-bromophenyl-, m.p. 135°, tri-(p-nitrophenyl-, m.p. 146°, tri-(p-tolyl-, m.p. 52°, and tri(benzyl-, m.p. 46°, -thiolmethyl)amines, respectively; 3RSH + (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub> → 2N(CH<sub>2</sub>-SR)<sub>3</sub> + 2NH<sub>3</sub>. With hydrobenzamide (II), the following reaction occurs: 2(CHPh·N)<sub>2</sub>CHPh + 3RSH → 3CHPh·N·CHPh·SR + NH<sub>3</sub>; benzylidene-α-phenylthiolbenzylamine, m.p. 79.5° [hydrolysed (AcOH-HCl) to PhSH, PhCHO, and NH<sub>3</sub>], -α-p-tolylthiolbenzylamine, m.p. 74°, and -α-benzylthiolbenzylamine, m.p. 67°, are prepared. 3:3':3''-Trinitrohydrobenzamide and PhSH similarly give m-nitrobenzylidene-m-nitro-α-phenylthiolbenzylamine, m.p. 122°; hydro-p-toluamide and hydrofurfuramide afford p-methylbenzylidene-α-phenylthiol-p-methylbenzylamine, m.p. 71°, and furfurylidene-α-phenylthiolfurfurylamine, m.p. 49°, respectively. n-Amyl mercaptan reacts slowly with (I) and (II); cryst. products have not been obtained.

H. B.

**Diastereoisomerides of 2:5-dibenzenesulphinyloquinol diacetate.** M. E. MACLEAN and R. ADAMS (J. Amer. Chem. Soc., 1933, 55, 4681—4683).—Oxidation (H<sub>2</sub>O<sub>2</sub>, AcOH) of 2:5-diphenylthiolquinol diacetate (I) gives α- (II), m.p. 207—208° (corr.; decomp.) (slight decomp. from 179°), and β- (III), m.p. 173.5—175° (corr.) to a red liquid (darkens from 166°). 2:5-dibenzenesulphinyloquinol diacetate; some monosulphoxide, m.p. 142.5—145.5° (corr.) (softens at 140°), is also formed. (II) and (III) are oxidised (H<sub>2</sub>O<sub>2</sub>, AcOH) to 2:5-dibenzenesulphonyloquinol diacetate, m.p. 270—271° (decomp.) (darkens from 220°), and reduced (Zn dust, AcOH) to (I). (II) and (III) are meso- and r-forms. H. B.

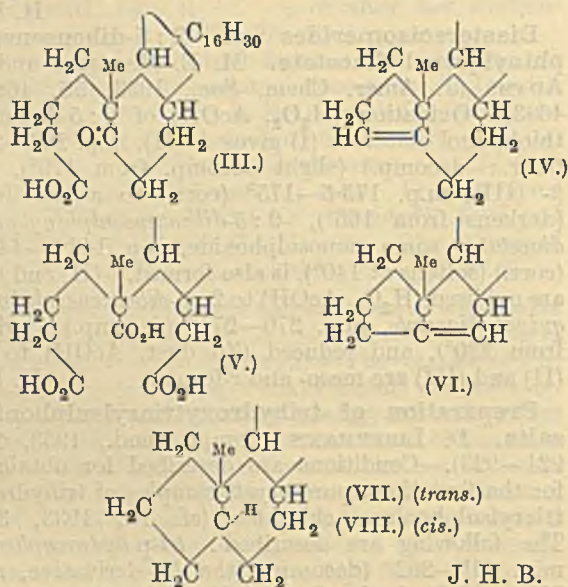
**Preparation of trihydroxytriarylsulphonium salts.** D. LIBERMANN (Compt. rend., 1933, 197, 921—923).—Conditions are described for obtaining, for the first time, pure cryst. samples of trihydroxytriarylsulphonium chlorides (cf. A., 1933, 389). The following are described: tri-p-hydroxyphenyl-, m.p. 261—262° (decomp.) [the Bz derivative, m.p. 35° (+H<sub>2</sub>O), is the Bz<sub>4</sub>, not Bz<sub>3</sub> derivative as stated in loc. cit.]; trihydroxytritolyl-, (1), from o-cresol, m.p. 190° (Bz<sub>4</sub> derivative, m.p. 39°); (2) from m-cresol, m.p. 273—274° (decomp.) (Bz<sub>4</sub> derivative, m.p. 42°); tri-α-hydroxynaphthyl-, m.p. > 350°, and two isomeric tri-β-hydroxynaphthyl-, m.p. 227° and 273—274°, -sulphonium chlorides. A. C.

**Preparation of homopiperonal.** H. ERDTMAN and R. ROBINSON (J.C.S., 1933, 1530—1531).—Safrole glycol, 3:4-CH<sub>2</sub>O<sub>2</sub>:C<sub>6</sub>H<sub>3</sub>·CH<sub>2</sub>·CH(OH)·CH<sub>2</sub>·OH, b.p. 233—236°/20 mm. (from safrole and aq. KMnO<sub>4</sub> at 0°), is oxidised [Pb(OAc)<sub>4</sub> in boiling C<sub>6</sub>H<sub>6</sub>] to homopiperonal, b.p. 123—125°/1 mm. [oxime, m.p. 121° (lit. 115°, 119—120°, 124—125°); 2:4-dinitrophenylhydrazones, m.p. 140—141°], which is converted by conc. HCl in AcOH into 6:7:3':4'-bismethylene-dioxy-2-phenylnaphthalene, m.p. 200—201° [Br<sub>3</sub>, m.p. 165—167°, and (probably) 6'-NO<sub>2</sub>, m.p. 225—228° (decomp.), -derivatives], and a compound, m.p. 206—208°. H. B.

**Cholesterol.** H. LETTRÉ (Z. physiol. Chem., 1933, 221, 73—89).—Wolff-Kishner reduction of cholestone (I) semicarbazone gives ψ-cholestene (II). CrO<sub>3</sub> oxidation of (II) affords a ketocarboxylic acid (III),



$C_{27}H_{46}O_3$  [semicarbazone, m.p.  $240^\circ$  (decomp.); oxime, m.p.  $165-166^\circ$ ]. Distillation of (III) yields a hydrocarbon (IV),  $C_{26}H_{44}$ , m.p.  $80^\circ$ ,  $[\alpha]_D^{25} +55.8^\circ$  in  $CHCl_3$ , which with  $O_3$  gives the keto-acid,  $C_{26}H_{44}O_3$ . Oxidation of (III) with Br yields a tricarboxylic acid (V),  $C_{27}H_{46}O_6$ , m.p.  $146^\circ$ , then  $202-203^\circ$ . These reactions indicate that the double linkings in (I) and (II) correspond. Distillation of (V) at  $240-260^\circ/14$  mm. gives a hydrocarbon (VI),  $C_{25}H_{42}$ , m.p.  $38-39^\circ$ ,  $[\alpha]_D^{25} -40.5^\circ$  in  $CHCl_3$ . Reduction of the pyroketone of the dicarboxylic acid from cholesterol with Zn-Hg in AcOH affords a hydrocarbon (cis) (VII),  $C_{26}H_{46}$ , m.p.  $78^\circ$ ,  $[\alpha]_D^{25} +25.1^\circ$  in  $CHCl_3$ . Wolff-Kishner reduction of the semicarbazone of the ketone  $C_{26}H_{44}O$  yields the trans-hydrocarbon (VIII),  $C_{26}H_{46}$ , m.p.  $46^\circ$ ,  $[\alpha]_D^{25} +33.2^\circ$  in  $CHCl_3$ . Hydrogenation of (IV) gives (VIII). Thus cholesterol is a derivative of trans- and coprostan of cis-decahydronaphthalene.



**isoCholesterol. II. Lanosterol.** C. DORÉE and D. C. GARRATT (J.S.C.I., 1933, 52, 355-361T; cf. A., 1933, 710).—Lanosterol (I),  $C_{30}H_{50}O_3$ , obtained from a neutral wool grease from which agnosterol (Windaus and Tschesche, A., 1930, 1179) was absent, had m.p.  $140.5-141^\circ$ ,  $[\alpha]_D^{25} +57.9^\circ$  (acetate, m.p.  $113.5^\circ$ ,  $[\alpha]_D^{25} +57.2^\circ$ ; benzoate, m.p.  $191.5^\circ$ ,  $[\alpha]_D^{25} +74.2^\circ$ ).  $CrO_3$  under restrained conditions acts on (I) giving lanostenone (II),  $C_{30}H_{48}O$ , m.p.  $116^\circ$ ,  $[\alpha]_D^{25} +71.9^\circ$  (semicarbazone, m.p.  $242^\circ$ ; phenylhydrazone, m.p.  $137^\circ$ ; 2:4-dinitrophenylhydrazone, m.p.  $207^\circ$ ), a ketone, m.p.  $89^\circ$ ,  $[\alpha]_D^{25} +54.4^\circ$  (2:4-dinitrophenylhydrazone, m.p.  $118^\circ$ ), and a ketonic acid,  $[\alpha]_D^{25} +64.2^\circ$  (2:4-dinitrophenylhydrazone, m.p.  $133^\circ$ ). Further oxidation gives  $COMe_2$  and a volatile aldehyde (traces). On reduction with Na in amyl alcohol (I) is reduced partly to  $\alpha$ -dihydrolanosterol (Windaus and Tschesche, loc. cit.); the greater portion is recovered as (?) an isomeride of (I), m.p.  $135^\circ$ ,  $[\alpha]_D^{25} +58.3^\circ$ , the acetate of which is identical with that of (I). Reduction of (I) with Na in EtOH gives lanosterol A, m.p.  $143^\circ$ ,  $[\alpha]_D^{25} +58.7^\circ$  (acetate, m.p.  $127^\circ$ ,  $[\alpha]_D^{25} +59.4^\circ$ ). With Br (I) gives a cryst. Br-derivative (III), m.p.  $177^\circ$ ,  $[\alpha]_D^{25} +50.0^\circ$ , probably a mixture of

substituted derivatives. Reduction of (III) with Zn-AcOH gives (I), and with Na in EtOH lanosterol B (IV), m.p.  $150^\circ$ ,  $[\alpha]_D^{25} +58.9^\circ$  (acetate, m.p.  $118^\circ$ ,  $[\alpha]_D^{25} +55.0^\circ$ ; benzoate, m.p.  $193^\circ$ ,  $[\alpha]_D^{25} +78.7^\circ$ ), which with  $CrO_3$  gives (II). (IV) is also formed by the action of Na in EtOH on lanosteryl acetate dibromide. (III) with  $CrO_3$  gives dibromolanostenone, m.p.  $188^\circ$ ,  $[\alpha]_D^{25} -10.5^\circ$  (2:4-dinitrophenylhydrazone, m.p.  $199^\circ$ ). A  $CHCl_3$  solution of (I) with  $O_3$  yields a mono-ozonide,  $C_{30}H_{50}O \cdot O_3$ , m.p.  $150^\circ$ , which with  $H_2O$  gives an acid,  $C_{30}H_{48}O_4$ , m.p.  $225^\circ$ ,  $[\alpha]_D^{25} +43.4^\circ$ , and a volatile aldehyde (?) of floral odour. Further attempts to isolate isocholesterol from samples of South African rubber latex gave negative results.

**Cinchol.** A. WINDAUS and M. DEPPE (Ber., 1933, 66, [B], 1689-1690).—Cinchol belongs to the sitosterol group and has the formula  $C_{29}H_{50}O$ , since it yields a m-dinitrobenzoate, m.p.  $200-202^\circ$ ,  $[\alpha]_D^{25} -10.9^\circ$  in  $CHCl_3$  (identical in m.p. and  $[\alpha]_D$  with the corresponding ester of rhamnol), and an acetate  $C_{31}H_{52}O_2$ , m.p.  $123^\circ$ ,  $[\alpha]_D^{25} -38.3^\circ$  in  $CHCl_3$ . Cinchol, m.p.  $136-137^\circ$ ,  $[\alpha]_D^{25} -33.5^\circ$  in  $CHCl_3$ , retains  $H_2O$  firmly. H. W.

**Vitamin of growth. V. Cryptoxanthine, a xanthophyll,**  $C_{40}H_{56}O$ . R. KUHN and C. GRUND-MANN (Ber., 1933, 66, [B], 1746-1750; cf. A., 1933, 431).—Physalien is accompanied in the berry and calyx of *Physalis franchetti* and *alkekengi* by cryptoxanthine (I),  $C_{40}H_{56}O$ , m.p.  $169^\circ$  (corr.; vac.; Berl) (isolation described). (I) cannot be distinguished spectroscopically from  $\beta$ -carotene (II) and zeaxanthine (III). It contains 1 OH (Zerevitinov) and gives a monoacetate, m.p.  $117-118^\circ$ . It absorbs 11  $H_2$ , thus containing 2 carbon rings. (I) is probably a hydroxy- $\beta$ -carotene in which the two halves of the mol. correspond, respectively, with (II) and (III). The intermediate position finds its expression in the behaviour towards  $CaCO_3$  and  $Al_2O_3$ , respectively. (I), (II), and (III) when oxidised with  $CrO_3$  give 4.85, 5.4, and 4.1 mols. of AcOH, respectively. (I) has  $[\alpha]_{589}^{25} \pm 6^\circ$  in  $C_6H_6$ . (I) shows pronounced vitamin-A action. H. W.

**Influence of  $p_H$  on aminated triphenylmethane dyes, and their decomposition by light.** P. C. HENRIQUEZ (Rec. trav. chim., 1933, 52, 991-1000).—The tautomerism of malachite-green (I) is followed photometrically for  $p_H$  1.0-8.0, and in ultra-violet light (II) up to  $p_H$  13, the equilibrium being displaced in the latter case to an extent proportional to the intensity of the light. The val. of the dissociation const. of the carbinol base is thus found to be  $1.29 \times 10^5$ . Exposure of aq. crystal-violet to light gives a red dye of intensity comparable with the original, and formed from it by demethylation; the presence of free  $NH_2$  is proved by diazotisation and coupling with 1:3:6- $NH_2 \cdot C_{10}H_5(SO_3H)_2$ . Under similar conditions (I) is converted into a violet dye (? Doebner's violet). Destruction of colour by light is more rapid the more basic is the solution. Exposure to (II) brings about oxidation of fuchsin by  $H_2O_2$  at room temp., the  $NH_2$  groups being unaffected. H. A. P.

**Changes in acid solutions of adrenaline.**—See A., 1933, 1256.



**Diazo-reaction of adrenaline.** G. NAKAYAMA (Japan J. Med. Sci., 1933, 2, 285—290).—When KOH is substituted for aq.  $\text{NH}_3$  in the Ehrlich diazo-reaction, adrenaline (I) gives a coloration with concns.  $> 1:25 \times 10^4$ . Pyrocatechol and 3:4-dihydroxy-adrenaline behave similarly to (I), whilst adrenalone yields a non-sp. yellowish-brown coloration. 2:4-Dihydroxyphenylalanine gives a stable orange-red and the 2:5-isomeride a transient reddish-yellow colour. F. O. H.

**Addition of hydrogen to acetylene derivatives.**  
**XXI. Synthesis of *s*-diphenyldi- $\alpha$ -naphthylbutenediol and its hydrogenation.** J. S. SALKIND and S. V. NEDZVETZKII (J. Gen. Chem. Russ., 1933, 3, 573—577).—The acetylenic glycol, *s*-diphenyldi- $\alpha$ -naphthylbutenediol, was synthesised and hydrogenated to ascertain whether stereoisomerides would be obtained. Interaction of  $\text{COPh}\cdot\text{C}_{10}\text{H}_7\cdot\alpha$  with the Grignard compound from dibromoacetylene, followed by hydrolysis in iced dil. AcOH, yields 42% of the glycol, m.p. 182—183°, but in only one stereoisomeric form. Hydrogenation (colloidal Pd), which was very slow, gave two stereoisomerides,  $\alpha$  and  $\beta$ , of  $\alpha\delta$ -diphenyl- $\alpha\delta$ -di- $\alpha$ -naphthyl- $\Delta^{\beta}$ -butene- $\alpha\delta$ -diol in the proportion 96:4. The  $\alpha$ -compound, m.p. 167°, gives a cryst. compound, m.p. 132—134°, with 1EtOH. When heated with  $\text{Ac}_2\text{O}$  and NaOAc the  $\gamma$ -oxide, 2:5-diphenyl-2:5-di- $\alpha$ -naphthyl-2:5-dihydrofuran, m.p. 221—222°, is formed, thus indicating that this glycol is the *cis*-isomeride. Further hydrogenation (very slow) with Pt-black gave  $\alpha\delta$ -diphenyl- $\alpha\delta$ -di- $\alpha$ -naphthylbutane- $\alpha\delta$ -diol (I), m.p. 220°. The  $\beta$ -isomeride, m.p. 231—232°, does not form a compound with EtOH. Further hydrogenation with Pt-black gave (I), thus proving that the  $\beta$ -isomeride is the *trans*-form. M. Z.

**Attempted resolution of substituted disulphonylmethanes and resolution of  $\alpha$ -*p*-carboxybenzenesulphonyl- $\alpha$ -*p*-tolylthiolethane.** F. B. KIPPING (J.C.S., 1933, 1506—1510).—*Et*-*p*-thiolbenzoate (I), b.p. 275° (slight decomp.), 162—164°/22 mm., from *p*- $\text{SH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  and EtOH-HCl [in some preps, *bis*-*p*-carbethoxyphenyl disulphide, m.p. 65—66°, is obtained; this is also prepared by oxidation (I-EtOH) of (I)], reacts (as Na salt) with  $\text{CH}_2\text{AcCl}$  in EtOH to give *p*-carbethoxyphenylthiolacetone, m.p. 53—54°, oxidised ( $\text{KMnO}_4$ , dil.  $\text{H}_2\text{SO}_4$ ,  $\text{CCl}_4$ ) to *p*-carbethoxybenzenesulphonylacetone (II), m.p. 88°. The Na salt of (II) and  $\text{CH}_2\text{PhI}$  in EtOH give  $\alpha$ -*p*-carbethoxybenzenesulphonyl- $\alpha$ -benzylacetone, m.p. 104°, hydrolysed (NaOH) to  $\alpha$ -*p*-carboxybenzenesulphonyl- $\beta$ -phenylethane, m.p. 232—233° (*Et* ester, m.p. 77—78°). Di-*p*-tolyl disulphoxide (III) (1 mol.), (II) (1 mol.), and NaOEt (1 mol.) in EtOH afford *p*-carbethoxybenzenesulphonyl-*p*-tolylthiolmethane (IV), m.p. 121°, and some  $\alpha$ -*p*-carbethoxybenzenesulphonyl- $\alpha$ -*p*-tolylthiolacetone, m.p. 86—87°; these are difficult to separate and are both hydrolysed (alkali) to *p*-carboxybenzenesulphonyl-*p*-tolylthiolmethane, m.p. 205—206° (Na salt), which is oxidised ( $\text{KMnO}_4$ , AcOH) to *p*-carboxybenzenesulphonyl-*p*-toluenesulphonylmethane (V), m.p. 240—242°. The *Et* ester, m.p. 147.5°, of (V), also prepared by similar oxidation of (IV), with  $\text{CH}_2\text{PhI}$  and EtOH-NaOEt gives the *Et* ester, m.p.

118—119°, of  $\alpha$ -*p*-carboxybenzenesulphonyl- $\alpha$ -*p*-toluenesulphonyl- $\beta$ -phenylethane (VI), m.p. 185—186° (*l*-menthylamine, m.p. 214—215°, nor-*d*- $\psi$ -ephedrine, m.p. 115—118°, *d*-*sec*-butylamine, m.p. 205—207°, *l*-phenylethylamine, m.p. 186°, quinine, m.p. 215°, and cinchonidine salts). (VI) could not be resolved.  $\text{Ph}_2$  disulphoxide, (V), and EtOH-NaOEt afford *p*-carboxybenzenesulphonyl-*p*-toluenesulphonylphenylthiolmethane, m.p. 212° (quinine, m.p. 209—210°, and *l*-menthylamine, m.p. 184—185°, salts), which could not be resolved. Oxidation ( $\text{KMnO}_4$ , dil.  $\text{H}_2\text{SO}_4$ ,  $\text{CCl}_4$ ) of the product from (I),  $\text{CHBrMeAc}$ , and EtOH-NaOEt gives  $\alpha$ -*p*-carbethoxybenzenesulphonylthyl *Me* ketone (VII), m.p. 66—67°, the Na salt of which with (III) affords [after hydrolysis (aq. EtOH-NaOH)] di- $\alpha$ -*p*-carboxybenzenesulphonyl- $\alpha$ -*p*-tolylthiolethane (VIII), m.p. 168—169° (*Me*, m.p. 112—113°, and *Et*, m.p. 72°, esters; acid chloride, m.p. 83—84°). This is resolved by *l*-menthylamine into *d*- (IX), m.p. 160°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +130° in  $\text{CHCl}_3$  [*l*-menthylamine salt, m.p. 199—202°; *Me*, m.p. 131—132°, and *Et* (X), m.p. 44—45°, esters; acid chloride, m.p. 101—102°], and *l*-forms, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -126° in  $\text{CHCl}_3$  (*Me* ester, m.p. 131—132°). (VIII) can also be resolved with quinine. (IX) racemises fairly rapidly in dil. aq. NaOH or  $\text{NH}_3$  at room temp. Oxidation ( $\text{H}_2\text{O}_2$ , AcOH) of (VIII) or (IX) gives the optically inactive  $\alpha$ -*p*-carboxybenzenesulphonyl- $\alpha$ -*p*-toluenesulphonylethane, m.p. 233—234° [*Et* ester, m.p. 120—121°, also prepared by similar oxidation of (X); *Me* ester, m.p. 141°; *l*-menthylamine, m.p. 187—191°, *l*-hydroxyhydrindamine, m.p. 208—210°, *l*-phenylethylamine, m.p. 214—215°, quinine, m.p. 211—212°, and cinchonidine, m.p. 177—178°, salts], which could not be resolved.

The Na salt of (VII) and *Me* *p*-toluenethiosulphonate in EtOH give (after hydrolysis)  $\alpha$ -*p*-carboxybenzenesulphonyl- $\alpha$ -methylthiolethane, m.p. 185° (decomp.) [*l*-hydroxyhydrindamine, m.p. 194° (decomp.), *l*-menthylamine, m.p. 174—177°, strychnine, m.p. 234° (decomp.), and quinine, m.p. 217°, salts], oxidised ( $\text{KMnO}_4$ , AcOH) to  $\alpha$ -*p*-carboxybenzenesulphonyl- $\alpha$ -methanesulphonylethane, m.p. 273° (*d*-hydroxyhydrindamine, m.p. 186—187°, *l*-phenylethylamine, m.p. 195—198°, *l*-menthylamine, m.p. 189—190°, quinine, m.p. 165—167°, and cinchonidine, m.p. 183—184°, salts). Neither of these acids could be resolved.

H. B.

**Relationship between the three forms of *cis*-cinnamic acid.** H. V. W. ROBINSON and T. C. JAMES (J.C.S., 1933, 1453—1454).—Rates of addition of Br to the three forms of *cis*-cinnamic acid in  $\text{CCl}_4$  with HBr as catalyst have been determined and indicate that the forms are identical in solution.

F. R. S.

**$\alpha$ -Methyl-*trans*-hexahydroindene-2-acetic acid and the reduction of  $\Delta^{\alpha}$ - and  $\Delta^{\beta}$ -unsaturated *trans*-hexahydrohydrindene (2) compounds.** R. S. THAKUR (J.C.S., 1933, 1485—1488; cf. A., 1932, 1033).—*Me* (or *Et*) 2-hydroxy- $\alpha$ -methyl-*trans*-hexahydrohydrindene-2-acetate when dehydrated (I) with  $\text{SOCl}_2$  (cf. A., 1911, i, 517) affords *Et*  $\alpha$ -methyl-*trans*-hexahydroindene-2-acetate (II), b.p. 150—151°/22 mm., unaccompanied by the  $\Delta^{3(\text{or } 8)}$ -isomeride (III), m.p. 81—83° (lit. 89—90°). (II) affords no (III)



with  $P_2O_5$ , and is hydrolysed by cold  $NaOH-H_2O$  to the acid (IV) (*amide*, m.p. 131—132°, from the undistilled acid chloride), which when oxidised by 3%  $KMnO_4$  in  $NaHCO_3$  followed by hot dil.  $HNO_3$  affords *trans*-hexahydrophthalic acid, m.p. 226—227° (lit., 222°), *trans*-hexahydrohomophthalic acid, and  $H_2C_2O_4$ . (IV) is reduced catalytically ( $H_2$ -Adams' catalyst) to  $\alpha$ -methyl-*trans*-hexahydrohydrindene-2-acetic acid (V), m.p. 104—105° (*amide*, m.p. 196°; *anilide*, m.p. 176—177°). Equilibration of (IV) with 25%  $KOH-H_2O$  in 3—4 days affords the  $\Delta^a$ -acid, m.p. 196—197°. (I) also gives some  $\alpha$ -methyl-*trans*-hexahydrohydrindylidene-2-acetic acid, which is reduced to (V), as is also the  $\Delta^a$ -acid, with Na-amyl alcohol or Na-Hg in  $Na_2CO_3-H_2O$ . The semicarbazone, m.p. 179—180°, of  $\alpha$ -methyl-*trans*-hexahydrohydrindyl-2-acetone (VI) regenerates with dil.  $H_2SO_4$  a ketone, b.p. 149°/23 mm. (*oxime*, m.p. 85—86° after shrinking). *trans*-Hexahydrohydrindylidene-2-acetic acid is reduced catalytically to *trans*-hexahydrohydrindene-2-acetic acid (VII), m.p. 102—103° after sintering (lit., 120°) [*amide*, m.p. 180° after shrinking; *anilide*, m.p. 132° (lit., 135°)], also obtained by reducing *trans*-hexahydroindene-2-acetic acid. Reduction of *trans*-hexahydrohydrindylidene-2-acetone affords *trans*-hexahydrohydrindyl-2-acetone, b.p. 130—134°/16 mm. [*semicarbazone* (VIII), m.p. 202—203° (decomp.)]. (VIII) affords a ketone, b.p. 141°/25 mm. (*oxime*, m.p. 68—70° after sintering). *trans*-Hexahydro-2-hydrindone and boiling  $HNO_3$  (d 1.42) afford *trans*-, m.p. 160—162°, in good yield and *cis* (?) hexahydrohomophthalic acid (cf. A., 1923, i, 220).

J. L. D.

**Decomposition of acetylsalicylic acid in aqueous solution.**—See A., 1933, 1250.

**Synthesis of  $\gamma$ -tolyl- $\gamma$ -butyrolactone.** H. WACHS (Riechstoffind., 1932, 7, 196—197; Chem. Zentr., 1933, i, 4056).— $\gamma$ -Tolyl- $\gamma$ -butyrolactone (I), m.p. 73°, b.p. 156°/7 mm., having a coconut-like odour, was obtained as follows:  $CO_2Et \cdot [CH_2]_2 \cdot CO_2Et \rightarrow CO_2H \cdot [CH_2]_2 \cdot CO_2Et \rightarrow COCl \cdot [CH_2]_2 \cdot CO_2Et \rightarrow C_6H_4Me \cdot CO \cdot [CH_2]_2 \cdot CO_2Et \rightarrow C_6H_4Me \cdot CO \cdot [CH_2]_2 \cdot CO_2H \rightarrow C_6H_4Me \cdot CH(OH) \cdot [CH_2]_2 \cdot CO_2Et \rightarrow$  (I). A. A. E.

**Action of potassium cyanide on meconine.** V. M. RODIONOV, S. J. KANEVSKAJA, and A. B. DAVANKOV (Ber., 1933, 66, [B], 1623—1627).—Meconine (I) is demethylated by KCN at 180—185° giving MeCN and 3-hydroxy-4-methoxyphthalide (II), m.p. 124—125°, with a small proportion of 4-hydroxy-3-methoxyphthalide (III), m.p. 87—88°. (II) and (III) are converted by  $p$ - $C_6H_4Me \cdot SO_3Me$  into (I). The *K* salt of (II) is transformed by  $p$ - $C_6H_4Me \cdot SO_3Et$  into 4-methoxy-3-ethoxyphthalide, m.p. 68—69°, oxidised by  $KMnO_4$  in alkaline solution to 4-methoxy-3-ethoxyphthalic acid (IV), m.p. 174—175° (anhydride, m.p. 105°). 4-Methoxy-3-ethoxyphthalylethylimide, m.p. 83—84°, is obtained from (IV) and 33%  $NH_4Et$ .

H. W.

**Reaction between acid chlorides and esters.** L. P. KYRIDES and M. N. DVORNIKOFF (J. Amer. Chem. Soc., 1933, 55, 4630—4632).—Slow addition of  $o$ - $C_6H_4(COCl)_2$  (I) (0.75 g.-mol.) to  $o$ - $C_6H_4(CO_2Et)_2$  (II) (0.75 g.-mol.) and  $ZnCl_2$  (0.2 g.) at 120° (and

finally up to 180°) gives  $EtCl$  (91%) and  $o$ - $C_6H_4(CO)_2O$  (nearly quant.). (I) and  $o$ - $C_6H_4(CO_2Bu)_2$  similarly afford  $BuCl$  (80%) and some butene (III);  $o$ - $C_6H_4(CO_2Bu \cdot sec.)_2$  yields *sec*-. $BuCl$  (50%) and much (III);  $(\cdot CH_2 \cdot COCl)_2$  and  $(\cdot CH_2 \cdot CO_2Bu \cdot sec.)_2$  give *sec*-. $BuCl$  (58%) and (III). Equiv. amounts of  $BzCl$  and  $EtOBz$  with 1% of  $ZnCl_2$  at 180—290° afford  $EtCl$  (77%),  $Bz_2O$  (77%), and a trace of anthraquinone.  $BzCl$  (2 mols.) and (II) (1 mol.) at 120—200° give  $EtCl$  (63%); reaction probably proceeds in two stages:  $o$ - $C_6H_4(CO_2Et)_2 + BzCl \rightarrow o$ - $C_6H_4(CO)_2O + EtCl + EtOBz$ ;  $EtOBz + BzCl \rightarrow Bz_2O + EtCl$ . (I) and  $EtOBz$  react similarly. Similar reactions with  $CH_2Ph$  esters did not give  $CH_2PhCl$ . Acyl chlorides and (II) afford large amounts of  $C_2H_4$  and  $HCl$  but no  $EtCl$ .

H. B.

**Michael condensation. I. Behaviour of ethyl phenylmalonate in the Michael condensation.** R. CONNOR (J. Amer. Chem. Soc., 1933, 55, 4597—4601).— $CHPh(CO_2Et)_2$  (I) does not undergo the Michael condensation. In  $EtOH-NaOEt$ ,  $Et_2CO_3$  and  $CH_2Ph \cdot CO_2Et$  are formed; the latter then reacts with the unsaturated ester or ketone. Thus, (I),  $Et$  crotonate, and  $EtOH-NaOEt$  give 80% of *Et*  $\alpha$ -phenyl- $\beta$ -methylglutarate, b.p. 156—158°/6 mm.;  $Et$  tiglate affords 70% of *Et*  $\alpha$ -phenyl- $\beta$ - $\gamma$ -dimethylglutarate, b.p. 157.5—159.5°/5 mm.;  $Et$  cinnamate yields 35% of  $Et$   $\alpha$ - $\beta$ -diphenylglutarate;  $Ph$  styryl ketone (II) furnishes 94% of  $Et$   $\gamma$ -benzoyl- $\alpha$ - $\beta$ -diphenylbutyrate (III).  $CNaPh(CO_2Et)_2$  and (II) in  $C_6H_6$  give 9% of *Et* 3-benzoyl-1:2:4:6-tetraphenyl- $\Delta^3$ -cyclohexene-1-carboxylate, m.p. 258°, also prepared from (II), (III), and  $NaOEt$  in  $C_6H_6$ .

H. B.

**Addition reactions of unsaturated  $\alpha$ -ketonic acids. III.** M. REIMER and H. H. KAMERLING (J. Amer. Chem. Soc., 1933, 55, 4643—4648).—*m*-Methoxybenzylidenepyruvic acid (I), m.p. 116—117° [*K* salt; *Me* ester, m.p. 57° (*Me\_2* acetal, m.p. 72°, obtained using warm  $MeOH-HCl$ ); *Et* ester], from  $m$ - $OMe \cdot C_6H_4 \cdot CHO$  and  $AcCO_2H$  (cf. A., 1931, 1155), and  $Br$  (1 mol.) in cold  $CHCl_3$  give a dibromide (not isolable), which loses  $HBr$  very readily and affords  $\beta$ -bromo-*m*-methoxybenzylidenepyruvic acid (II), m.p. 166—167° (*Me* ester, m.p. 95°). (II) is oxidised (alkaline  $H_2O_2$ ) to  $\alpha$ -bromo-*m*-methoxycinnamic acid, m.p. 122° (*Me* ester), which with  $Br$  (1 mol.) in  $CHCl_3$  gives  $\alpha$ :6-dibromo-3-methoxycinnamic acid (III), m.p. 167—169° (softens at 163°) (*Me* ester, m.p. 79°). (I) and  $Br$  (2 mols.) in  $CHCl_3$  afford  $\omega$ :6-dibromo-3-methoxystyrene, m.p. 99°. (II) is brominated to  $\beta$ :6-dibromo-3-methoxybenzylidenepyruvic acid, m.p. 137—139° (*Me* ester, m.p. 143°), oxidised ( $H_2O_2$ ) to (III). The results of Davies and Davies (A., 1928, 519) on the bromination of *m*-methoxycinnamic acid are confirmed.

H. B.

**Hydroxy-derivatives of  $\alpha$ - $\gamma$ -diphenylbutyric acid.** E. P. KOHLER and R. H. KIMBALL (J. Amer. Chem. Soc., 1933, 55, 4632—4639).—The diphenylcrotonolactone of Anschütz and Montfort (A., 1895, i, 179) is oxidised ( $KMnO_4$ ,  $MgSO_4$ , aq.  $COMe_2$ ) to  $\alpha$ - $\beta$ -dihydroxy- $\gamma$ -diphenyl- $\gamma$ -butyrolactone (I), m.p. 149° (cf. A., 1927, 262) [acetate, m.p. 138°; diacetate, m.p. 135°; dibenzoate (II), m.p. 144°; *Me\_2* ether (III), m.p. 118°; *Me* ether (IV), m.p. 143°, and *Me* ether, m.p. 77°

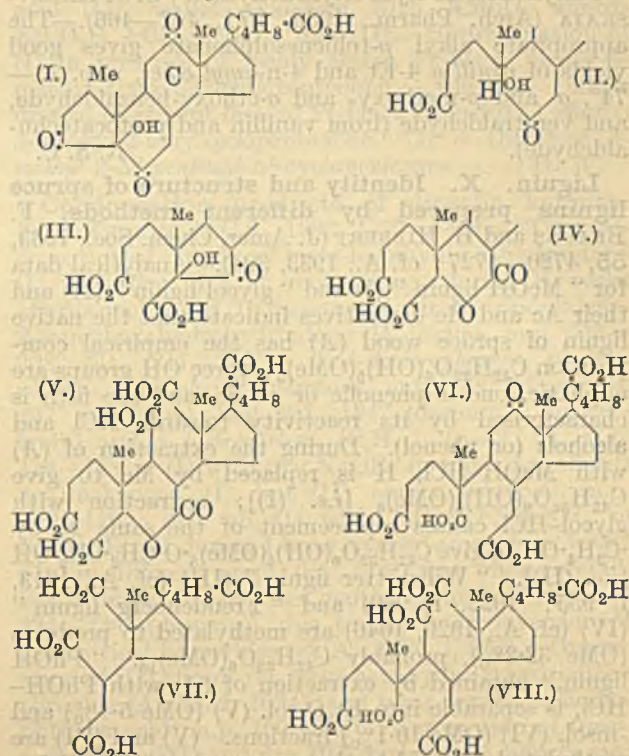


and 112° (dimorphous)].  $\alpha\beta\gamma$ -Trihydroxy- $\alpha\gamma$ -diphenylbutyric acid (V), m.p. 151° (with loss of H<sub>2</sub>O) {Na(+EtOH) and Ag salts; Me ester, decomp. 125° (softens at 115°) [ $\alpha\beta$ -dibenzoate, m.p. 178°; also prepared from (II) and MeOH-HCl;  $\alpha\beta$ -dibenzoate- $\gamma$ -acetate, m.p. 157°;  $\alpha\beta\gamma$ -triacetate, m.p. 153°]}, is obtained from (I) by the usual procedure. (I) and MeOH-HCl give Me  $\gamma$ -chloro- $\alpha\beta$ -dihydroxy- $\alpha\gamma$ -diphenylbutyrate, m.p. 124°. (I) could not be reduced with Na-Hg; with red P, HI (45%), and AcOH,  $\beta$ -benzoyl- $\alpha$ -phenylpropionic acid (VI) and some  $\alpha\gamma$ -diphenyl- $\gamma$ -butyrolactone result. Similar reduction of (II) gives  $\alpha\gamma$ -diphenylbutyric acid, m.p. 75°, also obtained by Clemmensen reduction of (VI). (III) is hydrolysed (EtOH-KOH) to  $\gamma$ -hydroxy- $\alpha\beta$ -dimethoxy- $\alpha\beta$ -diphenylbutyric acid (VII), m.p. 129° (decomp.) [K salt (+1.5H<sub>2</sub>O)], whilst methylation (Me<sub>2</sub>SO<sub>4</sub>, aq. NaOH) of (V) gives  $\alpha\beta$ -dihydroxy- $\gamma$ -methoxy-, m.p. 201°, a hydroxydimethoxy-, m.p. 148—149°, - $\alpha\gamma$ -diphenylbutyric acid, (III), and (IV). (VII) is readily convertible (by crystallisation) into (III). H. B.

**Cholatrienic acid. II. Photochemical change of cholatrienic acid and of choladienic acid.** Z. URAKI (Z. physiol. Chem., 1933, 221, 40—44; cf. A., 1932, 615).—Ultra-violet irradiation of  $\alpha$ -cholatrienic acid I, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -22.63° (which is a mixture of  $\alpha$ -cholatrienic acids III and IV), gives amorphous cholatrienic acid VI, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +2.4°, which, like acid III, affords cholanolic acid on hydrogenation (PtO<sub>2</sub>).  $\beta$ -Choladienic acid is unchanged on irradiation, indicating that the ultra-violet rays affect the  $\beta$ -ring of the acid I, changing the position of the double linking. J. H. B.

**Constitution of bile acids. LIII. Degradation of bromopyrodoxybilianic acid.** E. DANE and J. KLEE (Z. physiol. Chem., 1933, 221, 55—66; cf. A., 1932, 274).—Oxidation of pyrodoxybilianic acid with KMnO<sub>4</sub> gives a hydroxytriketocarboxylic acid (I), C<sub>23</sub>H<sub>32</sub>O<sub>6</sub>, which on hydrolysis affords a hydroxydiketodicarboxylic acid (II). Oxidation of (II) with fuming HNO<sub>3</sub> with heating gives biloidanic acid. With fuming HNO<sub>3</sub> in the cold, (II) yields a (?) nitrohydroxydiketodicarboxylic acid nitrate, decomp. 202°. KMnO<sub>4</sub> in AcOH oxidises (II) to the hydroxydiketotricarboxylic acid (III), C<sub>23</sub>H<sub>32</sub>O<sub>9</sub>, m.p. 227—228° (decomp.), already described, with probable formation of a 1 : 5-ketoaldehyde as intermediate product. (III) is probably a  $\beta$ -keto-acid. Oxidation of (II) with alkaline KMnO<sub>4</sub> or hydrolysis of (III) affords a ketolactonetetracarboxylic acid (IV), C<sub>23</sub>H<sub>32</sub>O<sub>9</sub>, m.p. 206°, (+H<sub>2</sub>O) sinters 150—160°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +51.3° in EtOH (Me<sub>2</sub> ester, m.p. 138—140°), and an isomeride, m.p. 243° (decomp.). With fuming HNO<sub>3</sub>, (IV) yields a  $\beta$ -lactonepentacarboxylic acid (V), C<sub>23</sub>H<sub>32</sub>O<sub>12</sub>·H<sub>2</sub>O, m.p. 245—250° (decomp.), [ $\alpha$ ]<sub>D</sub><sup>20</sup> +40.8° in EtOH (Me<sub>5</sub> ester, m.p. 165°). The acid (V), now called the  $\beta$ -form, is not identical with the  $\alpha$ -form previously described (A., 1932, 615), but is converted into it by conc. HCl. Oxidation of (I) with CrO<sub>3</sub> gives a ketotetracarboxylic acid (VI), C<sub>23</sub>H<sub>34</sub>O<sub>9</sub>, m.p. 160—163°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +71.8° in EtOH, and further oxidation with HNO<sub>3</sub> a tetracarboxylic acid (VII), C<sub>16</sub>H<sub>24</sub>O<sub>8</sub>, m.p. 218—220°, already obtained by oxidation of the diketodicarboxylic acid (Wieland and Schlichting,

A., 1924, i, 857). Oxidation of (I) with CrO<sub>3</sub> opens ring C, affording a  $\beta$ -solanellic acid (VIII), m.p. 217—218°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -11.4° in EtOH, which is converted by conc. H<sub>2</sub>SO<sub>4</sub> at 100° into  $\alpha$ -solanellic acid. The solanellic acids must differ in the arrangement of the substituents at C<sub>9</sub>.



J. H. B.

**Autoxidation of aldehydes.**—See A., 1933, 1249.

**Catalytic oxidations. II. Benzaldehyde. III. Pyruvic acid.**—See this vol., 37.

**Chloroimines. IV. Reactions of N-chloroaldehydes with bases.** C. R. HAUSER and E. MOORE (J. Amer. Chem. Soc., 1933, 55, 4526—4530).—The relative ease of removal of HCl from C<sub>6</sub>H<sub>4</sub>R·CH·NCl (R = *o*- and *m*-NO<sub>2</sub>, *p*-Cl, and *p*-OMe) with NaOH (2 mols.) in 95.6% EtOH at 0° or isoamylamine (I) (2 mols.) in C<sub>6</sub>H<sub>6</sub> at 30°, is in the same order as the ionisation constants of C<sub>6</sub>H<sub>4</sub>R·OH and C<sub>6</sub>H<sub>4</sub>R·CO<sub>2</sub>H and in the inverse order to those of C<sub>6</sub>H<sub>4</sub>R·NH<sub>2</sub>. (*p*-C<sub>6</sub>H<sub>4</sub>Cl)<sub>2</sub>C·NCl is decomposed only to a slight extent under the same conditions. The relative rates of reaction of *m*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CH·NCl with (I), piperidine, CH<sub>2</sub>Ph·NH<sub>2</sub>, NH<sub>2</sub>Ac, and NPh<sub>3</sub> in C<sub>6</sub>H<sub>6</sub> at 30° are in the same order as the ionisation constants of the bases. The first stage of the reaction is considered to be the withdrawal of a proton\* from H; this is followed by removal of Cl-. H. B.

**Reactions of aldoxime derivatives with bases.**

**I. Reactions of acetyl- $\beta$ -aldoximes with alkali.** C. R. HAUSER and C. T. SULLIVAN (J. Amer. Chem. Soc., 1933, 55, 4611—4613).—Acetyl- $\beta$ -*p*-methoxy-, -*m*-nitro-, -*p*-chloro-, and -3 : 4-methylenedioxy-benzaldoximes, prepared by a modification of Brady and McHugh's method (A., 1926, 69), are converted into



mixtures of the corresponding benzonitrile (I) and  $\beta$ -oxime (II) by aq. or EtOH-NaOH at 0° [(II) predominates] and 30° [(I) predominates]. The first two Ac derivatives and aq. Na<sub>2</sub>CO<sub>3</sub> at 0° or 30° give entirely (I). H. B.

**Alkylation of hydroxyaldehydes.** S. J. KANEVSKAJA (Arch. Pharm., 1933, 271, 462—466).—The appropriate alkyl *p*-toluenesulphonate gives good yields of *vanillin* 4-Et and 4-*n*-amyl ether, m.p. 73—74°, *o*- and *p*-methoxy- and *o*-ethoxy-benzaldehyde, and veratraldehyde (from *vanillin* and protocatechu-aldehyde). R. S. C.

**Lignin. X. Identity and structure of spruce lignins prepared by different methods.** F. BRAUNS and H. HIBBERT (J. Amer. Chem. Soc., 1933, 55, 4720—4727; cf. A., 1933, 394).—Analytical data for "MeOH lignin" (I) and "glycol lignin" (II) and their Ac and Me derivatives indicate that the native lignin of spruce wood (A) has the empirical composition C<sub>42</sub>H<sub>32</sub>O<sub>6</sub>(OH)<sub>5</sub>(OMe)<sub>5</sub>; three OH groups are aliphatic, one is phenolic or enolic, and the fifth is characterised by its reactivity towards HCl and alcohols (or phenol). During the extraction of (A) with MeOH-HCl, H is replaced by Me to give C<sub>42</sub>H<sub>22</sub>O<sub>6</sub>(OH)<sub>4</sub>(OMe)<sub>6</sub> [i.e. (I)]; extraction with glycol-HCl causes replacement of the same H by  $\cdot\text{C}_2\text{H}_4\cdot\text{OH}$  to give C<sub>42</sub>H<sub>32</sub>O<sub>6</sub>(OH)<sub>4</sub>(OMe)<sub>5</sub> $\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$  [i.e. (II)]. "Willstätter lignin" (III) (cf. A., 1913, i, 955; 1922, i, 989) and "Freudenberg lignin" (IV) (cf. A., 1929, 1046) are methylated to products (OMe 32.2%), probably C<sub>42</sub>H<sub>32</sub>O<sub>6</sub>(OMe)<sub>10</sub>. "PhOH lignin," obtained by extraction of (A) with PhOH-HCl, is separable into Et<sub>2</sub>O-sol. (V) (OMe 5.4%) and -insol. (VI) (OMe 10.1%) fractions. (V) and (VI) are methylated (CH<sub>2</sub>N<sub>2</sub>) to the same product (OMe 21.5—21.6%), indicating that they contain the same fundamental unit; further methylation (Me<sub>2</sub>SO<sub>4</sub>, NaOH) gives a product with OMe 28.2%. Acetylation of (VI) gives a compound (OMe:Ac=1:2), whilst methylation (CH<sub>2</sub>N<sub>2</sub>) and subsequent acetylation affords a compound (OMe:Ac=3:1); the change in the ratio OMe:Ac indicates that (VI) contains new free phenolic OH groups (arising from condensation of the lignin with PhOH). Condensation of (II) and its Me derivatives (CH<sub>2</sub>N<sub>2</sub>; Me<sub>2</sub>SO<sub>4</sub>) with PhOH followed by (a) methylation (CH<sub>2</sub>N<sub>2</sub>), (b) complete methylation, and (c) benzylation, and determinations of OMe and the ratios OMe:Bz indicate that three phenolic OH groups are introduced. "PhOH lignin" is C<sub>42</sub>H<sub>32</sub>O<sub>6</sub>(OH)<sub>4</sub>(OPh)(OMe)<sub>5</sub>(C<sub>6</sub>H<sub>4</sub>OH)<sub>3</sub>; this is obtained by condensation of PhOH with (IV) and (III) (in the last case, 8—10% of an almost OMe-free insol. residue is produced also). H. B.

**Reactions of substituted cyclohexanones.** R. E. MAYER (Helv. Chim. Acta, 1933, 16, 1291—1295).—Chlorination of *cyclohexanol* (I) suspended in H<sub>2</sub>O containing CaCO<sub>3</sub> at 20—25° yields small amounts of unchanged (I), *cyclohexanone*, 2-chloro*cyclohexanone* (II), b.p. 79°/7 mm., m.p. 22—23° (yield 56.6%), and more highly chlorinated products containing 2:6-dichloro*cyclohexanone*, b.p. 106°/7 mm., m.p. 72—73°. (II) is converted by excess of KCN in H<sub>2</sub>O into the readily oxidised 2-cyano*cyclohexanone* (III), b.p. 140—141°/15 mm., smoothly transformed by

10% NaOH into pimelic acid (best obtained from the crude nitrile). (III) is oxidised when exposed to air to adipic acid, the intermediate formation of  $\epsilon$ -hydroxy- $\epsilon$ -cyano-*n*-hexoic acid and  $\delta$ -aldehydo-*n*-valeric acid being postulated. H. W.

**Synthesis of some cyclic  $\Delta^{\alpha}$ -unsaturated ketones.** R. S. THAKUR (J.C.S., 1933, 1481—1485).— $\alpha$ -cyclohexylidenepropionyl chloride (I) [acid, m.p. 81—82° (lit., 79°)] when distilled and hydrolysed by 10% Na<sub>2</sub>CO<sub>3</sub>-H<sub>2</sub>O affords 45% of  $\Delta^{\beta}$ -acid, whereas *cyclohexylideneacetyl* chloride similarly treated exhibits no tautomerism (cf. A., 1932, 1033, 1111). Interaction of (I) (undistilled) and ZnMeI according to the Blaise-Maire reaction and treatment of the product with NH<sub>2</sub>·CO·NH·NH<sub>2</sub> affords, in different experiments, a semicarbazone of variable m.p. which depresses the m.p. of the  $\Delta^{\beta}$ -semicarbazone (II). Crystallisation gives  $\alpha$ -methylcyclohexylideneacetone-semicarbazone (III), m.p. 192—193° (rapid heating), different from (II), and a semicarbazone (IV), m.p. 155—160°, derived from the  $\Delta^{\alpha}$ -ketone. (III) with H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> affords  $\alpha$ -methylcyclohexylideneacetone (V), b.p. 97—98°/14 mm. (100%  $\Delta^{\alpha}$ -ketone), which is oxidised by KMnO<sub>4</sub> to *cyclohexanone*, whereas (IV) with H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> affords a ketone (VI), b.p. 100—101°/16—17 mm. (92.5%  $\Delta^{\alpha}$ -ketone). (VI) with NH<sub>2</sub>·CO·NH·NH<sub>2</sub> yields (III) and (IV). Catalytic reduction of (V) with Adams' catalyst followed by NH<sub>2</sub>·CO·NH·NH<sub>2</sub> gives a semicarbazone, m.p. 112—125°, from which  $\alpha$ -methylcyclohexenylacetone (100%  $\Delta^{\beta}$ -ketone) (cf. A., 1926, 952) is regenerated. Equilibration of (V) (cf. A., 1929, 927) leads finally to a ketone (10%  $\Delta^{\alpha}$ -isomeride) which gives a semicarbazone, m.p. 170°, identical with the  $\Delta^{\beta}$ -semicarbazone.  $\alpha$ -cyclohexylidenepropionic acid when catalytically reduced (Pt-H<sub>2</sub>) affords  $\alpha$ -cyclohexylpropionic acid (VII), m.p. 62° (amide, m.p. 156—157°; anilide, m.p. 135—136°; *p*-toluidide, m.p. 155—156°), whilst  $\alpha$ -cyclohexenylpropionic acid is only partly reduced under these conditions. Catalytic hydrogenation of  $\alpha$ -methyl- $\alpha$ -cyclohexenylacetone followed by the action of NH<sub>2</sub>·CO·NH·NH<sub>2</sub> on the product gives the semicarbazone (VIII), m.p. 84—106°, of  $\alpha$ -methyl- $\alpha$ -cyclohexylacetone (IX) together with  $\gamma$ -cyclohexylsec-butyl alcohol, b.p. 109—110°/15 mm., which is oxidised by CrO<sub>3</sub> to a ketone convertible into (VIII).  $\alpha$ -cyclohexylpropionyl chloride and ZnMeI according to the Blaise-Maire reaction give a ketone which affords (VIII), fractional crystallisation of which gives semicarbazones, m.p. 153—157° (X) and 130—131° (XI). (XI) is hydrolysed to (IX), b.p. 89—90°/13 mm., which gives a semicarbazone from which (X), the  $\Delta^{\beta}$ -semicarbazone, and impure (XI) are isolable. 2-Methylcyclohexylideneacetyl chloride and MgMeI in Et<sub>2</sub>O afford a crude product (XII) which gives 2-methylcyclohexylideneacetone-semicarbazone (XIII), m.p. 194° ( $\Delta^{\alpha}$ -isomeride) [the  $\Delta^{\beta}$ -isomeride is obtained from redistilled (XII)], which regenerates the pure  $\Delta^{\alpha}$ -ketone, b.p. 99—101°/12 mm. (cf. A., 1930, 1582). The regenerated  $\Delta^{\beta}$ -ketone has b.p. 102°/15 mm. Equilibration of the  $\Delta^{\alpha}$ - or  $\Delta^{\beta}$ -ketone affords a product (90%  $\Delta^{\beta}$ -) from which only the  $\Delta^{\beta}$ -semicarbazone can be isolated. Prepared similarly to (XII),  $\alpha$ -methyl-trans-decahydronaphthylidene-2-



acetone affords a semicarbazone, m.p. 214—215° (decomp.) (lit., 209—210°), which regenerates a mixture of  $\Delta^{\alpha}$ - and  $\Delta^{\beta}$ -ketones. Prolonged action of 2*N*-NaOEt on this mixture affords the  $\Delta^{\beta}$ -semicarbazone, m.p. 195—196°. An  $\alpha$ -Me group considerably retards the mobility of the cyclohexane (as does a 2-Me group) and *trans*- $\beta$ -decalin compounds.

J. L. D.

**Octahydrophenanthrene derivatives.** J. D. FULTON and R. ROBINSON (J.C.S., 1933, 1463—1466).—Interaction of cyclohexene (I) with  $\text{CH}_2\text{Ph}\cdot\text{COCl}$  in  $\text{CS}_2$  containing  $\text{SnCl}_4$  at  $-15^\circ$  during 2.5 hr. followed by  $\text{NPhEt}_2$  at  $180^\circ$  during 2 hr. affords  $\Delta^1$ -cyclohexenyl benzyl ketone, m.p. 44.5° (semicarbazone, m.p. 171—172°). Ethyl- $\Delta^1$ -cyclohexene gives no satisfactory product. cyclohexanone and  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{MgBr}$  (II) in  $\text{Et}_2\text{O}$  at  $-15^\circ$  afford 1- $\beta$ -phenylethyl-cyclohexanol (III), m.p. 56.5° and -cyclohexene, b.p. 112—113°/2 mm. (nitroschloride, m.p. 118—119°; nitrolpiperide, m.p. 117—118°), also obtained from (III) with  $\text{ZnCl}_2$ ,  $\text{Ac}_2\text{O}$ , or  $\text{PhNCO}$ . (I) reacts with (II) in  $\text{Et}_2\text{O}$  to give 2- $\beta$ -phenylethylcyclohexanol (IV), m.p. 17—18° (p-nitrobenzoate, m.p. 73.5°), a homogeneous product, apparently different from that of Bardhan and Sengupta (A., 1932, 1241). (IV) is oxidised by  $\text{CrO}_3$  in 0.5 hr. at  $55^\circ$  to 2- $\beta$ -phenylethylcyclohexanone (V), b.p. 135—136°/2 mm. {oxime, m.p. 74—75°; semicarbazone, m.p. 157° [lit., 179—180° (decomp.)]}. Dehydration of (IV) with  $\text{ZnCl}_2$  affords mainly an unsaturated compound (cf. Bardhan and Sengupta), but interaction of (IV) with  $\text{SOCl}_2$  in cold  $\text{C}_5\text{H}_5\text{N}$  during 1 hr. affords a sulphonyl chloride which decomposes when heated to give 2-chloro- $\beta$ -phenylethylcyclohexane, b.p. 130—134°/5 mm. (admixed with a hydrocarbon), cyclised by  $\text{AlCl}_3$  in warm light petroleum to 1:2:3:4:9:10:11:12-octahydrophenanthrene (VI), b.p. 135—137°/6.5 mm., which crystallises when cooled to  $-12^\circ$  and therefore differs stereochemically from Bardhan and Sengupta's product. (VI) is dehydrogenated by S to give phenanthrene (VII). (V) with  $\text{MgEtBr}$  in boiling  $\text{Et}_2\text{O}$  during 1 hr. affords 2- $\beta$ -phenylethyl-1-ethylcyclohexanol, b.p. 147—148°/3 mm. (easily dehydrated by  $\text{ZnCl}_2$  to 2- $\beta$ -phenylethyl-1-ethyl- $\Delta^1$ -cyclohexene, b.p. 113—114°), converted by  $\text{SOCl}_2$  into the chloride, which is cyclised ( $\text{AlCl}_3$ ) to a saturated hydrocarbon,  $\text{C}_{16}\text{H}_{22}$ , 12-ethyl-1:2:3:4:9:10:11:12-octahydrophenanthrene (?), b.p. 113—116°/<1 mm., dehydrogenated by S at  $170$ — $180^\circ$  in 40 hr. to (VII) and anthracene. Et 3:4-dimethoxycinnamate, m.p. 56°, gives with Br in artificial light, a dibromide, m.p. 107—108°, which when boiled with  $\text{EtOH}\cdot\text{KOH}$  (3 mols.) for 7 hr. affords 3:4-dimethoxyphenylpropionic acid, m.p. 154°, decarboxylated by  $\text{NPhEt}_2$  at  $150$ — $160^\circ$  to 3:4-dimethoxyphenylacetylene, m.p. 73—74° (VIII). (VIII) gives with  $\text{MgEtBr}$  a compound which does not react with (I). When similarly treated,  $\text{CPh}\cdot\text{CH}$  affords a hydrocarbon, m.p. 48—49°. Et homoveratrate, b.p. 159—160°/4 mm. (amide, m.p. 139°), is reduced with Na by the Bouveault reaction to give  $\beta$ -3:4-dimethoxyphenylethyl alcohol, m.p. 47—48° (phenylurethane, m.p. 99°; p-nitrobenzoate, m.p. 85° after softening). 3:4-Dimethoxymandelonitrile, m.p. 104—105°, is converted into the hydrochloride, m.p. 139—140°, of the related iminoethyl ester.

J. L. D.

**Jasmine perfumes. I. Constitution of jasmine.** L. RUZICKA and M. PFEIFFER (Helv. Chim. Acta, 1933, 16, 1208—1214).—Jasmine (I), regenerated from the semicarbazone, m.p. 209.5—210°, has b.p. 134—135°/12 mm.,  $\alpha_D +0^\circ$ . Ozonisation of (I) in  $\text{CCl}_4$  leads to  $\text{EtCHO}$ ,  $\text{CH}_2(\text{CO}_2\text{H})_2$ , and lævulic acid (II), whilst oxidation with  $\text{KMnO}_4$  affords  $\text{EtCO}_2\text{H}$ ,  $(\cdot\text{CH}_2\text{CO}_2\text{H})_2$ , and (II). Hydrogenation of (I) in presence of feebly active Pt-black yields 3-methyl-2-amyl- $\Delta^2$ -cyclopentenone, whereas more drastic treatment (active Pt-black from  $\text{PtO}_2$ ) affords 3-methyl-2-amylcyclopentanone. (I) is therefore 3-methyl-2- $\Delta^{\beta}$ -pentenyl- $\Delta^2$ -cyclopentenone. H. W.

**Condensation products of dicyclic ketones.** R. S. THAKUR (J.C.S., 1933, 1477—1481).—The condensation of 2 mols. of *trans*-hexahydro-2-hydrindone (I) with dry HCl at room temp. during 8 weeks affords unchanged (I), *trans*-hexahydrohydrindylidene-2-*trans*-hexahydrohydrindone (II) [oxime, m.p. 206—208° (lit., 211—212°); 2:4-dinitrophenyl-, p-nitrophenyl-, and phenyl-hydrazone, m.p. 248° (decomp.), 267° (decomp.), and 193—194° (decomp.), respectively] and a hydrocarbon,  $(\text{C}_9\text{H}_{12})_n$  [ $n=3$  (?)], m.p. 116—118°. (I) with dry NaOEt in a few hr. affords no unchanged (I), but (II) and a substance, m.p. 109—110°. (II) affords with  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$  in boiling EtOH during 1 hr. a semicarbazone, m.p. 180—210° in different preps. (lit., 140°), but when crystallised from EtOH or when gently warmed, it has m.p. 234—235° (decomp.), due to the interconversion of geometrical isomerides (cf. A., 1924, i, 652). Ozonisation of (II) affords (I), *trans*-hexahydro-2-hydrindone peroxide (A., 1932, 1034), and *trans*-hexahydrohomophthalic acid, m.p. 160—161°. Interaction of *trans*- $\beta$ -decalone (III) and dry HCl during 1 hr. affords two isomeric Cl-compounds,  $\text{C}_{20}\text{H}_{31}\text{OCl}$ , m.p. 130—131° (IV) and 118—119° (V), respectively. The crude mixture of (IV) and (V) with boiling  $\text{C}_5\text{H}_5\text{N}$  during 1.5 hr. [or by distillation of (IV)] affords a ketone,  $\text{C}_{20}\text{H}_{30}\text{O}$ , b.p. 228—230°/7 mm. (semicarbazone, m.p. 207°). (III) affords with dry NaOEt at room temp. during 8 days *trans*- $\beta$ -decalol, no unchanged (III) even after 1 day, and no identifiable condensation product (cf. A., 1925, i, 258), but a rosin-like substance which does not yield a semicarbazone, but with  $\text{NH}_2\text{OH}\cdot\text{HCl}$  gives a product, m.p. 255—256° (decomp.). The unhydrolysed residue (VI) obtained by interaction of (III) with  $\text{CH}_3\text{Br}\cdot\text{CO}_2\text{Et}$  or  $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$  and Zn (cf. A., 1932, 1032, 1033) affords  $\Delta^2$  (or  $\Delta^1$ )-*trans*-octahydronaphthyl-2-*trans*- $\beta$ -decalone (VII), m.p. 125—126° [semicarbazone, m.p. 212° (decomp.)], and a product (VIII), m.p. 75—80° [semicarbazone, m.p. 224—225° (decomp.)], different from *trans*- $\beta$ -decalol. (VII) and (VIII) afford the same phenyl-, m.p. 153—154°, and p-nitrophenyl-hydrazone, m.p. 208° (decomp.). (VII) gives a 2:4-dinitrophenylhydrazone, m.p. 175—176°, whilst (VIII) gives one of m.p. 194—195° (decomp.), although the latter does not depress the m.p. of the former. Ozonisation of (VI) affords (III) and *trans*-cyclohexane-1:2-diacetic acid, but no 1-carboxy-*trans*-cyclohexane-2-propionic acid.

J. L. D.

**Polyhalogeno-derivatives of acetomesitylene.** II. Bromination of 3:5-dichloroacetomesityl-



ene. C. H. FISHER (J. Amer. Chem. Soc., 1933, 55, 4594—4597; cf. A., 1933, 1296).— $p$ - $C_6H_4Cl$ -COME and excess of Br in absence or presence of solvent give the  $\omega\omega$ -Br<sub>2</sub>-derivative, m.p. 93.5—94.5° (lit. 92.5°); failure to obtain the  $\omega\omega\omega$ -Br<sub>3</sub>-derivative is probably due to the reducing action of the HBr formed (thus,  $\omega\omega\omega$ :3:5-pentabromo-2:4:6-trimethylacetophenone is reduced by 48% HBr in AcOH to the  $\omega\omega$ :3:5-Br<sub>2</sub>-derivative).  $\omega\omega$ :3:5-Tetrachloro-2:4:6-trimethylacetophenone (I), m.p. 106.5—107.5°, from acetomesitylene and Cl<sub>2</sub> in AcOH, is reduced (Zn dust, AcOH) to 3:5-dichloro-2:4:6-trimethylacetophenone (II), m.p. 107.5—109°, converted [as is (I)] by aq. NaOCl in C<sub>5</sub>H<sub>5</sub>N into  $\omega\omega\omega$ :3:5-pentachloro-2:4:6-trimethylacetophenone, m.p. 90—91°. (II) and excess of Br in AcOH give a 1:1 mixture (III), m.p. 103.5—104.5°, of 3:5-dichloro- $\omega\omega$ -dibromo- (IV), m.p. 121—122°, and 3:5-dichloro- $\omega\omega\omega$ -tribromo- (V), m.p. 84—85°, -2:4:6-trimethylacetophenones. (III) could not be separated by fractional crystallisation and is prepared from equimol. amounts of (IV) and (V). (V) is obtained from (II) or (III) and aq. NaOBr in C<sub>5</sub>H<sub>5</sub>N, whilst (IV) is prepared from (II) and Br (2 mols.) in AcOH.

H. B.

Asymmetric syntheses. III. Action of optically active nitrates on 1-keto-1:2:3:4-tetrahydronaphthalene. W. H. HORNE and R. L. SHRINER (J. Amer. Chem. Soc., 1933, 55, 4652—4654).—An optically inactive *K* salt of 2-nitro-1-keto-1:2:3:4-tetrahydronaphthalene, m.p. 67°, is obtained when 1-keto-1:2:3:4-tetrahydronaphthalene is treated with *d*-, *l*-, or *dl*- $\beta$ -octyl nitrate in EtOH-KOEt and Et<sub>2</sub>O, indicating the structure  $\cdot C(OK)C(NO_2)\cdot$  for the salt.

H. B.

Catalytic dehydration of ionone and constitution of ionene. M. T. BOGERT and V. G. FOURMAN (J. Amer. Chem. Soc., 1933, 55, 4670—4680).—Ionene (I), b.p. 114°/14 mm., 240—242°/752 mm., is best prepared by distillation of  $\alpha$ - or  $\beta$ -ionone with a little I. The work now and previously (A., 1933, 153) described establishes (I) as 1:1:6-trimethyl-1:2:3:4-tetrahydronaphthalene (cf. Barbier and Bouveault, A., 1897, i, 537). (I) is dehydrogenated (S) to 1:6- $C_{10}H_6Me_3$  and is oxidised (aq. KMnO<sub>4</sub>) to  $\beta$ -2:4-dicarboxyphenylisovaleric acid (+H<sub>2</sub>O), m.p. 220°, or  $\alpha$ -2:4-dicarboxyphenylisobutyric acid (II), m.p. 217° (*Me*<sub>3</sub> ester, m.p. 91°), and  $\alpha$ -keto- $\beta$ -2:4-dicarboxyphenylisovaleric acid (III), m.p. 140—145°, re-solidifying at 150° with m.p. about 206°, according to the conditions used; (II) and (III) are, respectively, the ioniregene- and ionegenone-tricarboxylic acid of Tiemann and Krüger (A., 1894, i, 80). Distillation of the *K* salt of (II) with soda-lime gives PhPr<sup>s</sup>. (I) and conc. H<sub>2</sub>SO<sub>4</sub> at 90° afford an ionenesulphonic acid [*Na* (+5H<sub>2</sub>O) and *Ba* (+3H<sub>2</sub>O) salts; chloride, m.p. 89°; amide, m.p. 157—158°], whilst (I), HNO<sub>3</sub> (*d* 1.5), and P<sub>2</sub>O<sub>5</sub> (or conc. H<sub>2</sub>SO<sub>4</sub>) in the cold give dinitroionene (IV), m.p. 103°. This is reduced (H<sub>2</sub>, PtO<sub>2</sub>, EtOH) to a nitroaminoionene, m.p. 171° (hydrochloride, decomp. 237—239°; *Ac* derivative, m.p. 158°), and oxidised (CrO<sub>3</sub>, AcOH, conc. H<sub>2</sub>SO<sub>4</sub>) to  $\alpha$ -dinitroionenone (V), m.p. 157° (*oxime*, m.p. 188.5°). (V) is isomerised by a little conc. H<sub>2</sub>SO<sub>4</sub> in Ac<sub>2</sub>O to

$\beta$ -dinitroionenone (VI), m.p. 99°, which is reconverted into (V) by dissolution in conc. H<sub>2</sub>SO<sub>4</sub> or EtOH-NaOH. (IV), (V), and (VI) are oxidised (Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, AcOH, conc. H<sub>2</sub>SO<sub>4</sub>) to  $\beta$ -dinitro-2-carboxyphenylisovaleric acid (+H<sub>2</sub>O), m.p. 150° (loss of H<sub>2</sub>O), re-solidifying with m.p. 177°, which when heated above its m.p. gives  $\beta$ -dinitrophenylisovaleric acid, m.p. 166.5—168.5°, and is oxidised (KMnO<sub>4</sub>, dil. H<sub>2</sub>SO<sub>4</sub>) to  $\alpha$ -dinitrophenylisobutyric acid, m.p. 170.5°. The irene of Tiemann and Krüger (*loc. cit.*) is probably (I).

H. B.

7-Phenylthiol derivatives of deoxybenzoin. W. A. MITCHELL and S. SMILES (J.C.S., 1933, 1529).—COPh·CPh(SPh)<sub>2</sub>, Zn, and AcCl in Et<sub>2</sub>O give 7'-acetoxy-7-phenylthiolstilbene, m.p. 141°, hydrolysed (EtOH-NaOEt) to 7-phenylthioldeoxybenzoin [*Ph*  $\alpha$ -phenylthiolbenzyl ketone], m.p. 81°. 7'-Acetoxy-7-(5-chloro-2-methoxyphenylthiol)stilbene, m.p. 114°, from COPh·CPh(S·C<sub>6</sub>H<sub>3</sub>Cl·OMe)<sub>2</sub>, is similarly hydrolysed to 7-(5-chloro-2-methoxyphenylthiol)deoxybenzoin, m.p. 102°, also prepared from 5-chloro-2-methoxythiophenol (I), benzoin, and EtOH-HCl [use of an excess of (I) in this condensation gives 7:7'-bis-(5-chloro-2-methoxyphenylthiol)stilbene, m.p. 208°]. The production of *Ph*  $\beta\beta$ -diphenylthiol- $\beta$ -phenylethyl sulphide (II), m.p. 82°, from PhSH (3 mols.), CH<sub>2</sub>Bz·OAc (1 mol.), and EtOH-HCl, together with the above change COPh·CPh(SAr)<sub>2</sub> → OAc·CPh·CPh·SAr, support Posner's assumption (A., 1902, i, 220) that the production of (CPh·SAr)<sub>2</sub> from ArSH and benzoin is preceded by the formation of (ArS)<sub>2</sub>CPh·CHPh·SAr. Attempts to remove a mol. of PhSH from (II) were, however, unsuccessful.

H. B.

Halogenated benzophenones. J. GANZMÜLLER (J. pr. Chem., 1933, [ii], 138, 311—312).—Prolonged heating of  $p$ -C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>, BzCl, and AlCl<sub>3</sub> gives 2:5-dichlorobenzophenone, m.p. 85—86°. 2:5:2'-Tri-, m.p. 145—147°, and 2:5:2':4'-tetra-, m.p. 176°, -chlorobenzophenones are similarly prepared using  $o$ -C<sub>6</sub>H<sub>4</sub>Cl·COCl and 2:4-C<sub>6</sub>H<sub>3</sub>Cl<sub>2</sub>·COCl, respectively.

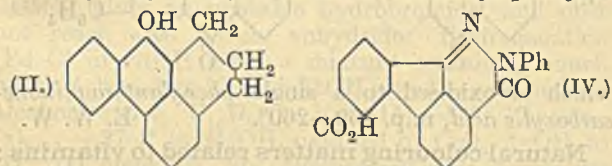
H. B.

Isomerism of halochromic compounds. II. P. PFEIFFER and H. KLEU (Ber., 1933, 66, [B], 1704—1711; cf. A., 1933, 1052).—Further examples are given of colourless ammonium salts (I), COR·CH:CH·C<sub>6</sub>H<sub>4</sub>·NMe<sub>2</sub>·HClO<sub>4</sub>, and coloured oxonium salts (II), NMe<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CH:CH·CR'·O·HClO<sub>4</sub> of unsaturated basic ketones (III). (I) are best prepared by dissolution of (III) in an excess of dil. aq. HClO<sub>4</sub> and crystallisation whereas (II) are obtained by partial hydrolysis of the diperchlorates or by dissolution of (III) in 70% HClO<sub>4</sub> which is slowly diluted. In cases of unusual difficulty (I) can be isomerised to (II) by crystallisation from CH<sub>2</sub>Cl·CO<sub>2</sub>H. The following compounds are described: *p*-chlorophenyl *p*-dimethylaminostyryl ketone, m.p. 140—140.5°, from *p*-NMe<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO and C<sub>6</sub>H<sub>4</sub>Cl·COME in NaOH-EtOH, its colourless and violet perchlorate; *p*-tolyl *p*-dimethylaminostyryl ketone, m.p. 122—123°, colourless and blue mono- and yellow di-perchlorate; *p*-anisyl *p*-dimethylaminostyryl ketone, m.p. 127°, colourless and coloured perchlorates; styryl *p*-dimethylaminostyryl ketone, m.p. 158°, its brownish-yellow and bluish-green monopерchlorate and orange-brown dipерchlorate;



Ph *p*-aminostyryl ketone, m.p. 152°, its yellow and pink perchlorate. H. W.

**Degradation of 1:9-benzanthrone-10 by oxidation.** G. CHARRIER and (SIGNA.) E. GHIGI (Gazzetta, 1933, 63, 685—697).—Oxidation of Bz-1-amino-benzanthrone (A., 1929, 1305) by  $\text{KMnO}_4$ -NaOH was unsuccessful as a method of degradation, yielding mainly anthraquinone-1-carboxylic acid (I), with a product, m.p. 180—185°. Hydroxytrimethyleneph-anthrene (II) was, however, thus oxidised to a small quantity only of (I) with 3:2'-dicarboxydiphenyl-2-



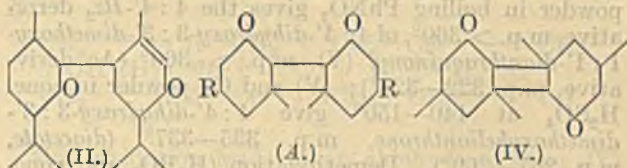
glyoxylic acid (III), m.p. 230° (decomp.) ( $\text{Na}_3$ ,  $\text{Ba}_{3/2}$  salts), also obtained by similar oxidation of benzanthrone. (III) forms a *phenylhydrazone*, m.p. 160° (decomp.), an *oxime anhydride*,  $\text{C}_{16}\text{H}_9\text{O}_6\text{N}$ , m.p. 250° (decomp.), and Na salt,  $\text{C}_{16}\text{H}_{10}\text{O}_7\text{NNa}$ , m.p. 270° (decomp.), and a *semicarbazone*, m.p. 220° (decomp.). When distilled from  $\text{Ca}(\text{OH})_2$  it gives  $\text{Ph}_2$ , and from Zn, fluorene. With dil.  $\text{H}_2\text{SO}_4$  and  $\text{MnO}_2$ , *diphenyl-2:3:2'-tricarboxylic acid*, m.p. 195—196° (decomp.), is formed; with conc.  $\text{H}_2\text{SO}_4$  the product is *fluorenone-1:5-dicarboxylic acid*, m.p. 295—299° (decomp.), which when distilled alone yields fluorenone, or with Zn, fluorene, and forms an *oxime*, m.p. 295—300° (decomp.), and a *phenylhydrazone*, m.p. about 290°. The last is converted below its m.p., or when heated in  $\text{AcOH}$ - $\text{Ac}_2\text{O}$ , into the *phthalazone* derivative (IV), m.p. 294—295°. E. W. W.

**Homogeneous catalysis of stereoisomeric change in oximes.**—See this vol., 36.

**Nitro-derivatives of  $\beta$ -diketones.** N. J. TOIVONEN, E. OSARA, and O. OLLILA (Suomen Kem., 1933, 6B, 67—68).—Nitration of 2:5:5-trimethylcyclohexane-1:3-dione (I) in conc.  $\text{HNO}_3$  affords 2-nitro-2:5:5-trimethylcyclohexane-1:3-dione (II), m.p. 145—147°, hydrolysed by conc. NaOH to  $\epsilon$ -nitro- $\delta$ -keto- $\beta\beta$ -dimethylheptonic acid, m.p. 60—62° [ $\text{Na}_2$  (III) and  $\text{Ag}_2$  salts]. (III) with  $\text{H}_2\text{O}$ -NaOBr affords  $\text{CMeBr}_2\text{NO}_2$  and  $\beta\beta$ -dimethylglutaric acid. Reduction of (II) affords (I). J. L. D.

**Polymerisation of  $\alpha\beta$ -unsaturated ketones by alkali and by light.** W. TREIBS (J. pr. Chem., 1933, [iii], 138, 299—305).—Polycarvone (I) (A., 1932, 1139) (structure suggested) is depolymerised by heat; it absorbs (Skita reduction) 1H per carvone unit (the resultant hydro-derivative is decomposed but not depolymerised by heat). Prolonged treatment of carvone or (I) with boiling  $\text{MeOH}$ -KOH gives a *dicarvone*,  $\text{C}_{20}\text{H}_{28}\text{O}_2$ , m.p. 115—116°, b.p. 230°/15 mm., in addition to that prepared by Ruzicka (A., 1921, i, 34); these are not depolymerised by heat. Piperitone is similarly converted into a *dipiperitone* (II), m.p. 105°. Irradiation (method; A., 1931, 95) of 3-methyl- $\Delta^2$ -cyclohexenone in aq.  $\text{MeOH}$  gives a saturated (Br;  $\text{KMnO}_4$ ) *dimeride* (A, R=H), m.p. 144—145° (impure *disemicarbazone*, m.p. >250°), and an unsaturated *dimeride*, an oil. 3:5-Dimethyl- $\Delta^2$ -cyclohexenone simi-

larly affords a *dimeride* (III) (A, R=Me), m.p. 161—162° (*disemicarbazone*, m.p. >250°), a little of the

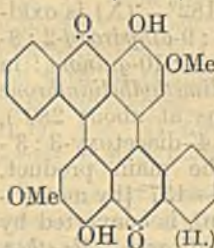


*dimeride* (IV) (*disemicarbazone*), and an unsaturated *dimeride*, b.p. 203—205°/17 mm. (III) is oxidised ( $\text{CrO}_3$ , = 40 per mol.,  $\text{AcOH}$ ) to 1:2-dimethyl-1:2-di- $\beta$ -carboxypropylcyclobutane-3:4-dicarboxylic acid, m.p. 261° (decomp.). H. B.

**Course of alkylation of enolates.** G. WANAG (Ber., 1933, 66, [B], 1678—1681).—Bindone (I) usually contains *isobindone* (II) from which it can be freed by  $\text{K}_2\text{CO}_3$  in  $\text{EtOH}$ , leaving a product, m.p. 209° (slight decomp.). Treatment of (I) with excess of  $\text{K}_2\text{CO}_3$  and  $\text{MeI}$  in  $\text{EtOH}$  leads to bindone *O*-Me ether, m.p. 174°, and (II). The formation of (II) is explained by the supposition that the primary product is bindone *O*-Me ether, which adds  $\text{H}_2\text{O}$  at the double linking and then loses  $\text{EtOH}$  with production of the K salt of (II). This is supported by the observation that the pure Me or Et ether of (I) freely yields (II) when treated with  $\text{K}_2\text{CO}_3$ . (I) does not give (II) when heated with  $\text{K}_2\text{CO}_3$  and  $\text{EtOH}$ . Homogeneous bindone *O*-Me ether, m.p. 217°, is obtained by treating (I) in  $\text{MeOH}$  with  $\text{HCl}$ ; hydrolysis with  $\text{K}_2\text{CO}_3$  in  $\text{MeOH}$  results in partial formation of (II), but this is not the case when  $\text{AcOH}$ - $\text{HCl}$  is used. H. W.

**Lipins of tubercle bacilli. XXXV. Constitution of phthiocol, the pigment isolated from human tubercle bacillus.** R. J. ANDERSON and M. S. NEWMAN (J. Biol. Chem., 1933, 103, 197—201).—The compound  $\text{C}_{11}\text{H}_{18}\text{O}_3$  (A., 1933, 1083), now termed *phthiocol* (I), gives ( $\text{Ac}_2\text{O}$ ,  $\text{C}_5\text{H}_5\text{N}$ ) a *monoacetate*, m.p. 101—102°, which on reductive acetylation affords a *triacetate*, m.p. 148° to an opaque melt which clears at 158—159°. (I) is oxidised (alkaline  $\text{H}_2\text{O}_2$ ) to *o*- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ . (I) is 3-hydroxy-2-methyl-1:4-naphthaquinone (synthesis to be reported later). H. B.

**Reduction products of hydroxyanthraquinones, XIV.** A. G. PERKIN and (in part) N. H. HADDOCK (J.C.S., 1933, 1512—1520).—The previously described (A., 1931, 355) 4:4'-dihydroxy-3:3'-dimethoxyhelianthrene (I) is now shown to be a mixture of (I) and 3:9-dihydroxy-2:8-dimethoxy-5:6:11:12-dibenzperylene-4:10-quinone (II). (I) is the main product when 1-hydroxy-2-methoxyanthrone (III) is oxidised with I in cold  $\text{C}_5\text{H}_5\text{N}$ ; in the hot, (II) predominates. Air oxidation of (III) or 1:1'-dihydroxy-2:2'-dimethoxydianthrene (*loc. cit.*) in boiling  $\text{C}_5\text{H}_5\text{N}$  gives mainly (II). The production of (II) from (III) and  $\text{I-C}_5\text{H}_5\text{N}$  probably occurs by loss of  $2\text{HI}$  from 10-iodo-1-hydroxy-2-methoxy-9-anthranol and subsequent oxidation of the so formed dihydro-derivative of (II). (I) is now syn-



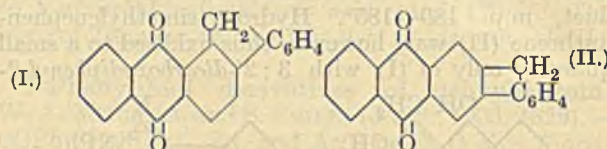


thesised as follows: the *Bz* derivative, m.p. 207—208°, of 4-bromoalizarin 2-Me ether (IV) with Cu powder in boiling  $\text{PhNO}_2$  gives the 4:4'-*Bz*<sub>2</sub> derivative, m.p. > 360°, of 4:4'-dihydroxy-3:3'-dimethoxy-1:1'-dianthraquinonyl (V), m.p. > 360° (Ac derivative, m.p. 322—326°); (V) and Cu powder in conc.  $\text{H}_2\text{SO}_4$  at 140—150° give 4:4'-dihydroxy-3:3'-dimethoxyhelianthrone, m.p. 335—337° (diacetate, m.p. 267—269°). Demethylation ( $\text{H}_3\text{BO}_3$  and conc.  $\text{H}_2\text{SO}_4$  at 140°) of (V) affords 3:4:3':4'-tetrahydroxy-1:1'-dianthraquinonyl (Eckert and Hampel, A., 1927, 881). 3:4:3':4'-Tetrahydroxyhelianthrone (VI) [from (I) and HBr (*d* 1.7) at 180—210°] is acetylated ( $\text{Ac}_2\text{O}$ ,  $\text{C}_5\text{H}_5\text{N}$ ) to its tetra-acetate (VII), m.p. 282—286°, and 3:4:3':4'-tetra-acetoxynaphthadanthrone (VIII), m.p. about 360°. Crystallisation of (VII) from  $\text{COMe}_2$  in daylight causes considerable conversion into (VIII). Reduction ( $\text{SnCl}_2$ , HCl, AcOH) of the Ac derivative of (IV) gives 4-bromo-1-hydroxy-2-methoxyanthrone (IX) and 4-hydroxy-3-methoxyanthranol, m.p. 198—200°. (IX),  $\text{Ac}_2\text{O}$ , and  $\text{C}_5\text{H}_5\text{N}$  afford 4-bromo-1-acetoxy-2-methoxy-9-anthranyl acetate, m.p. 185—188°. When (IX) is heated, it passes gradually into (II). (II) is also formed when (IX) is shaken with cold  $\text{C}_5\text{H}_5\text{N}$  or heated with  $\text{C}_5\text{H}_5\text{N}$ ,  $\text{PhNO}_2$ , or conc.  $\text{H}_2\text{SO}_4$ ; loss of 2HBr from 2 mols. of (IX) (anthranol form) and subsequent oxidation ( $\text{O}_2$ ) occur. (II) is not produced from (IX) and I in boiling  $\text{C}_5\text{H}_5\text{N}$ ; a dark brown powder results. 2:3:8:9-Tetrahydroxy-5:6:11:12-dibenzperylene-4:10-quinone [obtained by demethylation of (II) or oxidation ( $\text{I}-\text{C}_5\text{H}_5\text{N}$ ) of 1:2-dihydroxyanthrone (cf. *loc. cit.*)] and (VI) possess very similar dyeing properties (mordanted wool) (as do their  $\text{SO}_3\text{Na}$  derivatives). Digestion of (I) with 20% EtOH-KOH, evaporation to dryness, and treatment of the residue with  $\text{Me}_2\text{SO}_4$  and anhyd.  $\text{Na}_2\text{CO}_3$  at 90—140° gives 3:4:3':4'-tetramethoxyhelianthrone, m.p. 263—265° [oxidised ( $\text{CrO}_3$ , AcOH) to 3:4:3':4'-tetramethoxy-1:1'-dianthraquinonyl, m.p. 335—336°], and a compound,  $\text{C}_{30}\text{H}_{18}\text{O}_6$  (?), m.p. 285—287°; these are both converted by HBr (*d* 1.7) in cold AcOH into (I). (II) is similarly methylated to a  $\text{Me}_4$  ether (+AcOH), m.p. 317—319°, and a  $\text{Me}_3$  ether,  $\text{C}_{31}\text{H}_{20}\text{O}_6$ , m.p. 289—290°, both of which are converted by cold HBr-AcOH into (II); the former may be the 2:3:8:9- $\text{Me}_4$  ether, but since it gives a ppt. with EtOH-KOH in  $\text{C}_6\text{H}_6$ , it may contain free OH groups (formed by reduction during the original treatment with EtOH-KOH).

Reduction ( $\text{SnCl}_2$ , HCl, AcOH) of 1-hydroxy-2-methylantraquinone gives 1-hydroxy-2-methylanthrone (X), m.p. 136—138°, and 4-hydroxy-3-methylantranol, m.p. 197°. 1-Acetoxy-2-methyl-9-anthranyl acetate has m.p. 180—182°. (X) is oxidised by I in boiling  $\text{C}_5\text{H}_5\text{N}$  to 3:9-dihydroxy-2:8-dimethyl-5:6:11:12-dibenzperylene-4:10-quinone; in cold  $\text{C}_5\text{H}_5\text{N}$ , 4:4'-dihydroxy-3:3'-dimethylhelianthrone [diacetate, m.p. 297—300° (darkens at about 280°), readily converted (light) into 4:4'-diacetoxy-3:3'-dimethylnaphthadanthrone] is the main product. 3-Bromoalizarin  $\text{Me}_2$  ether, m.p. 136—137° [by methylation (as above) of 3-bromoalizarin], is converted by conc. HCl at 135—140° into 3-bromoalizarin 2-Me ether, m.p. 186—187° (acetate, m.p. 150—151°). H. B.

Occurrence of anthraquinone dyes in mineral kingdom (graebeite).—See A., 1933, 1268.

Condensation of *o*-2-fluorenylbenzoic acid. A. DANSI and A. SEMPRONJ (Gazzetta, 1933, 63, 681—684).—When this acid, prepared from fluorene and *o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ , best in  $\text{CS}_2$  as medium (cf. A., 1904, i, 168), is heated at 300—320° it condenses quantitatively to 1:2- (I) or 2:3-phthaloylfluorene (II),



which is oxidised to a single phenylantraquinone-carboxylic acid, m.p. 259—260°. E. W. W.

Natural colouring matters related to vitamins: carotenes and flavins. R. KUHN (Chem. and Ind., 1933, 981—986).—British Association lecture.

Cerebronic acid fraction. II. F. A. TAYLOR and P. A. LEVENE (J. Biol. Chem., 1933, 102, 535—540).—The higher fatty acids from the oxidation of cerebronic acid (cf. A., 1929, 1479) contain lignoceric acid (mixed m.p.). Evidence is offered that this is not present in the unoxidised acid. H. A. P.

Cerebronic acid. IX. P. A. LEVENE and P. S. YANG (J. Biol. Chem., 1933, 102, 541—556; cf. Klenk, A., 1928, 868, and preceding abstract).—Repeated fractional hydrolysis of the *Me* ester, m.p. 64°, of cerebronic acid (I) (*Et* ester, m.p. 64—65°) with cold NaOH in MeOH and re-esterification indicates that it is not homogeneous, but is free from lignoceric acid (II); the product finally obtained in this way is the acid  $\text{C}_{25}\text{H}_{50}\text{O}_3$  (titration). Confirmation that (I) contains near homologues is afforded by the behaviour on distillation of the  $\text{Me}_2$  derivative (ether-ester), m.p. 59°, obtained by action of MeI and  $\text{Ag}_2\text{O}$  in excess of  $\text{COMe}_2$ ; this is hydrolysed to the *OMe*-acid,  $\text{C}_{26}\text{H}_{52}\text{O}_3$ , m.p. 74—76°, thus disproving the presence of the lactide in (I). Oxidation of (I) with  $\text{KMnO}_4$  gives a mixture of acids of mol. wt. 340—380 consisting mainly of (II). H. A. P.

Plant colouring matters. LIV. Products of the methylation of zeaxanthine. P. KARRER and T. TAKAHASHI (Helv. Chim. Acta, 1933, 16, 1163—1165; cf. A., 1930, 1440).—Zeaxanthine (I) is converted by K *tert*-amyl oxide in boiling PhMe followed by MeI at 50° into a mixture of the *Me* (II), m.p. 153°, and  $\text{Me}_2$  (III), m.p. 176°, ethers in small yield. (II) and (III) are scarcely distinguishable from (I) by absorption spectrum, but differ considerably in their solubility and distribution between MeOH and light petroleum. H. W.

Modifications of gutta-percha hydrocarbon. III. A. W. K. DE JONG (Rec. trav. chim., 1933, 52, 1028—1032; cf. A., 1932, 1036).—By cooling a solution of the spongy form of gutta-percha in 25—30 vols. of light petroleum with ice two modifications are obtained, viz., *a*, which shrinks to a solid cylinder on drying, and *b*, a spongy form which may have closed or open pores. *a* is formed by rapid cooling of solutions prepared at relatively low temp. (40°), and therefore containing crystal nuclei, and is regarded



as composed of particles of colloidal size; *b* is deposited more slowly by solutions prepared at higher temp., and consists of longer and thicker crystals, the product with closed pores probably containing the *a*-form in its interstices.

H. A. P.

**Zierone.** A. E. BRADFIELD, A. R. PENFOLD, and J. L. SIMONSEN (J. Proc. Roy. Soc. New South Wales, 1933, 67, 200—205).—Zierone (I),  $C_{15}H_{22}O$  (cf. B., 1927, 28), b.p. 147—149°/18 mm. (2:4-dinitrophenylhydrazone, m.p. 95—97°; semicarbazone, m.p. 182°), is stable to  $H_2O_2$ -NaOH and  $KMnO_4$  in hot  $COMe_2$ , gives an unstable hydrobromide, and does not react with maleic anhydride. Hydrogenation (Pd-C) in EtOH gives a mixture containing much hydrocarbon, but Na and EtOH give the unsaturated alcohol, *zierol*,  $C_{15}H_{22}O$ , b.p. 151—152°/17 mm.,  $[\alpha]_{5461}^{20} + 37.4^\circ$  in MeOH, oxidised by  $CrO_3$ -AcOH to (I). (I) gives an oily hydroxymethylene derivative (2:4-dinitrophenylhydrazone, m.p. 155—157°), and with Se at 250—280° gives probably Se-guaiazulene (picrate, m.p. 110—111°; cf. A., 1931, 1301). (I) is oxidised by  $O_3$ , giving traces of  $CH_2O$  and no  $COMe_2$ . (I) is thus probably a tricyclic, mono-unsaturated compound, having a  $CH_2CO$  group; the ethylenic linking is probably not  $\alpha\beta$  to the CO group and forms part of a ring.  $[R_L]_D^{20}$  (66:93) suggests conjugation of a cyclopropane ring with both the ethylenic linking and the CO group.

R. S. C.

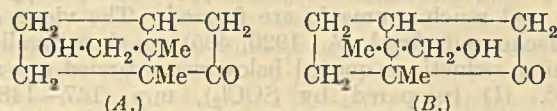
**Organic compounds with large molar depression of m.p.** J. PIRSCH (Ber., 1933, 66, [B], 1694—1697; cf. A., 1933, 770).—Compounds with high mol. m.p. depression belonging to the tricyclo-hydro-aromatic group have their mol. structure almost equally strongly developed in all three spatial directions. Further examples are: camphenilone, m.p. 38°,  $E=64.0$ , best obtained by alkaline hydrolysis of nitrocamphene and important because of its low m.p.; isocamphane, m.p. 65°,  $E=44.5$ , prepared by hydrogenation of camphene (Pd-BaSO<sub>4</sub> in EtOH); tricyclene, m.p. 66°,  $E=35.9$ , from camphorhydrazone and yellow HgO; bornylene,  $E=33.5$ ; camphane, m.p. 154°,  $E=29.5$ .

H. W.

**Occurrence of  $\pi$ -hydroxy-derivatives in campherol.** Y. ASAHINA and M. ISHIDATE (Ber., 1933, 66, [B], 1673—1677; cf. A., 1931, 358).—Further examination shows that “labile 5-ketocamphor” is a somewhat complicated mixture of structural isomerides and that the “1:5:5-trimethylcyclopentane-2:4-dione-1-acetic acid” should be deleted from the lit. Autoxidation of the mixture affords isoketopinac acid (I), m.p. 249—250°,  $[\alpha]_D^{20} + 3.17^\circ$  in EtOH (cf. Wedekind, A., 1923, i, 808) [semicarbazone, (II) m.p. 255° (decomp.); phenylhydrazone, m.p. 205° (decomp.)], and 2-keto- $\pi$ -apocamphane-7-carboxylic acid (III), m.p. 272°,  $[\alpha]_D^{20} + 67.2^\circ$  in EtOH [semicarbazone (IV), m.p. 215—216°] (cf. Hasselström, A., 1931, 626). Treatment of (II) with NaOEt-EtOH at 170—180° yields *l*- $\pi$ -apocamphane-7-carboxylic acid, m.p. 231°,  $[\alpha]_D^{20} - 18.16^\circ$  in EtOH, whilst similar treatment of (IV) gives *d*- $\pi$ -apocamphane-7-carboxylic acid, m.p. 231°,  $[\alpha]_D^{20} + 18.0^\circ$  in EtOH. Oxidation of (I) with  $KMnO_4$  leads to *trans-d*-camphortricarboxylic acid, m.p. (anhyd.) 197°,  $[\alpha]_D^{20} + 36.8^\circ$  in EtOH (Ag salt; anhydride, m.p. 254°).

G

In addition to 3- and 5-hydroxycamphor, campherol therefore contains the two  $\pi$ -hydroxycamphors *A* and *B*.



(A.)

(B.)

Mild oxidation leads to an aldehyde mixture (V) rapidly autoxidised to the 2-keto- $\pi$ -apocamphane-7-carboxylic acids. Treatment of (V) with  $NH_2 \cdot CO \cdot NH \cdot NH_2$  gives a *mono*-, m.p. 202° (decomp.), and a *di*-, m.p. about 360° (decomp.) after becoming discoloured at 300°, -semicarbazone which could not be hydrolysed to their components.

H. W.

**Isomeric myrtenols.** V. PAOLINI (Gazzetta, 1933, 63, 666—669).—The dextrorotatory myrtenol (A., 1905, i, 801) isolated through the H phthalate (Ag salt, m.p. 102°) from the saponified fraction of Calabrian myrtle essence, in which a laevorotatory form appears also to be present, is named  $\alpha$ -myrtenol.

E. W. W.

**Preparation of halogeno- and other 2-phenylbenzopyrylium salts.** (MRS.) C. G. LE FEVRE and R. J. W. LE FEVRE (J.C.S., 1933, 1532).—The appropriately substituted salicylaldehyde and CPhMe,  $HClO_4$ , and HCl give the benzopyrylium perchlorate in one stage (A., 1930, 217; 1932, 949). The following m.p. have been raised: 2-phenyl-, m.p. 180°; 6-bromo-, m.p. 250—251°; 6:8-dichloro-, m.p. 270—271°, and 6:8-dibromo-2-phenylbenzopyrylium perchlorate, m.p. 273—275°.

F. R. S.

**Synthetic experiments in the chromone group. X. Coumarin and chromone formation.** T. C. CHADHA, H. B. MAHAL, and K. VENKATARAMAN (J.C.S., 1933, 1459—1462).—A classification of the action of acid anhydrides and Na salts on phenolic ketones of different types. Phloracetophenone,  $Ac_2O$ , and  $CH_2Ph \cdot CO_2Na$  (I) form 5:7-diacetoxy-3-phenyl-4-methylcoumarin, m.p. 169°, hydrolysed to the (OH)<sub>2</sub>-compound, m.p. 282—283°. *o*-Hydroxyacetophenone,  $CH_2Ph \cdot COCl$ , and (I) form 3-phenyl-4-methylcoumarin, whilst the ketone,  $CH_2Ph \cdot CO_2Et$ , and Na dust give 2-benzylchromone, m.p. 86°. Ph phenylacetate, m.p. 50°, and  $AlCl_3$  give *o*-(II), m.p. 60° (2:4-dinitrophenylhydrazone, m.p. 219°), and *p*-hydroxyphenyl benzyl ketone, m.p. 151° (2:4-dinitrophenylhydrazone, m.p. 224°). (II) with NaOAc and  $Ac_2O$  affords 2-methylisoflavone, m.p. 140°, and with  $Bz_2O$  and NaOBz forms 2:3-diphenylchromone, m.p. 152°. Respropiofenone, (I), and  $Ac_2O$  form 7-acetoxy-3-phenyl-4-ethylcoumarin, m.p. 205°, hydrolysed to the 7-OH-compound, m.p. 254°.  $\beta$ - $C_{10}H_7$  phenylacetate, m.p. 87°, and  $AlCl_3$  give 1-phenylacetyl- $\beta$ -naphthol, m.p. 101°, which with  $Ac_2O$  and NaOAc affords 3-phenyl-2-methyl-1:4- $\beta\alpha$ -naphthapyrone, m.p. 161°, and with  $Bz_2O$  and NaOBz yields 2:3-diphenyl-1:4- $\beta\alpha$ -naphthapyrone, m.p. 188°. 1:2- $C_{10}H_6Bz \cdot OH$ ,  $Ac_2O$ , and (I) form 3:4-diphenyl-1:2- $\beta\alpha$ -naphthapyrone, m.p. 221—222°.

F. R. S.

**Coumarin series. II. Synthesis of some coumarinaldehydes.** Catalytic hydrogenation of acid chlorides. T. BOEHM [with G. SCHUMANN and H. H. HANSEN] (Arch. Pharm., 1933, 271, 490—514;



cf. A., 1931, 493).—Hydrogenation of coumarin-3-carboxyl chloride (I) in xylene at 100° gives 70–75% yields of coumarin-3-aldehyde (II); at 180°, 20% of (II) and much coumarin are formed. The views of Zetzsche and Arnd (A., 1926, 405) are thus invalid. Similar reductions quoted below were carried out at 100°. (I) (prepared by  $\text{SOCl}_2$ ), m.p. 147–148°, gives (II), m.p. 131–132° [oxidised by  $\text{CrO}_3$ -AcOH or 65%  $\text{HNO}_3$  to the acid; *p*-nitrophenylhydrazone, m.p. 287–288° (decomp.); semicarbazone, m.p. 265–266° (decomp.); oxime, m.p. 207° (decomp.)], which with  $\text{CH}_2(\text{CO}_2\text{H})_2$  and piperidine (III) in EtOH gives  $\beta$ -3-coumarylacrylic acid, m.p. 266° (Et ester, m.p. 122°), the chloride, m.p. 197–198°, of which is reduced to  $\beta$ -3-coumarylacraldehyde, m.p. 155–156° [p-nitrophenylhydrazone, m.p. 289–290° (decomp.); oxime, m.p. 206–207°; semicarbazone, m.p. 242° (decomp.)]. (II) with  $\text{MeNO}_2$  gives 3- $\omega$ -nitrovinylcoumarin, m.p. 143–144°. (II),  $\text{CH}_2(\text{CO}_2\text{Et})_2$ , and a little (III) in cold EtOH give Et, hydroxy-3-coumarylmethylmalonate, m.p. 117°, dehydrated by  $\text{Ac}_2\text{O}$ - $\text{C}_5\text{H}_5\text{N}$  to Et, 3-coumarylmethylenemalonate, m.p. 93–95°. (II) with  $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$  and (III) in EtOH gives a substance,  $(\text{C}_7\text{H}_5\text{O}_2)_2$ , m.p. 81–82°, with  $\text{CH}_2(\text{CN})_2$  in EtOH gives 3-coumarylmethylenemalonodinitrile, m.p. 198° (decomp.), with  $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$  and Na in EtOH  $\alpha$ -cyano- $\beta$ -3-coumarylacrylamide, m.p. 233°, and with  $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  Et  $\alpha$ -cyano- $\beta$ -3-coumarylacrylate, m.p. 202°. Tricarbomethoxygalloyl chloride gives 80% of the aldehyde. Resorcyaldehyde,  $\text{CH}_2(\text{CO}_2\text{Et})_2$ , and (III) give the *O*-piperidine salt of Et umbelliferone-3-carboxylate (Ac derivative, m.p. 153–154°). Acetylumbelliferone-3-carboxylic acid, m.p. 210–211°, gives the chloride, m.p. 189–190°, hydrogenated to acetylumbelliferone-3-aldehyde, m.p. 165–166° [ $\text{NaHSO}_3$  compound; p-nitrophenylhydrazone, m.p. 280° (decomp.)]. The following are similarly prepared: carbomethoxy-, m.p. 214–215°, and carbethoxy-umbelliferone-3-carboxylic acid, m.p. 167° (chloride, m.p. 144–145°), and -aldehyde, m.p. 134–135° [p-nitrophenylhydrazone, m.p. 263–265° (decomp.)], umbelliferone-3-aldehyde, decomp. > 300° [p-nitrophenylhydrazone, decomp. > 300°; oxime, m.p. 224–225° (decomp.)], Et daphnetin-3-carboxylate (from pyrogallolaldehyde), m.p. 231–232° (Ac<sub>2</sub> derivative, m.p. 129–130°), and the corresponding acid, m.p. 263° (Ac<sub>2</sub> derivative, m.p. 213–214°).

R. S. C.

**Synthesis of alkyl- and ar[alkyl]-coumarans.** J. B. NIEDERL and E. A. STOECH (J. Amer. Chem. Soc., 1933, 55, 4549–4555).—Distillation of the polymeride obtained from allyl alcohol (1 mol.) and a phenol (1 mol.) in boiling AcOH-conc.  $\text{H}_2\text{SO}_4$  gives an alkylcoumaran (50–65%) and a little of the corresponding *o*-isopropenylphenol. Thus, 2-methylcoumaran, b.p. 208–212°, is prepared using PhOH, whilst 2 : 4-, b.p. 103°/11 mm., 2 : 5-, b.p. 99–100°/11.5 mm., 2 : 6-, b.p. 253–258°, -dimethylcoumarans are obtained from *p*-, *m*-, and *o*-cresol, respectively. 3-isopropenyl-*o*-cresol and Br give a pentabromo-3-isopropyl-*o*-cresol, m.p. 190–191°. Cinnamyl alcohol and PhOH similarly afford (mainly) 2-benzylcoumaran, b.p. 308–311°, and  $\gamma$ -phenyl- $\beta$ -*o*-hydroxyphenyl- $\Delta^2$ -propene, b.p. 193–196°; *o*-cresol gives 2-benzyl-6-methylcoumaran, b.p. 318–322°, and

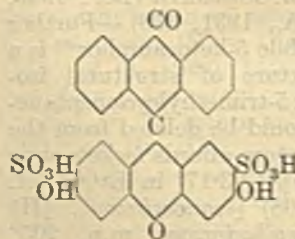
$\gamma$ -phenyl- $\beta$ -2-hydroxy-3-methylphenyl- $\Delta^2$ -propene, b.p. 212–216°; *m*-cresol yields 2-benzyl-5-methylcoumaran, b.p. 322–327°, and  $\gamma$ -phenyl- $\beta$ -2-hydroxy-4-methylphenyl- $\Delta^2$ -propene, b.p. 207–211°; *p*-cresol furnishes 2-benzyl-4-methylcoumaran, b.p. 320–325°, and  $\gamma$ -phenyl- $\beta$ -2-hydroxy-5-methylphenyl- $\Delta^2$ -propene, b.p. 208–212°. 2-Phenyl-1 : 4-dimethylcoumaran, b.p. 310–314° ( $\text{Br}_5$ -derivative, m.p. 249°), is prepared by Claisen and Tietze's method (A., 1925, i, 389).

H. B.

**Colouring matter on the stems of the tomato.** B. K. BLOUNT (J.C.S., 1933, 1528–1529).—The colouring matter is rutin. F. R. S.

**Synthesis of certain naphtha(1 : 2 : 4' : 3')-coumarin derivatives.** R. ROBINSON and J. D. ROSE (J.C.S., 1933, 1469–1472).—Resorcinol, Et benzoylsuccinate, and  $\text{H}_2\text{SO}_4$  give Et 7-hydroxy-4-phenylcoumarin-3-acetate, m.p. 177°, hydrolysed to the acid (I), m.p. 249–250° [*OMe*-derivative (II), m.p. 209°]. Methylation of (I) affords Me phenyl-2 : 4-dimethoxyphenylmethylenesuccinate, m.p. 101°, and of the Et ester of (I) yields the 1-Me 2-Et compound, m.p. 93°. (I) and  $\text{Ac}_2\text{O}$  give 4 : 7'-diacetoxy-naphtha(1 : 2 : 4' : 3')coumarin, m.p. 230°, hydrolysed to the 4 : 7'-(OH)<sub>2</sub>-compound, m.p. > 360°. (II) and  $\text{Ac}_2\text{O}$  form 4-acetoxy-7'-methoxynaphtha(1 : 2 : 4' : 3')coumarin, m.p. 184°, hydrolysed to the 4-OH-compound, m.p. 266–267° (decomp.), whilst (II) and  $\text{P}_2\text{O}_5$  yield 7'-methoxy-4-(7''-methoxy-4'-phenylcoumarin-3''-acetoxy)naphtha(1 : 2 : 4' : 3')coumarin, m.p. 237°. Veratroyl chloride, EtOH-NaOEt, and  $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$  give Et  $\alpha$ -veratroylacetylsuccinate, m.p. 98° (Et veratroylacetylacetate, m.p. 82°), which with resorcinol and  $\text{H}_2\text{SO}_4$  affords Et 7-hydroxy-4-veratroylcoumarin-3-acetate, m.p. 172°, hydrolysed to 4 : 7'-diacetoxy-5 : 6-dimethoxynaphtha(1 : 2 : 4' : 3')coumarin, m.p. 256–257°. Et *m*-methoxybenzoylacetate, Na, and  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$  yield Et *m*-methoxybenzoylsuccinate, b.p. 227°/17 mm., which does not condense with resorcinol. F. R. S.

**Condensation of *o*-benzoylbenzoic acid with resorcinol.** G. CHARRIER and (SIGNA.) E. GHIGI (Gazzetta, 1933, 63, 630–634).—The “rodonine” of Pavolini (A., 1932, 1038) contains S, being the disulphonic acid (probable formula annexed) of the condensation product (A., 1903, i, 640) of resorcinol and anthraquinone, and was patented in 1897 (G.P. 108,836). It may also be obtained by condensation of resorcinol-4 : 6-disulphonic acid with anthraquinone. E. W. W.



**Synthesis of homologues of dioxan.** R. CHRIST and R. K. SUMMERBELL (J. Amer. Chem. Soc., 1933, 55, 4547–4548; cf. A., 1932, 1141).—2 : 3-Dichlorodioxan (I) and  $\text{MgPhBr}$  give 2 : 3-diphenyldioxan, m.p. 49°, which when chlorinated at 125° and then hydrolysed (boiling  $\text{H}_2\text{O}$ ) affords Bz, and  $(\text{CHO})_2$ . Chlorination of (I) at 115° gives a (*s*-)tetraclorodioxan, m.p. 70° [hydrolysed to  $(\text{CHO})_2$ ], in addition to those



of m.p. 143—144° and b.p. 93—95°/11—12 mm. (cf. Butler and Cretcher, A., 1932, 949). H. B.

**Derivatives of dioxan.** IV. J. BÖESEKEN, F. TELLEGEN, and P. MALTHA (Rec. trav. chim., 1933, 52, 1067—1072; cf. A., 1933, 511).—Interaction of 2:3-dichlorodioxan with  $\text{HO} \cdot [\text{CH}_2]_3 \cdot \text{OH}$  in  $\text{C}_6\text{H}_6$  at the b.p. gives stereoisomeric forms, m.p. 157—158°, and 109.5—111°, of 2:3-dihydroxydioxan trimethylene ether,  $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{O} \cdot \text{CH} \cdot \text{O} \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{O} \cdot \text{CH} \cdot \text{O} \cdot \text{CH}_2 \end{smallmatrix}$ . The isomeride of higher m.p. appears to be converted by heat into a further modification from which it is regenerated by crystallisation from  $\text{Et}_2\text{O}$ . H. A. P.

**Thiophen derivatives.** III. I. J. RINKES (Rec. trav. chim., 1933, 52, 1052—1060).—Nitration of 3-methylthiophen ( $\text{HNO}_3\text{--Ac}_2\text{O}$  at  $-10^\circ$ ) gives 2-nitro-3-methylthiophen (I), m.p. 63°, b.p. 124°/20 mm., the orientation of which follows from its formation by the displacement of  $\text{CO}_2\text{H}$  by  $\text{NO}_2$  in the nitration of 3-methylthiophen-2-carboxylic acid (II). The constitution of 3-methylthiophen-5-carboxylic acid, obtained by oxidation of methathioxen (cf. A., 1887, 921), is proved by its nitration to the 2- $\text{NO}_2$ -compound (III), m.p. 180°, which on decarboxylation gives (I). Further nitration ( $\text{HNO}_3$ , d 1.51, and conc.  $\text{H}_2\text{SO}_4$  at  $-10^\circ$ ) of the Me ester, m.p. 93°, of (III) gives the 2:4-( $\text{NO}_2$ )<sub>2</sub>-ester, m.p. 64°, the free acid, m.p. 191°, of which is decarboxylated in quinoline to 2:4-dinitro-3-methylthiophen (IV), m.p. 96°, also formed together with (V) (below) by further nitration of (I). Nitration of (II) gives (I), (IV), and 4-, m.p. 208° (Me ester, m.p. 94°), and 5-nitro-3-methylthiophen-2-carboxylic acid, m.p. 182° (Me ester, m.p. 87°), further nitration of which eliminates  $\text{CO}_2\text{H}$  and gives (IV) and 2:5-dinitro-3-methylthiophen (V), m.p. 58°, respectively. H. A. P.

[Indigoid dyes. III.] R. TOBLER (Ber., 1933, 66, [B], 1757; cf. Dutta, A., 1933, 1169).—A question of priority. H. W.

**Preparation of glycyl-L-proline by E. Fischer's method.** E. ABDERHALDEN and W. NÜSSLER (Biochem. Z., 1933, 266, 216—220).—Material previously obtained (A., 1930, 1475) by Fischer's method (I) was impure. In the prep. of alanylproline and in many other cases the method of Bergmann *et al.* (A., 1933, 94) is greatly to be preferred. W. McC.

**Piperidine derivatives.** XIII. Phenyl- and phenylalkyl-substituted piperidinopropyl benzoates. L. A. WALTERS and S. M. McELVAIN (J. Amer. Chem. Soc., 1933, 55, 4625—4629).—2-Phenyl-, b.p. 270—272°/740 mm. (from  $\text{C}_5\text{H}_5\text{N}$  and LiPh in PhMe), 2- $\gamma$ -phenylpropyl-, b.p. 132—135°/2 mm., and 2- $\delta$ -phenylbutyl-, b.p. 142—145°/2 mm., -pyridines, prepared by Ziegler and Zeiser's method (A., 1931, 364), are reduced ( $\text{H}_2$ , Ni, methylcyclohexane at 150°) to 2-phenyl-, 2- $\gamma$ -phenylpropyl-, b.p. 161—163°/10 mm. (hydrochloride, m.p. 139—141°), and 2- $\delta$ -phenylbutyl-, b.p. 164—166°/9 mm. (hydrochloride, m.p. 129—131°), -piperidines, respectively.  $\delta$ -Phenoxy- $\alpha$ -phenylvaleronitrile, b.p. 190—195°/2 mm. (from  $\text{CH}_3\text{Ph} \cdot \text{CN}$ ,  $\gamma$ -phenoxypropyl bromide, and  $\text{NaNH}_2$  in  $\text{Et}_2\text{O}$ ), is reduced ( $\text{H}_2$ ,  $\text{PtO}_2$ ,  $\text{Ac}_2\text{O}$ ) to  $\epsilon$ -phenoxy- $\beta$ -phenylamylamine (hydrochloride, m.p. 127—128°),

which when treated with 48% HBr for 36 hr. and then with 10% NaOH in PhMe gives 3-phenylpiperidine, b.p. 255—256°/740 mm. (hydrochloride, m.p. 146—147°). The following benzoate hydrochlorides are prepared from  $\gamma$ -chloropropyl benzoate and the requisite piperidine:  $\gamma$ -2-, m.p. 186—187°, -3-, m.p. 180—181°, and -4-, m.p. 174—175°, -phenylpiperidinopropyl;  $\gamma$ -3-benzylpiperidinopropyl, m.p. 163—164°;  $\gamma$ -2- $\gamma$ -phenylpropylpiperidinopropyl, m.p. 103—105°, and  $\gamma$ -2- $\delta$ -phenylbutylpiperidinopropyl, m.p. 179—181°. The pharmacological properties of the esters are discussed (cf. A., 1930, 786). H. B.

**Behaviour of the pyridine ring on electrochemical oxidation.** IV. Piperidine. M. YOKOYAMA and K. YAMAMOTO (Bull. Chem. Soc. Japan, 1933, 8, 306—312; cf. A., 1932, 758).—Electrolytic oxidation of piperidine produces acids. By oxidation in 2N- $\text{H}_2\text{SO}_4$  at 22°  $\delta$ -aminovaleric, glutaric, succinic, and formic acids,  $\text{CO}_2$ , CO, and  $\text{NH}_3$  are obtained; an aldehyde, probably  $\delta$ -aminovaleraldehyde, is also formed. R. S. C.

**Oxidation of pyridine to a 2-pyridylpyridinium salt.** P. BAUMGARTEN and E. DAMMAN (Ber., 1933, 66, [B], 1633—1638).—Oxidation of  $\text{C}_5\text{H}_5\text{N}$  by  $\text{K}_2\text{S}_2\text{O}_8$  in  $\text{H}_2\text{O}$  at 100° affords 2-pyridylpyridinium sulphate [corresponding acetate, hygroscopic hydrochloride and perchlorate;  $(\text{C}_{10}\text{H}_8\text{N}_2)_2\text{PtCl}_6$ , m.p. 213—214° (decomp.)], hydrolysed by KOH-EtOH to glutacondialdehydedianil and 2-aminopyridine. Electrochemical oxidation of  $\text{C}_5\text{H}_5\text{N}$  in  $\text{H}_2\text{SO}_4$  appears to follow a similar course. H. W.

**Reactions of dinitriles [ $\beta$ -amino- $\beta$ -arylacrylonitriles] with aromatic hydroxyaldehydes.** N. PALIT (J. Indian Chem. Soc., 1933, 10, 529—535).— $\beta$ -Amino- $\beta$ -phenyl- (I), - $\beta$ -p-tolyl- (II), and - $\beta$ -anisyl- (III), m.p. 117°, -acrylonitriles are best prepared from MeCN, ArCN, and "mol." Na in  $\text{Et}_2\text{O}$ . (II) and  $o\text{-OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$  (IV) in boiling  $\text{H}_2\text{O}$  give a compound,  $\text{C}_{24}\text{H}_{18}\text{O}_2\text{N}_2$ , m.p. 217—218° (Ac derivative, m.p. 180—181°), hydrolysed (conc. HCl at 180—185°) to a substance,  $\text{C}_{14}\text{H}_{20}\text{O}_2\text{N}_2$ , m.p. 198° (shrinking) (Me ether, m.p. 100—110°). 3:5-Dicyano-2:6-di-p-tolyl-4-o-hydroxyphenyl-1:4-dihydropyridine, m.p. 266—267°, is obtained from (II) and (IV) in AcOH at 100° (bath). Compounds,  $\text{C}_{23}\text{H}_{16}\text{O}_2\text{N}_2$ , m.p. 225—226°, and  $\text{C}_{24}\text{H}_{18}\text{O}_3\text{N}_2$ , m.p. 247—248°, are similarly obtained (in  $\text{H}_2\text{O}$  or AcOH) from (I) and (III), respectively; in AcOH-HCl, (I) gives a substance,  $\text{C}_{23}\text{H}_{16}\text{O}_2\text{N}_2$ , m.p. 291—292°. With  $p\text{-OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$  in AcOH, (I), (II), and (III) afford 3:5-dicyano-2:6-diphenyl-, m.p. 218—219°, -2:6-di-p-tolyl-, m.p. 259—260°, and -2:6-dianisyl-, m.p. 385° (softens at 379°), -4-p-hydroxyphenyl-1:4-dihydropyridine, respectively; these are oxidised ( $\text{N}_2\text{O}_3$  in EtOH) to the corresponding pyridines, m.p. 265° (shrinks at 255°), 245—246°, and 248—250°, respectively. 3:5-Dicyano-2:6-diphenyl-, m.p. 267—268°, -2:6-di-p-tolyl- (V), m.p. 269—270°, and -2:6-dianisyl- (VI), m.p. 218—220°, -4-m-hydroxyphenyl-1:4-dihydropyridines are similarly prepared using  $m\text{-OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$ . (V) and (VI) are oxidised ( $\text{N}_2\text{O}_3$ ) to the compound,  $m\text{-OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{CO} \cdot \text{CN})_2$ , m.p. 256—257°. H. B.

**Isatogens and indoles.** XII. Oxidative fission of indoxyl derivatives by atmospheric oxygen in



alkaline solution. P. RUGGLI, A. ZIMMERMANN, and O. SCHMID (Helv. Chim. Acta, 1933, 16, 1249—1256; cf. A., 1933, 602).—6-Nitro-2-phenylisatogen (improved prep.) is reduced by  $\text{NHPh}\cdot\text{NH}_2$  in EtOH to 6-nitro-2-phenylindoxyl (I), m.p. 215°. (I) in EtOH containing a little NaOH at 35° is transformed by air into *Et* 4-nitrobenzoylanthranilate (II), m.p. 179—180°, and 4-nitrobenzoylanthranilic acid (III), m.p. 251° (decomp.), when rapidly heated (*K*, *Na*, and *Ag* salts). (III) is obtained in very poor yield by oxidation of *o*-nitro-*o*-benztoluidide with  $\text{KMnO}_4$  in  $\text{H}_2\text{O}$ ; addition of  $\text{C}_6\text{H}_5\text{N}$  is not helpful. Preferably, 4-nitro-*o*-acetotoluidide is oxidised by  $\text{KMnO}_4$  to 4-nitro-2-acetamidobenzoic acid, m.p. 220°, which is hydrolysed (HCl in  $\text{H}_2\text{O}$ -EtOH) and benzoylated. (III) is esterified with great difficulty (*Ag* salt used) hence it is improbable that (II) is derived from (III) during oxidation of (I). Similarly 6-nitro-2-phenyl-5-styrylindoxyl is oxidised to 4-nitro-5-styrylbenzoylanthranilic acid, m.p. 279° (decomp.). H. W.

**Binuclear isomerism of the diphenyl type.** II. (MISS) A. J. CHALMERS and F. LIONS (J. Proc. Roy. Soc. New South Wales, 1933, 67, 178—199; cf. A., 1931, 631).—*Et*  $\alpha\beta$ -dibenzoylpropionate, m.p. 65—68° (lit. 55—58°), led to 2:5-diphenyl-1- $\alpha$ -naphthylpyrrole-3-carboxylic acid, m.p. 278—280° (lit. 271—272°). Phenylacetoveratronephenylhydrazone, m.p. 153—154°, and HCl-EtOH give 3-phenyl-2-(3':4'-dimethoxyphenyl)indole, m.p. 197°.  $\beta$ -3:4-Dimethoxybenzoylpropionic acid (modified prep.), m.p. 163° (6- $\text{NO}_2$ -derivative, m.p. 115°), gives the *as*-phenylmethylhydrazone, m.p. 171°, which with HCl in boiling xylene gives a poor yield of 2-(3':4'-dimethoxyphenyl)-1-methylindole-3-acetic acid, m.p. 153—156° (*Br*-derivative, m.p. 206—207°).  $\beta$ -2:4-Dimethoxyphenylisobutyric acid and  $\text{NHPh}\cdot\text{NHMe}$  in hot AcOH give 2-(2':4'-dimethoxyphenyl)-1-methylindole-3-acetic acid, m.p. 210°. *Et*  $\alpha$ -*o*-bromobenzylacetate, b.p. 165—180°/2 mm., and 2:5-dichlorobenzene diazonium chloride give *Et*  $\alpha$ -*o*-bromobenzyl- $\alpha$ -2:5-dichlorobenzeneacetate, m.p. 142—143°, which with HCl-EtOH gives *Et* *o*-bromophenylpyruvate-2:5-dichlorophenylhydrazone, m.p. 108—109°, hydrolysed to the corresponding acid, m.p. 197°, which is re-esterified by HCl-EtOH, no indole ring-closure taking place. By the diazonium salt-hydrazone method are prepared *Et* 4:7-dichloro-3-phenylindole-2-carboxylate, m.p. 130° (corresponding acid, m.p. 246—248°), *Et* 3-*o*-bromophenylindole-2-carboxylate, m.p. 164—165° [corresponding acid, m.p. 235° (softening at 224°), and  $+\text{CHCl}_3$ , m.p. 231—232°], and *Et* 3-*o*-bromophenyl-4:5- and -5:6-benzoindeole-2-carboxylate, m.p. 245° and 217°, respectively, or *vice versa* [corresponding acids, m.p. (anhyd. or  $+\text{COMe}_2$ ) 228—230° ( $\text{NO}_2$ -derivative, m.p. 285°) and 188—189° ( $\text{NO}_2$ -derivative, m.p. 227°), respectively, do not form alkaloidal salts]. 3:4-Dimethoxybenzoylpyruvic acid and  $\text{NHPh}\cdot\text{NHMe}$  in hot EtOH give 3-(3':4'-dimethoxyphenyl)-1-methylindole-2-carboxylic acid, m.p. 194°, which with EtOH-HCl gives 3-(3':4'-dimethoxyphenyl)-1-methylindole, m.p. 104° ( $\text{NO}_2$ -derivative, m.p. 166°). R. S. C.

**Poly-membered heterocyclic compounds.** I. *cyclo*Octamethyleneimine, *cyclopentadecamethyleneimine*, *cyclohexadecamethyleneimine*,

and *dicyclopentadecamethylenedi-imine*. J. RUZICKA, M. W. GOLDBERG, M. HURBIN, and H. A. BOEKENOOGEN (Helv. Chim. Acta, 1933, 16, 1323—1334).—*cyclo*Octanoneoxime is converted by  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  (4:1 by vol.) into *cyclo*octanoneisooxime (I)  $[\text{CH}_2]_7\text{<}\begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix}$ , b.p. 164—166°/14 mm., m.p. 72—73°, also obtained from *cyclo*octanone,  $\text{N}_3\text{H}$ , and conc.  $\text{H}_2\text{SO}_4$  in  $\text{C}_6\text{H}_6$ . (I) is converted by successive action of  $\text{K}_2\text{S}$  and  $\text{P}_2\text{S}_5$  in xylene into *cyclo*octanoneithioisooxime (II)  $[\text{CH}_2]_7\text{<}\begin{smallmatrix} \text{CS} \\ \text{NH} \end{smallmatrix}$ , m.p. 89°, preferably prepared from (I) and  $\text{P}_2\text{S}_5$  in xylene with subsequent addition of NaOH. Reduction of (I) with Na and boiling EtOH leads to *cyclo*octamethyleneimine (III)  $[\text{CH}_2]_8\text{>NH}$ , b.p. 69°/17 mm. (yield > 10%) [hygroscopic hydrochloride, m.p. 153—155°; picrate, m.p. 148—149°], *o*-hydroxyoctylamine, m.p. 45° (*o*-hydroxyoctyl-carbamide, m.p. 94°, and *phenyl*carbamide, m.p. 147—148°), and an unidentified compound, m.p. 68—69°. (III) is not obtained in appreciable amount by treatment of (II) with Zn dust or Na-Hg in AcOH or with Al-Hg or Mg-Hg in  $\text{H}_2\text{O}$ ; better results are obtained with Na and AcOH-EtOH and an 85% yield results by electrolytic reduction in 55%  $\text{H}_2\text{SO}_4$  at a Pb cathode. *cyclo*Pentadecanoneoxime is transformed by  $\text{H}_2\text{SO}_4$  into *cyclopentadecanoneisooxime*, b.p. about 170°/0.2 mm., m.p. 133—134°, and thence into *cyclopentadecanoneithioisooxime*, m.p. 104—105°, reduced (Na and AcOH-EtOH) to *cyclopentadecamethyleneimine*, b.p. 112—114°/0.05 mm., m.p. 48—49° [hydrochloride, m.p. 170—173° (decomp.) after softening at 165°; acetate, m.p. (indef.) 60—80°; picrolonate, m.p. 221—222° (decomp.) after softening and darkening at 215°]. *cyclo*Hexadecanone,  $\text{N}_3\text{H}$ , and  $\text{H}_2\text{SO}_4$  in  $\text{C}_6\text{H}_6$  yield *cyclohexadecanoneisooxime*, m.p. 125—126°, whence successively *cyclohexadecanoneithioisooxime*, m.p. 104—105°, and *cyclohexadecamethyleneimine* (Tafel reduction), b.p. 126—127°/0.2 mm., m.p. 58—59° (picrolonate, m.p. 208—210°; non-cryst. acetate; tartrate, m.p. about 154°). *cyclo*Triacontane-1:16-dionedioxime is isomerised to *cyclo*triacontane-1:16-dionediisooxime, m.p. 178—179°, whence *cyclo*triacontane-1:16-dionedithioisooxime, m.p. 177°, reduced by Na and AcOH-amyl alcohol to *cyclo*dipentadecamethylenedi-imine,  $\text{NH}<\begin{smallmatrix} [\text{CH}_2]_{15} \\ [\text{CH}_2]_{15} \end{smallmatrix}\text{NH}$  or  $\text{NH}<\begin{smallmatrix} [\text{CH}_2]_{16} \\ [\text{CH}_2]_{14} \end{smallmatrix}\text{NH}$ , m.p. 62—63° [dihydrochloride, decomp. > 260°; diacetate, m.p. (indef.) 120°].

H. W.

**Addition of 8-hydroxyquinoline by thorium and uranium 8-hydroxyquinolates.** F. J. FRERE (J. Amer. Chem. Soc., 1933, 55, 4362—4365).—Th and  $\text{UO}_2$  8-quinoloxides (I) form an additive compound with 8-hydroxyquinoline (II). On heating (II) is driven off, but (I) combines with a further quantity of (II) to nearly the former val. E. S. H.

**Derivatives of 8-aminoquinoline as antimalarials.** II. Influence of the length of the chain in position 8. O. J. MACIDSON and I. T. STRUKOV (Arch. Pharm., 1933, 271, 569—580; cf. A., 1933, 956, 1071).— $\gamma$ -Diethylaminopropyl alcohol (prepared in 72% yield from  $\gamma$ -chloropropyl acetate and  $\text{NH}_4\text{Et}_2$ )



and  $\text{SOCl}_2$  in  $\text{C}_6\text{H}_6$  give *diethyl- $\gamma$ -chloropropylamine*, b.p.  $82^\circ/28$  mm.,  $169\text{--}171^\circ/760$  mm., the hygroscopic *hydrochloride*, m.p.  $62\text{--}64^\circ$ , of which with 8-amino-6-methoxyquinoline in dry EtOH at  $100^\circ$  gives 8- $\gamma$ -diethylaminopropylamino-6-methoxyquinoline (I), b.p.  $198\text{--}201^\circ/1\text{--}2$  mm. [meconate, m.p.  $133\text{--}134^\circ$  (decomp.)]. The 6-OEt-analogue, b.p.  $214\text{--}218^\circ/2\text{--}3$  mm., similarly prepared, and 40% HBr at  $150^\circ$  give 6:8-dihydroxyquinoline, m.p.  $230^\circ$ .  $\text{NEt}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$  and  $\text{CHNa}(\text{CO}_2\text{Et})_2$  give *Et*<sub>2</sub>  $\beta$ -diethylaminomalonate, b.p.  $136\text{--}142^\circ/12$  mm., which led to *Et* 8-diethylaminobutyrate, b.p.  $103\text{--}105^\circ/16\text{--}17^\circ$  mm., 8-diethylaminobutyl alcohol, b.p.  $90\text{--}92^\circ/7\text{--}9$  mm., and chloride, cryst., and 8-8-diethylaminobutylamino-6-methoxyquinoline (II), b.p.  $200\text{--}210^\circ/3$  mm. (dihydrochloride, cryst., hygroscopic). Similarly were obtained *Et*<sub>2</sub>  $\gamma$ -diethylaminopropylmalonate, b.p.  $149\text{--}151^\circ/4$  mm., *Et* 8-diethylaminovalerate, b.p.  $130\text{--}131^\circ/25$  mm.,  $\epsilon$ -diethylaminoamyl alcohol, b.p.  $131^\circ/23\text{--}24$  mm., and chloride (hydrochloride, m.p.  $55\text{--}56^\circ$ ),  $\epsilon$ -diethylaminoamylamino-6-methoxyquinoline (III), b.p.  $216\text{--}221^\circ/2\text{--}3$  mm. [meconate, m.p.  $120\text{--}122^\circ$  (decomp.)], 8- $\beta$ -hydroxy- $\gamma$ -diethylamino- (IV), b.p.  $240\text{--}245^\circ/2$  mm., and (from  $\gamma$ -piperidinopropyl chloride) 8- $\gamma$ -piperidino-propylamino-6-methoxyquinoline (V), b.p.  $227\text{--}232^\circ/2\text{--}3$  mm. (NO-compound, cryst.). Piperidine and  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$  at  $100^\circ$  give  $\alpha\beta$ -dihydroxy- $\gamma$ -piperidinopropane, b.p.  $128\text{--}130^\circ/7$  mm., m.p.  $67\text{--}68^\circ$ . 8-Amino-6-ethoxyquinoline and  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Me}$  at  $50^\circ$  give 8-ethylamino-6-ethoxyquinoline, b.p.  $168\text{--}173^\circ/3$  mm., m.p.  $53^\circ$  (*p*-toluenesulphonate, m.p.  $68^\circ$ ; hydrochloride, m.p.  $200\text{--}201^\circ$ ), which led to 8-N-ethyl-N-( $\beta$ -diethylaminoethyl)amino-6-ethoxyquinoline (VI), b.p.  $192\text{--}193^\circ/1$  mm., and (by  $\gamma$ -diethylaminopropylene glycol and Na in xylene at  $120\text{--}150^\circ$ ) 8-N-ethyl-N-( $\beta$ -hydroxy- $\gamma$ -diethylaminopropyl)amino-6-ethoxyquinoline (VII), b.p.  $207\text{--}212^\circ/1$  mm. 8-Nitro-6-hydroxyquinoline and  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{NEt}_2$  in hot NaOH-EtOH give 8-nitro-6- $\beta$ -diethylaminoethoxyquinoline, m.p.  $47\text{--}5^\circ$ , reduced by  $(\text{NH}_4)_2\text{S}$  to the 8-NH<sub>2</sub>-compound (VIII) (hydrochloride,  $+2\text{H}_2\text{O}$ , m.p.  $209\text{--}212^\circ$ ; Ac derivative, m.p.  $141^\circ$ ); the Bz derivative, m.p.  $57^\circ$  (hydrochloride, m.p.  $200\text{--}201^\circ$ ), with KOEt and EtI gives 8-N-benzoyl-N-ethylamino-6- $\beta$ -diethylaminoethoxyquinoline (dihydrochloride, m.p.  $182\text{--}183^\circ$ ). 8-N-Benzoyl-N-( $\beta$ -diethylaminoethyl)amino-6- $\beta$ -diethylaminoethoxyquinoline (trihydrochloride, m.p.  $83^\circ$ ) was similarly obtained.  $D_{\text{tol.}}/D_{\text{cur.}}$  for 8- $\beta$ -diethylaminoethylamino-6-methoxyquinoline, (I), (II), (III), (IV), (VI), (VII), (V), and (VIII) against malaria in canaries is 6, 26.5, 10.6, 25, 14, 0, 0, 6, and 0, respectively. In clinical tests (I) effected 90% of cures in tertiary and quaternary, and 50% in tropical, malaria. It is less toxic than plasmoquine and less often causes complications. It acts on the gametes. R. S. C.

Attempts to find new antimalarials. VI. Preparation of  $\beta$ -6:7-dimethoxyquinaldyl(4)-ethylamine dihydrochloride. K. MIKI and R. ROBINSON (J.C.S., 1933, 1467—1469).— $\beta$ -2-Nitro-4:5-dimethoxybenzoylpropionic acid (cf. Haq *et al.*, A., 1933, 1060) is reduced to the NH<sub>2</sub>-compound, which condenses with  $\text{COMe}_2$  to  $\beta$ -6:7-dimethoxyquinaldyl(4)-propionic acid (I), m.p.  $249^\circ$  [hydrochloride, m.p.  $216^\circ$

(decomp.)]. The acid is converted successively into the Me ester, m.p.  $101.5\text{--}102^\circ$ , hydrazide, m.p.  $188.5^\circ$ , azide, decomp.  $94\text{--}95^\circ$ , and  $\beta$ -6:7-dimethoxyquinaldyl(4)-ethylurethane, m.p.  $154^\circ$ , and -ethylamine, m.p.  $249^\circ$  (dihydrochloride). (I), EtOH, and NaOH give a substance, m.p.  $271\text{--}272^\circ$  (decomp.). F. R. S.

Symmetrical sec.-hydrazides of pyridine- and quinoline-monocarboxylic acids. R. GRAF [with H. RUDLER] (J. pr. Chem., 1933, [ii], 138, 289—291).—sec.-Hydrazides,  $(\text{NH}\cdot\text{CO}\cdot\text{R})_2$ , where R is 2-, m.p.  $218\text{--}219^\circ$ , 3-, m.p.  $227\text{--}228^\circ$ , and 4-, m.p.  $254\text{--}255^\circ$ , -pyridyl, 2-, m.p.  $239\text{--}240^\circ$ , and 4-, m.p.  $254\text{--}256^\circ$ , -quinolyl, and 2-phenyl-4-quinolyl, m.p.  $328\text{--}329^\circ$  (decomp.) (previous darkening), are prepared from the appropriate  $\text{R}\cdot\text{COCl}$  and  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  in  $\text{C}_6\text{H}_6$ . H. B.

N-Methylolamides of pyridine- and quinoline-monocarboxylic acids. R. GRAF [with H. RUDLER] (J. pr. Chem., 1933, [ii], 138, 292—298).—The following are prepared from the appropriate amide, 40%  $\text{CH}_2\text{O}$ , and aq.  $\text{K}_2\text{CO}_3$  (or KOH): pyridine-2-, m.p.  $102\text{--}104^\circ$ , and -3-, m.p.  $141\text{--}142^\circ$  (decomp.), 6-methylpyridine-2-, m.p.  $95^\circ$  (sinters from  $90^\circ$ ), quinoline-2-, m.p.  $129\text{--}131^\circ$ , and 2-butoxyquinoline-4-, decomp. from  $129^\circ$  (loss of  $\text{CH}_2\text{O}$ ) (clear melt at  $140^\circ$ ), -carboxy-N-methylolamides. Treatment of 2-butoxyquinoline-4-carboxylamide, m.p.  $161\text{--}162^\circ$  (from 2-chloroquinoline-4-carboxylamide and  $\text{BuOH}\cdot\text{NaOBu}$ ), with 40%  $\text{CH}_2\text{O}$  and  $\text{NH}_4\text{Et}$  in MeOH gives 2-butoxyquinoline-4-carboxydiethylaminomethylamide (I), m.p.  $69\text{--}71^\circ$ , which possesses anaesthetic properties but is rapidly hydrolysed by dil. acids. Hydrolysis (20% HCl) of (I) gives methylenedi-(2-butoxyquinoline-4-carboxylamide), m.p.  $> 290^\circ$ ;  $\text{NHBz}\cdot\text{CH}_2\cdot\text{NEt}_2$  is hydrolysed (10% HCl) to  $\text{CH}_2(\text{NHBz})_2$  (Einhorn *et al.*, A., 1906, i, 245). 3-Cyanopyridine is a by-product in the prep. of pyridine-3-carboxylamide from the chloride and dry  $\text{NH}_3$  in  $\text{C}_6\text{H}_6$ . H. B.

Complex bromo-compounds of antimony.—See this vol., 43.

Acridine derivatives. (SIGNA.) L. MONTI (Gazzetta, 1933, 63, 724—730).—N-Hydroxymethylchloroacetamide and -benzamide with acridine and  $\text{H}_2\text{SO}_4$  give, respectively, N-acridylmethylchloroacetamide and -benzamide, m.p.  $172\text{--}174^\circ$  and  $162\text{--}164^\circ$ , either of which can be hydrolysed to acridylmethylamine [picrate, m.p.  $202\text{--}204^\circ$  (decomp.)] by acid, but is decomposed by alkali. 9-Methylacridine in HCl with  $\text{CH}_2\text{O}$  and  $\text{NHMe}_2$  or piperidine yields, respectively,  $\beta$ -9-acridylethylidimethylamine dihydrochloride, m.p.  $185\text{--}190^\circ$  (decomp.) (corresponding picrate, decomp.  $130\text{--}135^\circ$ ), or 9- $\beta$ -piperidinoethylacridine dihydrochloride, m.p.  $169\text{--}170^\circ$  (corresponding picrate, m.p.  $138\text{--}140^\circ$ ). E. W. W.

Effect of unsaturated aliphatic groups in barbituric acids. H. A. SHONLE and J. H. WALDO (J. Amer. Chem. Soc., 1933, 55, 4649—4652).— $\delta$ -Chloro- $\Delta^8$ -pentene, b.p.  $58^\circ/155$  mm.,  $\delta$ -chloro- $\Delta^8$ -hexene, b.p.  $73\text{--}76^\circ/136$  mm., and  $\gamma$ -bromohexane, b.p.  $65.8\text{--}67^\circ/49$  mm., are prepared from the corresponding alcohols and  $\text{HHal}$  in the cold. *Et* isoamylpropargyl, b.p.  $142^\circ/11$  mm.— $151^\circ/14$  mm., ethyl-( $\alpha$ -methyl- $\Delta^8$ -butenyl)-, b.p.  $135\text{--}138^\circ/15$  mm., ethyl-( $\alpha$ -ethyl- $\Delta^8$ -butenyl)-, b.p.  $143.4\text{--}144.6^\circ/15$  mm., ethyl-( $\alpha$ -ethyl-



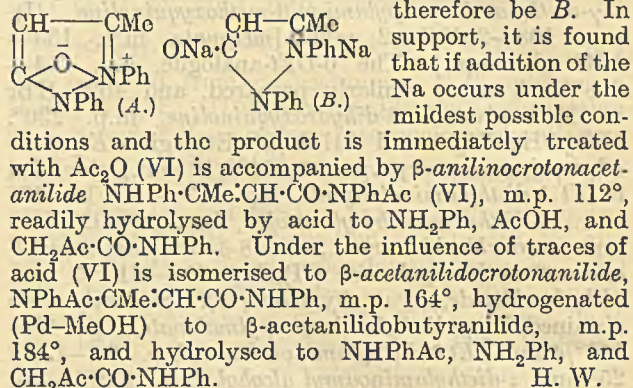
*butyl*-, b.p. 132.8°/8.5 mm.—135°/9 mm., and *propyl*-*sec*-.*butyl*-, b.p. 112°/6 mm.—114°/5 mm., -malonates are prepared and purified by the method previously described (A., 1930, 1047). 5-*sec*-.*Butyl*-5-*propargyl*-, m.p. 167—168°, 5-*isoamyl*-5-*propargyl*-, m.p. 163—164°, 5-*ethyl*-5- $\alpha$ -*methyl*- $\Delta^{\beta}$ -*butenyl*- (I), m.p. 114.5—116°, 5-*ethyl*-5- $\alpha$ -*ethyl*- $\Delta^{\beta}$ -*butenyl*- (II), m.p. 93—94°, 5-*ethyl*-5- $\alpha$ -*ethylbutyl*-, m.p. 112—115°, and 5-*propyl*-5-*sec*-.*butyl*-, m.p. 136—138°, -barbituric acids are prepared by the usual method. (I) and (II) have smaller hypnotic actions than the corresponding saturated compounds; they cause convulsions even in small doses. H. B.

**Microscopic determination of barbital and dial by ammoniacal silver nitrate; crystallographic study.** C. STRYZOWSKI and L. DEVERIN (Helv. Chim. Acta, 1933, 16, 1288—1291).—Detailed description is given of the microscopic characters of the crystals obtained by the interaction of diethyl- and diallyl-barbituric acid with  $\text{NH}_3\text{-AgNO}_3$  under varied conditions. H. W.

**Microchemical behaviour of antipyrine.** C. VAN ZIJP (Pharm. Weekblad, 1933, 70, 1243—1248).—Antipyrine (I) with  $\text{KNO}_3\text{-HNO}_3$  (dil.) gives blue-green dichroic crystals of the oximino-compound, which is converted by 50%  $\text{HNO}_3$  at 90—100° into a reddish-violet compound, of characteristic appearance under crossed nicols. (I) sublimes at 90° and crystallises from  $\text{H}_2\text{O}$  in rectangular, hexagonal (angles 116°, 128°) and rhombic (angles 114°, 66°) plates. Salipyrine gives the  $\text{HNO}_3$  reaction but does not crystallise like (I). Pyramidone does not give the reddish-violet colour. S. C.

**Constitution of antipyrine. Action of sodium on 1:2-diphenyl-3-methylpyrazolone.** A. HEYMONS and W. ROHLAND (Ber., 1933, 66, [B], 1654—1661).—Interaction of hydrazobenzene with  $\text{CH}_3\text{Ac-CO}_2\text{Et}$  at 130—150° and, after removal of  $\text{EtOH}$  and  $\text{H}_2\text{O}$ , at 160—180° leads to 1:2-diphenyl-3-methylpyrazole-5-one (I), m.p. 130° (*picrate*, m.p. 138°), identical with the "phenylhydroxymethylquinizine" of Müller and of Perger. (I) is transformed by Br in  $\text{CHCl}_3$  into 4-bromo-1:2-diphenyl-3-methylpyrazol-5-one, m.p. 145°, and by HCl and  $\text{NaNO}_2$  into non-cryst. 4-nitroso-1:2-diphenyl-3-methylpyrazol-5-one (II), converted by  $\text{NHPH-NH}_2$  in boiling  $\text{EtOH}$  into the compound  $\text{C}_{22}\text{H}_{21}\text{O}_2\text{N}_5$ . (II) is reduced by  $\text{SnCl}_2$  and HCl to 4-amino-1:2-diphenyl-3-methylpyrazol-5-one, m.p. 165°. Treatment of (I) with Na and  $\text{CO}_2$  in xylene leads to  $\text{NH}_2\text{Ph}$  and acetoacetanilide (due to hydrolysis of  $\beta$ -anilinocrotonanilide) and small amounts of 1:2-diphenyl-3-methylpyrazolidone-3-carboxylic acid (II), decomp. 122° (*Me* ester, m.p. 130°), which readily loses  $\text{CO}_2$  with production of 1:2-diphenyl-3-methylpyrazolid-5-one (III), m.p. 126°, very resistant towards dehydrogenation. Evidence of the position of  $\text{CO}_2\text{H}$  in (II) is found in its non-formation from  $\text{CO}_2$  and the Na enolate (IV) of (III). In absence of  $\text{CO}_2$  (I) adds 2Na giving a product (V) converted by the successive action of  $\text{Ac}_2\text{O}$  and  $\text{CO}_2$  into 4-acetyl-1:2-diphenyl-3-methylpyrazolid-5-one-3-carboxylic acid (VI), m.p. 165° (decomp.), passing by loss of  $\text{CO}_2$  into 4-acetyl-1:2-diphenyl-3-methylpyrazolid-5-one, m.p. 135° [also obtained from (IV) and  $\text{Ac}_2\text{O}$ ]. Reasons are advanced

for considering the production of (V) and consequently of (II) to occur secondarily from a common intermediate. This can be derived without difficulty only from the phenol-betaine form A of (I) and must therefore be B. In support, it is found that if addition of the Na occurs under the mildest possible conditions and the product is immediately treated with  $\text{Ac}_2\text{O}$  (VI) is accompanied by  $\beta$ -anilinocrotonanilide  $\text{NHPH-CMe:CH-CO-NPhAc}$  (VI), m.p. 112°, readily hydrolysed by acid to  $\text{NH}_2\text{Ph}$ ,  $\text{AcOH}$ , and  $\text{CH}_3\text{Ac-CO-NHPH}$ . Under the influence of traces of acid (VI) is isomerised to  $\beta$ -acetanilidocrotonanilide,  $\text{NPhAc-CMe:CH-CO-NHPH}$ , m.p. 164°, hydrogenated ( $\text{Pd-MeOH}$ ) to  $\beta$ -acetanilidobutyranilide, m.p. 184°, and hydrolysed to  $\text{NHPHAc}$ ,  $\text{NH}_2\text{Ph}$ , and  $\text{CH}_3\text{Ac-CO-NHPH}$ . H. W.



**Complex compounds of nitroso- and bromo-antipyrine.** R. RĂSCANU (Ann. Sci. Univ. Jassy, 1933, 18, 72—97).—The following complex salts are described ( $N$  = nitroso-,  $B$  = bromo-antipyrine):  $[\text{UO}_2, N_4](\text{NO}_3)_2$ ;  $2N, \text{H}_2\text{PtCl}_6, 2\text{H}_2\text{O}$ ;  $N, \text{HAuCl}_4, 2\text{H}_2\text{O}$ ;  $\text{CdCl}_2, 2(N, \text{HCl}), 2\text{H}_2\text{O}$ ;  $\text{H}_2\text{SnCl}_6, 3(N, \text{HCl}), 4\text{H}_2\text{O}$ ;  $[\text{UO}_2, B_2](\text{NO}_3)_2$ ;  $[\text{UO}_2, B_2]\text{Cl}_2$ ;  $[\text{UO}_2, B_2]\text{Br}_2$ ;  $N, \text{HBr}$  (by action of 40% aq.  $\text{HBr}$ ); and antipyrine hydrobromide, m.p. 179—180° (from perbromoantipyrine and boiling  $\text{COMe}_2$ ). All are decomposed by boiling  $\text{H}_2\text{O}$ , the  $\text{UO}_2$  compounds being most stable. H. A. P.

**2-Thiol-4(5)-hydroxymethylglyoxaline.** A. O. JACKSON and C. S. MARVEL (J. Biol. Chem., 1933, 103, 191—195).— $\text{o-C}_6\text{H}_4(\text{CO})_2\text{N} \cdot \text{CH}_2\text{-CO-CH}_2\text{Br}$  (I) and  $\text{NaOAc}$  in  $\text{EtOH}$  give  $\omega$ -acetoxyacetonylphthalimide, m.p. 141—142° [and not the  $\omega$ -OH-derivative as stated by Gabriel (A., 1911, i, 644)], hydrolysed (20%  $\text{HCl}$  at 85—95°) to  $\alpha$ -amino- $\gamma$ -hydroxyacetone hydrochloride, m.p. 136—137°. This and aq.  $\text{KCNS}$  afford 2-thiol-4(5)-hydroxymethylglyoxaline (II), m.p. 203—204°, converted by aq.  $\text{FeCl}_3$  into 4(5)-hydroxymethylglyoxaline. (II) and  $\text{SOCl}_2$  (or  $\text{HCl}$  in  $\text{CHCl}_3$  at 20—25° or conc.  $\text{HCl}$  at 70—75° give the pentahydrochloride, decomp. 265°, of a polymeric base,  $\text{C}_{20}\text{H}_{22}\text{ON}_{10}\text{S}_5$ , decomp. 300°, which gives the colour reactions of a 2-thiolglyoxaline. (I) and  $\text{CN-CH}_2\text{-CO-NH}_2$  afford cyanoacetyl- $\omega$ -phthalimidoacetonylamide, m.p. 196—197°, which with Br in  $\text{AcOH}$  gives  $\text{Br}_1$ -, m.p. 299—300° (Maquenne block), and  $\text{Br}_2$ -, m.p. 345—346° (Maquenne block), -derivatives. H. B.

**Methylation of pyrazoles with diazomethane.** K. VON AUWERS and O. UNGEMACH (Ber., 1933, 66, [B], 1690—1694).—Et 4-phenylpyrazole-5-carboxylate (I) is converted by treatment with  $\text{Me}_2\text{SO}_4$  and  $\text{NaOH}$  and subsequently with  $\text{EtOH-HCl}$  into 4-phenyl-1-methylpyrazole-5-carboxylic acid, m.p. 210—211° (decomp.) [transformed with difficulty into the *Et*, m.p. 52.5—53.5°, and *Me* (II), m.p. 69°, ester], and Et 4-phenyl-1-methylpyrazole-3-carboxylate [corresponding acid, m.p. (hydrated) about 100°, m.p. (anhyd.) 132°]. Treatment of (I) in  $\text{Et}_2\text{O}$  with  $\text{CH}_2\text{N}_2$  leads almost exclusively to (II) accompanied by only traces of the 1:3-derivative. Me 3-phenylpyrazole-5-carboxylate and  $\text{CH}_2\text{N}_2$  yield a product hydrolysed almost



exclusively to 3-phenyl-1-methylpyrazole-5-carboxylic acid. Similar differences in behaviour on treatment with KOH and  $\text{Me}_2\text{SO}_4$  or MeI or with  $\text{CH}_2\text{N}_2$  are not observed with 5(3)-chloro-3(5)-methylpyrazole.

H. W.

**Piperazine derivatives as local anaesthetics.** W. BRAKER and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1933, 22, 950—953).—*N*-Carbethoxymethylpiperazine, b.p. 153—159°/9—11 mm., obtained from piperazine and  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ , gives with  $\gamma$ -chloro-*n*-propyl alcohol *N*-carbethoxymethyl-*N'*- $\gamma$ -hydroxy-*n*-propylpiperazine (I), an oil. (I) is converted by  $\text{SOCl}_2$  into the corresponding chloropropyl derivative, an oil, which, with  $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Na}$  in dry EtOH, gives the *O*-*p*-aminobenzoyl derivative of (I), an oil. *NN'*-Bis-( $\beta$ -hydroxy- $\beta$ -methylhexyl)piperazine (Fournneau and Samdahl, A., 1930, 1597) forms a bisphenylurethane, m.p. 180—181°. The products are either unsuitable for biological trial, or exhibit little local anaesthetic activity.

W. S.

**Bis-2-pyridylaniline and *N*-2-pyridylpiperidine.** J. P. WIBAUT and G. TILMAN (Rec. trav. chim., 1933, 52, 987—990).—Interaction of 2-bromopyridine (I) with  $\text{NH}_2\text{Ph}$  at the b.p. gives 2-pyridylaniline (picrate, m.p. 219°), which with (I) and Cu-bronze in  $s\text{-C}_6\text{H}_5\text{Me}_3$  at the b.p. gives bis-2-pyridylaniline, m.p. 93° (corr.), which is non-basic. With  $\text{C}_5\text{H}_{11}\text{N}$  at 145° (I) gives *N*-2-pyridylpiperidine, b.p. 85°/0.06 mm. (picrate, m.p. 137.5—138.5°; picrolonate, m.p. 168°).

H. A. P.

**Pyrimidines. Molecular rearrangement of ethyl 2-ethylthiol-6-thiocyanopyrimidine-5-acetate.** Y. F. CHU and C. M. MA (J. Amer. Chem. Soc., 1933, 55, 4655—4657).—Et 6-chloro-2-ethylthiolpyrimidine-5-acetate (I), b.p. 174°/4 mm. (from the 6-OH-ester and  $\text{POCl}_3$  at 100°), and KCNS in  $\text{C}_6\text{H}_6$  give (impure) Et 2-ethylthiol-6-thiocyanopyrimidine-5-acetate (II), which with  $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  affords Et 2-ethylthiol-6-thiopyrimidine-5-acetate, m.p. 130—131°, also prepared from (I) and NaHS. (I) and KCNS in boiling PhMe give Et 2-ethylthiol-6-thiocarbamidopyrimidine-5-acetate (III), b.p. 190—200°/4 mm., which when distilled repeatedly passes into a polymeric form, b.p. 220°/4 mm., m.p. 140—141°. (II) is isomerised slowly at the b.p. to (III). Et 2-ethylthiol-6-thiocarbamidopyrimidine-5-acetate, m.p. 135—136° (free acid, m.p. 220—221°; acid amide, m.p. 230°), Et 2-ethylthiol-6-phenylthiocarbamidopyrimidine-5-acetate, m.p. 112.5—113°, and 2-ethylthiol-6-thiourethanopyrimidine-5-acetic acid, m.p. 146—148°, are prepared from (III) and the appropriate reagents.

H. B.

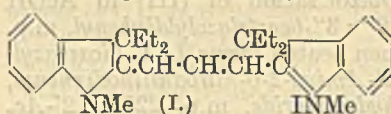
**Reactive capacity of the methyl group. I. Synthesis of 6 : 6'-dibenzoylindigotin.** L. CHARONNENS (Helv. Chim. Acta, 1933, 16, 1295—1302).—3-Nitro-4-methylbenzophenone (I) condenses with PhCHO in presence of piperidine at 150—155° to 2-nitro-4-benzoylstilbene, m.p. 120—121°. (I) and  $p\text{-NO}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$  in boiling EtOH containing anhyd.  $\text{Na}_2\text{CO}_3$  slowly afford 2-nitro-4-benzoylbenzaldehyde-*p*-dimethylanil (II), m.p. 174—175°; the corresponding Et<sub>2</sub> compound (III), m.p. 146—147°, is similarly prepared. (II) and (III) are hydrolysed by HCl- $\text{H}_2\text{O}$  in presence of  $\text{C}_6\text{H}_6$  to 2-nitro-4-benzoylbenzaldehyde (IV), m.p. 102.5—103° (phenylhydrazine, m.p. 206°;

2-nitro-4-benzoylbenzoic acid, m.p. 187—189°); a substance, m.p. 215°, was on one occasion obtained as by-product. (IV) condenses with  $\text{COMe}_2$  in presence of NaOH to 6 : 6'-dibenzoylindigotin, m.p. about 355—360° (decomp.). Bz thus appears able to activate the Me.

H. W.

**Alkylindoleninium iodide reds. (SIGNA.) E. GHERI (Gazzetta, 1933, 63, 698—701).—**

$\text{CHEt}_2\cdot\text{CMe}\cdot\text{N}\cdot\text{NH}_2 + \text{ZnCl}_2$  in MeOH form 2-methyl-3 : 3-diethylindolenine (A., 1899, i, 450) (picrate,



m.p. 188—189°), the methiodide of which with  $\text{CH}(\text{OEt})_3$  gives the indocyanine

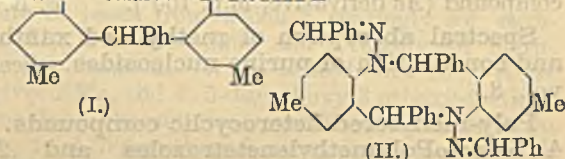
$\text{C}_{29}\text{H}_{37}\text{N}_2\text{I}$  (I), m.p. 271°. The ethiodide yields the compound " $\text{C}_{31}\text{H}_{42}\text{N}_2\text{I}$ " [ $\text{C}_{31}\text{H}_{41}\text{N}_2\text{I}$ ?], m.p. 293—294°; similar compounds  $\text{C}_{27}\text{H}_{33}\text{N}_2\text{I}$  and  $\text{C}_{35}\text{H}_{33}\text{N}_2\text{I}$ , m.p. 254° and 272°, are derived from 2 : 3-dimethyl-3-ethyl- and -3-phenyl-indolenines. All these indocyanines are intensely coloured.

E. W. W.

**Condensation of aldehydes with hydrazones.**

**VIII. Eight-membered heterocyclic nuclei. A. GLACALONE (Gazzetta, 1933, 63, 764—766).—**The substance (I) is prepared by diazotising and reducing 2 : 2'-diamino-5 : 5'-dimethyltriphenylmethane to the 2 : 2'-dihydrazino-compound, of which the hydrochloride, m.p. 190°, gives with PhCHO the 2 : 2'-di-

$\text{CHPh}\cdot\text{N}\cdot\text{N}\cdot\text{CHPh}\cdot\text{N}\cdot\text{N}\cdot\text{CHPh}$



benzylidenehydrazino-compound, and with further PhCHO and  $\text{H}_2\text{SO}_4$  the substance (I), m.p. 151—152°. This is not identical with the product from PhCHO and its *p*-tolylhydrazine (A., 1933, 402), which is probably (II). *p*-Benzylidenehydrazinobenzoic acid, m.p. 221°, does not condense further with PhCHO. E. W. W.

**Hydrolysis and reduction of hydan-toin-oxindoles.** H. R. HENZE and C. M. BLAIR (J. Amer. Chem. Soc., 1933, 55, 4621—4625).—Hydrolysis [aq.  $\text{Ba}(\text{OH})_2$  at 115—120°] of hydan-toin- $\Delta^5:3'$ -oxindole (I) gives oxindole; hydan-toin- $\Delta^5:3':5'$ -methyl-oxindole (II), m.p. > 310° (from 5-methylisatin, hydan-toin, AcOH,  $\text{Ac}_2\text{O}$ , and NaOAc at 150°), similarly affords 5-methyl-oxindole (III). Reduction of (I) by the method of Hill *et al.* (A., 1930, 480) gives hydan-toin-5 : 3'-oxindole, m.p. 281—282° (corr.; decomp.) (lit. 276°), hydrolysed (as above) to 2-keto-1 : 2-dihydroquinoline-4-carboxylic acid and not the 2 : 3-dihydroxy-3 : 4-dihydro-derivative (cf. Kotake, A., 1927, 1199). 1-Acetylhydan-toin- $\Delta^5:3'$ -1'-acetyl-oxindole has m.p. 258° (corr.; decomp.) (sinters at 240—245°) (cf. *loc. cit.*). Reduction [HI (*d* 1.7), AcOH] of (II) gives hydan-toin-5 : 3'-5'-methyl-oxindole, m.p. 306—307° (corr.; decomp.), hydrolysed (as above) to (III); reduction with red P, HI (*d* 1.7), and AcOH at 150° affords 2-keto-6-methyl-1 : 2 : 3 : 4-tetrahydroquinoline-4-carboxylic acid, m.p. 219—220°



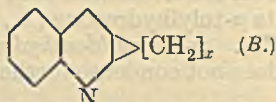
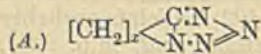
(corr.). 2-Keto-6-methyl-1:2:3:4-tetrahydroquinoline has m.p. 114—115° (corr.) (lit. 106°). H. B.

**Dicarbazyls.** IV. Synthesis of 1:1'-dicarbazyl. T. F. MACRAE and S. H. TUCKER. V. Synthesis of 3:9'-dicarbazyl. (MISS) M. C. NELNES and S. H. TUCKER (J.C.S., 1933, 1520—1523, 1523—1525).—IV. 2:2'-Diaminodiphenyl (I),  $\text{o-C}_6\text{H}_4\text{Cl-NO}_2$  (II), and  $\text{BaCO}_3$  give 2:2'-di-o-nitroanilinodiphenyl, m.p. 188.5—189.5° (NN'-Ac<sub>2</sub> derivative, m.p. 246—249°), reduced to the  $\text{NH}_2$ -compound (III), m.p. 225—227°. Diazotisation of (III) in AcOH affords 2:2'-di-1":2":3"-benztriazolyldiphenyl, m.p. 194—196°, which when heated forms 1:1'-dicarbazyl, m.p. 205—207°. 2'-Amino-2-o-nitroanilinodiphenyl, m.p. 113—114.5° (hydrochloride, m.p. 222°; 2'-Ac<sub>2</sub> compound, m.p. 192—194°), is obtained by heating (I) with (II) and  $\text{K}_2\text{CO}_3$  at 205—208° for 35 hr. 1:1'-Dicarbazyl is not identical with any of the products of oxidation of carbazole.

V. 9-p-Aminophenylcarbazole, obtained from the  $\text{NO}_2$ -derivative (improved prep.), with (II) and  $\text{Na}_2\text{CO}_3$  gives 9-p-(o-nitroanilino)phenylcarbazole, m.p. 181—185° (Ac derivative, m.p. 205—207°), reduced to the  $\text{NH}_2$ -compound (IV), m.p. 115—116° (picrate, m.p. 137°; o-Ac derivative, m.p. 180—181°). (IV) on diazotisation affords 9-p-1":2":3"-benztriazolylphenylcarbazole, m.p. 163°, converted into 3:9'-dicarbazyl, m.p. 212—214° (9-Ac derivative, m.p. 197°). Carbazole, (II), and  $\text{K}_2\text{CO}_3$  form 9-o-nitrophenylcarbazole, m.p. 156°, reduced to the  $\text{NH}_2$ -compound (Ac derivative, m.p. 150°). F. R. S.

**Spectral absorption of methylated xanthenes and constitution of purine nucleosides.**—See this vol., 8.

**Poly-membered heterocyclic compounds.** II. 4:5-cycloPolymethylenetetrazoles and 2:3-cyclopolymethylenequinolines. L. RŮŽICKÁ, M. W. GOLDBERG, and M. HURBIN (Helv. Chim. Acta, 1933, 16, 1335—1339; cf. this vol., 82).—A substance



$\text{C}_6\text{H}_{11}\text{N}_5$ , m.p. 90—91°, is derived from cyclohexanone,  $\text{H}_2\text{SO}_4$ , and  $\text{N}_3\text{H}$ . Treatment of cycloheptanone with  $\text{N}_3\text{H}$  and  $\text{H}_2\text{SO}_4$  in  $\text{C}_6\text{H}_6$  yields 4:5-cyclohexamethylene-tetrazole (A;  $x=6$ ), m.p. 66—68°. 4:5-cycloHeptamethylenetetrazole (A;  $x=7$ ), b.p. 145—146°/0.1 mm., and 4:5-cyclotetradecamethylenetetrazole (A;  $x=14$ ), m.p. 97—98°, are similarly obtained. cycloOctanone is converted by  $\text{o-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  in EtOH containing a little NaOH into 2:3-cyclohexamethylenequinoline (B;  $x=6$ ), b.p. 130—135°/0.1 mm. (hydrochloride, m.p. 200—202°; picrate, m.p. 212°). Similarly, cyclopentadecanone affords 2:3-cyclotridecamethylenequinoline (B;  $x=13$ ), b.p. 197°/0.1 mm. (picrate, m.p. 169—171°; hydrochloride; sulphate; phosphate). The physiological action of the compounds is described.

H. W.

**Chlorophyll-like bacterial pigment.**—See this vol., 112.

**Dioximes.** C. G. PONZIO. CI. M. MILONE. CII. E. DURIO (Gazzetta, 1933, 63, 730—743, 744—

746, 747—751).—C. Mol. wt. determinations show that the Ac derivative (A., 1923, i, 1020) of  $\alpha$ -phenylglyoxime peroxide is bimol.; it is renamed as the Ac<sub>2</sub> derivative of dibenzoylfuroxandioxime [3:4-diacetoximinodibenzyl-1:2:5-oxadiazole 2-oxide] (I), new m.p. 117—118°. When heated at 125—130°, (I) is converted into an isomeride (II), m.p. 130°; (I) or (II) in 20% NaOH with EtOH is hydrolysed in the cold to dibenzoylfuroxandioxime (III), m.p. 110° (decomp.), which is converted by  $\text{HNO}_3$  ( $d$  1.40) into a compound  $\text{C}_{16}\text{H}_{11}\text{O}_3\text{N}_3$ , m.p. 122°. At 100° (III), or (I) or (II) with EtOH, is isomerised by 5% NaOH to 3-benzoylformyl-4-phenyl-1:2:5-oxadiazole- $\alpha$ -dioxime (IV) (A., 1933, 726). (IV) can also be obtained from the compound described (A., 1931, 1157) as the dimeride of the Bz derivative of oximino-phenylacetone nitrile oxide, and now renamed as the Bz<sub>2</sub> derivative of dibenzoylfuroxandioxime [3:4-dibenzoximinodibenzoyl-1:2:5-oxadiazole 2-oxide]. Similarly the substance described (A., 1924, i, 294) as the Ac derivative of the oxide of  $p$ -toluoyl cyanide oxime is renamed as the Ac<sub>2</sub> derivative of di- $p$ -toluoylfuroxandioxime; it is converted by 5% NaOH + EtOH into 3- $p$ -toluoylformyl-4- $p$ -tolyl-1:2:5-oxadiazole- $\alpha$ -dioxime (V) (A., 1933, 726). The corresponding Bz derivative (A., 1931, 1157) is renamed as a Bz<sub>2</sub> derivative; it also yields (V). The Ac<sub>2</sub> derivatives of diaroyloxadiazole dioximes with  $\text{NHPh}\cdot\text{NH}_2$  give osazones, not of the diaroyloxadiazoles, but isomeric, and hence probably of the aroylformylaryloxadiazoles,  $\text{NHPh}\cdot\text{N}\cdot\text{C}(\text{Ar})\cdot\text{C}(\text{N}\cdot\text{NHPh})\cdot\text{C}_3\text{N}_2\text{O}\cdot\text{Ar}$ . Benzoylformylphenyloxadiazoleosazone, m.p. 177—178°, like dibenzoyloxadiazoleosazone (new m.p. 175—176°), resists acid or alkaline hydrolysis.  $p$ -Toluoylformyl- $p$ -tolylloxadiazoleosazone has m.p. 179°.

CI. The action of ultra-violet light on the  $\alpha$ -phenyl-,  $p$ -tolyl-, and -phenylmethyl-glyoximes, and on the  $\alpha$ - and  $\gamma$ -diphenylglyoximes (benzildioximes of m.p. 211° and 163°), causes isomerisation into the  $\beta$  forms (determined by their complex Ni salts), which are therefore considered the more stable. The change is more rapid in EtOH solution than in the solid.

CII. Glyoxime, and its Me, Me<sub>2</sub>, Me Et, and  $\alpha$ - and  $\beta$ -Ph,  $p$ - $\text{C}_6\text{H}_4$ ·Me, and Ph Me derivatives, all fail to react with  $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$ , as do the oximino-derivatives of CPhEt and COMe·CH<sub>2</sub>Ph.  $\beta$ -Chloroglyoxime, and chloro-oximino-acetone, -acetophenone, and - $p$ -methylacetophenone (best prepared by action of  $\text{Cl}_2$  on oximino- $p$ -methylacetophenone in AcOH) react to form 3-o-phenylenediaminoquinoxaline, m.p. 160—170°, and its 2-methyl, m.p. 242° (decomp.) (hydrolysable to 3-hydroxy-2-methylquinoxaline), 2-phenyl, decomp. 217—218° [Ac derivative, m.p. 155—156° (decomp.)], and 2- $p$ -tolyl, m.p. 217° (decomp.), derivatives; the last are also obtainable from the corresponding substituted chloroglyoximes.

E. W. W.

**Directive effect of [nuclear] substituents on cyclisation of  $s$ -diarylthiocarbamides.** II. Effect of the fluorine atom on thiazole cyclisation of  $p$ -fluoro- $s$ -diphenylthiocarbamides by bromine. III. Effect of the carbethoxy-group on formation of anilinobenzthiazoles from  $p$ -carbethoxy- $s$ -diphenylthiocarbamides and bromine. M. O. FAROOQ and R. F. HUNTER (J. Indian Chem.



Soc., 1933, 10, 465—470, 563—571; cf. A., 1933, 168).—II.  $p$ - $C_6H_4F \cdot NCS$  and the appropriate  $ArNH_2$  give 4-fluoro-4'-methyl-, m.p. 169°, 4-chloro-4'-fluoro-, m.p. 158—159°, 4-bromo-4'-fluoro-, m.p. 164—165°, and 4-fluoro-4'-nitro-, m.p. 170—171°, -s-diphenylthiocarbamides, which are converted by Br in  $CHCl_3$  into 4'-fluoro-5-methyl-, m.p. 183°, 5-chloro-4'-fluoro-, m.p. 222—223°, 5-bromo-4'-fluoro-, m.p. 222—223°, and 5-fluoro-4'-nitro-, m.p. 252—253°, -1-anilinobenzthiazole (intermediate hydroperbromides described), respectively. F thus resembles the other halogens (A., 1929, 582; 1930, 1452). 4'-Fluoro-5-nitro-1-anilinobenzthiazole has m.p. 278—279°. 1-Chloro-5-fluorobenzthiazole, m.p. 97—98°, is prepared from 5-fluoro-1-aminobenzthiazole.

III.  $p$ -Carbethoxy-s-diphenylthiocarbamide (I), m.p. 129—130° (from  $p$ - $CO_2Et \cdot C_6H_4 \cdot NCS$  and  $NH_2Ph$ ), and Br in  $CHCl_3$  give *Et* 1-anilinobenzthiazole-4'-carboxylate, m.p. 182—183° (hydroperbromide). 4-Bromo-4'-carbethoxy-, m.p. 158—159°, 4-carbethoxy-4'-methyl-, m.p. 160—161°, 4-chloro-4'-carbethoxy-, m.p. 159—160°, and 4-nitro-4'-carbethoxy-, m.p. 154—155°, -s-diphenylthiocarbamides similarly afford *Et* 5-bromo-, m.p. 227—228° [also obtained from (I) and an excess of Br], 5-methyl-, m.p. 206—207°, and 5-chloro-, m.p. 226°, -1-anilinobenzthiazole-4'-carboxylate and *Et* 4'-nitro-1-anilinobenzthiazole-5-carboxylate, m.p. 241—243°, respectively. *Et* 5-nitro-1-anilinobenzthiazole-4'-carboxylate, m.p. 242—243°, and analogous compounds are synthesised from the 5-substituted-1-chlorobenzthiazoles and the appropriate  $p$ - $C_6H_4R \cdot NH_2$ . The esters isolated (by cyclisation) are often impure. 1-Chloro-5-bromo-, m.p. 101—102° (lit. 89°), and 1:5-dichloro-, m.p. 101°, -benzthiazole are prepared from the 5-halogeno-1-aminobenzthiazoles. 1-Chlorobenzthiazole and cold  $HNO_3$  (d 1.5) give the 5- $NO_2$ -derivative.

H. B.

Thiazoles. XIX. Synthesis of "2-(*m*-nitrophenyl)benzothiazolyl *pp'*-disulphide" [2:2'-dinitro-4:4'-bisbenzthiazolyldiphenyl disulphide]. M. T. BOGERT and R. B. CONKLIN (Coll. Czech. Chem. Comm., 1933, 5, 443—447).—Interaction of 4-chloro-3-nitrobenzoyl chloride with ( $o$ - $NH_2 \cdot C_6H_4 \cdot S$ ) $_2$ Zn gives 2-(4'-chloro-3'-nitrophenyl)benzthiazole, m.p. 165.5—166.5° (corr.), which with  $Na_2S$  and S in boiling EtOH gives 2:2'-dinitro-4:4'-bisbenzthiazolyldiphenyl disulphide, m.p. 292—293° (corr.).

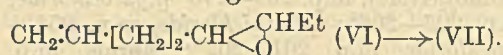
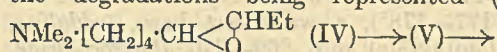
H. A. P.

Volatile alkaloid in *Helvella esculenta*. D. AYE (Arch. Pharm., 1933, 271, 537—539).—Fresh, but not dried, *H. esculenta* contain a small amount of a volatile, liquid alkaloid,  $C_8H_{12}$ (or  $14$ ) $N_2$  (impure picrate, m.p. 145—150°).

R. S. C.

Constitution of conhydrine. E. SPÄTH and E. ADLER (Monatsh., 1933, 63, 127—140).—Dehydration of conhydrine (I) ( $P_2O_5$  in PhMe at 120—140°) and reduction of the mixed coniceines ( $H_2$ -Pd in 20% AcOH) gives dihydroconiceine (II), the 2:4-dinitrobenzoyl derivative, m.p. 138—138.5°, of which racemises the corresponding derivative of (+)-coniine, thus confirming Loeffler's conclusion (A., 1909, i, 180) that (II) is identical with (−)-coniine. Hofmann degradation of the base from *N*-methylconhydrine methiodide (III), m.p. 221—223°, affords conhydrine-

methine (IV), b.p. 91°/10 mm.,  $[\alpha]_D^{25} + 30.36^\circ$  (picrate, m.p. 109—110° in vac.) (no double linking, CO, or OH group), which by long keeping with  $H_2O$  and subsequent addition of NaI re-forms (III). With MeI in  $COMe_2$  (IV) gives a methiodide (V), m.p. 134—135°,  $[\alpha]_D^{25} + 16.6^\circ$  in  $H_2O$ , Hofmann degradation of which gives a compound (VI), b.p. 157—159°/744 mm.,  $[\alpha]_D^{25} + 28.7^\circ$  [converted by  $H_2O$  at 170—180° into (VII)], and  $\epsilon\zeta$ -dihydroxy- $\Delta^8$ -*n*-octene (VII), m.p. 75—76°, reduced by  $H_2$ -Pd in  $H_2O$  to  $\gamma\delta$ -dihydroxy-*n*-octane (VIII), m.p. 94—96°. Low-temp. oxidation of (VII) with  $H_2SO_4$ - $KMnO_4$  gives EtCHO (as its dimedon compound) and  $(CH_2 \cdot CO_2H)_2$ , whereas (VIII) similarly treated affords *n*-valeric acid. These results confirm that (I) is 2- $\alpha$ -hydroxypropylpiperidine, the degradations being represented (III)→



J. W. B.

Cactus alkaloids. X. Constitution of peltotine and anhalonidine. E. SPÄTH and F. BOSCHAN (Monatsh., 1933, 63, 141—153).—The methiodide of peltotine (I) is converted by  $CH_2PhCl$  and NaOH in EtOH into its *O*- $CH_2Ph$  ether, m.p. 193—195°, and with EtI similarly into *O*-ethylpeltotine methiodide, m.p. 185—186°, converted by AgCl into the methochloride, which when heated with 4% Na-Hg in  $H_2O$  gives a basic oil, reduced ( $H_2$ -Pd in AcOH) to a mixture of bases from which a sparingly sol. methiodide (II), m.p. 238—239°, and a readily sol. methiodide are obtained. When heated with 25% KOH (II) gives  $NMe_3$  and 4:5-dimethoxy-3-ethoxy-2-ethylstyrene (not characterised), oxidised by  $KMnO_4$  in  $COMe_2$  to 4:5-dimethoxy-3-ethoxy-2-ethylbenzoic acid, m.p. 102—103°, which with  $HNO_3$  at  $-14^\circ$  affords 5:6-dinitro-3:4-dimethoxy-2-ethoxyethylbenzene (III), reduced by Zn-HCl to the corresponding 5:6-diamine (IV), m.p. 80.5—81° (*Bz* $_2$  derivative, m.p. 229—230°), the structure of which is proved by the following synthesis. 2-Hydroxy-3:4-dimethoxyacetophenone (V) (A., 1903, i, 272) is reduced (Clemmensen) to 2-hydroxy-3:4-dimethoxyethylbenzene, b.p. 124°/10 mm., the 2-Et ether, b.p. 122—123°/10 mm., of which is nitrated to (III), reduced to a diamine identical with (IV). The structure of (V) is proved by condensation with PhCHO, oxidation to 2-hydroxy-3:4-dimethoxybenzoic acid (A., 1904, i, 808), the 2-Et ether of which is identical with the acid obtained by ethylation and subsequent oxidation of 2-hydroxy-3:4-dimethoxybenzaldehyde (A., 1931, 1411). The revised structure of (I) (A., 1933, 77) and therefore of anhalonidine is thus confirmed.

J. W. B.

Hedyotine, an alkaloid from the root of *Hedyotis auricularia*. B. B. DEX and S. LAKSHMINARAYANAN (Arch. Pharm., 1933, 271, 485—490).—The roots of *H. auricularia*, Linn., yield to MeOH 0.12—0.28% of hedyotine,  $C_{16}H_{22}O_9N_2$ , unstable, not isolated pure (OMe absent) [hydrochloride, m.p. 245° (sinters at 227°; decomp. 250°); nitrate, m.p. 252° (decomp.) after sintering at 238°; picrate, m.p. 265° (decomp.); aurichloride, m.p. 305—310° (decomp.); platini-chloride; tetrachloroiodide, m.p. 167—170° (decomp.)];



(?) *perbromide*, m.p. from 240°; *dichromate*; compounds with metallic salts, amorphous]. R. S. C.

Reactions between amino-acids and nicotine. I. S. JAITSCHNIKOV (Biochem. Z., 1933, 265, 426—428).—Monoamino-diacids (aspartic and glutamic) and hippuric acid react with nicotine, but the monoamino-mono-acids (glycine, leucine) and asparagine do not. P. W. C.

*Toddalia aculeata* (Pers.). I. Two alkaloids and a neutral, crystalline substance from its root-walls. B. B. DEY and P. P. PILLAY (Arch. Pharm., 1933, 271, 477—485).—The root-walls of *T. aculeata* contain, besides known constituents, a lactone,  $C_{16}H_{20}O_6$ , m.p. 132—135° ( $Ac_2$  derivative, m.p. 111—112°; gives with very dil. NaOH an acid, m.p. 177—178°), a weak *tert.* base, *toddaline*,  $C_{17}H_{12}O_2(OMe)_2(NMe)$ , m.p. 269—270° [*hydrochloride*,  $+H_2O$ , m.p. 205—206°; *platinichloride*, m.p. 254—256°; *aurichloride*, m.p. 201—202°; *nitrate*, m.p. 239° (decomp.) after sintering at 235°; *picrate*, m.p. 237—238°; *sulphate*, m.p. 236—239° (decomp. from 210°)], and a strong base, *toddalinine*,  $C_{17}H_9O_3(OMe)(NMe)$ ,  $+0.5H_2O$ , m.p. 180—200° (decomp.) [*hydrochloride*,  $+2H_2O$ , m.p. 283—285°; *platinichloride*, m.p. 231—232° (decomp.); *picrate*, decomp. 230—235°]. Colour reactions differentiate the bases from berberine, which is not present in the root (cf. J.C.S., 1895, 67, 413). R. S. C.

Compounds from sparteine and cyclic substituted barbituric acids. F. MERCIER and L. J. MERCIER (Compt. rend., 1933, 197, 941—943).—The prep. and properties of the neutral (1:2) salts *sparteine* 5-phenyl-5-ethylbarbiturate (I), m.p. 148—150°, and 5-phenyl-5-methylbarbiturate (II), m.p. 154—156°, are described. No definite basic salts were obtained. (I) is more stable than (II). A. C.

Lupin alkaloids. VIII. Synthesis of  $\beta$ -lupinane. K. WINTERFELD and F. W. HOLSCHNEIDER (Ber., 1933, 66, [B], 1751—1756; cf. A., 1933, 78).—The Grignard compound from Et  $\gamma$ -bromopropyl ether transforms 2-acetylpyridine (I) into 2-pyridylmethyl- $\gamma$ -ethoxypropylcarbinol, b.p. 142—144°/11 mm., the *hydrochloride* of which is hydrogenated ( $PtO_2$ -Pt-black-abs. EtOH) to 2-piperidylmethyl- $\gamma$ -ethoxypropylcarbinol (II), b.p. 152—153°/12 mm. (II) is transformed by boiling HI into  $\beta$ -lupinane (*picrate*, m.p. 163°; *aurichloride*, m.p. 143—144°); further amounts of the base are obtained by treatment of the residues with NaOEt. The intermediate production of 2-8-iodo- $\alpha$ -methylbutylpiperidine is assumed. Analogous attempts to obtain 2-pyridylmethyl- $\gamma$ -phenoxypropylcarbinol from (I) gave  $\alpha,\epsilon$ -diphenoxyhexane, m.p. 83°, and unchanged (I). Treatment of (II) with  $PBr_5$  leads to a lupinane-like base. H. W.

Derivatives of 1-methyltropane. B. K. BLOUNT and R. ROBINSON (J.C.S., 1933, 1511—1512).—Lävulaldehyde (improved prep.),  $CO(CH_2CO_2)_2Ca$ , and  $NH_2Me$  yield 1-methyltropinone, b.p. 124°/27 mm. [*picrate*, m.p. 201° (decomp.); *methiodide*, m.p. 273—282° (decomp.)], reduced (Na-BuOH) to 1-methyl- $\psi$ -tropine, m.p. 71° [*picrate*, explodes 280°; *hydrobromide*, m.p. 286°], which with  $Bz_2O$  gives benzoyl-1-methyl- $\psi$ -

tropine (methyltropacocaine), b.p. 210°/15 mm. (*picrate*, m.p. 163—164°). F. R. S.

Green coloration of solutions of quinine salts. M. BACHSTETZ and G. CAVALLINI (Annali Chim. Appl., 1933, 23, 490—494).—The green coloration appearing in solutions of quinine salts (with or without urethane) on sterilisation or ageing is dependent on the presence of Cu and on an oxidising reaction catalysed by Cu. The compound  $(C_{20}H_{24}O_2N_2.HCl.2H_2O)_3.CuCl_2$  is described. The coloration may be avoided by crystallising the salt repeatedly and excluding  $O_2$  from the bottle containing the solution (cf. Erben, A., 1925, i, 573). T. H. P.

*Strychnos* alkaloids. LXXVII. Benzylidene and C-benzyl derivatives of brucine and strychnine and their sulphonic acids. H. LEUCHS and H. S. OVERBERG (Ber., 1933, 66, [B], 1711—1718; cf. A., 1933, 1061).—C-Benzylstrychninesulphonic acid I,  $[\alpha]_D^{20} -159^\circ$  in 0.1N-NaOH, is obtained by reduction of the C-CHPh derivative by Na-Hg and  $H_2O$ . Strychninesulphonic acid II, PhCHO, and NaOH afford C-benzylidene-,  $[\alpha]_D^{20} -441^\circ$  in 0.1N-NaOH, whence C-benzyl-,  $[\alpha]_D^{20} -123.3^\circ$  in 0.1N-NaOH, -strychninesulphonic acid II. C-Benzylidene- and C-benzyl-, m.p. 205° (decomp.), -strychninesulphonic acid III are analogously prepared. Benzylidene-strychnine is reduced to C-benzylstrychnine (I), m.p. (from EtOH) about 65°, decomp. about 90°, m.p. (from MeOH) 102—105° (decomp.),  $[\alpha]_D^{20} -76^\circ/d$  in EtOH (*methiodide*, decomp. about 305°). Oxidation of (I) with  $KMnO_4$  in  $COMe_2$  affords C-benzylstrychninonic acid, m.p. 208—210° (decomp.) after softening at 200°,  $[\alpha]_D^{20} -19.0^\circ$  in 0.1N-NaOH, and C-benzylstrychninolic acid, m.p. 220—223°, readily converted into benzylstrychninolone. C-Benzylidihydrostrychnine, m.p. 187—189° (vac.),  $[\alpha]_D^{20} -13.4^\circ/d$  in abs. EtOH [*methiodide*, m.p. about 310° (decomp.)], is prepared by reduction (Na-Hg in EtOH) of the corresponding CHPh derivative. Oxidation of benzylidenebrucine (II) ( $CrO_3$ ,  $O=18$ ) leads to the compound  $C_{23}H_{24}O_4N_2$  (*perchlorate*,  $[\alpha]_D^{20} -229^\circ/d$  in  $H_2O$ ). Reduction of (II) by Na-Hg in EtOH leads to C-benzylbrucine [*methiodide*, m.p. 255—258° (decomp.)], which is not advantageously oxidised by  $CrO_3$ , whereas hydrogenation ( $PtO_2$ ) leads to non-cryst. C-benzylidihydrobrucine (non-cryst. *methiodide*). Brucinesulphonic acid I, NaOH, and PhCHO in  $H_2O$ -EtOH afford benzylidenebrucinesulphonic acid I,  $[\alpha]_D^{20} -232^\circ$  in 0.1N-NaOH, reduced to benzylbrucinesulphonic acid I,  $[\alpha]_D^{20} -146.3^\circ$  in 0.1N-NaOH, which yields only BzOH as cryst. product of oxidation by  $CrO_3$  and oxidised by  $CrO_3$  in  $AcOH-H_2SO_4$  to the compound  $C_{23}H_{24}O_4N_2S$ , plates or prisms, which does not react with  $NH_2.CO.NH.NH_2$  or  $BaO_2$ . The  $CH_2Ph$  derivative of the Hanssen  $C_{16}$ -sulphonic acid has  $[\alpha]_D^{20} -104^\circ$  in 0.1N-NaOH.

[With DORNOV.] C-Benzylidenebrucinesulphonic acid II,  $[\alpha]_D^{20} -386.5^\circ$  in 0.1N-NaOH, is reduced (Na-Hg) to C-benzylbrucinesulphonic acid II,  $[\alpha]_D^{20} -112^\circ$  in 0.1N-NaOH. H. W.

Metathebainone. L. F. SMALL and E. MEITZNER (J. Amer. Chem. Soc., 1933, 55, 4602—4610).—Metathebainone (I) is reduced [ $H_2$ ,  $PtO_2$ , 0.2N-HCl



(sufficient for neutralisation)] to *metathebainol* (II), (+CHCl<sub>3</sub>), m.p. 87—88°, (+MeOH), m.p. 92—93°,  $[\alpha]_D^{25}$  —66.7° in EtOH (using solvent-free base) [*hydrochloride* (+EtOAc), m.p. 162° (decomp.), re-solidifying with decomp. > 220°; *hydriodide* (+H<sub>2</sub>O); *methiodide*, m.p. 225°; *Ac* derivative, m.p. 150° (becoming red; turns pink at about 143°); *Ac*<sub>2</sub> derivative, m.p. 140°, hydrolysed (aq. EtOH—KOH) to a new base, m.p. 150°, which could not be reduced (Na; Na—Hg; catalytic). Reduction of (I) by Kondo and Ochiai's method (A., 1929, 1088) gives 65% of (II) and 5% of dihydrometathebainone (III); reduction does not occur in EtOH or dil. AcOH using Pt or Pd. (III) is reduced (H<sub>2</sub>, PtO<sub>2</sub>, EtOH) to *dihydrometathebainol*, m.p. about 120° (*hydriodide* + 2H<sub>2</sub>O,  $[\alpha]_D^{25}$  +16.4° in H<sub>2</sub>O). Reduction (Wolff-Kishner) of (I) gives *dihydrodeoxymetacodeine*, b.p. 130—135°/0.001 mm.,  $[\alpha]_D^{25}$  —93.8° in EtOH; (III) similarly affords *tetrahydrodeoxymetacodeine* (*hydriodide*,  $[\alpha]_D^{25}$  —12.5° in H<sub>2</sub>O). (II) and EtOH—KOH at 160° give *anhydrometathebainol*, C<sub>18</sub>H<sub>21</sub>O<sub>2</sub>N, b.p. 130°/0.001 mm.,  $[\alpha]_D^{25}$  —201° in EtOH [(+MeOH), m.p. 107°; *Ac* derivative, m.p. 166°], reduced (H<sub>2</sub>, PtO<sub>2</sub>, EtOH) to *dihydroanhydrometathebainol*, b.p. 130°/0.001 mm. The so-called β-dihydrothebainone of Kondo and Ochiai (*loc. cit.*) is a mixture of (II) and (III). The existence of a diastereoisomeride of (III) has not yet been demonstrated.

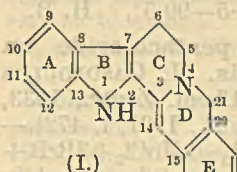
H. B.

**Synthesis of physostigmine (eserine). VIII.** F. E. KING, R. ROBINSON, and H. SUGINOME. **IX.** Improvement of the synthesis of *dl-eserethole*. F. E. KING, M. LIGUORI, and R. ROBINSON (J.C.S., 1933, 1472—1475, 1475—1477).—VIII. The product, m.p. 170°, obtained by decarboxylation (cf. A., 1932, 287) is 3-*keto-4-o-carboxybenzoyl-10-ethoxy-7-methyl-3:4:5:6-tetrahydro-4-ψ-carboline*. *l*-Eserethole forms a *H d-tartrate*, m.p. 164—165°, a *H d-racemate*, m.p. 159°, and a *H l-tartrate*, m.p. 172—173°. *dl*-Noreserethole and Me *p*-toluenesulphonate give *dl-eserethole H l-tartrate*, (+H<sub>2</sub>O), m.p. 125—140°, and the *methopicate*, m.p. 184—186°. 1-Eserethole *methopicate* has m.p. 190° (decomp.), and *dl-eserethole picrate*, 138—140°. αγ-Dibromobutane and PhOH give a phenoxybromide which condenses with Et methylmalonate to *Et ε-phenoxy-γ-methylpentane-ββ-dicarboxylate*, b.p. 211—212°/17 mm. The general correctness of the conclusions of Part II (*loc. cit.*) has been confirmed.

**IX.** γ-Phenoxy-α-methylbutaldehyde (improved yield; 2:4-dinitrophenylhydrazones, m.p. 109—110°) and *p*-methoxyphenylhydrazine give 5-methoxy-3-methyl-3-β-phenoxyethylindolenine, purified through the *picrate*, m.p. 157° (*methiodide*, m.p. 180—181°). The methochloride could not be heated with aq. HBr without suffering deep-seated change. γ-Phthalimido-α-methylbutyric acid forms successively the *amide*, m.p. 162—163°, the *nitrile*, m.p. 102°, and the *aldehyde* (2:4-dinitrophenylhydrazones, m.p. 191°), which with *p*-ethoxyphenylhydrazine gives 5-ethoxy-3-methyl-3-(β-phthalimidoethyl)indolenine, identical with the substance described in Part II. F. R. S.

**Yohimbine.** G. BARGER and C. SCHOLZ (Helv. Chim. Acta, 1933, 16, 1343—1354; cf. A., 1933,

840).—Distillation of yohimbine (I) with Se dust yields yobirine (II), which is C<sub>19</sub>H<sub>16</sub>N<sub>2</sub> instead of C<sub>10</sub>H<sub>18</sub>N<sub>2</sub> advocated by Mendlik *et al.* (A., 1931, 369); their "dihydroxybyrine" is consequently *tetrahydroxybyrine* (III). The nucleus E, obtained as *o*-C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)<sub>2</sub> by oxidation of (II), is tetra- and



hexa-hydrogenated in (III) and (I), respectively. The rings A, B, and C are identified in harmnan (*loc. cit.*) and D is identified by the oxidation of (III) with HNO<sub>3</sub> to berberonic [pyridine-1:4:5-tricarboxylic] acid. The structure explains the production of isoquinoline by distillation of (I) with Zn dust, rupture of ring C taking place. In general, ring D suffers preferential fission, thus explaining the production of 2:3-dimethylbenzoic acid by fusion of keto-yobirine (IV) with KOH (Mendlik *et al.*, *loc. cit.*); moderation of the action by use of KOH in amyl alcohol leads to the identification of norharman as second product of fission and thus renders account of all the atoms of (IV). Degradation can occur so that C-14 remains attached to ring C since *m*-toluic acid results from treatment of (I) or yohimboic acid with superheated steam or molten KOH. The possibility that the same C—N scaffolding is not present in (I) and (II) is discussed. For the primary product (III) conditions appear more favourable; its isolation from (V) by means of molten KOH or steam at 300° is described and it possibly results by distillation of (V) with CaO at 4 mm. pressure. The presence of NMe in (I) could not be detected. Oxidation of (I) gives only (·CH<sub>2</sub>·CO<sub>2</sub>H)<sub>2</sub>. H. W.

**Arsinic acids of the fluorenone and the fluorenol series.** G. T. MORGAN and (Miss) J. STEWART (J.C.S., 1933, 1454—1457).—Na aminofluorenone-2-arsinate and the appropriate carbamide yield *fluorenone-7-glycine-ureide* (Na salt), *-methylureide* [Na salt (+H<sub>2</sub>O)], and *-phenylureide-2-arsinic acid* (Na salt; Na<sub>2</sub> salt). Na 7-carbamylmethoxyfluorenone-2-arsinate, from 7-hydroxyfluorenone-2-arsinic acid, has increased trypanocidal activity. 9-Fluorenone-2-arsinic acid (Na salt) is obtained from 2-amino-9-fluorenol. Na 7-aminofluorenone-2-arsinate (I) (acid), by reduction of the fluorenone, with Ac<sub>2</sub>O gives 7-acetamido-9-fluorenone-2-arsinic acid (Na salt) and subsequently the 9-acetoxyfluorenone compound. (I), NH<sub>2</sub>·CO·CH<sub>2</sub>Cl, and NaI form a mixture of 9-fluorenone-7-glycineamide-2-arsinic acid (Na salt) and 9-O-carbamylmethylfluorenone-7-glycineamide-2-arsinic acid (Na<sub>2</sub> salt). (I) with KCNO in AcOH gives 7-carbamido-9-fluorenone-2-arsinic acid [Na salt (+2H<sub>2</sub>O)], with MeNCO forms the 7-Me derivative [Na<sub>2</sub> salt (+0.5H<sub>2</sub>O)], and with PhNCO yields the 7-Ph derivative [Na<sub>2</sub> salt (+3H<sub>2</sub>O)]. F. R. S.

**Preparation of derivatives of germanium triphenyl by means of sodium triphenylgermanide.** C. A. KRAUS and C. S. SHERMAN (J. Amer. Chem. Soc., 1933, 55, 4694—4697).—GePh<sub>3</sub>Pr<sup>a</sup>, m.p. 86—86.5°, GePh<sub>3</sub>Bu<sup>a</sup>, m.p. 84.5—85.5°, GePh<sub>3</sub>n-amyl, m.p. 42—43°, and GePh<sub>3</sub>benzyl, m.p. 82.5—83.5°, are prepared from NaGePh<sub>3</sub> and the requisite halide in liquid NH<sub>3</sub>.



$\text{NaGePh}_3$  and  $\text{GeEt}_3\text{Br}$  in  $\text{C}_6\text{H}_6$  give *triphenyltriethyl-digermane*,  $\text{GePh}_3\cdot\text{GeEt}_3$ , m.p. 89.5—90.5°. H. B.

**Action of molybdenum pentachloride on organomagnesium compounds.** I. GASOPOULOS (Praktika, 1932, 7, 180—183; Chem. Zentr., 1933, ii, 534; cf. Bennett and Turner, A., 1921, i, 472).—The reaction,  $6\text{MgRCl} + 2\text{MoCl}_5 = 2\text{MoCl}_2 + 3\text{R}\cdot\text{R} + 6\text{MgCl}_2$ , is energetic; the  $\text{MoCl}_5$  must be added in small portions to an  $\text{Et}_2\text{O}$  solution of excess of the Mg compound.  $\text{Ph}_2$ ,  $(\text{CH}_2\text{Ph})_2$ , 4:4'-ditolyl,  $(\cdot\text{CH}_2\text{Pr}^\beta)_2$ , and  $[\cdot\text{CH}_2\cdot\text{CH}_2\text{Pr}^\beta]_2$  have been prepared. A. A. E.

**New complex organomagnesium compound:  $\beta$ -magnesyphenylacetoneitrile.** D. IVANOFF and I. PAOUNOFF (Compt. rend., 1933, 197, 923—925).— $\text{CH}_2\text{Ph}\cdot\text{CN}$  and  $\text{RMgX}$  ( $\text{R}=\text{Ph}$ ,  $\text{Et}$ , and  $\text{Pr}^\beta$ ) yield  $\text{RH}$  and the Mg derivative  $\text{CN}\cdot\text{CHPh}\cdot\text{MgX}$  (I), converted by  $\text{CO}_2$  into  $\text{CN}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$  (II). The best yield (40%) of (II) is obtained when  $\text{R}=\text{Pr}^\beta$ . (I) reacts with  $\text{COPh}_2$  yielding, in addition to polymerides,  $\beta$ -hydroxy- $\alpha\beta$ -triphenylpropionitrile, m.p. 140—141°, and  $\alpha\beta$ -triphenylacrylonitrile. A. C.

**Labilities or electronegativities of unsaturated alkyl radicals as determined by hydrogen chloride scission of organo-lead compounds.** H. GILMAN, E. B. TOWNE, and H. L. JONES (J. Amer. Chem. Soc., 1933, 55, 4689—4693).—Mg  $\Delta^r$ -butenyl bromide and  $\text{PbPh}_3\text{Cl}$  give *Pb Ph<sub>3</sub>  $\Delta^r$ -butenyl*, m.p. 84—86°, which with  $\text{HCl}$  in  $\text{CHCl}_3$  at 40—45° affords *Pb Ph<sub>3</sub>  $\Delta^r$ -butenyl chloride*, m.p. 134—135° (decomp.), and  $\text{C}_6\text{H}_6$ . The following are prepared similarly, the fission products with  $\text{HCl}$  being given in parentheses: *Pb Et<sub>3</sub>  $\Delta^r$ -butenyl*, b.p. 78°/3 mm. (*Pb Et  $\Delta^r$ -butenyl dichloride* and  $\text{C}_2\text{H}_6$ ); *Pb Ph<sub>3</sub>  $\beta$ -styryl*, m.p. 107—109° (*PbPh<sub>3</sub>Cl* and styrene); *Pb Ph<sub>3</sub>  $\alpha$ -naphthyl* (62.5% of  $\text{C}_{10}\text{H}_8$ ); *Pb Ph<sub>3</sub> di- $\alpha$ -naphthyl* (*PbPh<sub>3</sub>Cl* and  $\text{C}_{10}\text{H}_8$ ); *Pb Ph<sub>3</sub> benzyl*, m.p. 91° ( $\text{C}_6\text{H}_6$  and *Pb Ph<sub>3</sub> benzyl chloride*, sinters at 157°); *Pb Ph<sub>3</sub> allyl* (*PbPh<sub>3</sub>Cl* and  $\text{C}_3\text{H}_6$ ) (cf. Austin, A., 1931, 1317). From the above and previous work (A., 1933, 71), the relative order of labilities is  $\alpha$ -thienyl,  $\alpha$ - $\text{C}_{10}\text{H}_7$  >  $\text{Ph}$  >  $\text{Et}$ ,  $\text{CH}_2\text{Ph}$  (as found for other organo-metallic compounds) and allyl,  $\beta$ -styryl >  $\text{Ph}$  >  $\Delta^r$ -butenyl. H. B.

**1:4-Selenothian.** C. S. GIBSON and J. D. A. JOHNSON (J.C.S., 1933, 1529—1530).—1:4-Selenothian,  $\text{S} \begin{smallmatrix} \text{CH}_2\text{CH}_2 \\ \text{CH}_2\text{CH}_2 \end{smallmatrix} \text{Se}$ , m.p. 107°, is prepared from  $(\text{CH}_2\text{Cl}\cdot\text{CH}_2)_2\text{S}$  (I) and aq.  $\text{Na}_2\text{Se}$ . (I) and  $\text{Al}_2\text{Se}_3$  at 150—170° give (after decomp. with  $\text{H}_2\text{O}$  and steam distillation) dithian and much  $\text{H}_2\text{Se}$ .  $(\text{CH}_2\text{Cl}\cdot\text{CH}_2)_2\text{Se}$  and aq.  $\text{Na}_2\text{S}$  afford  $\text{C}_2\text{H}_4$  (?) and  $\text{Se}$ . H. B.

**Vegetable proteins. II. Purified edestin and edestan.** G. FLORENCE, J. ENSELME, and M. POZZI (Bull. Soc. Chim. biol., 1933, 15, 1113—1116; cf. A., 1932, 1262).—In alkaline solution the ultra-violet absorption band of edestin (I) at 280  $\text{m}\mu$  tends to disappear. Edestan (II) shows an increased absorption in alkaline solution. (I) and (II) contain the same quantity of phenolic  $\text{NH}_2$ -acids but differ in ultra-microscopic appearance. H. D.

**Protein salts of organic bases.** M. A. LISSITZIN (Biochem. Z., 1933, 266, 25—28).—Caseinogen and similar proteins react with equiv. amounts of org.

bases (including alkaloids) to give compounds (I) many of which are  $\text{H}_2\text{O}$ -sol. (I) are not coagulated by heat unless a salt (e.g., of  $\text{Ca}$ ) is present but are pptd. unchanged by  $(\text{NH}_4)_2\text{SO}_4$ . W. McC.

**Validity of the mass action law in the reaction of proteins with acids and bases.**—See this vol., 36.

**Optical rotatory power of heat-denatured ovalbumin.** H. A. BARKER (J. Biol. Chem., 1933, 103, 1—12).—The  $[\alpha]$  of alkali-denatured ovalbumin increases with time of heating to a limiting val. (independent of temp.) which is reached the more quickly the higher is the temp. This val. is a function of the  $p_{\text{H}}$  and protein concn. of the solution. Any change of these factors after heating has little influence on  $[\alpha]$ . The  $p_{\text{H}}$  of an ovalbumin solution decreases in acid and increases in alkaline solution when heated.  $[\alpha]$  is the only property suitable for the quant. characterisation of a denatured protein. M. S. B.

**Secondary reaction between ovalbumin and acid.** G. ETTISCH and G. V. SCHULZ (Biochem. Z., 1933, 265, 370—374).—The secondary reaction (see A., 1933, 788) of ovalbumin with acid increases with rise of temp. and is associated with acid hydrolysis. P. W. C.

**Protamines of some species of fish.**—See this vol., 96.

**Action of heavy metals on cysteine and on thiol groups of proteins.** S. M. ROSENTHAL and C. VOEGTLIN (U.S. Pub. Health Rep., 1933, 48, 347—364).—Conditions for oxidative degradation of cysteine and coagulated ovalbumin (I) in presence of  $\text{Cu}$  are given.  $\text{Fe}$  and  $\text{Mn}$  cause cysteine  $\rightarrow$  cystine. With (I)  $\text{Mn}$  causes half the  $\text{O}_2$  absorption given with  $\text{Cu}$ , where oxidation of  $\cdot\text{SH}$  is suggested. The effects of  $\text{Fe}$  and  $\text{Cu}$  on dialysed tissues are described. NUTR. ABS. (m).

**Effect of ultra-violet, radium, and X-ray radiation on glutathione in pure solution.** G. E. WOODWARD (Biochem. J., 1933, 27, 1411—1414).—The concn. of total and reduced glutathione (I) after ultra-violet irradiation varied with the time of exposure and  $p_{\text{H}}$  of the solution. For  $p_{\text{H}}$  6.8 and  $t=4$  hr. the total (I) recovered was 62%, and the  $\text{SO}_4^{''}$  formed was 12.6%, the rest being sulphones and org. sulphides.  $\beta$ - and  $\gamma$ -rays exert a slight oxidative and destructive effect on (I); X-rays do not. H. D.

**Cystine from deaminised casein.** A. WHITE (J. Biol. Chem., 1933, 103, 295—297).—The proportion of cystine yielded by casein (I) on hydrolysis is uninfluenced by preliminary deamination of (I). H. D.

**Ter Meulen method for direct determination of oxygen in organic compounds.** W. W. RUSSELL and J. W. FULTON (Ind. Eng. Chem. [Anal.], 1933, 5, 384—386).—The method is improved by vaporising the substance in an electric furnace and using a Pt-coated  $\text{SiO}_2$  cracking surface and  $\text{ThO}_2$ -Ni as hydrogenation catalyst. R. S. C.

**Semimicro-determination of nitrogen by the Dumas method.** E. P. CLARK (J. Assoc. Off. Agric. Chem., 1933, 16, 575—580).—An improved apparatus and technique are described to deal with 15—25 mg.



of sample, a special feature being a cartridge composed of a mixture of sample and CuO powder between layers of fine CuO powder, the whole being held in position in the combustion tube by coils at each end produced by heating Cu and immersing while hot in MeOH (which ignites) and cooling in vac. Errors due to contaminated CO<sub>2</sub>, the v.p. of the KOH, and drainage in the azotometer are negligible, but allowance must be made for air occluded in the filling; the max. error was  $\pm 0.17\%$  for org. compounds containing 4–15% N. J. G.

**Determination of picric acid, and its separation from aqueous solution.** A. ZACHAROV (J. Appl. Chem. Russ., 1933, 6, 998–1001).—Picric acid (I) is quantitatively pptd. as

[C<sub>6</sub>H<sub>2</sub>(NO<sub>2</sub>)<sub>3</sub>O]<sub>2</sub>Cu(NH<sub>3</sub>)<sub>4</sub>·3H<sub>2</sub>O (II) by aq.-ammoniacal CuSO<sub>4</sub> (III). (I) can be determined gravimetrically as (II), or volumetrically by adding standard (III) until the colour changes from orange to green. Pure (I) can be recovered from factory waste H<sub>2</sub>O as (II), from which (I) is regenerated by aq. H<sub>2</sub>SO<sub>4</sub>. R. T.

**Fractionation and purification of organic substances by chromatographic adsorption.** I. Application. II. Chlorophylls. A. WINTERSTEIN and G. STEIN (Z. physiol. Chem., 1933, 220, 247–263, 263–277).—I. Chromatographic analysis is useful for separating ergosterol-cholesterol, oleanol-oleanylene, dipalmityl ketone-hentriacontane, and similar mixtures. Activated Al<sub>2</sub>O<sub>3</sub> is a useful adsorbent.

II. Using sucrose as adsorbent, chlorophylls *a* and *b* may be separated; the extinction coeffs. offer a criterion of purity. The absorption bands of the pure preps. are given. J. H. B.

**Hammarsten reaction of cholic acid.** K. YAMASAKI (J. Biochem. Japan, 1933, 18, 311–322).—The visual and spectroscopic appearances of the bile acids, their derivatives, and similar compounds on treatment with 25% (A., 1909, ii, 836) or 37% HCl are described. F. O. H.

**Detection of local anaesthetics.** R. FISCHER (Arch. Pharm., 1933, 271, 466–470).—By m.p. determinations of the ppts. with trinitroresorcinol

(I), C<sub>6</sub>H<sub>2</sub>(NO<sub>2</sub>)<sub>3</sub>·CO<sub>2</sub>H, PtCl<sub>4</sub>, and picric acid, 13 common local anaesthetics (0.3 mg.; micro-technique) can be identified. The crystal forms are variable. An unstable modification of (I) has m.p. 165–166°. R. S. C.

**Reactions for differentiating novocaine and panthesin.** P. DUQUENOIS (Bull. Sci. pharmacol., 1933, 40, 287–289; Chem. Zentr., 1933, ii, 583).—2% aq. AgNO<sub>3</sub> gives with novocaine (I) a white ppt., but no reaction with panthesin (II). The following give no ppt. with (I), but with (II) form ppts.: saturated aq. NaHCO<sub>3</sub> or Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, white, Na<sub>2</sub>Fe(NO)(CN)<sub>5</sub> dirty white, Na nitrophenoxide (1%) or PtCl<sub>4</sub> (2.5%) + HgCl<sub>2</sub> (5%) yellow. A. A. E.

**Gravimetric and volumetric determination of antipyrine as hydroferrocyanide in presence of amidopyrine.** I. M. KOLTHOFF (J. Amer. Pharm. Assoc., 1933, 22, 947–950).—The iodometric determination of antipyrine (I) is inapplicable in presence of amidopyrine, which, however, has little influence on the pptn. of the former as cryst. (C<sub>11</sub>H<sub>12</sub>N<sub>2</sub>O)<sub>2</sub>·H<sub>4</sub>Fe(CN)<sub>6</sub> in acid solution (0.5N-HCl). The ppt., which is appreciably sol. in several aq. solutions, should be washed with its own saturated aq. solution and either dried and weighed, or dissolved in standard alkali and determined acidimetrically. The qual. sensitivity is 400 p.p.m. of (I), but  $\geq 0.1$  g. should be used for a determination. W. S.

**Micro-chemistry of the opium alkaloids.** L. KOFER (Oesterr. Chem.-Ztg., 1933, 36, 174–176).—A lecture. These alkaloids cannot be distinguished by crystal forms, which are variable. Anhyd. morphine (I) sublimes in two forms, m.p. 197° (metastable) and 240° (decomp.) (stable), respectively. Crystallographic data are given for (I) and its hydrate [m.p. 300° (decomp. from 200°)] and for its anhyd. and hydrated (m.p. about 140°) hydrochloride. R. S. C.

**Spectroscopic characterisation of organic dyes and other coloured substances.** J. FORMANEK (Coll. Czech. Chem. Comm., 1933, 5, 411–414).—Polemical against Chloupek (A., 1933, 844). D. R. D.

**Analysis of protein solutions.**—See this vol., 121.

## Biochemistry.

**Apparatus for automatically measuring respiratory exchange of small animals.** H. H. LEWIS and J. M. LUCK (J. Biol. Chem., 1933, 103, 209–226).—Air is pumped through the animal chamber, fitted with a device for recording the muscular activity of the rat during the experiment, into a CO<sub>2</sub>-absorption unit; during its return to the pump O<sub>2</sub> is automatically added and the cycle begins again. The CO<sub>2</sub> absorbed is measured by the decrease in conductivity of a dil. Ba(OH)<sub>2</sub> solution. The O<sub>2</sub> consumption is measured by recording the compensating flow of H<sub>2</sub>O into the O<sub>2</sub> reservoir on a kymograph and subsequent determination of the total vol. of H<sub>2</sub>O entering. The animal chamber, absorption cell, and O<sub>2</sub> reservoir are immersed in a

H<sub>2</sub>O thermostat, and the entire apparatus in an air thermostat. The average fasting metabolic rate of eighteen white rats at 28° was 744 g.-cal. per day per sq. m. body-surface. H. D.

**Spectroscopic detection of carbon monoxide in blood.** J. KOLLER (Deut. Z. ges. gerichtl. Med., 1933, 21, 275–277; Chem. Zentr., 1933, ii, 915–916).—For blood containing  $> 20\%$  CO the use of Na<sub>2</sub>SnO<sub>2</sub> is preferred to that of (NH<sub>4</sub>)<sub>2</sub>S; for  $< 20\%$  neither reagent is satisfactory. A. A. E.

**Detection and determination of carbon monoxide in blood.** A. A. CHRISTMAN and E. L. RANDALL (J. Biol. Chem., 1933, 102, 595–609).—The method depends on the colorimetric determination



of excess  $\text{PdCl}_2$  with KI after reduction with the CO liberated by  $\text{K}_3\text{Fe}(\text{CN})_6$ . NO and CN' interfere;  $\text{H}_2\text{S}$  is without effect on the determination. A. L.

**Gas and electrolyte equilibria in blood. XVII. Effect of oxygenation and reduction on the carbon dioxide absorption curve and  $p_{K'}$  of whole blood.** D. D. VAN SLYKE and J. SENDROY, jun. (J. Biol. Chem., 1933, 102, 505—519).—The effect of oxygenation and reduction on the  $\text{HCO}_3'$  content and buffer val. of dog blood is studied and previous data on horse blood are recalc. with the more accurate const. available. At  $p_{\text{H}}$  7.4 the increase in combined  $\text{CO}_2$  caused by removing 1 millimol. of  $\text{O}_2$  averages 0.52 millimol. for horse blood and 0.45 millimol. for dog blood, these vals. differing to almost the same extent as the vals. 0.66 and 0.60 previously found for solutions of the cryst. hæmoglobin (I) from the two species at the same  $p_{\text{H}}$ . The buffer val. (II) of dog blood per unit of (I) content is also slightly < the (II) of horse blood, this difference again being similar to that between solutions of the cryst. (I). The Hasselbalch  $p_{K'}$  vals. for whole blood of varying (I) content and oxygenation are recalc. and expressed in a line chart. A. L.

**First dissociation constant  $p_{K'}$  of carbonic acid in hæmoglobin solutions and its relation to the existence of a combination of hæmoglobin with carbon dioxide.** R. MARGARIA and A. A. GREEN (J. Biol. Chem., 1933, 102, 611—634).—The apparent first dissociation const.  $p_{K'}$  of  $\text{H}_2\text{CO}_3$  is determined in the presence of varying concn. of hæmoglobin (I),  $\text{H}_2\text{CO}_3$ , and  $\text{CO}_2$ , the  $p_{\text{H}}$  of the mixtures being determined with a glass electrode. At const. ionic strength (II) and (I) concn.  $p_{K'}$  varies approx. linearly with the  $p_{\text{H}}$ , and the difference between  $p_{K'}$  in the presence of, and  $p_{K'}$  in the absence of, (I) at const. (II) is the greater the higher is the (I) concn. At very low (II),  $p_{K'}$  at const.  $p_{\text{H}}$  increases with increasing (II), and at high (II)  $p_{K'}$  is lower the lower is the proportion of  $\text{NaHCO}_3$  making up the total electrolyte concn. If the deviation of  $p_{K'}$  from  $p_{K'}$  be assumed to be entirely due to the combination of  $\text{CO}_2$  with (I), and this quantity is calc., the amount found for low (II) increases with increase in the calc.  $[\text{HCO}_3']$ . The difference between  $p_{K'}$  and  $p_{K'}$  is greater in reduced than in oxy-(I) solutions, so that combination of  $\text{CO}_2$  with (I) may take place more easily in the first case.  $\text{O}_2$  dissociation curves at const.  $p_{\text{H}}$  and (II) in  $\text{NaHCO}_3$ - $\text{CO}_2$  solution are moved to the right of those in the absence of  $\text{CO}_2$  under identical conditions of (II),  $p_{\text{H}}$ , and (I) concn.  $p_{K'}$  in a 1% hæmatin solution of 0.04N-Na' is the same as in the absence of hæmatin in a solution of the same (II). These results are believed to indicate the real existence of a  $\text{CO}_2$  or  $\text{HCO}_3$ -(I) compound. A. L.

**Existence of a carbhæmoglobin.** R. JANZEN and H. NETTER (Pflüger's Archiv, 1933, 232, 349—356; Chem. Zentr., 1933, ii, 239).—The existence of a  $\text{CO}_2$ -hæmoglobin complex has not been confirmed. A. A. E.

**Preparation of pure hæmoglobin solutions by electrodialysis.** G. ETTISCH and G. GROSCURTH (Biochem. Z., 1933, 266, 441—447).—A method is described for the prep. of pure hæmoglobin solutions

by electrodialysis for 2½ hr. of hæmolysed red corpuscles using glycine-collodion anodic and parchment cathodic membranes. P. W. C.

**Sedimentation constants, mol. wts., and isoelectric points of respiratory proteins.** T. SVEDBERG (J. Biol. Chem., 1933, 103, 311—325).—The sedimentation consts. (I) of the respiratory proteins (II) of the blood from many different species were determined by the ultra-centrifuge, use being made of their sp. absorption in the long ultra-violet to measure the migration. The (I) of the (II) in corpuscles are generally < of those contained in plasma; biological kinship is usually accompanied by identity in the (I) of (II). Comparison of the mol. wts. of (II) as calc. from (I) shows them to be multiples of 34,500. The isoelectric points (III) of the (II) vary from species to species and are lower in invertebrates than in vertebrates. The (I) and mol. wts. can be used as group characteristics, whilst (III) are species characteristics. H. D.

**Availability of iron from different sources for hæmoglobin formation.** C. A. ELVEHJEM, E. B. HART, and W. C. SHERMAN (J. Biol. Chem., 1933, 103, 61—70).—The dipyriddy reagent indicates that  $\text{FeCl}_3$ , Fe glutamate,  $\text{Fe}_4(\text{P}_2\text{O}_7)_3$ ,  $\text{FePO}_4$ , 47% of total Fe in wheat and yeast, and 57% of Fe in oats are available for hæmoglobin production. H. G. R.

**Iron. VIII. Differentiation of the "readily eliminated" blood-iron from the hæmoglobin-iron and from the inorganic iron.** G. BARKAN (Z. physiol. Chem., 1933, 221, 241—251; cf. A., 1933, 623).—The "readily eliminated" blood-Fe may be separated from other compounds containing Fe, since it is not taken up by  $\text{Al}(\text{OH})_3$  under conditions in which hæmoglobin and inorg. Fe added to blood are strongly adsorbed. J. H. B.

**Blood-iron in animals with hæmocyanin and the dissociation of copper from hæmocyanin.** G. BARKAN (Klin. Woch., 1933, 12, 546—547).—The blood of the crab (*Astacus fluviatilis*) incubated for 24 hr. with 0.4% HCl gives an ultrafiltrate containing per c.c. of blood approx.  $9 \times 10^{-7}$  mol. of Cu but practically no Fe. NUTR. ABS. (m).

**Detection of bloodstains on green leaves.** R. M. MAYER (Deut. Z. ges. gerichtl. Med., 1933, 20, 577—582; Chem. Zentr., 1933, i, 3994).—For the detection of old bloodstains on green leaves isolation as protoporphyrin in 3% HCl is recommended. Spectroscopic confirmation is necessary. A. A. E.

**"Fluorinated" methæmoglobin. Spectrophotometric study and its application to the determination of methæmoglobin and fluorides.** R. FABRE and S. BAZILLE (J. Pharm. Chim., 1933, [viii], 18, 465—470).—The presence of 10% of methæmoglobin (I) in oxyhæmoglobin can be determined by addition of NaF and subsequent spectroscopic examination; the band at  $\lambda$  6320 Å. [for (I)] is displaced at  $\lambda$  6100. Determination of the optical density of the max. (for  $\lambda$  6100—6200) of solutions of (I) containing various amounts of NaF can be used to detect 0.1—2 mg. of NaF. H. B.

**Rôle of proteins in regulating the resistance of red blood-cells.** G. PETRÁNYI and S. BLAZSÓ (Z.



ges. exp. Med., 1933, 88, 610—615).—Administration of peptone and milk to rabbits leads to an increase of the protein of the red cells. There is no correlation between corpuscular resistance and plasma-protein or non-protein-N of plasma or corpuscles.

NUTR. ABS. (m)

**Enzymes of leucocytes. IX. Amylases. II.** R. WILLSTATTER and M. ROHDENWALD (Z. physiol. Chem., 1933, 221, 13—32; cf. A., 1932, 292).—There are eight amylases now classified on the basis of solubility in glycerol (*G*), inhibition by *G* (*a*), and dependence on added  $\text{PO}_4'''$  (*b*) as follows: I lyo- and desmo-amylase,  $+a+b$ , inhibited by *G* and independent of added  $\text{PO}_4'''$ ; II lyo- and desmo-amylase,  $+a-b$ , inhibited by *G* and needing addition of  $\text{PO}_4'''$ ; III lyo- and desmo-amylase,  $-a+b$ , not inhibited by *G* and independent of  $\text{PO}_4'''$ ; IV lyo- and desmo-amylase,  $-a-b$ , not inhibited by *G*, inactive without added  $\text{PO}_4'''$ .  $\alpha$ -Lyo-amylase becomes IV lyo-amylase. *G* extracts from dry leucocytes I lyo-amylase, which becomes active on dialysis of the *G* and undergoes conversion into III. This enzyme and probably IV lyo-amylase is present in the living leucocytes. Three at. groups in the mol. are held responsible for the behaviour of these amylases, the specifically active group and those influencing *a* and *b*, respectively. The leucocyte amylases belong to the  $\alpha$ - or dextrinogen type. J. H. B.

**Blood picture of the turtle after complete anoxia.** J. M. JOHLIN and F. B. MORELAND (J. Biol. Chem., 1933, 103, 107—114).—After complete absence of  $\text{O}_2$  for 28 hr., blood-sugar rises from 50 to 1200 and lactic acid to 1000 mg. per 100 c.c., and blood- $p_{\text{H}}$  is decreased from 7.9 to 6.8.  $\text{CO}_2$  expired is  $>$  the total  $\text{HCO}_3$  of the blood. H. G. R.

**Diurnal variations in the blood of fish. L.** BAUDIN (Compt. rend., 1933, 197, 1353—1354).—In various fish (*Blennius gattorugine*, *Crenilabrus melops*, and *Perca fluviatilis*) the no. of cells and the  $\text{O}_2$  capacity of the blood increase to a max. in early afternoon and then diminish towards evening. The degree of  $\text{O}_2$  saturation shows a large decrease in the afternoon, but the (more nearly const.)  $\text{CO}_2$  content passes through a min. about noon. J. W. B.

**Electrodialysis of serum with the glycine-collodion membrane.** G. ETTISCH and J. A. DE LOUREIRO (Biochem. Z., 1933, 266, 422—435).—Using as anodic diaphragm a membrane prepared from a collodion solution shaken with solid glycine, electrodialysis of 50 c.c. of serum is complete in 35 min., the reaction remaining unchanged for the first 30 min. and no protein being pptd., the final reaction with almost complete elimination of electrolytes being attained in the subsequent 5 min. P. W. C.

**Fractionation of serum by electrodialysis.** G. ETTISCH (Biochem. Z., 1933, 266, 436—440).—The use of the ultracentrifuge is discussed. P. W. C.

**Analysis of serum with the ultracentrifuge.** P. VON MUTZENBECHER (Biochem. Z., 1933, 266, 226—249).—Serum-albumin and -globulin can be separated in the ultracentrifuge using the refraction method, and the relative amounts determined from the curves obtained. Normal horse and human sera examined in

this way show the presence of four different mols., the sedimentation consts. for which in very dil. solution are 4.5, 6.8, 9, and 17. The first two are identical with those for pure albumin and globulin, and form the chief part of the serum-protein. The sedimentation consts. of human sera decrease more slowly with increasing concn. of the serum than those of horse serum. With two pathological sera considerable deviations occur, in one case a mol. which normally was present only in small amount being increased to 50% of the total protein. P. W. C.

**Fractions of serum.** P. VON MUTZENBECHER (Biochem. Z., 1933, 266, 250—258).—The sedimentation consts. (I) of globulin are redetermined. Serum-globulin pptd. with  $(\text{NH}_4)_2\text{SO}_4$  contains chiefly a mol. of mol. wt. 138,000 and (I) of  $7.1 \times 10^{-13}$ , together with smaller amounts of mols. having (I) of  $9.0 \times 10^{-13}$  and  $19 \times 10^{-13}$ . In all albumin preps. the chief fraction has (I) of  $4.5 \times 10^{-13}$ . Albumin purified by dialysis contains in addition small amounts of smaller mols., but after pptn. by full saturation with  $(\text{NH}_4)_2\text{SO}_4$  it contains also mol. aggregates of albumin. P. W. C.

**Dissociation and association of serum molecules.** P. VON MUTZENBECHER (Biochem. Z., 1933, 266, 259—265).—When increasing amounts of  $(\text{NH}_4)_2\text{SO}_4$  are added to serum (I) the no. of small mols. increases, and these are difficultly sedimented. The sedimentation const. (II) of the albumin fraction also decreases. Electrodialysis of (I) causes a partial association of the protein remaining in solution. Proteins of (I) in 0.1*N*-salt solution are stable between  $p_{\text{H}}$  3.5 and 11.5, but (II) begins to diminish above  $p_{\text{H}}$  10 and below  $p_{\text{H}}$  5. P. W. C.

**Precipitation of proteins by neutral salts.** G. SANDOR, A. BONNEFOI, and J. J. PÉREZ (Compt. rend., 1933, 197, 1254—1256).—Pptn. of the globulins and albumins of horse serum by  $(\text{NH}_4)_2\text{SO}_4$  is studied and discussed. J. L. D.

**Basic amino-acids of serum-proteins.** R. J. BLOCK (J. Biol. Chem., 1933, 103, 261—267).—Serum-albumin and -globulin prepared by pptn. with different concns. of  $\text{MgSO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ , and NaCl contained varying quantities of total N, histidine, arginine, and lysine. H. D.

**Determination of blood-cholesterol.** H. BANERJI (J. Indian Chem. Soc., 1933, 10, 573—576).—Oxalated blood (0.25 c.c.) is dried on fat-free filter-paper at 37°, the cholesterol extracted with  $\text{CHCl}_3$ , and determined colorimetrically ( $\text{Ac}_2\text{O}$ , conc.  $\text{H}_2\text{SO}_4$ ). The method gives more accurate results than that of Myers *et al.* (A., 1918, ii, 461). H. B.

**Determination of blood-cholesterol. I. Extraction and gravimetric methods. II. Combination of colorimetric and digitonin methods.** K. KUSUI (J. Biochem. Japan, 1933, 18, 227—236, 237—241).—I. For the determination of cholesterol (I) in blood or serum, the method of Onizawa (A., 1929, 952) or of Mühlbock and Kaufmann (A., 1931, 755) achieves complete extraction whilst that of Fox (A., 1920, i, 697) does not. A simplified gravimetric method for the determination of (I) and its esters is described.



II. Free (I) in blood or serum (2.5 c.c.) is determined gravimetrically by digitonin pptn., and esters of (I) colorimetrically by treatment with  $\text{Ac}_2\text{O}$  and  $\text{H}_2\text{SO}_4$ . F. Ö. H.

**Glycogen content of blood.** Its significance for metabolic processes. E. BONG (Pflüger's Archiv, 1933, 232, 482—499).—In adult dogs the glycogen content (I) of the blood varies from 13 to 30 mg. per 100 c.c. (average 21); in puppies (II) it averages 18 mg. In fasting dogs (I) varies directly with the liver-glycogen (III). After carbohydrate-rich diet there is a rapid rise in (I) to supernormal vals. (63 mg.) and after the third day a gradual fall to normal or subnormal: in (II) the rise is more marked and rapid. High (I) is accompanied by low blood-sugar (IV); while (I) and (III) fall the blood- and liver-fat increase. Support is given to Junkersdorf's theory that overloading of the liver with glycogen leads to functional inefficiency of the liver, and therefore to defective regulation of (IV). High-carbohydrate diet with insulin leads to a very marked lowering of (I) (average 9 mg.): there is a rise in the glycogen and fat of muscle, but (III) is < without insulin. Dogs treated with phloridzin show an increase of (I). After injection of thyroxine there is a rise of (IV) and (I) and fall of muscle-glycogen and (III). In dogs with an Eck fistula the lowest vals. for (I) are found, supporting the view that (I) and (III) are correlated.

NUTR. ABS. (m)

**Distribution of blood-sugar.** F. KERTI and F. STENGEL (Z. ges. exp. Med., 1933, 88, 78—91).—The relative sugar concn. of whole blood (I), plasma, and serum differs by as much as 20% in healthy individuals and 30% in diabetics (II), in whom the sugar of (I) is more frequently lower than that of plasma or serum. The relative concns. vary in the same person from day to day; sex, age, ingestion of food, or the presence of hyperpiesia has no const. effect in (II) or non-diabetics (III). In the blood of (II) and (III) kept at 18—25° in sterile tubes for 14 days various changes in the distribution of the sugar occur.

NUTR. ABS. (m)

**Micro-analysis of urine and blood by the step photometer.** X. Determination of blood-sugar. C. URBACH (Biochem. Z., 1933, 265, 390—400).—The method is described and a table gives comparative vals. by this and the usual analytical methods for samples of blood of rat, cat, rabbit, and man. P. W. C.

**Normal urea level in human blood.** H. GEMEINHARDT (Z. ges. exp. Med., 1933, 88, 622—629).—The NaOBr method for blood-urea (I) gives results averaging 1.1 mg. per 100 c.c. > the urease method. The average (I) of patients without renal disease is 36.05 mg. per 100 c.c. In women (I) is 3 mg. per 100 c.c. lower and tends to increase with age: there is no correlation between (I) and either wt. or height, although there is a slight correlation with Rohrer's index ( $100P/L^3$ , where  $P$ =wt. in g. and  $L$ =height in cm.). In non-renal diseases lack of salts, tissue- $\text{H}_2\text{O}$ , and secretions, and toxic effects on the kidneys play a part in the rise in (I).

NUTR. ABS. (m)

**Manometric micro-Kjeldahl and blood-urea determinations.** D. D. VAN SLYKE and V. H.

KUGEL (J. Biol. Chem., 1933, 102, 489—497).—The determination of blood-urea and  $\text{-NH}_3$  using separate solutions of NaOH and Br in aq. KBr has advantages over that using alkaline NaOBr. The procedure is described. Somogyi's method (A., 1930, 1055) of pptg. blood-proteins with  $\text{Zn(OH)}_2$  removes most of the non-urea substances present in tungstic acid filtrates, and using this in conjunction with the above on bloods with < 50 mg. urea-N per 100 c.c., the average error is  $\pm 0.02$  mg. A. L.

**Determination of ammonia in blood.** D. D. VAN SLYKE and A. HILLER (J. Biol. Chem., 1933, 102, 499—504).—The procedure for the removal of  $\text{NH}_3$  from blood by the Nash-Benedict aëration method (A., 1922, i, 191) and its colorimetric determination with  $\text{HOCl}$  and  $\text{PhOH}$  (I) (cf. Thomas, A., 1912, ii, 991) is described. (I) is more sensitive than Nessler's reaction and the product does not flocculate. A. L.

**Conditions for the formation in serum of colloid-calcium-phosphorus complexes.** M. LASKOVSKI (Biochem. Z., 1933, 265, 401—412).—Increase of serum-Ca (I) causes decrease of  $\text{PO}_4$  in the ultrafiltrate (II), the product of the Ca and P contents of (II) remaining const. Increase of serum- $\text{PO}_4$  (III) decreases the Ca content of (II), but to only a certain limiting val. (3.5—4.0 mg. per 100 c.c.) and thereafter the  $\text{Ca} \times \text{P}$  product in (II) increases with the increase of  $\text{PO}_4$ . With simultaneous increase of (I) and (III), providing the Ca/P ratio does not exceed 1, the Ca of (II) is often unchanged. P. W. C.

**Spectrophotometric detection of bile acids in blood.** N. SCHEINFINKEL (Biochem. Z., 1933, 265, 380—385).—A modification of the Aldrich and Bledsoe method (A., 1928, 788) and its adaptation for use with the spectrophotometer are described. The bile acid content of dog's blood is 0.8 mg. per 100 c.c.

P. W. C.

**Biochemical properties of bile-pigments.** II. Influence of calcium cations on agglutinating and hæmolytic power of bilirubin. A. CLEMENTI and F. CONDORELLI (Biochem. Z., 1933, 266, 221—225).—The characteristic agglutinating action of bilirubin previously obtained with red cells suspended in Ringer's solution (A., 1931, 1179) proceeds only slowly when the cells are suspended in 0.9% NaCl, the  $\text{Ca}^{++}$  of the Ringer's solution (also  $\text{Ba}^{++}$  and  $\text{Sr}^{++}$ ) accelerating the process considerably. P. W. C.

**Photobiological sensitisation and desensitisation in the ultra-violet.** W. HAUSMANN and F. M. KUEN (Klin. Woch., 1933, 12, 711—712; Chem. Zentr., 1933, ii, 405).—Serum, pinakryptol, glucose, and fructose arrest, whilst resorcinol and  $\text{Na}_2\text{SO}_3$  increase, hæmolysis following irradiation of erythrocytes in presence of hæmatoporphyrin. A. A. E.

**Coagulation.** V. Isoelectric point of fibrin. K. KLINKE and K. BALLOWITZ (Z. ges. exp. Med., 1932, 84, 224—229; Chem. Zentr., 1933, ii, 899).—The isoelectric point of fibrinogen is  $p_H$  4.4 (4.29—4.54), and of fibrin 5.23—5.66; hence the substances are colloid-chemically distinct. Thrombin-fibrin and fibrin formed by heat-coagulation have practically the same isoelectric point. A. A. E.



**Chemical nature of thrombin.** F. KRAUS and H. J. FUCHS (Biochem. Z., 1933, 266, 458).—Fischer's work (A., 1933, 1065) is criticised. P. W. C.

**Potentiometric determination of antibody-haptene equilibrium.** H. ERLÉNMEYER, E. BERGER, and M. LEO (Biochem. Z., 1933, 266, 355—359).—Preliminary work for determination of the concn. of atoxyl-antibody in atoxyl-antiserum, depending on potential changes in the reduction-oxidation system  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{As}^{\text{V}}\text{O}_3\text{H}_2[\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{As}^{\text{III}}\text{O}_2\text{H}_2]$ , is described. P. W. C.

**Specificity of brominated and iodinated proteins.** M. H. FINKELSTEIN (J. Immunol., 1933, 25, 179—182).—Iodinated and brominated (I) proteins (Wormall) showed close antigenic relationship. (I) (Wormall) showed only slight immunological relationship with (I) (Bruynoghe), which probably suffered oxidation. CH. ABS.

**Electric charge of antibodies.** L. OLITZKI (J. Immunol., 1933, 24, 505—512).—Experiments on protein-free solutions show that agglutinins (H- and O-type) carry a negative charge over the range  $p_{\text{H}}$  10.0—3.4; below this point they are too sensitive to acid reactions to make measurement possible. CH. ABS.

**Specific precipitation test for the standardisation of type I antipneumococcus serum.** R. BROWN (J. Immunol., 1933, 25, 149—154).—Pptn. tests agreed (92.3%) with mouse protection tests. CH. ABS.

**Lipoidal content of antipneumococcic horse serum.** L. D. FELTON and G. KAUFFMANN (J. Immunol., 1933, 24, 543—548).—Immune sera (types I and II) contain, per 100 c.c., 1.34 g. (normal 1.05 g.) of material sol. in  $\text{EtOH}-\text{Et}_2\text{O}$ ; this has not been correlated with the lipin and total N content or with protection. CH. ABS.

**"Super-contraction" and "set" in animal hairs.** H. J. WOODS (Nature, 1933, 132, 709—710).—The mechanism of the behaviour of animal hairs under various conditions of stress or relaxation is discussed in terms of mol. structure. L. S. T.

**Spectral absorption of visual purple before and after illumination.** Y. HOSOYA and V. BAYERL (Pflüger's Archiv, 1933, 231, 563—570; Chem. Zentr., 1933, i, 3959).—2% aq. panatoxin (from *Panax ginseng*) is recommended for the extraction of visual purple from the frog's retina. Max. absorption is at 520  $\text{m}\mu$ . A. A. E.

**Calcium salts of bone.** C. M. BURNS (J. Physiol., 1933, 78, 1—2r).—The Ca:P ratio in old bones (rat, cat) is 2.0 to 2.2 and in young bones (I) 1.85 to 2.0. Allowing for the Ca present as  $\text{CaCO}_3$  these ratios suggest that (I) contain not only  $\text{Ca}_3(\text{PO}_4)_2$  but also compounds (II) of the type  $\text{CaRPO}_4$ , where R is org. or inorg. Such (II) may explain the reactions of growing (I) to madder. NUTR. ABS. (m)

**Sulphur in the animal organism.** L. SILBERSTEIN (Compt. rend., 1933, 197, 1068—1069).—The S content of animals and animal organs has been determined. W. O. K.

**Total phosphorus in the young rat.** A. LEULLIER and G. BÉRUARD (Compt. rend. Soc. Biol., 1933, 112, 483).—The total P increases from 12.50—13.04 mg. at the age of 1 day to 218.7 mg. at 30 days and 500 mg. at 70 days. After weaning the rat grows more quickly and retains more P. The % of P is doubled between birth and the eighth day, after which it remains steady. NUTR. ABS. (b)

**Mineral content of the muscles of fish in water containing increased concentration of mineral salts.** S. KAPLANSKI and N. BOLDIREVA (Biochem. Z., 1933, 265, 422—425).—With increase of NaCl and  $\text{CaCl}_2$  content of  $\text{H}_2\text{O}$  to 1.5—2%, the corresponding cation contents of the musculature of fish greatly increase, but of the blood remain unchanged. On the other hand, the Cl' content of the muscle is unchanged, but of the blood is greatly increased. P. W. C.

**Iron in the liver of the foetal calf.** G. ROUSSEL and Z. GRUZEWSKA (Compt. rend., 1933, 197, 943—944).—A min. val. of 0.007—0.01% Fe (fresh organ) was observed at 6—7 months, and a max. of 0.179% at 8.5—9 months. A. C.

**Histospectrographic detection of copper in the normal and pathological liver.** A. POLICARD (Bull. d'Histol. appl., 1933, 10, 94—103).—By the method described the presence of Cu in various types of normal and pathological (I) livers is confirmed. Such (I) include those of rabbits treated with powdered Cu suspended in lard. Human livers normally contain Cu; those of normal rats, in two cases out of three, contained none. NUTR. ABS. (m)

**Physiological products of the lac insect. I.** N. K. R. RAO and M. SREENIVASAYA (J. Indian Inst. Sci., 1933, 16A, 76—83).—Extraction of the incrustation deposited by lac insects with 0.9% aq. NaCl yields a globulin-like protein, polypeptides resembling protamines, and a fat (I val. 30.4, sap. val. 182, acid val. 5.0). F. O. H.

**Physiological products of the lac insect. II. Water-soluble nitrogenous constituents.** N. K. R. RAO (J. Indian Inst. Sci., 1933, 16A, 97—102).—From the aq. extract of the lac insect, various fractions isolated include four containing N, two of which are pptd. by phosphotungstic acid (I), and the other two are not pptd. by (I). These account respectively for about 40% and 25% of the total N, whilst tyrosine accounts for 2.5%. W. O. K.

**Nitrogen content of organisms and its significance.** A. ROCHE (Compt. rend. Soc. Biol., 1933, 113, 105—107).—The N content of rats of various ages and nutritional levels varies between 1.5 and 4.6% of the fresh wt. (I) (average of 3.1% for the well-nourished adult rat). In complete inanition or after N starvation the vals. range from 3.6 to 4.6%. As the fat and  $\text{H}_2\text{O}$  content of the animals calc. on (I) vary greatly the N vals. are of doubtful significance. NUTR. ABS. (m)

**Determination of residual nitrogen in organs. I. Liver.** H. ELIAS and H. KAUNITZ (Biochem. Z., 1933, 266, 323—328).—A method is described for the prep. of aq. liver suspensions (depending on the use of



rapid freezing and trituration with sand) in which the residual N and its fractions can be determined.

P. W. C.

**Protamines of some species of fish.** M. A. LISSITZIN and N. S. ALEXANDROVSKAYA (Z. physiol. Chem., 1933, 221, 156—164).—Protamines were isolated as sulphates: from *Luciperca sandra*, percin (I),  $[\alpha]_D^{20}$  —55° in H<sub>2</sub>O (sulphate,  $[\alpha]_D^{20}$  —67·4° in H<sub>2</sub>O); from *Huso huso* or *Acipenser huso*, acipenserin (II) (sulphate,  $[\alpha]_D^{20}$  —45° in H<sub>2</sub>O). (I) and (II) contain, respectively, 76·7, 78·6% of arginine-N, 7·6, 11·2% of histidine-N, 0·0, 7·2% of lysine-N, 9·5, 0·0% of mono-NH<sub>2</sub>-acid-N. (I) (equiv. wt. 244) combines with caseinogen (III) (equiv. wt. 1227) in the wt. ratio 1:5. The compound (IV) is insol. in H<sub>2</sub>O, but sol. in 10% aq. NaCl from which it is pptd. on dilution. (IV) is decomposed into its constituents by alkali and acid; the dissolution and pptn. effects obtained are those of (III). (IV) is salted out by (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and the solution in 10% NaCl is coagulated by heat in presence of a trace of Ca. (II) forms a (IV) with similar properties.

J. H. B.

**Analysis of muscles of marine invertebrates.** D. M. NEEDHAM, J. NEEDHAM, E. BALDWIN, and J. YUDKIN (Z. physiol. Chem., 1933, 222, 63—64).—The detection of creatinephosphoric acid in various genera by Riesser and Hansen (A., 1933, 1094), which is contrary to the authors' observations (A., 1932, 532), is probably due to their having used the method of Lohmann and Jendrassik, which is untrustworthy.

J. H. B.

**Determination of protein-nitrogen. Nitrogenous non-protein substances in spermine preparations.** I. S. JAITSCHNIKOV (J. Gen. Chem. Russ., 1933, 3, 434—436).—Fassbender's Cu(OH)<sub>2</sub> reagent, Pb(OAc)<sub>2</sub>, and phosphotungstic acid ppt. not only proteins, but also purine and hexone bases. Pharmaceutical preps. of spermine contain xanthine and arginine, with traces of guanine, hypoxanthine, adenine, and lysine.

R. T.

**Occurrence of betaines in *Arca Noæ*.** F. KUTSCHER and D. ACKERMANN (Z. physiol. Chem., 1933, 221, 33—39).—The so-called lysine fraction of *A. Noæ* contains glycinebetaine and, in smaller amounts,  $\gamma$ -butyrobetaine, carnitine, stachydrine, and a substance C<sub>7</sub>H<sub>10</sub>O<sub>2</sub>N<sub>2</sub> (aurichloride; hydrochloride, m.p. 168—172°), an isomeride of trigonelline.

J. H. B.

**Trimethylamine oxide and other nitrogenous bases in crab's muscle.** F. A. HOPPE-SEYLER (Z. physiol. Chem., 1933, 221, 45—50).—NMe<sub>3</sub>O was isolated from the lobster (*Homarus vulgaris*) and shown indirectly to be present in the river-crab (*Astacus fluviatilis*). Lobster muscle also contains NMe<sub>3</sub>, *d*-arginine, betaine, probably choline, and a base (I), C<sub>7</sub>H<sub>7</sub>O<sub>2</sub>N, similar to but not identical with trigonelline. In presence of conc. HCl it gives a regular, m.p. 185—190°, decomp. 191°, and with dil. HCl an irregular, aurichloride (C<sub>7</sub>H<sub>7</sub>O<sub>2</sub>N)<sub>4</sub>·3HAuCl<sub>4</sub>, m.p. 139—143°. (I) was also obtained from *Arca Noæ*.

J. H. B.

**Preparation of glutathione.** M. T. RÉGNIER (J. Pharm. Chim., 1933, [viii], 18, 369—376).—Brewer's yeast is extracted with aq. EtOH (45—70%

according to the H<sub>2</sub>O content of the yeast), Pb(OAc)<sub>2</sub> added, the ppt. washed with 45% EtOH and H<sub>2</sub>O, dissolved in 0·5N-H<sub>2</sub>SO<sub>4</sub>, the solution filtered and pptd. with Cu<sub>2</sub>O at 40°, the ppt. washed free from sulphate, decomposed in aq. suspension by H<sub>2</sub>S, and the filtered solution evaporated at < 30°/vac. Glutathione is crystallised from the resulting syrup by adding EtOH; yield approx. 1 g. per 1000 g. of fresh yeast.

H. A. P.

**Glutathione content of the suprarenal glands.**

A. D. MARENZI and B. BRAIER (Anal. Farm. Biochim., 1933, 4, 50—54).—The apparent high content of glutathione (I) in the suprarenals is in part due to the simultaneous determination of ascorbic acid (II) and adrenaline (III) (cf. Birch and Dann, A., 1933, 541). Approx. determinations may be made by destroying successively (II) by heating the alkaline extract to 40° for 2 hr., and (III) by autoclaving for 30 min. at 0·5 atm.

R. K. C.

**Thiol and ascorbic acid content of the lens of the eye.** H. VON EULER and C. MARTIUS (Z. physiol. Chem., 1933, 222, 65—69).—In the ox-lens about  $\frac{1}{2}$  of the total reduction (I titration) is due to ascorbic acid (I) (indophenol titration). The (I) normally present in the human lens cannot be detected in cataract, and the glutathione is much diminished.

J. H. B.

**Fermentable sugar in heart and skeletal muscle.** G. T. CORI, J. O. CROSS, and C. F. CORI (J. Biol. Chem., 1933, 103, 13—24).—Fermentable sugar (I) in skeletal muscle of rats is 10—12 and 13—53 mg. per 100 g. at plasma-sugar (II) levels of 80—120 and 140—380 mg. per 100 c.c. Adrenaline causes a larger rise in (I) than can be accounted for by the rise in (II), which is probably due to breakdown of muscle-glycogen, whereas moderate insulin hypoglycemia (III) causes a decrease in (I). Heart muscle at (II) levels of 130—180 contains 46—59 mg. per 100 g. of (I), and during (III) is reduced to 14—24. Tetanic stimulation of muscle is accompanied by an increase in (I).

H. G. R.

**Extraction from heart-muscle of a hæmin differing from blood-hæmin.** E. NEGELEIN (Biochem. Z., 1933, 266, 412—416).—A hæmin is extracted from horse heart-muscle with HCl-COMe<sub>2</sub> which on dissolving in aq. C<sub>5</sub>H<sub>5</sub>N gives a hæmochromogen absorption band at 587 m $\mu$ . The corresponding bands of phæohæmin-*b* from chlorophyll and *Spirographis* hæmin are at 584 m $\mu$ , whilst for blood-hæmin the band is at 557 m $\mu$ . The hæmin was obtained cryst. as the C<sub>5</sub>H<sub>5</sub>N-hæmochromogen, but the free hæmin (as the FeCl<sub>3</sub> compound) was not obtained cryst. The amorphous ferrichlorohæmin contained 6·5% Fe and contained 1 atom Fe for 4 atoms of N. P. W. C.

**Isolation of hepatoflavin.** K. G. STERN (Nature, 1933, 132, 784—785).—The isolation of cryst. "hepatoflavin" (I), from horse liver is described. Aq. solutions of (I) are lemon yellow in colour, and exhibit a strong green fluorescence in filtered ultra-violet light. All fractions containing (I), with or without protein, show a strong absorption band near 2600 Å. Absorption at longer  $\lambda$  is less uniform and depends on  $p_H$  and other factors. Intensive irradiation of



flavin preps. in alkaline solution gives a greenish-coloured photo-decomp. product (II) which displays absorption bands at 2630, 3650, and 4420 Å. The absorption of (II) is identical with that of the corresponding photo-decomp. products obtained by Warburg and Christian (A., 1932, 1285) from yeast, and by other workers (A., 1933, 847) from various mammalian tissues.

L. S. T.

**A. Unsaturated fatty acids of the oleic series in Japanese sardine oil.** **B. Unsaturated fatty acid,  $C_{20}H_{38}O_2$ , in Japanese sardine oil.** M. TAKANO (J. Soc. Chem. Ind. Japan, 1933, 36, 549—550B, 550—551B; cf. B., 1926, 758; A., 1930, 451).—A. Zoomaric and oleic acid (mainly), also gadoleic (?) and eicetoleic acid, are isolated.

**B. Fatty acids, b.p. 220—225°/6 mm., are isolated;** fractional crystallisation of the Li salts affords eicosenoic acid (I), m.p. 22—23°, hydrogenated to arachidic acid. Decomp. of the ozonide of (I) affords undecolic and azelaic acid.

J. L. D.

**Fat of *Rana temporaria*.** E. KLENK (Z. physiol. Chem., 1933, 221, 264—270).—The fatty acids of the fat consist of saturated acids,  $C_{14}$ , 4%,  $C_{16}$ , 11%,  $C_{18}$ , 3%; singly unsaturated  $C_{16}$ , 15%; one to two double linkings,  $C_{18}$ , 52%; about three double linkings,  $C_{20}$ ,  $C_{22}$ , 15%. Myristic, palmitic, stearic, linolenic, linoleic, oleic (?), arachidonic, and elupanodonic acids were detected. The composition is intermediate between those of the fats of mammals and fishes.

J. H. B.

**Phosphatides. VII. Sphingomyelins of heart-muscle. VIII. Fatty acids of the liver-phosphatides and liver-oils of *Rana temporaria*.** E. KLENK (Z. physiol. Chem., 1933, 221, 67—72, 259—264; cf. A., 1933, 846).—VII. A phosphatide obtained from ox-heart is a mixture of lignoceryl- and stearyl-sphingomyelin.

**VIII. The phosphatide-fatty acids consist of saturated, mainly of chain-length  $C_{16}$ , 25%; one to two double linkings, mainly  $C_{18}$ , 42%, and about three double linkings,  $C_{20}$  and  $C_{22}$ , 33%. The liver-oils contain saturated acids,  $C_{16}$ , 19—23%, one to two double linkings,  $C_{16}$  and  $C_{18}$ , 61%, about three double linkings,  $C_{20}$  and  $C_{22}$ , 16—20%.**

J. H. B.

**Lipins of animal organs. VIII. Occurrence of lignocerylsphingosine in ox-spleen.** C. TRÖPP and V. WIEDERSHEIM (Z. physiol. Chem., 1933, 222, 39—43; cf. A., 1933, 967).—Lignocerylsphingosine was isolated from ox-spleen in yields of 0.06—0.16%. No cerebrosides were detected.

J. H. B.

**Pigments of silk.** G. BARBERA (Annali Chim. Appl., 1933, 23, 501—508).—The pigments of silk consist, for the native (Italian) yellow races of silkworm, of mixtures of carotenoids, and for the Japanese green race, of substances of flavone character.

T. H. P.

**Determination of bile salts in bile.** S. A. PEOPLES (Proc. Soc. Exp. Biol. Med., 1933, 30, 1117—1120).—The bile salts are flocculated with 1% aq.  $FeCl_3$  and the Fe in the ppt. is determined colorimetrically (Lyons). Each 0.1 mg. of Fe is associated with 2.5 mg. of glycocholic or with 2.98 mg. of taurocholic acid.

NUTR. ABS. (m)

**Occurrence of taurocholic acid in hen's bile.** K. YAMASAKI (J. Biochem. Japan, 1933, 18, 323—324).—Treatment of the bile with aq.  $FeCl_3$  and extraction with EtOH etc. yields a product which on hydrolysis affords cholic acid, m.p. 195—196°,  $[\alpha]_D^{20} +30.05^\circ$  in EtOH, and taurine. The yields indicate that the bile has a very low content of taurocholic acid.

F. O. H.

**Gastric secretion in dogs with Eck's fistula.** S. I. LEBEDINSKAJA (Z. ges. exp. Med., 1933, 88, 264—270).—In dogs with Pavlov pouches the gastric secretion is greatly increased in vol. and duration after the formation of Eck's fistula, whilst acidity increases and digestive activity diminishes. The changes in gastric secretion become more marked with time. Normal hepatic function is necessary for a physiological gastric secretion. NUTR. ABS. (m)

**$p_H$  of stomach contents and its electrometric titration.** L. KISS (Magyar orvosi Arch., 1933, 34, 145—151; Chem. Zentr., 1933, ii, 571).—The  $p_H$  is not characterised by the usual determination of free HCl; the latent acidity is linearly proportional to the protein content.

A. A. E.

**Determination of protein- and non-protein-nitrogen in gastric juice.** L. MARTIN (J. Amer. Med. Assoc., 1933, 100, 1475—1478).—Normal gastric juice contains N in the following fractions in mg. per 100 c.c.: 48 total (I), 22.6 as protein, 25.5 non-protein (II), of which 7.2 as  $NH_2$ -acid, 2.6 as urea, and 5.2 as  $NH_3$ . In peptic ulcer the (I) and (II) are slightly increased. In benign achlorhydria and pernicious anaemia, vals. up to 109 mg. per 100 c.c. for (I) occur. In gastric carcinoma (I) and (II) show average vals. of 200 and 105, respectively.

NUTR. ABS. (m)

**Enzymes in human colostrum. II. Oxidoreductase, catalase. III. Carbohydrase, diastase, and invertase. IV. Esterase, monobutyrase, tributyrase, castor-oil- and olive-oil-decomposing enzymes.** Y. KATSU (Japan. J. Obstet. Gynecol., 1933, 16, 2—8, 10—20, 21—44).—II. Catalase was present in human colostrum and milk during the first week after parturition (I), particularly in the milk of primipara. Much catalase was present in the serum of the puerperal woman; the quantity decreased gradually after (I).

III. Human colostrum or milk contains much diastase during the first week after (I). Colostrum contains a little invertase (optimum  $p_H$  6.24—6.42).

IV. Monobutyrase and tributyrase are present in the colostrum of the healthy puerperal woman. Enzymes decomposing castor oil or olive oil were not found.

CH. ABS.

**Human milk. XIV. Determination of nitrogenous constituents.** B. N. ERICKSON, N. STONER, and I. G. MACY (J. Biol. Chem., 1933, 103, 235—248).—By analysis of the N constituents of human milk filtrates after pptn. with  $H_2WO_4$  under different conditions an optimal pptn. was obtained by addition of 0.1 c.c. of 10%  $Na_2WO_4$  and 0.2 c.c. of  $H_2SO_4$  per c.c. of milk. Considerable differences in non-protein-N were found in the filtrates according as  $H_2WO_4$  or  $CCl_3CO_2H$  was used for pptn.; the discrepancy



increases with the time of keeping of the milk before pptn., indicating the presence of proteolytic decomp. products. An increased  $\text{NH}_2$ -acid-N in both filtrates after hydrolysis demonstrates the presence of simple peptides in fresh milk. H. D.

**Carbohydrate and caseinogen variations during milking in women.** C. VINCENT and J. VIAL (Compt. rend. Soc. Biol., 1933, 113, 113—114).—During a milking the carbohydrate content (I) of the milk at various stages is almost const., with a slight fall about the middle. The % of caseinogen varies considerably with a marked max. generally when (I) shows its min. NUTR. ABS. (m)

**Quantity and fat content of milk from the two human breasts.** C. VINCENT and J. VIAL (Compt. rend. Soc. Biol., 1933, 113, 111—113).—During simultaneous manual expression of milk from the two human breasts (period of several weeks) a larger quantity of milk is obtained from one breast, and this breast always gives the higher yield at all milkings. The side differs in different subjects. There is no marked difference in the % of fat in the milk of the two breasts. NUTR. ABS. (m)

**Unreported fatty acids in butter-fat.** A. W. BOSWORTH and J. B. BROWN (J. Biol. Chem., 1933, 103, 115—134).—The following acids have been identified in butter: decenoic and tetradecenoic, hexadecenoic and eicosenoic (doubtful). There is evidence for a  $\text{C}_{20}$ , a  $\text{C}_{22}$ , or a  $\text{C}_{24}$  acid with two double linkings, highly unsaturated acids of the arachidonic type, probably  $\text{C}_{22}$  series, and tetracosic with small amounts of behenic and cerotic acids. Linoleic acid was not found. H. G. R.

**Linoleic and linolenic acid content of butter-fat.** H. C. ECKSTEIN (J. Biol. Chem., 1933, 103, 135—140).—Butter-fat contains 0.17—0.25% of linoleic acid and 0.07—0.17% of linolenic acid (II). (II) can be increased by adding linseed meal to the feed. H. G. R.

**Alteration of the titratable acidity of milk by addition of calcium chloride.** A. KERN (Milch. Forsch., 1933, 15, 501—506).—The titratable acidity of milk increases on the addition of a small quantity of aq.  $\text{CaCl}_2$ . The increase in titration is const. for the same milk even when it has turned sour. There is a difference in the apparent increase of acidity in diseased or colostrual milk. E. B. H.

**Correlation between properties of milk and type of inflammation in acute mastitis.** R. B. LITTLE and F. S. JONES (J. Amer. Vet. Med. Assoc., 1933, 82, 818—825).—In cows suffering from udder disease there is incomplete correlation between increase in leucocyte content and in whey proteins and change in  $p_{\text{H}}$  of the milk. In acute attacks all properties considered, in less severe cases only one or two, may change. The changes in the milk are indicative of the severity and character of the inflammation. NUTR. ABS. (m)

**Ethyl sulphide formation in the animal organism.** J. WOHLGEMUTH (Z. physiol. Chem., 1933, 221, 207—208).— $\text{Et}_2\text{S}$  excreted by the dog is probably formed by intestinal bacteria, and is not an endo-

genous metabolic product (cf. Christomanos, A., 1931, 976). J. H. B.

**Identification of catatonin.** E. DINGEMANSE and J. FREUD (Acta Brev. néerl. Physiol., 1933, 3, 59—51; Chem. Zentr., 1933, ii, 568).—Urine (1 litre) affords: men 4—12, women 0.5—2, children and diseased persons 0.25—0.5, mental patients 0.125—0.25 units. There are probably considerable losses during isolation. Catatonin is possibly identical with nicotine. A. A. E.

**Crystalline urine-urobilin. Stercobilin and copromesobiliviolin.** C. J. WATSON (Z. physiol. Chem., 1933, 221, 145—155).—Cryst. urobilin (I) was isolated from urine; it is probably identical with stercobilin (II) (*Cu* salt). An improved separation of copromesobiliviolin (III), m.p. 170—180°, decomp. 240—250° (*Cu* salt), is described. (III) is spectroscopically identical with mesobiliviolin (IV) from mesobilirubinogen (V). The blue pigments accompanying (III) and (IV) are similarly identical. (I) was obtained by oxidation of (V) *in vitro*. The blue and violet oxidation products of bilirubin are spectroscopically similar to, but not identical with, (IV). J. H. B.

**Renal threshold of bilirubin.** II. E. H. BENSLEY (J. Biol. Chem., 1933, 103, 71—79).—The direct type of bilirubin only is excreted in urine, and there is no evidence of any threshold in the kidney. H. G. R.

**Determination of urinary protein by polarisation.** SEILER (Schweiz. Apoth.-Ztg., 1933, 71, 264—265; Chem. Zentr., 1933, ii, 582).—Readings obtained on ordinary apparatus are within the error of observation. A. A. E.

**Filtration and secretion of exogenous creatinine in man.** N. JOLLIFFE and H. CHASIS (Amer. J. Physiol., 1933, 104, 677—680).—In man the average clearance vals. (I) (c.c. plasma cleared per min. per sq. m. body-surface) for xylose (II), urea, and creatinine (III) are respectively 52.9, 36.6, 91.4. The val. for (III) is > that for (II), and as (II) is excreted solely by filtration it follows that (III) is excreted partly by secretion in the tubules. The (I) vary for different subjects, but the ratios of one to another are fairly const. for all. NUTR. ABS. (m)

**Urea clearance in dogs.** R. L. HOLMAN (Amer. J. Physiol., 1933, 104, 615—623).—The clearance vals. (I) are not const. for each animal. A rise in blood-urea due to fasting reduces (I) whilst a fall due to injury to the liver raises it. NUTR. ABS. (m)

**Reaction of kidneys to different water-salt loads.** I. In resting condition. II. During muscular activity. A. M. SIMKINA and A. A. MICHELSON (J. Physiol. U.S.S.R., 1932, 15, 353—365, 366—369).—I. In the dog the optimal solution for max.  $\text{H}_2\text{O}$ -retention (I) is 1% aq.  $\text{NaCl}$ . Other concns. give a smaller (I), whilst 2.5%  $\text{NaCl}$  produces a diuresis (II). At the height of (II) the concn. index falls continuously. The (II) produced by  $\text{H}_2\text{O}$  and 0.5%  $\text{NaCl}$  during an ordinary diet occurs at the expense of normal reabsorption; in many cases using higher concns. of  $\text{NaCl}$  (II) was due to increased



filtration; in the case of a Cl-deficient diet both factors operate.

II. During muscular activity (II) is much less, and the solution for max. (I) is 1% NaCl. Directly after activity an anuresis is observed, dependent on the quantity and quality of the ingested solution, and due to the increased reabsorption. It is followed by an increase in (II). H. D.

Prevention of anæmia in suckling pigs, with observations on the blood picture. T. S. HAMLTON, G. E. HUNT, and W. E. CARROLL (J. Agric. Res., 1933, 47, 543—563).—Conditions leading to anæmia are examined. Preventive treatment consisting of wetting the sow's udder with solutions of Fe or Fe and Cu salts is described. Relationships between the hæmoglobin content and cell vol. of the blood are traced. A. G. P.

Rôle of iron in anæmias. I. Iron content of liver, liver extracts and preparations. II. Iron content of normal and pathological blood, its relation to hæmoglobin content and factors affecting it. A. H. MÜLLER (Z. ges. exp. Med., 1933, 88, 776—781, 782—792).—I. The Fe of liver is not an important factor in the therapeutic results obtained by liver administration. Fe is present in traces only in liver preps.

II. The blood-Fe (I) varies greatly in health and in anæmia. There is no const. relationship between (I) and hæmoglobin (II). Administration of ferrum reductum leads to an increase of (I) which occurs before the final rise of (II). The increase in (I) appears to be independent of its original level and is not closely related to the amount of Fe administered. There is no increase of (I) in pernicious anæmia after the administration of Fe, but this occurs after combined liver-Fe therapy. NUTR. ABS. (m)

Filterable agent of Rous chicken sarcoma. W. NAKAHARA and H. NAKAJIMA (Gann, 1933, 27, 202—214).—The substance is poorly adsorbed on kaolin, but well on  $\text{Al}(\text{OH})_3$ , at  $p_{\text{H}}$  7—10. Adsorption on  $\text{Al}(\text{OH})_3$  is slight at  $p_{\text{H}}$  4—6. After removal from  $\text{Al}(\text{OH})_3$  (with  $M/7\text{-NaH}_2\text{PO}_4$  or  $N/25\text{-NH}_3$ , but not by buffer solutions at  $p_{\text{H}}$  4—6 or by glycine or  $\text{NH}_4\text{H}_2\text{PO}_4$ ) the substance was much less active. CH. ABS.

Metabolism of heterotransplanted tumours. O. ROSENTHAL (Biochem. Z., 1933, 265, 413—421).—The carbohydrate metabolism of tumours arising in rats by transplantation of mouse sarcoma S37 resembles that of the Jensen sarcoma in rats and differs from the original metabolism. The change in biochemical behaviour is discussed. P. W. C.

Relationship between tumour growth and blood-amino-acid content. S. L. MALOWAN (Arch. wiss. prakt. Tierheilk., 1932, 65, 279—284).—The presence of tumours produced no change in protein-N in men, but gave a lower val. in rats and mice;  $\text{NH}_2\text{-N}$  was slightly raised in men and unchanged in rats and mice. In rats and mice there is no increased activity of the proteases in cancer. NUTR. ABS. (b)

Effect of X-rays on blood-gases and alkali reserve in cancer. A. GREMME (Arch. Gynäk., 1933, 152, 667—678).—In women, after irradiation

of carcinoma the alkali reserve of the blood falls concomitantly with the  $\text{CO}_2$  tension, but the vals. generally rise to normal again. Sometimes the  $\text{O}_2$  saturation of the blood falls, but not the  $\text{CO}_2$  tension. NUTR. ABS. (m)

Cancer chemotherapy. XI. Effect of  $\text{CO}$ ,  $\text{HCN}$ , and pituitrin on tumour growth. L. C. MAXWELL and F. BISCHOFF (J. Pharm. Exp. Ther., 1933, 49, 270—282).—Exposure of mice bearing transplantable tumours (I) to  $\text{CO}$  or  $\text{HCN}$  reduced the rate of increase of body-wt. (II) and of tumour growth (III), whilst treatment with sublethal doses of pituitrin reduced (II) but did not affect (III). Changes in the lipin (IV) and cholesterol of (I), and in the (IV) and glycogen of the body tissues, were not found. W. O. K.

Recent developments in the study of dental caries. R. W. BUNTING (Science, 1933, 78, 419—424). L. S. T.

Periodicity of carbohydrate metabolism and rhythmic functioning of the liver. Significance in insulin treatment of diabetes. J. MÖLLERSTRÖM (Arch. Int. Med., 1933, 52, 649—663; cf. A., 1933, 302).—The periodicity of liver function is independent of meal times, and insulin therapy should be conducted in relation to the former rather than the latter. P. G. M.

Histochemical study of diabetic arteritis. F. RATHERY and S. DOUBROW (Compt. rend. Soc. Biol., 1933, 113, 56—57).—The fat in the intimal coat of the vessel in diabetic arteritis consists mostly of palmitates and stearates. Oleic fats would be most suitable in the diet for prophylaxis. NUTR. ABS. (m)

Hypercholesterolaemia. Disturbance of cholesterol excretion. R. SCHÖNHEIMER (Z. klin. Med., 1933, 123, 749—763; Chem. Zentr., 1933, ii, 1050).—The blood contained excess of cholesteryl ester. On ingestion of cholesterol (I), no (I) or dihydro-(I) was found in the faeces, but the latter was isolated from the blood. The condition was ameliorated by a vegetable diet. A. A. E.

Effect of organ extracts on blood-pressure of hypertonics and the blood-adenylic acid in pathological blood-pressure. K. A. BOCK (Z. ges. exp. Med., 1933, 87, 799—805; Chem. Zentr., 1933, ii, 567).—In hypertension of various origins there is no lack of blood-adenylic acid. A. A. E.

Glucose metabolism in hyperthyroidism. H. GOTTA and M. YRIART (Compt. rend. Soc. Biol., 1933, 113, 454—456).—In patients suffering from hyperthyroidism ingestion of glucose results in a rise of blood-sugar which is > that obtained with normal persons; nevertheless in the former more of the ingested glucose is oxidised than in the latter, as judged by the R.Q. The abnormal blood-sugar curves are therefore to be attributed rather to inadequate formation of glycogen in the liver than to deficiency of insulin secretion. NUTR. ABS. (m)

Inter-relations of liver functions. Rôle of glycogen in the physiology of the liver. F. K. GASSMANN (Z. ges. exp. Med., 1933, 88, 593—598).—The percentage output of bilirubin in patients with



hepatic inefficiency is increased by administration of sugar and diminished in hepatic disease and health by withdrawal of sugar by means of insulin injection. The improvement in hepatic function is attributed to increased formation of new liver-cells. Owing to the dependence of cell growth on glycolysis (I) and better (I) from fructose (II) than from glucose, (II) is said to be more efficient. NUTR. ABS. (m)

**Storage of glycogen in the diseased liver after administration of different sugars.** F. K. GASSMANN (Z. ges. exp. Med., 1933, 88, 599—604).—In the livers of dogs administration of fructose (I) leads to a much greater glycogenogenesis than does that of glucose (II); intravenous administration (III) gives the best results. Simultaneous injection of insulin increases glycogenogenesis with (II), but decreases it slightly with (I). In the treatment of hepatic disease in man (III) of 20—40 c.c. of 20% (I) or 10% (I) at the rate of 100 c.c. per hr. is recommended. NUTR. ABS. (m)

**Glycogen-storing disease.** P. KIMMELSTIEL (Beitr. pathol. Anat., 1933, 91, 1—18).—Excessive deposits of glycogen (I) were found in the liver, brain, muscles, and heart of an infant which died of the disease; the kidneys contained little (I) and all other organs were free, whilst the deposits in the brain were localised. Diastatic fermentation of the child's liver-(I) was slower than that of (I) from dog's liver and commercial preps. An abnormal type of (I), resistant to diastase, is laid down in (I)-storing disease. NUTR. ABS. (m)

**Use of 3:5-di-iodothyronine in the treatment of myxœdema.** A. B. ANDERSON, C. R. HARRINGTON, and D. M. LYON (Lancet, 1933, 125, 1081—1084).—3:5-Di-iodothyronine relieves symptoms of myxœdema, and restores and maintains the basal metabolic rate at an approx. normal level. L. S. T. NUTR. ABS. (m)

**Clinical applications of dinitro-*o*-cresol.** E. C. DODDS and J. D. ROBERTSON (Lancet, 1933, 125, 1137—1139, 1197—1198).—Dinitro-*o*-cresol (I) has a powerful action in increasing the metabolic rate in normal adults, but is of no use in alleviating symptoms of myxœdema. This indicates that the increase in metabolism induced by (I) may be different from the normal metabolic process. L. S. T.

**Water excretion as a measure of equilibrium with environment.** D. N. PARFITT (Brit. Med. J., 1933, i, 1102—1103).—In states of emotional tension there is a delay in H<sub>2</sub>O secretion. A simple H<sub>2</sub>O excretion test is described. The results show general agreement with those obtained by the hyperglycæmic index test on the same patients. Such tests give increased accuracy of prognosis in certain mental diseases. NUTR. ABS. (m)

**Muscle-potassium in some neurological conditions.** A. LEULIER, B. POMMÉ, and A. BERNARD (Compt. rend. Soc. Biol., 1933, 112, 1413—1414).—In cases of lower motor neurone lesions but not in parkinsonian post-encephalitis there is reduction in the K content of the affected muscles. In diphtheritic peripheral neuritis the affected quadriceps contains 3.11 mg. of K per 100 g., whilst the normal muscle contains 4.21. NUTR. ABS. (m)

**Acid-base equilibrium in relation to œdema.** O. L. E. DE RAAFT (Klin. Woch., 1933, 12, 224—225).—Nephritic, nephrotic, and cardiac œdema are all due to acidosis due to insufficiency of the kidney or of the circulation. The formation of NH<sub>4</sub>HCO<sub>3</sub> in acidotic tissues leads to retention of H<sub>2</sub>O and NaCl for further neutralisation, through the reaction: NaCl + (NH<sub>4</sub>)HCO<sub>3</sub> = NaHCO<sub>3</sub> + NH<sub>4</sub>Cl. Hunger-œdema is due to the same mechanism. NUTR. ABS. (b)

**Behaviour of atoxyl-resistant lipase after gastric operations.** H. DIBOLD and M. TAUBENHAUS (Klin. Woch., 1933, 12, 857—860).—After resection of the stomach an increased atoxyl-resistant lipase content of the blood is observed (12 out of 27 cases). Similar results are obtained in evident pancreatic disease (9 out of 11), but seldom in other cases (6 out of 39). NUTR. ABS. (m)

**Colloid-chemical investigations on the swelling of gelatin jellies in the serum of gynæcological patients.** N. M. MOGILEVSKAJA (Kolloid-Z., 1933, 65, 234—236).—The effect of the blood-serum on the elasticity of a gelatin jelly gives an indication of disease. E. S. H.

**Serum-calcium and -phosphorus during pregnancy.** J. W. MULL and A. H. BILL (Proc. Soc. Exp. Biol. Med., 1933, 30, 854—856).—Serum-Ca shows a decline until about a week before delivery, when a rise begins and continues until the second week *post partum*. The vals. in the period Jan. to Apr. are generally < those in May to Dec. Serum-P decreases very slightly *ante partum* with a sharp rise just prior to and after delivery: it exhibits no seasonal variation. NUTR. ABS. (m)

**Calcium content of the cerebrospinal fluid in normal pregnancy and in eclampsia.** Cerebrospinal fluid-calcium in infants. D. F. ANDERSON (Brit. J. Exp. Path., 1933, 14, 155—159).—In eclampsia (16 cases) the Ca of the fluid ranges from 4.1 to 5.9 mg. (average 5.3) and in normal pregnancy (27 cases) from 4.3 to 6.2 mg. per 100 c.c. (average 5.2). These figures and others from cases taken at random are within physiological limits; abnormal variations which could be connected with the occurrence of convulsions are not found. In infants a few days old having convulsions the vals. range from 6.1 to 6.9 mg. per 100 c.c. (average 6.5). NUTR. ABS. (m)

**Carbohydrate metabolism in cases of unexplained miscarriages.** E. C. P. WILLIAMS (Lancet, 1933, 225, 858—861).—A lowered tolerance for glucose has been observed in 90% of cases of unexplained repeated miscarriage. L. S. T.

**Carbohydrate metabolism in pregnancy and after.** I, II. Sugar and diastase in blood. P. GOLDSCHMIDT-FURSTNER (Arch. Gynäkol., 1933, 153, 417—426, 427—433).—During pregnancy the diastatic activity of the blood falls progressively from the normal val., but rises again after parturition (I); the blood-sugar (II) rises during (I) and then falls. Injection of extracts of pituitary results in a rise of (II) and diastase (III), whilst injection of glucose or adrenaline results in a fall of blood-(III), which later



risers as (II) falls. The changes following the injection of insulin are irregular, but in general (III) falls and later rises. NUTR. ABS. (m)

**Absorption and assimilation of protein in pregnancy.** O. BOKELMANN and W. SCHERINGER (Arch. Gynäkol., 1933, 153, 201—212).—The absorption of protein is the same in pregnant and non-pregnant women. During pregnancy there is no retention of  $\text{NH}_2$ -acids, non-protein-N, or coagulable N in the blood; N is not retained in the tissue fluids. Hence the N is retained as protein in the tissues (probably in the liver). NUTR. ABS. (m)

**Protein metabolism and renal function during pregnancy and the early puerperium.** O. BOKELMANN and W. SCHERINGER (Arch. Gynäkol., 1933, 153, 447—467).—In early pregnancy the metabolic effect of a large meal (650 g.) of meat is as in non-pregnant women. During the early puerperium the condition of N-sparing and reduced protein catabolism characteristic of pregnancy is reversed. A condition of functional renal insufficiency after parturition, distinct from true "pregnancy kidney," is evidenced by disturbances of acid-base equilibrium and  $\text{NH}_3$  production after a protein meal: simultaneous administration of acid emphasises this condition. NUTR. ABS. (m)

**Thyroid hormone and the blood of menstruating and pregnant women.** C. MÜLLER (Arch. Gynäkol., 1933, 153, 244—251; Chem. Zentr., 1933, ii, 404).—The hormone was not detected. A. A. E.

**Parathyroid hormone in the blood in pregnancy.** F. HOFFMANN (Arch. Gynäkol., 1933, 153, 181—200; Chem. Zentr., 1933, ii, 404—405).—Blood-plasma of pregnancy affords a prep. which raises dogs' blood-Ca and has other properties of parathyroid hormone. A. A. E.

**Potassium and sodium in regulation of mineral metabolism by the kidneys in renal disease.** H. GLATZEL (Klin. Woch., 1933, 12, 853—855).—In nephritis (I) there is delayed excretion and lower concn. of Na and K in the urine. The total eliminated  $\text{Na} + \text{K}$  in the same subject is the same whether the diet fed is rich in either. In (I) therefore a max. alkali concn. exists in the urine, in which Na and K can replace each other to a certain extent. In normal subjects on acid or alkaline diet the acid-base equilibrium (III) of the blood and tissues is maintained mainly by the excretion of  $\text{NH}_3$  or org. acids, and Na, Ca, and Cl, K taking no part in this regulating mechanism (II). In kidney diseases (II) is upset and (III) can be maintained only by the help of the fixed ions. The excretion of K then plays an important part in the regulation of  $p_{\text{H}}$ , so that a significant loss of K may result. NUTR. ABS. (m)

**Calcium content of muscles and liver of normal and starved guinea-pigs, or afflicted with acute or chronic scurvy.** A. MICHAUX (Compt. rend., 1933, 197, 1453—1455).—The muscle-Ca of guinea-pigs fed on a scorbutic diet is the greater the larger is the dose (4—5%) of Ca lactate added to the normal diet, and is very high in severe cases of acute or chronic scurvy, but the liver-Ca is < in animals fed

on a normal diet, and is approx. the same as in those given distilled  $\text{H}_2\text{O}$  only. All animals received only  $\text{H}_2\text{O}$  for the 15 hr. preceding death. J. W. B.

**Silicosis.** W. R. JONES (J. Chem. Met. Soc. S. Africa, 1933, 34, 99—123).—The mineral in silicotic lungs responsible for the disease consists of minute acicular fibres, usually sericite and not quartz (cf. A., 1933, 1192). Preventive methods are discussed. W. O. K.

**Variations in blood-sugar after splenectomy.** F. RATHERY and I. COSMULESCO (Compt. rend. Soc. Biol., 1933, 113, 548—551).—The changes in the sugar content of the blood of dogs, produced by splenectomy, are variable. NUTR. ABS. (m)

**Effect of work on gas exchange in pulmonary tuberculosis.** T. EBINA and I. SATO (Tōhoku J. Exp. Med., 1933, 21, 125—136).—As regards  $\text{O}_2$  consumption (I) tuberculous subjects are divided into: (a) those with markedly increased (I) during work and a quick return to the resting val.; (b) those with a smaller increase during work and a prolonged recovery period; and (c) those who behave like controls. NUTR. ABS. (m)

**Plasma-phosphatase in pulmonary tuberculosis.** L. BINET and J. PAUTRAT (Compt. rend., 1933, 197, 945—946).—The phosphatase content of venous plasma increases in fibrous pulmonary tuberculosis. A. C.

**Lipolytic power of the liver of the normal and the tuberculous pig.** M. GHIRON (Annali Chim. Appl., 1933, 23, 495—501).—A glycerol extract of pig's liver (previously extracted with  $\text{COME}_2$  and  $\text{Et}_2\text{O}$ ) shows marked lipolytic action on tributyrin,  $\text{PrCO}_2\text{Me}$ , neutral olive oil, and fats extracted from dried tubercle bacilli by  $\text{COME}_2$ , the last being emulsified in a system of activators formed from  $\text{CaCl}_2$  and ovalbumin. The results obtained similarly with an extract of tuberculous pig's liver indicate that the disease stimulates the production of lipolytic enzymes of the liver (cf. B., 1932, 622). T. H. P.

**Micro-incineration of tubercles.** E. R. LONG (Proc. Soc. Exp. Biol. Med., 1933, 30, 1090—1092).—The nuclei of the cells (man, guinea-pig) ignited at  $540^\circ$  for 4 hr. are richest in ash (I), and the cytoplasm is generally low in mineral content. The (I) from regions of degeneration and necrosis is < that of corresponding undegenerated tissue because sol. mineral material diffuses away. In late stages of human tuberculosis there is increase of (I) in the necrotic tissue. In tuberculous rabbits treated with viosterol remineralisation seems to increase. NUTR. ABS. (m)

**Gastric pepsin. II. Secretion of pepsin in cases of duodenal ulcer and pseudo-ulcer.** F. R. VANZANT, A. E. OSTERBERG, W. C. ALVAREZ, and A. B. RIVERS (J. Clin. Invest., 1933, 12, 557—565).—In cases of healed duodenal ulcer peptic activity (I) generally fell within normal limits, although the average was above normal. In cases with definite symptoms of duodenal ulcer the average (I) was 2.5 times the normal mean, with gastric ulcer it was only slightly > normal, and with duodenal or jejunal ulcer after gastro-enterostomy (I) was high.



In patients with symptoms of duodenal ulcer but in whom this was not present it was as high as in the ulcer patients. This test is a more sensitive index than the determination of free HCl.

#### NUTR. ABS. (b)

**Physiology of bone-marrow.** K. FELIX, A. GRASSMÜCK, K. HUCK, and K. MATZEN (Z. physiol. Chem., 1933, 221, 137—144).—The  $O_2$  uptake of red marrow (I) of calves is 0.28—0.32 c.c. per g., of fatty marrow (II), 0.09—0.15 c.c. in 5 hr. The optimum  $p_H$  is 8.3. The purine-N of (I) is 0.18—0.24%, of (II) 0.06—0.08%. The  $O_2$  uptake increases with the purine-N content. It is also increased by alanine, the anti-anæmic and other substances in preps. from liver and gastric mucosa, probably by proline and tryptophan, but not by aspartic or glutamic acid, glycine, or glycylglycine.

J. H. B.

**Effect of restricted diet on oxidative processes.** I. KANAI (Z. ges. exp. Med., 1933, 88, 725—732).—In rats fed on diets consisting chiefly of protein (I), fat, or carbohydrate (II), respectively, the C:N and "Vacat":O (III):N ratios are low with (I) and high with fat and (II). (III):C is lowest with (I) and highest with (II). The total amount of (III) is greatest with (I). Although the total amount of incompletely oxidised material in the urine is greatest with (I), oxidation during intermediate metabolism is then relatively much better.

#### NUTR. ABS. (m)

**Respiration of *Diphyllobothrium latum* (L.). Respiration enzymes.** E. A. H. FRIEDHEIM and J. G. BAER (Biochem. Z., 1933, 265, 329—337).—The respirations of *D. latum* (egg, larva, and adult) and of *Triacnophorus lucii* (adult) are not inhibited by CO in presence of only 5%  $O_2$ , the effects being the same for anaerobically living worms and aerobically developing eggs. The KCN inhibition, however, is incomplete with the worm, but complete with the egg. The presence of cytochrome c is indicated.

P. W. C.

**Eosin and tissue respiration.** R. DEL ZOPPO (Arch. Farm. sperim., 1933, 56, 536—542).—Intravenous injection of 20—30 c.c. of 1% eosin into rabbits causes a diminution of respiratory activity of the liver, kidney, spleen, and testicle, and an increase in  $O_2$  content of the blood, particularly venous blood.

R. K. C.

**Intermediate metabolism of the endocrine glands.** A. UTEVSKI, S. EPSTEIN, V. OSSINSKAJA, and E. MMA (Biochem. Z., 1933, 265, 320—328).—The thymus (I) and thyroid (II) glands contain small amounts of glycogen. In the ox, the lactic acid (III) content of (I) is much > that of (II). The (III) content of the glands in exophthalmic goitre (IV) and strumatic diseases is much > in the glands of normal animals. Alanine increases the formation of (III) in (I), but not in (II). In (IV) the formation of (III) is slightly increased in presence of alanine. MeCHO is formed only in small amounts in both (I) and (II), which are poor in carboxylase. The amount of MeCHO is increased on adding glycogen or glucose.

P. W. C.

**Fate in the animal body of anthocyanins from Concord grapes.** M. K. HORWITT (Proc. Soc. Exp.

Biol. Med., 1933, 30, 949—951).—Anthocyanins are not easily absorbed from the intestine. The small quantity which passes through is apparently excreted unchanged by the kidney.

NUTR. ABS. (m)

**Changes in blood-constituents produced by partial inanition and muscular fatigue.** F. W. SCHLUTZ, A. B. HASTINGS, and M. MORSE (Amer. J. Physiol., 1933, 104, 669—676).—In dogs, blood analysis shows that swimming is much more fatiguing than treadmill exercise. Exercise accompanied by under-nutrition produces changes in the same direction, but of greater magnitude than in the normal animal. Return to the normal level is delayed in malnutrition.

NUTR. ABS. (m)

**Rigor of muscle and changes induced by various physiological factors. I. Calf muscle of guinea-pigs and rats.** W. LENKEIT (Arch. Tierernähr. Tierzucht, 1933, 9, 266—349).—Relationships are examined between the post-mortal rigor of muscles and their colloidal condition as shown by  $H_2O$ -absorbing properties when placed in contact with hyper-, iso-, and hypo-tonic solutions of alkali chlorides.

A. G. P.

**Effect of  $p_H$  on carbohydrate changes in isolated anaerobic frog muscle.** M. KERLY and E. RONZONI (J. Biol. Chem., 1933, 103, 161—173).—During anaerobic breakdown of muscle-carbohydrate at an alkaline reaction the lactic acid (I) increase balances the carbohydrate (II) decrease, there is a small increase in hexose monophosphate (III), and the formation of lower (II) from glycogen (IV) is small. As the reaction becomes more acid, (I) decreases while (III) increases to balance (II). At  $p_H$  6 considerable quantities of glucose and an intermediary (II) are formed from (IV).

H. G. R.

**Disappearance of hexose phosphate from intact frog muscle.** E. RONZONI and M. KERLY (J. Biol. Chem., 1933, 103, 175—181).—Under anaerobic conditions at  $p_H$  6, 70—80 mg. of hexose phosphate (I) are formed per 100 g., the phosphocreatine (II) almost completely hydrolysed, and 50% adenosine triphosphate (III) is dephosphorylated in 2½ hr., but no lactic acid (IV) is formed. On treatment with  $O_2$  the normal level for these substances is again reached, with increased consumption of  $O_2$  which becomes normal when (II) is reconstituted. In  $N_2$  at  $p_H$  9, the breakdown of (II) is slower with little change in (I) and a normal production of (IV). There is no reconstitution of (II) and (III).

H. G. R.

**Chemical processes accompanying the activity of muscle.** E. M. KREPS (J. Physiol. U.S.S.R., 1932, 15, 258—275).—A summary.

T. H. P.

[Carbohydrate metabolism in muscle.] A. HAHN (Z. Biol., 1933, 94, 97—98).—Meyerhof's views (A., 1933, 742) of the source of  $AcCO_2H$  in muscle extracts and of the presence of natural H acceptors are discussed.

A. G. P.

**Lactic acid metabolism of the dog's isolated heart.** A. RÜHL and H. ROLSHOVEN (Klin. Woch., 1933, 12, 776—777).—The amount of lactic acid (I) removed from the blood by the heart is not increased when the work of the heart-muscle is increased. Poisoning of the heart with histamine, somnifen, and



avertin does not decrease removal of (I) nor does treatment with strophanthin, caffeine, or adrenaline. The amount removed is greater when the blood-(I) is high. Synthesis of carbohydrate from the lactate (II) is assumed, although there is no connexion between the  $O_2$  uptake and the amount of (II) absorbed. After poisoning with cyanide, the heart loses (II).

NUTR. ABS. (m)

**Bile acids and carbohydrate metabolism.** XXIX. Influence of bile acids on tissue oxidation and carbohydrate utilisation. Z. URAKI (J. Biochem. Japan, 1933, 18, 207—225).—Dehydrogenation and the oxidation of glucose, fructose, glycogen, and glycerophosphoric, lactic, and succinic acids by muscle- and liver-tissues are inhibited by cholic acid; the oxidation of hexose mono- and di-phosphate is, however, not influenced. The mechanism of the inhibition is discussed.

F. O. H.

**Is d-glucose absorbed from the dog's stomach?** S. J. MADDOCK, H. C. TRIMBLE, and B. W. CAREY, jun. (J. Biol. Chem., 1933, 103, 285—294).—Determination of the glucose in the blood from the peripheral and intra-abdominal vessels of dogs with ligatured pylori before and after ingestion of glucose in quantities of from 5 to 27 g. shows practically no gastric absorption; a similar result was obtained by a method dispensing with the use of anaesthetics and fistulae.

H. D.

**Citric acid metabolism.** A. C. KUYPER and H. A. MATTILL (J. Biol. Chem., 1933, 103, 51—60).—Serum-citrate is decreased by alkalosis (I) and inanition and increased by acidosis (II). Citric acid (III) in urine is increased after meals and by (I) and decreased by (II) and exercise. (III) is not completely oxidised by the human organism, and no correlation was observed between the oxidation and any particular tissue.

H. G. R.

[Glycuronic acid.] I. Origin in the urine of rabbits. C. O. MILLER and J. CONNOR. II. Metabolism in the dog. C. O. MILLER, F. G. BRAZDA, and E. C. ELLIOT. III. Glycuronic acid as a growth factor in guinea-pigs. C. O. MILLER, A. E. SIEHRS, and F. G. BRAZDA (Proc. Soc. Exp. Biol. Med., 1933, 30, 630—633, 633—636, 636—638).—I. The rabbit is apparently unable to synthesise glycuronic acid (I) from carbohydrates (II) or  $NH_2$ -acids (III), or only very slowly. The acid, which is produced by the digestion of mucin, was readily available when required by the body for combination with certain toxic substances.

II. The dog is probably provided with a store of (I) or may be able to synthesise it from (II) or (III). When stores of (I) were depleted, borneol given by stomach tube rapidly exerted a toxic effect. Mucin, included in the diet, protected against comparatively large doses of borneol, presumably because of (I) provided by its digestion.

III. (I) did not protect guinea-pigs on a scorbutic diet from developing scurvy nor reduce the severity of the disease. It did, however, postpone the period of loss of wt., and facilitated wt. recovery when orange juice was added to the diet. Like the rabbit, the guinea-pig either cannot synthesise (I), or only slowly.

NUTR. ABS. (b)

**Nutritive value of calcium gluconate.** T. TAKAHASHI, T. ASAI, and M. KANEKO (J. Agric. Chem. Soc. Japan, 1933, 9, 567—572).—Ca as  $CaCl_2$ ,  $CaCO_3$ , lactate, and gluconate (I) was given to rats (0.6% of standard feed); (I) was the best source of Ca.

CH. ABS.

**Complete utilisation of heat of combustion of ethyl alcohol by homeotherms in thermoneutrality.** E. LE BRETON and G. SCHAEFFER (Compt. rend., 1933, 197, 1066—1068).—In warm-blooded animals in a temp. thermally neutral, the ingestion and combustion of EtOH does not result in the liberation of extra heat.

W. O. K.

**Glycogen formation in the white rat after oral administration of propionic, butyric, valeric, and hexoic acids.** H. C. ECKSTEIN (J. Biol. Chem., 1933, 102, 591—594).—Using the Cori technique, increases in liver-glycogen (I) are shown to result from the administration of  $EtCO_2H$ . With butyric, valeric, and hexoic acids, no increase in (I) was apparent, although absorption had taken place. Mobilisation of body-glycogen did not occur throughout the experiments.

A. L.

**Dietary production of fatty livers in rats.** N. R. BLATHERWICK, E. M. MEDLAR, P. J. BRADSHAW, A. L. POST, and S. D. SAWYER (J. Biol. Chem., 1933, 103, 93—106).—Fatty livers are produced by feeding whole liver or eggs, whereas lecithin tends to decrease the fat, which appears to be that normally present. Lipins of blood and kidneys are not materially altered.

H. G. R.

**Physiology of intermediate metabolism after Claude Bernard's piqure.** IV. Alkali reserve and blood-chloride. V. Residual nitrogen and certain other blood-components. G. D. OBRATZSOV, E. T. MINKER-BOGDANOVA, and M. N. KALLINKOVA (J. Physiol. U.S.S.R., 1932, 15, 206—211, 212—217).—With the rabbit, piqure causes alteration of the acid-base equilibrium, the alkali reserve falling and the blood-Cl' rising at once, but gradually becoming normal later. The residual N undergoes no sp. change, inorg.  $PO_4'''$  increases, org.  $PO_4'''$  and Ca decrease, and K shows no clear change. From these and earlier results it appears that piqure causes, besides hyperglycaemia, other changes in the blood-components similar to those produced by adrenaline.

T. H. P.

**Calorigenic action of glycine.** H. G. LEWIS and J. M. LUCK (J. Biol. Chem., 1933, 103, 227—233).—In doses above 0.6 g. per kg. body-wt. glycine (I) administered subcutaneously to fasting rats produces an excess metabolism < that produced by (I) administered orally. Above 2.2 g. (I) is toxic, and often produces a lowered metabolic rate. The increased metabolism induced by moderate doses occurs soon after dosage and lasts > 1 hr.

H. D.

**Specific dynamic action of protein and its relation to post-prandial excretion of urea.** E. MAY and A. MEYER-HEINE (Compt. rend. Soc. Biol., 1933, 112, 1311—1313).—In normal subjects 1½ hr. after a test meal of 200 g. veal, 100 g. bread, and 100 c.c.  $H_2O$  there is an average increase of 20% in the metabolic rate (min. increase 10%). Urea excre-



tion during the same period runs parallel to the sp. dynamic action. NUTR. ABS. (m)

**Blood-urea and nutrition.** G. V. DERVIS and A. V. LYSLOVA (J. Physiol. U.S.S.R., 1932, 15, 439—445).—On a meat diet the blood-urea (I) is 2—3 times that on a carbohydrate (II) diet and even greater when meat is taken without drinking. A single meal of meat produces a considerable rise in (I), which reaches a max. in 8 hr. A single meal of (II) produces a small decrease in (I). H. D.

**Residual nitrogen and creatinine on different diets.** E. A. KAFIYEVA (J. Physiol. U.S.S.R., 1932, 15, 446—450).—On a meat diet (I) the residual N (II) is twice as great as on a carbohydrate diet. The increase of creatine-creatinine (III) on (I) runs parallel with that of (II), the increase of N corresponding with the increase in (III) being 5% of the increase in (II). H. D.

**Effect of restriction of protein intake on the serum-protein concentration of the rat.** A. L. BLOOMFIELD (J. Exp. Med., 1933, 57, 705—720).—Rats receiving for 21 weeks a diet low in protein (2.6% from yeast and 0.3% from lucerne), but otherwise adequate, show no significant decrease in the serum-protein except for an initial fall of about 10%. NUTR. ABS. (m)

**Nutritive protein value of five varieties of rice.** A. J. HERMANO (Philippine J. Sci., 1933, 51, 567—572).—Young rats fed on a diet containing approx. 5—10% of protein never attained normal maturity. Mancasar rice, although containing less protein than three other varieties, appears to have the highest nutritive val. No relation exists between ash, carbohydrate, and fat contents, and nutritive val. J. G.

**Comparative study of the paired and *ad libitum* feeding methods for determining amino-acid deficiencies of foods.** C. L. SHREWSBURY and J. W. BRATZLER (J. Assoc. Off. Agric. Chem., 1933, 16, 582—584).—Statistical analysis of the results obtained with rats using 10 and 15% of soya-bean protein in a purified diet and 6% as a supplement to maize showed that paired feeding (with equalised consumption) gave the more trustworthy results. L. S. T.

**Outlook in the science of nutrition.** L. B. MENDEL (Science, 1933, 78, 317—322).—A survey. L. S. T.

**Metabolism in high external temperatures on different diets.** A. A. MITTELSTEDT (J. Physiol. U.S.S.R., 1932, 15, 424—438).—Men were maintained in a room at 50° and 29 mm. aq. v.p. on a diet (I) containing sufficient protein and on one (II) deficient in protein. On (I) retention of N and no increased intensity of oxidation (III) were observed, whilst on (II) increased N excretion and increased (III) occurred. Cl<sup>-</sup> excretion on (I) was > that on (II). The excretion of salts showed no regularities. H. D.

**Chemistry of embryonic growth. III. Embryonic growth of the pig in relation to nitrogen compounds.** V. A. WILKERSON and R. A. GORTNER (Amer. J. Physiol., 1932, 102, 153—166).—Total N remains const. after the embryo has reached 50 mm., following an early fall. Glutathione and S increase

rapidly up to 30—50 mm. and then gradually decrease. H<sub>2</sub>O content is const. from 15 to 160 mm. after an initial rapid decline, and then decreases gradually until after birth. The arginine content is highest in young embryos; histidine and tyrosine also decrease during development. There is a continuous rise in ash content up to 240 mm. P. G. M.

**Influence of varied nutrition of pregnant sows on the development of the piglings.** D. DJAPARIDSE (J. Landw., 1933, 81, 249—280). A. G. P.

**Uric acid synthesis in the bird. I. Pigeon. II. Hen and goose.** W. SCHULER and W. REINDEL (Z. physiol. Chem., 1933, 221, 209—231, 232—240; Klin. Woch., 1933, 12, 736—738).—I. Both liver and kidneys are concerned in uric acid synthesis in the pigeon. An unknown precursor (not a purine) is produced in both organs by an enzymic reaction with  $p_H$  and temp. optima of 7.6—7.7 and 40°, respectively. The same precursor is present in muscle and other organs, but is not there produced by enzymic synthesis. The actual synthesis of uric acid from the precursor takes place only in the kidney. This reaction has an optimum  $p_H$  of 7.1 and is a function of living tissue. The N sources for the synthesis are NH<sub>2</sub>-acids (degraded by way of NH<sub>3</sub>) but not urea. The sources of C are not glycerol, or lactic or tartronic acid.

II. In the hen and goose the synthesis of uric acid follows the same course as in the pigeon, but here the surviving liver as well as kidney tissue is able to transform the precursor into uric acid. The precursor is identical in all three species. J. H. B.

**Purine metabolism in fish and amphibia.** E. STRANSKY (Biochem. Z., 1933, 266, 287—300).—Fish and amphibia excrete urea (I). Uric acid (II) and allantoin (III) cannot be detected with certainty in frog's urine. The livers of these animals convert (III) and (II) by way of (III) into (I). (III) and allantoic acid (IV) give a positive Ehrlich aldehyde reaction. (III) and (IV) may be differentiated by xanthhydrol. The glyoxylic acid reaction is not characteristic for (III) and is given strongly by (IV). Vertebrates are classified according to the end-products of their purine and protein metabolism. P. W. C.

**Rate of change of alkali reserve after ingestion of organic salts. I. Normal variations in acid-base balance under basal conditions.** J. CAPE and E. L. SEVRINGHAUS (J. Biol. Chem., 1933, 103, 257—260).—The  $p_H$ , CO<sub>2</sub> content, and total base in the sera of normal individuals under basal conditions showed no significant variations over a morning period of 5 hr. H. D.

**Calcium and phosphorus metabolism of normal young children. II. Variation in calcium and phosphorus storage.** T. PORTER-LEVIN (J. Amer. Dietetic Assoc., 1933, 9, 22—35).—The mineral intake of children is remarkably const. (average Ca intake 1.010±0.004 g. per day; average P intake 1.050±0.004 g.). The average excretion of Ca is 87 and of P 83%. The average "per kg." retentions (I) are 0.007 g. Ca and 0.008 g. P per day, but the retentions vary greatly from period to period, P retention being slightly less variable than that of Ca.



15 to 21 consecutive days are required to cover the entire range of variation in these (I).

#### NUTR. ABS. (m)

**Relation of milk ingestion to calcium metabolism in children.** A. L. DANIELS, M. K. HUTTON, E. KNOTT, G. EVERSON, and O. WRIGHT (Proc. Soc. Exp. Biol. Med., 1933, 30, 1062—1063).—The amount of Ca, P, and N retained by a child on an adequate or abundant consumption of milk depends primarily on physiological condition. When the previous diet has been below requirements, more of these factors is retained, at least in earlier stages, than if the previous diet had been adequate. Well-nourished children retain approx. the same quantity of Ca whether receiving a pint or a quart of milk per day.

#### NUTR. ABS. (m)

**Effect of calcium-deficient roughages on milk-production and welfare of dairy cows.** R. B. BECKER, W. M. NEAL, and A. L. SHEALY (Florida Agric. Exp. Sta. Bull., 1933, No. 262, 28 pp.).—Cows on low-Ca pasture from acid sandy soils showed lowered bone strength, and milk yields were subnormal even when high-protein supplements were used. Addition of 2% bone meal and 5% lucerne hay increased bone strength to > normal and increased milk yields without additional storage of fat. The Ca and P required for reproduction was much < that for lactation.

#### A. G. P.

**Iron in the nutrition of infants. III. Metabolism of iron in infants breast-fed for the first year.** A. WALLGREN (Rev. franc. Pédiat., 1933, 9, 196—235).—The daily Fe balance varied from -0.274 to +1.054 mg., but was usually positive. The retention of Fe was less in the first 5 months, but there was no fall in blood-haemoglobin even when the Fe balance was negative. The amount of Fe contained in breast-milk (average 0.642 mg. per 1000 g.) was sufficient for the requirements of the infants. The Fe contained in the tissues of the normal, new-born infant together with that liberated from dead red cells may amplify the small intake. The relatively large amounts of Fe found in the faeces in the early months indicate that some of the endogenous Fe is excreted.

#### NUTR. ABS. (b)

**Copper and iron as dietary factors.** H. L. KEIL, H. H. KEIL, and V. E. NELSON (Proc. Soc. Exp. Biol. Med., 1933, 30, 1153—1155).—Normal haemoglobin regeneration in milk-fed anaemic rats occurs with 0.15 mg. colloidal Fe and 0.002 mg.  $\text{CuSO}_4$  injected intraperitoneally, daily, in addition to a daily oral dose of 0.5 mg. Fe as  $\text{FeCl}_3$ . Rats on milk, Cu, and Fe in the first generation reproduce as well as do rats on a mixture of NaI, NaF,  $\text{K}_2\text{SO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{MnSO}_4$ , and  $\text{Na}_2\text{SiO}_3$ , but in the former case, the mortality of the young is considerably greater and their wt. at birth is less.

#### NUTR. ABS. (m)

**Action of copper and other elements in iron metabolism.** E. MUNTWYLER and R. F. HANZAL (Proc. Soc. Exp. Biol. Med., 1933, 30, 845—846).—Administration of Fe for 14 days to rats rendered anaemic by a milk diet results in increase in the Fe content (I) of the liver and improvement in the blood count (II). Succeeding administration of milk diet only causes decrease in (I) and (II). Addition of Cu

only, as a dietary supplement at the end of this period, produces a rise in (II), but a fall in (I). The Cu mobilises the Fe stores of the liver to produce haemoglobin and erythrocytes.

#### NUTR. ABS. (m)

**Chlorine metabolism. II. Blood-chlorine and -nitrogen after chlorine-free and low-chlorine diets. III. Blood-chlorine and -nitrogen after administration of sodium chloride.** G. FERRO-LUZZI (Arch. Farm. sperim., 1933, 56, 477—486, 502—511; cf. A., 1933, 531).—II. With a Cl-free diet patients suffer general discomfort after 8—10 days, and the urinary Cl falls, but neither Cl nor N in the blood changes significantly. The diet is better tolerated after addition of milk.

III. After ingestion of 10 g. of NaCl by human patients the blood-Cl rises markedly and the blood-N slightly, whilst the no. of red corpuscles falls. The rise in blood-N is regarded as an effect of functional interference with the kidney as a result of varying the mol. concn. of the blood.

#### R. K. C.

**Action of the brain cortex on respiration.** R. P. OLNJANSKAYA (J. Physiol. U.S.S.R., 1933, 15, 314—329).—Mental stimuli and irritants acting on persons doing work cause changes in the rate of respiration.

#### A. L.

**Widmark's method for determining blood-alcohol and its forensic significance.** J. KOLLER (Deut. Z. ges. gerichtl. Med., 1933, 21, 269—274; Chem. Zentr., 1933, ii, 915).—The method is satisfactory; the significance of the results is discussed.

#### A. A. E.

**Action of amino-acids on the alcohol content of blood.** E. M. P. WIDMARK (Biochem. Z., 1933, 265, 237—240).—Addition of glycine or alanine to an alcoholic drink administered to fasting dogs leads to a decreased blood-EtOH during the post-absorptive period.

#### P. W. C.

**Anæsthetic action of a series of naphthalene derivatives.** M. E. FISK and F. P. UNDERHILL (J. Pharm. Exp. Ther., 1933, 49, 329—336).—Of seven compounds tested of the general formula

$\text{R}\cdot\text{CO}_2\cdot[\text{CH}_2]_n\cdot\text{NAlk}_2$  ( $n=2$  or  $3$  and  $\text{R}=\text{C}_{10}\text{H}_7$ ,  $\text{OH}\cdot\text{C}_{10}\text{H}_6$ , or  $\text{OEt}\cdot\text{C}_{10}\text{H}_5$ ), all possess local anæsthetic action, but most produce considerable local irritation.  $\text{NEt}_2\cdot[\text{CH}_2]_3$  2-ethoxy-3-naphthoate was superior to the others.

#### W. O. K.

**Effect of calcium administration on the toxicity of carbon tetrachloride in mice.** F. WOKES (Quart. J. Pharm., 1933, 6, 413—417).—Addition of  $\text{CaCO}_3$  (0.2—3%) or Ca lactate (0.15—0.3 g. per kg.) to the diet produced no and a slight protection again the poison, respectively.

#### R. S. C.

**Variation in the susceptibility of mice to certain anæsthetics.** J. C. GAGE (Quart. J. Pharm., 1933, 6, 418—426).—The ratio anæsthetic dose/toxic dose for mice for paraldehyde and avertin *per rectum*, nembutal and pernocton intravenously, is about 1 : 2, the doses causing anæsthesia for 1 hr. being about 0.1 c.c., 0.03 c.c., 6 mg., and 0.06 c.c. per 100 g. body-wt., respectively. A small proportion of mice is abnormally susceptible.

#### R. S. C.

**Permeability of the placenta to barbituric acid derivatives.** R. FABRE (J. Pharm. Chim., 1933,



[viii], 18, 417—418).—Veronal passes unchanged through the placenta, and may be detected in foetal blood and organs. S. C.

**Copper metabolism. II. Copper content of liver.** S. SUMEGI (Frankfurter Z. Path., 1933, 44, 490—507).—In the livers of rabbits poisoned with  $\text{CHCl}_3$  a severe necrosis of the central zone of the lobuli is of fibrinous character at first, but after some weeks regeneration takes place. The Cu content of the  $\text{CHCl}_3$ -livers is increased above the max. normal val. in 58% of the cases and is independent of the amount of  $\text{CHCl}_3$  given. After some weeks the difference decreases, but persists even if large amounts of Cu be given. A pigment containing a varying amount of Cu appears mostly in the healthy liver cells and represents a definite stage in excretion. The necrotic cells do not contain it; the regenerated cells only slowly acquire the power of excreting it. Haemosiderosis was observed especially at the beginning of the Cu injections as a result of the hæmotoxic action of Cu. The increase of Cu found in human cirrhotic livers is the result of acute parenchymatous lesions. NUTR. ABS. (b)

**Effect of anæsthetics on blood-sugar before and after bulbar puncture.** J. VIDAL (Compt. rend. Soc. Biol., 1933, 112, 760—762).—With the rabbit, neither somnifen nor chloralose has any appreciable effect on the blood-sugar level, but they inhibit piqûre hyperglycæmia (I). Urethane causes slight (I), but does not prevent piqûre-(I).

NUTR. ABS. (b)  
**Disturbances of carbohydrate metabolism in narcosis. Effect of pernocton on carbohydrate metabolism.** H. HELLER and P. NATHAN (Deut. med. Woch., 1933, 59, 956—958).—Changes (hyperglycæmia, loss of liver-glycogen) in carbohydrate metabolism during general anæsthesia may be dangerous. Since pernocton (I) anæsthesia has no effect on blood-sugar or blood-lactic acid, (I) is recommended for diabetics and in liver disease. NUTR. ABS. (m)

**Nervous regulation of blood-sugar. Decerebration hyperglycæmia.** J. J. R. MACLEOD and S. DONHOFFER (Klin. Woch., 1933, 12, 778—781).—Puncture of the floor of the fourth ventricle of the brain of starved, deeply anæsthetised (barbituric derivatives) rabbits does not produce hyperglycæmia (I). In rabbits, similarly starved and under intravenous amytal or local anæsthesia, decerebration (II) at the pons, but not at other levels, produces a considerable (I). (I) is not necessarily accompanied by a diminution of liver-glycogen, but practically always by a fall of muscle-glycogen (III); the total glycogen which disappears is insufficient to account for (I). Blood-lactic acid is increased, probably from (III). The respiratory exchange is unaffected. In normally fed animals (I) is prevented by double adrenalectomy, vagotomy, and atropine or atropine and ergotamine; when the liver contains much glycogen (> 5%) (II) leads to (I) under these conditions. Two physiological types of glycogen are postulated: (a) a storage form which is readily released by a stimulus unaffected by atropine etc.; (b) a gluconeogenic form, a new product from protein and fat, the release of which requires other conditions. Amytal and luminal arrest

the decerebration (I), an effect connected with the absence of rise of blood-sugar with these anæsthetics.

NUTR. ABS. (m)

**Operative interference with carbohydrate metabolism.** Y. KOMATSU (Arch. klin. Chirurg., 1933, 174, 65—97).—Postprandial hyperglycæmia (I) of the dog is less pronounced after denervation (II) of the liver; adrenaline hyperglycæmia (III) is usually affected in a similar way. These changes occur a few days after operation and remain fairly const. (I) and (III) increase after partial removal of the pancreas (IV). This effect may diminish in a few months, but never disappears completely. 3—4 months after (IV). (II) reduces (I) to a normal level, provided no severe diabetes has meanwhile developed. Simultaneous (II) may suppress completely the effect of (IV). (II) has no effect on (III) after (IV).

NUTR. ABS. (b)

**Blood-sugar-depressant principle of onions (*Allium sativum*) active per os.** I. P. LALAND and O. W. HAVREVOLD (Z. physiol. Chem., 1933, 221, 180—196).—Onion extract administered per os depresses the blood-sugar (I) of rabbits and depancreatized dogs. The active principle is volatile in steam and sol. in  $\text{Et}_2\text{O}$ . A substance is also present which increases (I). The depressant fractions lost their activity in 1—10 days at  $0^\circ$ . By fractionation in high vac. and recrystallisation, an alkaloid (?), m.p.  $174^\circ$ , was isolated. The presence of S, which occurs in the active fractions as allyl and diallyl sulphides, together with the alkaloid, appears necessary for the production of the effect. A "picrate fraction" obtained from potatoes had a similar depressant effect on (I). J. H. B.

**Substances decreasing blood-pressure.** I. M. TOKI, Z. MIYOSHI, and N. UYEDA (J. Agric. Chem. Soc. Japan, 1933, 9, 625—631).—The depressor substance in yeast is insol. in org. solvents and stable towards enzyme action. When yeast is autolysed the pressor substance, unstable and sol. in  $\text{EtOH}$ , is produced and then disappears; finally only the depressor action is retained. CH. ABS.

**Effect of cocainisation on the depressor action of limiting doses of  $\beta$ -methyladrenaline.** RAYMOND-HAMET (Compt. rend. Soc. Biol., 1933, 112, 452—453; Chem. Zentr., 1933, ii, 897).

**Detoxication of veronal with ephedrine.** L. NIERHOFF (Z. ges. exp. Med., 1933, 88, 430—436; Chem. Zentr., 1933, ii, 740).—In rats and cats the abs. mortality after veronal poisoning is not diminished by ephedrine, although in 50% of the cases it produced a favourable symptomatic-therapeutic effect.

A. A. E.

**[Pharmacology of] morphine, codeine, and their derivatives. III. Morphine methochloride and codeine methochloride.** N. B. EDDY (J. Pharm. Exp. Ther., 1933, 49, 319—328).—The methochlorides (I) of morphine (II) and codeine (III) exhibit many of the pharmacological actions of (II) and (III), but usually in diminished strength, and the differences between the two quaternary salts are generally similar to those between (II) and (III). Both (I) have a curare-like action on frogs. W. O. K.



**Relative activity of ergotoxine and ergotamine.** **Assay of ergot preparations.** E. LOZINSKI, G. W. HOLDEN, and G. R. DIVER (Quart. J. Pharm., 1933, 6, 395—398).—Ergot alkaloids contain about 60% of ergotoxine (I). Ergotamine (II) has about 60% of the biological activity of (I). Agreement between the colorimetric determination and biological assay using (II) as standard is a result of these relations.

R. S. C.

**Pharmacology of acetyl- $\beta$ -methylcholine and the ethyl ether of  $\beta$ -methylcholine.** J. H. COMROE, jun., and I. STARR, jun. (J. Pharm. Exp. Ther., 1933, 49, 283—299).—The actions of acetyl- $\beta$ -methylcholine (I) and of  $\beta$ -methylcholine Et ether (II) on animals closely resemble that of muscarine and are similar to the effect of stimulation of the parasympathetic together with peripheral vasodilation. (I) is more active than (II).

W. O. K.

**Hippuric acid in the animal organism.** VII. **Hydrazine intoxication and hippuric acid synthesis in the rabbit.** V. T. TULANE, A. A. CHRISTMAN, and H. B. LEWIS. IX. **Rate of synthesis and excretion of hippuric and phenacetic acids by the rabbit.** V. T. TULANE and H. B. LEWIS (J. Biol. Chem., 1933, 103, 141—150, 151—160).—VII. Synthesis and excretion of hippuric acid (I) are delayed by  $N_2H_4$  intoxication. The decreased excretion of (I) in the early stages is not accompanied by increased excretion of BzOH (II) in any other form.

IX. When  $CH_3Ph-CO_2Na$  (III) is fed, the excretion of phenacetic acid (IV) is small, but increases to 6% when (II) is added and to 21% with glycine. The time for excretion of "extra" (IV) when (III) is fed is considerably > for (I) when (II) is fed.

H. G. R.

**Excretion of foreign protein. Prolonged albuminuria due to injection of egg-white.** L. BRULL (Compt. rend. Soc. Biol., 1933, 113, 67—69).—In dogs receiving subcutaneous injections of ovalbumin containing up to 2 g. of N for periods up to 1 month, 4—68% of the protein is excreted. Renal elements are absent from the urine and there is no evidence of subsequent renal disturbance. The non-protein-N of the blood does not increase.

NUTR. ABS. (m)

**Glutathione in tissues following administration of "Tiargirio."** G. PARADISO (Arch. Farm. sperim., 1933, 56, 487—501).—Reduced glutathione (I) has been determined in the blood, liver, and heart of rabbits and dogs by Tunnicliffe's method (A., 1925, i, 752), which is recommended. No change in (I) is produced by injection of "Tiargirio," a prep. of Hg thiosalicylate.

R. K. C.

**Poisonous principles of *Dimorphotheca spectabilis*, Schltr., and *Dimorphotheca Zeyheri*, Sond.** C. RIMINGTON (18th Rep. Director Vet. Services, Union S. Africa, 1932, 955—972).—The toxic substance in the two plants is linamarin or phaseolutin (cryst. form). It is hydrolysed by an enzyme present in the plants, but not appreciably by emulsin or maltase. *D. spectabilis* yielded about 1.7 g. of HCN by enzymic hydrolysis in the fresh state and *D. Zeyheri* about 1.1 g. per 100 g. (dry wt. basis). Dried plant powder produced typical HCN poisoning in rabbits. The unhydrolysed glucoside

in doses equiv. to 1 min. lethal dose in terms of HCN was not toxic, but was so when previously hydrolysed with plant powder.

NUTR. ABS. (b)

**Constituents of leaves of *Solanum tuberosum* determining alimentation of the larvæ of *Leptinotarsa decemlineata*.** M. RAUCOURT and B. TROUVELOT (Compt. rend., 1933, 197, 1153—1154).—The substance(s) is contained in the green solid part of the expressed juice and is also obtained by extraction of the leaves with EtOH. It is only slightly sol. in  $C_6H_6$ , light petroleum,  $Et_2O$ ,  $COMe_2$ , and  $CHCl_3$ , it is non-volatile, is not decomposed at 105°, but is destroyed by fermentation.

H. B.

**Physico-chemical factors in the oecology of anopheline larvæ at Tongking.** H. G. S. MORIN and H. BADER (Ann. Inst. Pasteur, 1933, 51, 656—668).—An investigation of the "carbonic index" (I) (a measurement of the excess of free and half-combined over the potential  $CO_2$ ) of the  $H_2O$  of the rivers of Tongking at various points and at different seasons. A parallelism exists between (I) and the anopheline population of the various waters.

A. W.

**Theory of diffusion in cell models.** L. G. LONGSWORTH (J. Gen. Physiol., 1933, 17, 211—235).—The differential equations for the simultaneous diffusion of  $H_2O$  and salt in a cell model have been solved. The theoretical time curves for the diffusing substances accurately reproduce the characteristics of the experiment.

H. G. R.

**Potassium as an adrenaline-producing element.** R. HAZARD (Compt. rend., 1933, 197, 1455—1458).—Intravenous injection of KCl into chloralosed dogs produces hypertension (I) and hyperglycæmia (II), and other effects like those of adrenaline (III). The excitation causing (III) secretion is peripheral, since paralysis of the ganglia by a previous injection of sparteine increases and prolongs (I) without modifying (II). (I) is replaced by hypotension in animals previously submitted to the action of yohimbine.

J. W. B.

**Excretion of calcium after injection of barium.** Y. POURBAIX (Compt. rend. Soc. Biol., 1933, 112, 1556—1559).—Subcutaneous or intraperitoneal injection of Ba gluconate or chloride into guinea-pigs on a neutral diet causes increase of Ca in the urine. The excess Ca eliminated is much > equiv. to the Ba injected.

NUTR. ABS. (m)

**Calcium and the resistance of *Nereis* to brackish water.** W. G. ELLIS (Nature, 1933, 132, 748).—Wt. curves show that the resistance of *N. diversicolor* to immersion in brackish  $H_2O$  depends on the presence of Ca in the environment.

L. S. T.

**So-called normal lead in the human body.** F. WEYRAUCH and H. MÜLLER (Z. Hyg., 1933, 115, 216—220; Chem. Zentr., 1933, ii, 1047).—The organs of men not brought into contact with Pb in their work are free from Pb, but the bones contain > 0.25 mg. Pb in 3 g. of ash.

A. A. E.

**Sodium iodobismuthite (iodobismutol). Muscular absorption of bismuth.** P. J. HANZLIK and J. B. SPAULDING (J. Pharm. Exp. Ther., 1933, 49, 257—269).—Intramuscular injection of therapeutic



doses of iodobismutol [6% Na iodobismuthite and 12% NaI in  $(\cdot\text{CH}_2\cdot\text{OH})_2$ ] into animals is followed by prompt absorption of the Bi, frequently almost complete after 24 hr. W. O. K.

Irritation and toxicity of sodium iodobismuthite (iodobismutol) prepared with propylene glycol and diethylene glycol. P. J. HANZLIK, H. G. MEHRTESS, and J. B. SPAULDING (J. Pharm. Exp. Ther., 1933, 49, 300—305).—The replacement of  $(\cdot\text{CH}_2\cdot\text{OH})_2$  (I) in iodobismutol by propylene glycol does not alter or only slightly increases its local irritant action in man when injected intramuscularly, whilst it decreases its general toxicity, whereas replacement of (I) by diethylene glycol increases its toxicity. W. O. K.

Effect of water containing the isotope of hydrogen on fresh-water organisms. H. S. TAYLOR, W. W. SWINGLE, H. EYRING, and A. H. FROST (J. Chem. Physics, 1933, 1, 751).—Water containing 92% of  $\text{H}^2$  killed tadpoles of *Rana clamitans* (I), the fish *Lebistes reticulatus* (II), the flatworm *Planaria maculata* (III), and the protozoan *Paramecium caudatum* (IV). 30% heavy  $\text{H}_2\text{O}$  did not affect (I), (II), and (III), and 15—20% did not affect (IV).

H. S. P.  
Effect of preservatives on enzyme action. H. KLUGE (Z. Unters. Lebensm., 1933, 66, 412—435).—BzOH (I) does not interfere with the action of amylase and lipase. Pancreatin is inhibited by (I),  $\text{CH}_3\text{O}$ , salicylic acid,  $\text{Na}_2\text{SO}_3$ , and NaF. (I) and NaOBF have no effect on normal, but have a harmful effect on scorbutic, guinea-pigs. E. C. S.

Cryolysis and the mechanism of enzyme action. F. F. NORD [with G. WEISS] (Ergebn. Enzymforsch., 1933, 2, 23—49; Chem. Zentr., 1933, ii, 72).—Ovalbumin, gelatin, gum arabic, saponin, and Na oleate in solution or emulsion suffer irreversible physical change at low temp., as indicated by surface tension, viscosity, conductivity, gas absorption, etc. Emulsions made with frozen material have a somewhat increased stability. Surface tension measurements with ovalbumin and Na oleate solutions charged with  $\text{C}_2\text{H}_4$  have also been made. After 2 hr. at  $-18^\circ$  the colloids exhibit increased gas absorption, attributed to diminution of particle size. A. A. E.

Influence of mitogenetic radiation on enzymic processes. S. MARDASHEV and M. MOGILEVSKI (Biochem. Z., 1933, 265, 429—436).—The systems arginine+arginase or sucrose+invertase can be used in place of yeast as detector of mitogenetic radiation, the action of the enzyme being usually depressed by the radiation. P. W. C.

Mitogenetic spectral analysis of polysaccharide degradation. J. S. KLENITZKI and E. G. PROKOFIEVA (Biochem. Z., 1933, 265, 375—379).—The mitogenetic spectrum is sp. for the degradation of a particular mol. structure. Thus, the same mitogenetic spectrum is obtained for the hydrolysis of starch by salivary or pancreatic amylase, of maltose, and of salicin. The spectrum for hydrolysis of sucrose, on the other hand, is the same whether hydrolysis is by invertase or acid, but is different from that of the above reactions. P. W. C.

Intracellular enzymes of tissues and glands. III. Pancreatic amylase. R. WILLSTÄTTER and M. ROHDEWALD (Z. physiol. Chem., 1933, 221, 202—206; cf. A., 1933, 864).—In pig's pancreas  $\approx 0.2\%$  of the amylase (I) present is desmo-amylase. In 100% glycerol pancreatic (I) rapidly becomes irreversibly inactivated, although stable in 87%. Pancreatic (I) is only slightly inhibited by glycerol. J. H. B.

Combined rôle of H and Cl ions in the activation of amylase. L. AMBARD and S. TRAUTMANN (Compt. rend. Soc. Biol., 1933, 112, 1532—1534).—Possibly nascent HCl (not Cl') is the co-enzyme which promotes the action of amylase on starch.

NUTR. ABS. (m)  
Adsorption of amylases by starch grains. P. T. BOEKESTEIN (Acta Brev. néerl. Physiol., 1932, 2, 132—134; Chem. Zentr., 1933, ii, 397—398).—Pancreatic (I), but not malt, amylase is adsorbed on rice, wheat, and potato starches; on rise of temp. the adsorption of purified (Willstätter) (I) diminished considerably. The starch grains were not attacked by the enzyme. The relation of  $p_H$  to absorption has been studied. Starch treated with *N*-HCl absorbs less enzyme. The effect of glycogen, starch solution, maltose, fructose, glucose, and sucrose on the absorption has been examined. In this way (I) containing only traces of lipase and trypsin, and giving greatly weakened protein reactions, has been prepared. A. A. E.

Limited saccharification of starch and amylase "complement." K. MYRBÄCK and S. MYRBÄCK (Svensk Kem. Tidskr., 1933, 45, 230—236).—Peptic hydrolysates of bottom yeast do not accelerate the maltose formation (I) from starch by malt-amylase (II). The hydrolysis by pancreatic (II) is also not affected by yeast "complement" or glutathione. The extent of (I) by green malt extract is  $>$  that by  $\alpha$ - or  $\beta$ -(II) prepared from it, the two isolated forms having the same activity. (I) is also not appreciably influenced by the proportion of  $\alpha$ - and  $\beta$ -(II) nor by the abs. amount of (II). Amylose (J.C.S., 1923, 123, 2666), however, exhibits a 70% (I) with  $\beta$ -(II), but is completely hydrolysed by a mixture of  $\alpha$ - and  $\beta$ -(II). The results of Pringsheim (A., 1932, 100) are probably due to the character of the substrate employed. F. O. H.

Amylosynthase. XII. Regeneration. XIII. Amylosynthase of glutinous rice. T. MINAGAWA (J. Agric. Chem. Soc. Japan, 1933, 9, 547—549, 549—552). XII. Amylosynthase (I) is inactivated by acids, alkalis,  $\text{HgCl}_2$ , and heat; it is not reactivated by neutralisation,  $\text{H}_2\text{S}$ , and cooling. When (I) pptd. by  $\text{CdCl}_2$  is treated with  $(\text{NH}_4)_2\text{SO}_4$ , enzymic activity is restored.

XIII. The optimum  $p_H$  of (I) from glutinous rice (prep. described) is 6.7—6.8. It differs from (I) of yeasts; sol. glycogen and hexahexosan are not polymerised. CH. ABS.

Determination of diastase. O. FISCHER (Z. ges. exp. Med., 1933, 86, 258—268; Chem. Zentr., 1933, ii, 232).—The dextrin (I)- and starch-decomposing powers of diastase are parallel. For the determination of diastase in urine, (I) is added and the amount of



(I) undecomposed is determined colorimetrically after addition of a solution of I in aq. KI.

A. A. E.

**Emulsin. XII. I. Fission of phenyl- $\beta$ -D-isorhamnoside by emulsin.** B. HELFERICH, H. ROHR, and E. GÜNTHER. **II. Fission of  $\beta$ -D-glycuronides (paired glycuronic acids) by emulsin.** B. HELFERICH and G. SPARNBERG. **III. Deterioration of emulsin produced by ultra-violet rays.** B. HELFERICH and G. BRIEGER. **IV. Influence of formaldehyde on the fission of  $\beta$ -glucosides and  $\beta$ -galactosides by emulsin.** B. HELFERICH and S. WINKLER (Z. physiol. Chem., 1933, 221, 90—92, 92—94, 94—98, 98—100; cf. A., 1933, 635).—I. Phenyl- $\beta$ -D-isorhamnoside, m.p. 161—162° (corr.),  $[\alpha]_D^{25}$  —80.8° in  $\text{CHCl}_3$  [ $\text{Ac}_3$  derivative, m.p. 134—135° (corr.),  $[\alpha]_D^{25}$  —7.3° in  $\text{CHCl}_3$ ], is hydrolysed by different preps. of emulsin at rates bearing a const. ratio to the rates of hydrolysis of the corresponding glucoside.

**II.** The fission of Na 1-menthyl- $\beta$ -D-glycuronate (+1.5  $\text{H}_2\text{O}$ ),  $[\alpha]_D^{25}$  —98.4° in  $\text{H}_2\text{O}$ , does not run parallel with the fission of l-menthyl- and phenyl- $\beta$ -D-glucosides.

**III.** Only ultra-violet rays of  $\lambda$  254 m $\mu$  are harmful to emulsin. Purified enzyme is more affected than the crude product. The destruction of activities towards phenyl- $\beta$ -D-glucoside and -galactoside run parallel, indicating that the same enzyme is responsible for both hydrolyses. The difference in loss of activity towards  $\beta$ -D-glucoside and  $\alpha$ -D-mannoside indicates that the enzymes here are different.

**IV.** Destruction by  $\text{CH}_2\text{O}$  indicates that  $\beta$ -D-galactoside and  $\beta$ -D-glucoside differ, which is contrary to previous results.

J. H. B.

**Glucosides acting on the heart. III. Scillarenase.** A. STOLL, W. KREIS, and A. HOFMANN (Z. physiol. Chem., 1933, 222, 24—38; cf. A., 1933, 1146).—Scillarenase (I) hydrolyses scillarene A to proscillaridin A with elimination of 1 mol. of glucose. (I) is a desmo-enzyme and is obtained as an autolysate, talc-prep., or cell-residue prep., from the sea-onion.  $\text{EtOAc}$  partly,  $\text{MeOH}$  completely, destroys the activity.  $\text{EtOH}$  and  $\text{COMe}_2$  do not permanently affect activity, although  $\text{EtOH}$  shows inhibition. The  $p_H$  and temp. optima are 5—6 and 37°, respectively. (I) is inactivated in 1 hr. at 98°. It is not liberated from the cell by papain or diastase. (I) does not hydrolyse digilane A, deacetyldigilane A, or scillabiose.

J. H. B.

**Dilatometric studies in enzyme action. III. Contraction constants of enzyme-substrate reactions.** H. B. SREERANGACHAR and M. SREENIVASAYA (J. Indian Inst. Sci., 1933, 16A, 69—75).—The system emulsin (I)—salicin, but not (I)—amygdalin, (I)—arbutin, or (I)—asculin, gives a depression in the dilatometer (A., 1932, 880) during hydrolysis. "Contraction consts." were determined for the hydrolysis of starch and glycogen by ptyalin and taka-, malt-, and pancreatic diastase.

F. O. H.

**Cytochrome c.** K. ZEILE and F. REUTER (Z. physiol. Chem., 1933, 221, 101—116).—The mesoporphyrin was obtained by way of the hæmatoporphyrin from cytochrome c (I); the ester proved

identical with mesoporphyrin ester IX from blood-hæmin. Thus (I) contains a porphin nucleus as derivative of ætioporphyrin III with the same arrangement of side-chains as in the natural blood-pigment. The mol. wt. of the smallest unit of (I), based on the hæmin content, is 18,700. Determination of (I) makes use of the fact that oxidised (I) is, and reduced (I) is not, adsorbed by kaolin. (I) of 92% purity was obtained by fractional pptn. at varying  $p_H$ . The diffusion coeff. of (I) gives a mol. wt. up to 10 times the min. unit based on hæmin content.

J. H. B.

**Supposed direct spectroscopic observation of the "oxygen-transporting ferment."** D. KEILIN (Nature, 1933, 132, 783).—Warburg and Negelein's observations on *B. pasteurianum* (I) (A., 1933, 862) are in the main confirmed, but their interpretation is criticised. The absorption spectrum (II) of the cytochrome of (I) varies with the strain of the organism, the culture medium, and the age of the culture. The effect of CO on (II) also varies with the culture. These results, together with spectroscopic investigations of other bacteria, show that the shading in the yellow (590 m $\mu$ ) and the band in the red (630 or 636 m $\mu$ ) are not the absorption bands of the O-transporting enzyme, but are those of derivatives of cytochrome and probably of its component a.

L. S. T.

**Reactions of the yellow [oxidation] enzyme.** O. WARBURG and W. CHRISTIAN (Biochem. Z., 1933, 266, 377—411).—The yellow enzyme (I) consists of a colloidal carrier and a pigment (II) which can be eluted slowly by  $\text{MeOH}$ . (II) on irradiation in alkaline solution gave a substance  $\text{C}_{13}\text{H}_{12}\text{O}_2\text{N}_4$ , m.p. 320° (decomp.), the spectrum of which showed its close relationship with (II); on treatment with  $\text{BaO}$  it gave urea and a substance  $\text{C}_9\text{H}_{10}\text{O}_2\text{N}_2$ , m.p. 213° (decomp.). The leuco-form of (I) with atm.  $\text{O}_2$  gave (I) +  $\text{H}_2\text{O}_2$  and with methylene-blue gave (I) + leucomethylene-blue. Since (I) contains no metal, the O transport of (I) is not inhibited by either CO or HCN. (I) is responsible for the O transport in anaërobic lactic acid cultures and is present in all cells, including those of higher animals.

P. W. C.

**Inactivation of mussel catalase by oxygen.** G. W. MARKS and D. L. FOX (J. Biol. Chem., 1933, 103, 269—283).—Mussel catalase (I) is prepared by keeping the minced tissue over-night at 20° in contact with  $\text{PO}_4^{3-}$  buffer and filtering. (I) stored under  $\text{N}_2$  is inactivated more slowly than when kept under  $\text{O}_2$  or air. By plotting the log. activity against  $t$  a straight line is obtained between 7 and 19 days; the quantity of  $\text{H}_2\text{O}_2$  decomposed by a given extract is proportional to the concn. of extract except in high concns. By substituting in the unimol. equation vals. of  $k$  are obtained for the inactivation of (I) showing a steady drift. The Arrhenius equation is applicable for the variation of  $k$  with temp. The inactivation in air is uninfluenced by the presence of  $\text{H}_2\text{O}_2$ .

H. D.

**Peroxidase reaction. XL. Short-timed peroxidase reaction of blood-leucocytes of mothers secreting, and of sucklings nursed with, "aper-**



oxidatic milk." M. CHIBA and J. ABE. **XLI.** Prolongation of short-timed peroxidase reaction of leucocytes as a sign of avitaminosis-B, and effect of vitamin-B on it. M. CHIBA (Tôhoku J. Exp. Med., 1932, 19, 479—485, 486—512).

CH. ABS.

Membrane potential of peroxidases and oxidases in equilibrium with metallic ions. M. PADOA and G. TEDESCHI (Biochem. Z., 1933, 266, 452—457).—The membrane potential of oxidase in equilibrium with  $Mn^{++}$  is nil up to  $p_H$  6.2, then increases up to 40 mv. at  $p_H$  7, and above this decreases due to coagulation of enzyme.  $Mn^{++}$  also increased the activity of the oxidase, the increase varying with  $p_H$  and disappearing below 6.2.

P. W. C.

Micro-method for determination of phenolase. S. BLAZSÓ (Biochem. Z., 1933, 266, 281—286).—The oxidation of pyrocatechol is studied using the  $H_3Fe(CN)_6$  technique of Hagedorn and Jensen and a table constructed which permits the reading of the amount of phenol in terms of the  $Na_2S_2O_3$  used in back-titration. The method is employed in determinations of the phenolase contents of rabbit's skin and blood.

P. W. C.

Alcohol-oxidase. H. MIZUSAWA (J. Biochem. Japan, 1933, 18, 243—258).—EtOH is rapidly dehydrogenated by alcohol-oxidase (I), a max. action occurring in 0.04*M*-EtOH. The main source of (I) is the liver, from which it can be prepared by pptn. of aq. extracts by  $COMe_2$ . MeOH, PrOH, glycol, glycerol, erythritol, and sorbitol are also dehydrogenated by (I). Ultra-violet and X-rays, KCN,  $C_4H_4N$ , and adrenaline inhibit, whilst extracts of adrenal cortex accelerate, (I). (I), which, unlike methylene-blue, has a significant reduction potential, has a stronger action in alcoholised than in normal animals.

F. O. H.

Decomposition of lactic acid by yeast enzymes. A. HAHN, E. FISCHBACK, and H. NIEMER (Z. Biol., 1933, 94, 58—66).—The isolation from yeast of a lactic acid dehydrase is described. In the presence of a H acceptor [methylene-blue,  $C_6H_4(NO_2)_2$ ] lactic acid is converted into  $AcCO_2H$  and  $MeCHO$ . The action is unaffected by the presence of  $O_2$ .

A. G. P.

Mechanism of oxidation processes. **XXXVI.** Enzymic dehydrogenation of lactic acid, pyruvic acid, and methylglyoxal by yeast. H. WIELAND, O. B. CLAREN, and B. N. PRAMANIK (Annalen, 1933, 507, 203—212).—Aërobic dehydrogenation of lactic acid (I) proceeds similarly to that of EtOH (A., 1933, 865) when "impoverished" yeast (II) (A., 1932, 303) is used;  $AcOH$ , EtOH, and (mainly)  $CO_2$  are produced. The following reactions probably occur: (i)  $OH\cdot CHMe\cdot CO_2H \rightarrow AcCO_2H$ ; (ii)  $AcCO_2H \rightarrow MeCHO + CO_2$ ; (iii)  $2MeCHO + H_2O \rightarrow AcOH + EtOH$ ; (iv)  $MeCHO + O \rightarrow AcOH$ . In two cases, small amounts of succinic acid were isolated. The carbohydrate content and wt. of (II) do not increase during these experiments (cf. Hoffert, A., 1926, 642). Dehydrogenation of (I) is more dependent on the substrate concn. than in the cases of EtOH and  $AcOH$ ;  $O_2$  consumption occurs much more rapidly

at the higher concns. studied ( $M/32-M/4$ ).  $AcCO_2H$  (III) (as Na salt) is first decarboxylated to  $MeCHO$  (which then reacts as above). A smaller amount of (III) [compared with (I)] is oxidised completely; reaction (iii) (above) appears to be inhibited by (III). The  $O_2$ -consumption is much greater at the higher concns.  $AcCHO$  (IV) is also dehydrogenated to (mainly)  $MeCHO$ ; in some cases, (III) is isolated and probably results thus:  $AcCH(OH)_2 - 2H \rightarrow (III)$ . Re-synthesis of (IV) to carbohydrate does not occur. The course of the dehydrogenation of (IV) appears to differ from that of EtOH,  $AcOH$ , or (I). (IV) exhibits a retarding action on the oxidation.

H. B.

Indoxyluria. G. LAROCHE and J. DESBORDES (Ann. Méd., 1932, 32, 221—224; Chem. Zentr., 1933, ii, 738).—Experiments on surviving liver of guinea-pigs and rabbits disclosed considerable accumulation and rapid oxidation of indole to indoxyl. Conversion in other tissues is slower.

A. A. E.

Reducing power of liver tissue in presence of alkaloids, bases, salts, and mineral waters. A. BOUTARIC and T. JACQUINOT (Bull. Acad. Méd., 1932, 107, 1054—1057; Chem. Zentr., 1933, ii, 233).—Theobromine, pilocarpine, strychnine, aconitine, emetine, sparteine, morphine, and cocaine, HCl,  $H_2SO_4$ , and HCN retard, whilst mineral  $H_2O$ ,  $NH_3$ , NaOH, and KOH accelerate, the decolorisation of methylene-blue by pig's liver. Corresponding behaviour is exhibited by acid- or basic-reacting salts.

A. A. E.

Reductases of liver and milk and the zymosthenic action of mineral waters. M. LOEPER, A. MOUGEOT, and V. AUBERTOT (Bull. Acad. Méd., 1933, 109, 179—182; Chem. Zentr., 1933, ii, 233).—The mineral waters examined accelerated the reduction of methylene-blue by the reductase of pig's liver and cow's milk; the "zymosthenic index" is the ratio of the time necessary in distilled to that in mineral  $H_2O$ . Vals. are given for various waters.

A. A. E.

Carboxylase. I. W. LANGENBECK, R. JÜTTEMANN, O. SCHAEFER and H. WREDE (Z. physiol. Chem., 1933, 221, 1—9).—In the purification of carboxylase, most of the protein is pptd. by MeOH and the remainder by tannin, excess of which is removed by hide powder. After adsorption on  $Al(OH)_3$  B and elution with  $KH_2PO_4$  solution the product is dialysed. The temp. is maintained at about  $-20^\circ$  except during dialysis and the reagents are dissolved or suspended in 30% MeOH which prevents freezing. The final prep. has 1000 times the activity of the original yeast maceration juice.

J. H. B.

Esterase of intestinal secretion. L. REALE (Arch. Farm. sperim., 1933, 56, 512—535).—The secretion of the dog has a ratio of lipase to esterase activity of 0.29. The esterase is not dialysable. On pptn. by  $MgSO_4$  or  $(NH_4)_2SO_4$  it is found in both albumin and globulin fractions. Electrophoresis causes migration to the anode at  $p_H$  8.3—5.0 and to the cathode at  $p_H$  < 4.5, the isoelectric point being at  $p_H$  4.7. The secretion has  $p_H$  7.3. The activity is maximal at  $p_H$  7.3 and  $37^\circ$ .

R. K. C.



**Physiology of digestion in infants. XVI. Gastric lipase.** H. LICHTENBERG (Z. Kinderheilk., 1933, 54, 732—741).—Gastric lipase (I) attacks best short-chain, and pancreatic lipase long-chain, triglycerides, whilst human milk-lipase attacks intermediate fats. For (I) in presence of peptic digestion products the optimal  $p_H$  is 5; in the presence of tryptic digestion products (II) it is 7. (II) promote the action of lipase. NUTR. ABS. (m)

[Lipase.] **IV. Inhibitory effect of primary alcohols on the lipase of carp-liver.** J. C. KERNOT and H. W. HILLS (Z. physiol. Chem., 1933, 222, 11—15; cf. A., 1933, 534).—The inhibitory effect of primary alcohols on the hydrolysis of Et butyrate (I) and crotonate (II) by carp- and pig-liver lipase increases with chain length. The rate of hydrolysis of (I) is about 14 times that of (II). J. H. B.

**Autolysis of the skin of pigmented and non-pigmented animals.** S. BLAZSÓ (Biochem. Z., 1933, 266, 266—273).—There is little or no difference between the autolytic powers (I) at  $p_H$  3.8, 5.7, and 7.32 of the skins of albino, black, or brown rabbits, so long as the skins themselves are unpigmented. The (I) of pigmented skin, however, may be 300% > that of unpigmented skin. No difference was obtained in (I) of the skins of old and young animals. P. W. C.

**Muscle autolysis. II. Changes of the total amount of reducing substances, lactic and phosphoric acids.** I. A. SMORODINCEV, N. V. SCHIROKOV, and L. A. PHILIPOVA (Biochem. Z., 1933, 266, 274—280).—During the storage of flesh, the amount of reducing substances increases at room temp. by 50% in 24 hr. and by > 100% in 3 days, at 4—8° by 50%, and at 17—25° by 200% in 3 days. The increase of lactic acid reaches max. vals. after 24 hr., when it is three times the amount obtained in the first hr., the increase in the same time at 4—8° being 185% and at 17—25° 283% of that in the first hr. Changes in org. and inorg. P amount to only 20—25% of the vals. for the first hr. P. W. C.

**Enzymic ammonia elimination from thymonucleic acid by rabbit-liver.** E. BÜDING (Z. physiol. Chem., 1933, 222, 6—10).—The enzyme system of rabbit's liver which deaminates thymonucleic acid (I) can be separated into H<sub>2</sub>O-sol. and -insol. components. Both are heat-sensitive and inactive alone, but reactivated on mixing. Part of the deamination of nucleoproteins and (I) occurs in the guanine nucleus. J. H. B.

**Fermentative uricolysis.** H. KLEINMANN (Klin. Woch., 1933, 12, 712; Chem. Zentr., 1933, ii, 726).—Human tissue, unlike pig's tissue, contains no uricase. Uricolysis is optimal at  $p_H$  8.85 and 10.03; it is increased by O<sub>2</sub> and arrested by NaCN and H<sub>2</sub>S. The fission products are: allantoin (40—50% of theory), CO<sub>2</sub>, urea, and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. A. A. E.

**Hæmatoporphyrin, an artificial proteolytic enzyme.** M. J. BOYD (J. Biol. Chem., 1933, 103, 249—256).—Fibrinogen (I) exposed to light for 5 hr. in presence of hæmatoporphyrin (II) loses its clotting power and heat-coagulability with the formation of an albumose. With shorter exposures a heat-

coagulable protein appears as an intermediate product. A serum-albumin solution containing (II) undergoes hydrolysis on exposure to light, but not so rapidly as (I); serum-globulin and ovalbumin failed to react similarly. In an atm. of H<sub>2</sub> no hydrolysis of (I) and no loss of (II) occur, although the fluorescence of (II) appears to be uninfluenced. The phenomenon is one of photo-sensitisation. H. D.

**Proteolytic enzymes in pancreatic and intestinal juice.** E. LE BRETON and F. MOCOROA (Ann. Physiol. Physicochim. biol., 1933, 7, 215—219; Chem. Zentr., 1933, ii, 559).—Pure pancreatic juice does not attack ovalbumin or caseinogen unless activated with kinase or CaCl<sub>2</sub>; hence it contains a prokinase and an inactive proteinase. It decomposes scombrin, clupein, and chloroacetyltyrosine, and hence contains active carboxypolypeptidase. It does not attack di- and tri-peptides. Dog's intestinal juice contains no tryptic enzyme, but two enzymes of the erepsin class (dipeptidase and aminopolypeptidase) and a very active kinase. A. A. E.

**Action of papain on milk.** A. UNDERRAIN (Milch. Forsch., 1933, 15, 433—447).—Papain acts on milk even when the latter is at b.p. The optimum temp. for papain is 87°. Albumin and globulin act as protective agents against the action of papain on caseinogen. E. B. H.

**Absorption of pepsin by crystalline proteins.** J. H. NORTHROP (J. Gen. Physiol., 1933, 17, 165—194).—With a ratio of pepsin (I) to edestin (II) of 2:1 and at  $p_H$  4.0, the formation of the insol. complex (III) is a max. The peptic activity of (III) is equiv. to the amount of (I) present and may be extracted with cold 0.25N-H<sub>2</sub>SO<sub>4</sub>. On dissolving (III) in acid ( $p_H$  2.0), (II) is rapidly digested and (I) may be isolated. H. G. R.

**Action of pepsin on muscle-globulin and collagen.** I. A. SMORODINCEV and A. N. ADOVA (J. Biochem. Japan, 1933, 18, 325—332).—Muscle-globulin is more readily hydrolysed by pepsin than is collagen (I). Unlike that of gelatin, the viscosity (II) of (I) increases during digestion. This increase is unaccompanied by combination with alkali, which, however, occurs at a later stage when (II) diminishes. The first phase of protein hydrolysis is a flocculation of the micellæ accompanied by an increase in (II); fission of the peptide linking does not occur. F. O. H.

**Determination of trypsin.** M. L. ANSON and A. E. MIRSKY (J. Gen. Physiol., 1933, 17, 151—157).—After pptn. of the undigested hæmoglobin with CCl<sub>3</sub>-CO<sub>2</sub>H, the blue colour obtained with the Folin-Ciocalteu reagent (A., 1927, 892) is taken as a measure of the tryptic activity. H. G. R.

**Determination of active native trypsin in presence of inactive denatured trypsin.** M. L. ANSON and A. E. MIRSKY (J. Gen. Physiol., 1933, 17, 159—164).—An alkaline solution of urea prevents the change of inactive denatured trypsin into the active native variety and may be used as a medium for determination of the latter. H. G. R.

**Chemistry of alcoholic fermentation.** A. HARDEN (J. Inst. Brew., 1933, 39, 644—646).—A review of new theories of fermentation. R. H. H.



Increase of yeast fermentation. IX. By urine of healthy and pathological subjects. X. By animal, plant, and chemical substances. H. ZELLER (Biochem. Z., 1933, 266, 360—366, 367—376).—IX. Tables show the changes of induction time (I) and of fermentation power (II) of yeast on adding normal and pathological urines. Autoclaving the urine increases (I) and decreases (II). (II) is increased by night urine of adults by > 100%, of children by 200%, by urine in fevers of adults by 300%, and of children by 500%. The effect of urines in fever cases is in part dependent on the readily hydrolysable  $\text{NH}_3$  of the urine.

X. A table shows the effect on fermentation of many org. and inorg. substances, and the results are discussed in relation to the effect on the early and later part of the fermentation cycle. P. W. C.

Nitrogenous metabolism of yeast. II. Yeast growth and fermentation in synthetic media. III. Ability of certain pure chemical compounds to function as nitrogen sources for yeast. R. S. W. THORNE (J. Inst. Brew., 1933, 39, 597—607, 608—621; cf. B., 1932, 203).—The extent of growth of yeast in artificial media is 15—20% of that usual in wort. English yeast (I) does not grow or ferment as energetically as Froberg yeast (II), but addition of bios to (I) produced favourable effects.  $(\text{NH}_4)_2\text{HPO}_4$  is a very good nutrient for (II) and for (I) in the presence of bios.  $\text{NH}_2$ -acids except cystine function as nutrients, but  $\text{KNO}_3$ ,  $\text{NH}_2\text{Ac}$ ,  $\text{EtCO}\cdot\text{NH}_2$ , alloxan, allantoin, betaine, and choline are useless.

R. H. H.

Kinetics of the accumulation of organic substance in cultures containing two types of yeast. G. F. GAUSE (Biochem. Z., 1933, 266, 352—354).—In an investigation of the accumulation of org. substance (yeast vol.) in a culture composed of two yeasts, *Saccharomyces cerevisiae* and *Schizosaccharomyces kefir*, the coeffs.  $\alpha$  and  $\beta$  calc. according to a given equation agree with the corresponding coeffs. for the production of  $\text{EtOH}$ , and the applicability of the equation for such cultures is regarded as proved.

P. W. C.

Effect of cyanides on the development of yeast. M. N. MEISSEL (Zentr. Bakt. Par., 1933, II, 88, 449—459).—The toxicity of cyanides to yeast was in the order  $\text{Hg}(\text{CN})_2 > \text{NaCN} > \text{KCN} > \text{NH}_4\text{CNS}$ . Exposure to  $\text{KCN}$  solution resulted in increased fat production by the yeast. Morphological and physiological effects of cyanides are described. A. G. P.

"Radium yeasts." G. A. NADSON and E. J. ROCHLIN (Arch. Mikrobiol., 1933, 4, 189—208; Chem. Zentr., 1933, ii, 560).—"Radium yeasts-A, -B, and -C," produced by the action of Rn on Berlin press-yeast XII, have sp. morphological and physiological properties; -B is particularly active.

A. A. E.

Formation of gluconic acid by *Aspergillus niger*. E. KARDO-SYSSOJEVA (Biochem. Z., 1933, 266, 337—351).—A strain of *A. niger* is grown at 30—35° on a solution containing 20% sucrose and the usual salts, the substrate removed, and the mycelium (under surface) washed and floated on solutions containing 20% sucrose, or sucrose with

varying amounts of salts with and without addition of  $\text{CaCO}_3$ . Decreased concn. of salts or addition of  $\text{CaCO}_3$  favours the formation of gluconic acid (I). Increase of N-containing salts stimulates accumulation of (I) in acid medium, but inhibits in presence of  $\text{CaCO}_3$ . When an established mycelium is floated on a solution containing 1/25 the usual salts, the amount of (I) formed is 100% of the sugar utilised or 50% of the sugar present in the medium. P. W. C.

Direct conversion of nitrates into ammonia by the mycelium of the lower fungi. D. BACH and D. DESBORDES (Compt. rend., 1933, 197, 1463—1465).—At  $p_{\text{H}}$  1.16—2.65 the disappearance of  $\text{NO}_3\text{-N}$  (I) from a nitrate-glucose- $\text{NaCl}$  medium (Ca citrate buffer) in contact with *Aspergillus repens* is almost exactly accounted for by the amount of  $\text{NH}_3\text{-N}$  (II) appearing in the medium, no gain in wt. of the mould being observed. Above  $p_{\text{H}}$  4.4 ( $p_{\text{H}}$  6.6), however, the very rapid disappearance of (I) is accompanied by the appearance of only traces of (II), loss of  $\text{NH}_3$  from the cell by exosmosis being now prevented and resulting in rapid increase in the wt. of the mould. J. W. B.

Evolutionary cycle of *Actinomyces* in cultures after ultrafiltration through collodion. A. SARTORY, R. SARTORY, and J. MEYER (Compt. rend., 1933, 197, 1465—1467).—When incubated under various conditions, the ultrafiltrates of cultures of *A. bovis*, Harz, show both typical and atypical forms ("symplastic," pseudo-diphtheria and -streptococcus, filamentous with arthrospores, etc.) which appear to represent labile and stable evolutionary phases of the morphology of the organism. F. O. H.

A chlorophyll-like bacterial pigment. K. NOACK and E. SCHNEIDER (Naturwiss., 1933, 21, 835).—Bacteriochlorin from the S-free purple bacteria (absorption band in  $\text{Et}_2\text{O}$  at 595—550  $\text{m}\mu$ ) resembles chlorophyll in basicity and contains Mg which can be removed by acid. Bacteriopheophytin, which remains, closely resembles pheophytin. The application of Stoll's method for the direct prep. of pheophorbide yields (I) a crystallisable compound of relatively slight basicity,  $\text{C}_{34}\text{H}_{35}\text{O}_5\text{N}_4\cdot\text{OMe}\cdot 0.5\text{H}_2\text{O}$ , corresponding with a semi-hydrated pheophorbide *b* (Me ester,  $\text{C}_{36}\text{H}_{40}\text{O}_6\text{N}_4$ ); (II) a non-cryst. *a* modification. The action of  $\text{HI}\cdot\text{AcOH}$  yielded a mixture of porphyrins of which the spectrum resembles that of phyloerythrins. With  $\text{Fe}\cdot\text{HCO}_2\text{H}$  two porphyrins are obtained, spectroscopically resembling pheophorphyrin,  $\text{C}_{33}\text{H}_{33}\text{O}_6\text{N}_4$  (HCl no.=5), and  $\text{C}_{33}\text{H}_{32}\text{O}_5\text{N}_4\cdot\text{OMe}$  (HCl no.=9). It is suggested that the name bacteriochlorin be altered to bacteriochlorophyll.

W. O. K.

Carotenoids of bacteria. E. CHARGAFF (Compt. rend., 1933, 197, 946—948).—The distribution of pigments in *Sarcina lutea* (A., 1933, 97), *S. aurantiaca* (I), *Staph. aureus* (II), and *Mycobacterium phlei* (III) has been determined by the method of Kuhn and Brockmann (A., 1932, 785). (I) contains  $\beta$ -carotene, and its xanthophyll fraction is zeaxanthin, which is the only pigment in (II). Lutein is probably the xanthophyll ester in (III), the hydrocarbons of which are separable by adsorption, and consist mainly of  $\beta$ - with 4% of  $\gamma$ -carotene (A., 1933, 431). A. C.



**Bacteria fermenting xylan.** R. PATRICK and C. H. WERKMAN (Iowa State Coll. J. Sci., 1933, 7, 407—418).—A medium containing xylan 2.5,  $\text{NH}_4\text{Cl}$  2, and  $\text{K}_2\text{HPO}_4$  1 g. in 1 litre of  $\text{H}_2\text{O}$ , at  $p_{\text{H}}$  7.0, was fermented by various bacilli with the production of acid but not gas.

CH. ABS.

**Gaseous metabolism of *L. pentoaceticus* with reference to the *Lactobacillus* group.** G. A. HUNT (J. Bact., 1933, 26, 341—360).—*L. pentoaceticus* (I) differs from other organisms of the group in utilising relatively large proportions of  $\text{O}_2$  during the fermentation of carbohydrates and producing an approx. equal vol. of  $\text{CO}_2$ . Xylose and lactates are readily utilised by (I) with the same ratio of  $\text{O}_2$  intake to  $\text{CO}_2$  produced. All members of the group examined are inhibited by 0.1N-NaF and by 0.0001N- $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$  but not by KCN solutions of  $< 1\%$ . Methylene-blue and pyocyanine accelerate  $\text{O}_2$  consumption either in the presence or absence of KCN. Acids produced by (I) under aerobic conditions have a higher ratio of volatile to non-volatile constituents than those obtained under anaerobic conditions.

A. G. P.

**Action of nitrates on the fermentation of glucose by *B. coli*.** J. TIKKA (Suomen Kem., 1933, 6, B, 67).—Glucose (buffered at  $p_{\text{H}}$  7) is fermented by *B. coli* in presence of  $\text{KNO}_3$  (I) to give much less  $\text{H}_2$  and lactic acid, and more  $\text{AcOH}$ , than without (I).

J. L. D.

**Propionic acid bacteria. II. Classification.** C. H. WERKMAN and R. W. BROWN (J. Bact., 1933, 26, 393—429).—Chemical and morphological characteristics are recorded and a system of classification is described.

A. G. P.

**Propionic acid bacteria.** F. DOMKE (Milch. Forsch., 1933, 15, 480—500).—Methods for detecting their presence in dairy products are considered.

E. B. H.

**Putrefaction of hydroxyproline.** W. KEIL and A. GÜNTHER (Z. physiol. Chem., 1933, 221, 10—12).—Putrefactive organisms convert *l*-hydroxyproline into  $\text{NH}_2\cdot[\text{CH}_2]_4\cdot\text{CO}_2\text{H}$ . Proline and  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$  were not detected in the reaction products.

J. H. B.

**Effect of light on the carbon monoxide inhibition of butyric acid fermentation.** W. KEMPNER and F. KUBOWITZ (Biochem. Z., 1933, 265, 245—252).—The  $\text{CO}$  inhibition of anaerobic  $\text{PrCO}_2\text{H}$  fermentation with *Clostridium butyricum*, like that of the  $\text{O}_2$  respiration of aerobic cells, can be removed by irradiation, but for the former process a lower temp. and light of greater intensity are required. The reaction reverses on darkening.

P. W. C.

**Vibrio isolated at Damascus from cases of summer diarrhoea in man. *Vibrio enteriditis* (n. sp.).** M. HURI (Ann. Inst. Pasteur, 1933, 51, 640—649).—The organism is strictly aerobic, and grows well with all ordinary media, with optimum  $p_{\text{H}}$  8—8.2 and best at 37°. Inoculation experiments with various types of animals, and serological tests, are described. It differs from other known vibrios in complete absence of proteolytic properties, and also in biochemical and serological characteristics.

A. W.

**Differentiation between Gram-positive and Gram-negative micro-organisms by the use of enzymes.** D. W. BRUNER (J. Bact., 1933, 26, 361—371).—An aged glycerol extract of pancreas added in appropriate amounts to the medium permitted the growth of Gram-positive but prevented that of Gram-negative organisms. Trypsin effects a lysis of the latter organisms.

A. G. P.

**Importance of peptone as a nutrient substrate for aerobic bacteria. Utilisation of peptone by *Staphylococcus aureus*.** J. HIRSCH and A. W. MÜLLER (Z. Hyg., 1933, 115, 443—494).—Peptone (I) serves as a source of energy as well as of N for bacteria. The production of  $\text{NH}_3$  from (I) by *S. aureus* occurs only in the presence of  $\text{O}_2$ .  $\text{NH}_3$  is derived directly from the free  $\text{NH}_2$  groups of (I), and the amount produced is directly proportional to the concn. of (I) in the substrate. Addition to the medium of energy sources other than (I) retards  $\text{NH}_3$  formation. The requisite energy is derived from the oxidative deamination process. (I) also contains substances stimulating the reproduction of bacteria. The val. of meat extracts in culture media depends more on the proportion of stimulating substance than on the nutrient or energy sources which they contain.

A. G. P.

**Action of normal blood on the transmissible lysis of *Staphylococcus aureus*.** W. MUTSAARS (Ann. Inst. Pasteur, 1933, 51, 605—625).—The strong, temporary inhibitory action of normal sera on the lysis of *S. aureus* (I) by the corresponding bacteriophage (II) is due to a protective action of the serum-albumin; it does not occur with other varieties of staphylococci. An extract of leucocytes (III), made by the method of Gengou, acts like (III) in destroying (II), and this destructive action is lost completely by heating to 100°, and very largely by filtration through an L3 Chamberland candle or after adsorption by emulsions of cholera vibrio. Blood-platelets have no fixing or destructive action on staphylococcal (II).

A. W.

**Staphylolysin.** J. FORSSMAN (Biochem. Z., 1933, 265, 291—319).—Using a described method of titration, the sensitivity of the blood-cells of various animals, the effect of the lysin at different temp., the influence of dilution (I) and of the no. of cells (II), and the adsorption of the lysin by the various cells are determined. The activity of staphylolysin decreases almost in proportion to (I) and increases almost in proportion to (II), usually displaying its greatest activity at 37°. More resistant cells often adsorb considerable amounts of, and sensitive cells often adsorb no, lysin.

P. W. C.

**Immunisation of the rabbit by diphtheria anatoxins of different antigenic values.** Y. ASAKAWA (Ann. Inst. Pasteur, 1933, 51, 565—583).—The degree of immunity induced in rabbits by two subcutaneous injections of diphtheria anatoxin (I), with an interval of 3 weeks between the injections, varies considerably from one animal to another. In general, immunity, as measured by intradermal tests, increases rapidly a few days after the second injection, with progressive increase up to or beyond the third month. The average antitoxin titre of the blood of



the immunised rabbits increases during the second and third weeks after the second injection of (I), and then falls to a fairly const. level. A. W.

**Merthiolate as a preservative for biological products. II. Diphtheria toxoid.** L. C. MORGAN, W. A. JAMIESON, and H. M. POWELL (J. Immunol., 1933, 25, 121—126). CH. ABS.

**Substance inhibiting bacterial growth produced by strains of lactic streptococci.** H. R. WHITEHEAD (Biochem. J., 1933, 27, 1793—1800).—Two streptococci (I), which inhibited the growth of normal cheese lactic acid cocci, were identified as strains of *S. cremoris* and *S. mastiditis*. The inhibition persists after the destruction of (I). Acid production is similarly inhibited in caseinogen broth. A conc. solution of the inhibiting substance (II) was obtained from milk incubated with (I) by EtOH extraction from the conc. whey. (II) is a protein derivative; it is destroyed by trypsin and resistant to pepsin. H. D.

**Hæmolytic action of bacterial cells of streptococci.** K. MATSUNAGA (Kitasato Arch. Exp. Med., 1933, 10, 196—206).—The hæmolytic power of the bacterial cells of hæmolytic streptococci is > 10 times that of the corresponding sol. hæmolysin. It is inseparable from the cells and vanishes before their death. The effect is weakened or destroyed by 30 min. at 50—55°, and is unaffected by changes in  $p_H$  between 6.0 and 8.0. It is inhibited by PhOH, AgNO<sub>3</sub>, and PhMe. CH. ABS.

**Influence of salts on the hæmolytic action of the bacterial cells of streptococci and other conditions that determine the hæmolysis.** K. MATSUNAGA (Kitasato Arch. Exp. Med., 1933, 10, 207—219).—Mg and Ca are essential for the hæmolysis of erythrocytes by streptococci. The reaction caused in presence of Mg is inhibited by Ca and promoted by K; that in presence of Ca is inhibited by K. Salt-free peptone has little effect. CH. ABS.

**Serum-proteins of healthy hill bulls and their variations during rinderpest and after recovery.** K. C. SEN and A. C. ROY (Indian J. Vet. Sci., 1933, 3, 39—64).—In fatal rinderpest the serum-total protein (I), -globulin, and -euglobulin were low, but the latter two were normal relatively to (I). Considerable fluctuation occurred after recovery. In rinderpest associated with piroplasmosis and/or coccidiosis the serum underwent gelation when kept. CH. ABS.

**Fractional precipitation of the anti-body-containing protein of anti-rinderpest serum.** I. J. R. HADDOW, K. C. SEN, and A. C. ROY (Indian J. Vet. Sci., 1933, 3, 149—159).—The total globulin fraction is more potent than the H<sub>2</sub>O-insol. protein or the euglobulin. CH. ABS.

**Fractionation of antimeningococcus serum.** P. P. MURDICK and S. M. COHEN (J. Immunol., 1933, 24, 531—541).—Agglutinative, precipitative, and antitoxic activity is associated with the H<sub>2</sub>O-insol. globulin, separation of which is described. CH. ABS.

**Syphilis antigens.** E. BALBI (Z. Immunität., 1933, 78, 524—539; Chem. Zentr., 1933, ii, 1051—

1052).—Immunisation and complement-formation experiments with EtOH extracts of brain after treatment with COMe<sub>2</sub> and Et<sub>2</sub>O are described. Brain-antigen is adsorbed on Al(OH)<sub>3</sub>-B but not on Al(OH)<sub>3</sub> (Merck). The antigen is removed from heart extracts by Al(OH)<sub>3</sub>. A. A. E.

**Bacteriophage and fatigue of soils cultivated with lucerne.** A. DEMOLON and A. DUNEZ (Compt. rend., 1933, 197, 1344—1346).—Bacteriophage (I) is detected in the nodules (max.), roots, and stems, but not in the leaves, of lucerne > 1 year old, but not in young plants. (I) passes into the soil and thence into new plants. In agreement with the known period in which soil becomes fatigued, diffusion of (I) to the whole region occupied by the roots occurs in 2 years. J. W. B.

**Determination of chemotherapeutical substances fixed by spirochaetes and trypanosomes.** E. SINGER and V. FISCHL (Naturwiss., 1933, 21, 787).—Determination of As by a method based on that of Sanger and Black shows that spirochaetes and trypanosomes in the blood of animals treated with arsenicals take up and fix the latter. Similar results have been obtained with metallic compounds other than arsenicals. W. O. K.

**[Bacterial growth]-arresting and toxic effect of silver nitrate in nutrients and electrolytes.** G. GLÜCK (Arch. Hyg. Bact., 1933, 110, 38—60; Chem. Zentr., 1933, ii, 559).—The effect of AgNO<sub>3</sub> on *B. coli* in H<sub>2</sub>O and non-interfering electrolytes is slow but considerable. It is diminished by proteins. A. A. E.

**Presence of a substance resembling acetylcholine in the venous blood of the tongue of dogs on excitation of the nervus lingualis.** W. FELDBERG (Pflüger's Archiv, 1933, 232, 88—104; Chem. Zentr., 1933, ii, 239).—The substance is considered to be acetylcholine. A. A. E.

**Adrenal cortex and sex. Effect of cortical extract on normal and castrated rats.** S. I. SIMPSON, A. KOHN-SPEYER, and V. KORENCHESKY (Lancet, 1933, 125, 1194—1196).—No effect of a potent cortical extract on the sexual, endocrine, or some other organs of normal or castrated male rats could be obtained. This is apparently not in harmony with clinical evidence of the effect of adrenal tumours on primary and sexual characteristics. L. S. T.

**Ergotamine and the effect of adrenaline on blood-lactate.** M. W. GOLDBLATT (J. Physiol., 1933, 78, 96—105).—In cats anaesthetised with amytal and urethane the hyperglycaemia and rise in blood-lactate observed after injection of adrenaline is inhibited by previous injection of ergotamine. NUTR. ABS.(m)

**Action of organ extracts on adrenaline.** F. SCHÜTZ (Biochem. Z., 1933, 265, 282—290).—A thermolabile substance is extracted from liver which at  $p_H$  6.1—6.4 accelerates the oxidation of *l*-adrenaline to the red oxidation product and also accelerates the oxidation of *d*-adrenaline and more slowly of *l*-dihydroxyphenylalanine but does not act on *l*-tyrosine. P. W. C.



**Effect of active substances of the adrenal cortex and of adrenaline on the behaviour of muscle of normal and adrenalectomised frogs.** K. WACHHOLDER and V. MORGENSTERN (Pflüger's Archiv, 1933, 232, 444—453; Chem. Zentr., 1933, ii, 564).—High concns. (5—25 mg. per 100 c.c.) of Schmitz and Kühnau's cortical hormone-B abolish reactivity towards acetylcholine (I) in both cases; 0.01—0.05 mg. per 100 c.c. increases (I) contraction, whilst 0.02—0.2 mg. per 100 c.c. retards fatigue, especially in adrenalectomised animals. Hormone-A has a similar but weaker action. With Swingle and Pfiffer's eucortone increased performance of isolated muscle was observed only with adrenalectomised animals and at high concn. Adrenaline at a concn. 1 in  $5 \times 10^5$  has a slightly stimulating action, but at other concns. is depressant. A. A. E.

**Adrenaline hyperglycæmia.** M. ROTHCHILD (Z. ges. Exp. Med., 1933, 88, 33—41).—Adrenaline hyperglycæmia (I) in rabbits increases when sugar is given 3—8 hr. before the injection of adrenaline (II), the blood-sugar (III) being normal before the (II) is injected. (I), which depends on the capacity of the individual to store glycogen, is greater when alimentary hyperglycæmia is lower. Removal of the thyroid causes rise in (I), which is reduced by previous feeding with thyroxine. Injection of 20 units of parathyroid extract reduces (III) by 10—20 mg. per 100 c.c. in 1—2 hr., but has no effect on (I). NUTR. ABS. (m)

**Influence of thyroid in tissue oxidation.** W. BÜNGELER (Klin. Woch., 1933, 12, 933—934; Chem. Zentr., 1933, ii, 236).—Addition of thyroxine to the suspension liquid did not increase the  $O_2$  demand of the tissues examined. Prolonged feeding with thyroid increased that of isolated organs. A. A. E.

**Effect of alkali on the absorption of thyroxine from the gastro-intestinal tract.** Intravenous injection of thyroxine. W. O. THOMPSON, P. K. THOMPSON, L. F. N. DICKIE, and J. M. ALPER (Arch. Int. Med., 1933, 52, 809—820).—The  $Na_2$  salt (I) is 75 times as effective as pure thyroxine when administered *per os*; the Na salt is only one third as effective as (I). Intravenous injection is somewhat more effective than oral administration. Synthetic and natural thyroxine are equally effective in the treatment of myxœdema. P. G. M.

**Water exchange.** XVII. **Effect of thyroxine on excretion of urine.** J. HATAFUKU and S. TAKAHASHI (Tôhoku J. Exp. Med., 1933, 21, 102—106).—Perfusion of the toad's kidney through the renal artery with Ringer's solution containing thyroxine (II) usually produces diuresis (I) with low concn. of (II) and oliguria (III) with large concn. (I) results from diminished tubular re-absorption under (II), but this, in excessive amount, so increases the  $O_2$  consumption of the kidney that asphyxia and consequent lowered functional capacity result in oliguria. Perfusion through the renal portal vein produces slight (I) only, and (III) extremely rarely. NUTR. ABS. (m)

**Antagonism between di-iodotyrosine and thyroxine and the rôle of diet in hyperthyroidism.** I. ABELIN and A. SCHÖNENBERGER (Z. ges. exp. Med.,

1933, 88, 528—542).—Administration of di-iodotyrosine (I) to dogs rendered hyperthyroid by thyroid gland (II) or thyroxine (III) reduces the increased basal metabolic rate (IV), cardiac and respiratory activity, and nervous hyper-excitability and leads to an increase in wt., although feeding of (II) or (III) is continued. Continued administration removes hyperthyroidism (V) and (IV) occasionally becomes subnormal. The dosage depends on the degree of (V), since excess leads to increased secretion of (III). With occasional intermissions, administration of (I) can be continued with efficient results for long periods. NUTR. ABS. (m)

**Determination of parathyroid hormone.** F. J. DYER (Quart. J. Pharm., 1933, 6, 426—430).—The rise of Ca content in the urine of male rats following injection of parathyroid extract (I) is confirmed, but is too variable to be used as a standard for estimating the activity of (I). R. S. C.

**Effect of parathyroid extract on secretion of insulin.** E. ZUNZ and J. LA BARRE (Compt. rend. Soc. Biol., 1933, 112, 1544—1545).—Crossed circulation experiments on dogs under chloralose show that injection of 5—10 units of parathyroid extract into the donor causes a considerable fall of blood-sugar in the recipient. The suprarenals play no part. NUTR. ABS. (m)

**Physiology of the liver.** XXIV. **Effect of insulin on blood-sugar following total removal of the pancreas and liver.** F. C. MANN and J. L. BOLLMAN (Amer. J. Physiol., 1933, 103, 45—47).—Using a depancreatized dog, the observation by Mann and Magath that insulin exerts its hypoglycæmic action in absence of the liver was confirmed. NUTR. ABS. (b)

**Effect of insulin on the respiratory quotient, oxygen consumption, sugar utilisation, and glycogen synthesis in the normal mammalian heart in hyper- and hypo-glycæmia.** E. W. H. CRUICKSHANK and C. W. STARTUP (J. Physiol., 1933, 77, 365—395).—Hyperglycæmia was associated with an increase in  $O_2$  consumption (I), sugar utilisation (II), and glycogen synthesis (III). The reverse occurred in hypoglycæmia (IV), but the R.Q. throughout remained at unity except in progressive and marked insulin-(IV) when it was lowered. Insulin increased slightly the (I) and (II), and largely (III). NUTR. ABS. (b)

**Relation of insulin to liver-glycogen.** R. C. BODO and I. NEUWIRTH (Amer. J. Physiol., 1933, 103, 5—17).—In dogs fed on high-carbohydrate diet and anaesthetised with morphine and chloralose, there occurred a steady decrease in liver-glycogen (I). With a continuous intravenous infusion of glucose (II), however, (I) increased, whilst its distribution in the liver remained uniform. When, with (II) infusion, relatively large amounts of insulin were administered in single injections, (I) fell. A continuous slow infusion of insulin prevented storage of (I). NUTR. ABS. (b)

**Liver-glycogen storage in diabetic animals.** R. C. BODO, F. C. TUI, and L. FARBER (Amer. J. Physiol., 1933, 103, 18—24).—In completely depancreatized dogs, after fasting for 48 hr., the liver



is free from glycogen (I). On administering glucose (II), with or without anaesthesia, (I) is restored to a max val. of 1%. Administration of both (II) and insulin produces in the depancreatized animal a still greater recovery of (I). NUTR. ABS. (b)

**Heat-precipitation of insulin.** V. DU VIGNEAUD, R. H. SIFFERD, and R. R. SEALOCK (J. Biol. Chem., 1933, 102, 521—533).—The heat-pptn. (I) of insulin by  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{H}_3\text{PO}_4$  at varying concn. compared with the amount of  $\text{NH}_3$  liberated under the same conditions indicates that the  $\text{NH}_3$  liberation is merely coincidental with (I). Inactivation of insulin by  $\text{H}_2\text{S}$  or  $\text{NaCN}$  prevents (I); the isolation, however, of an inactive heat-ppt. from insulin after treatment with  $6N\text{-H}_2\text{SO}_4$  indicates that the groups responsible for the activity and (I) are not the same. Regenerated heat-ppt. yields a heat-ppt. again with  $0.1N\text{-HCl}$  or  $\text{-H}_2\text{SO}_4$  more readily than the original insulin. A. L.

**Diastase inhibition in the liver in fatal insulin hypoglycaemia.** H. POPPER and O. WOZASEK (Virchow's Archiv, 1933, 288, 673—681).—A non-diabetic child, which died in hypoglycaemia after treatment with insulin for malnutrition, had a large amount of liver-glycogen; there was also a powerful inhibition of liver-diastase. NUTR. ABS. (m)

**A blood-sugar-increasing substance from the pancreas.** H. TANGL and F. THAN (Biochem. Z., 1933, 266, 448—451).—The aq. extract of an acidified  $\text{CCl}_4$  extract of pancreas (3 kg.) gave on neutralisation and evaporation 0.1—0.8 g. of a substance which increased the blood-sugar of dogs by 100—200%. P. W. C.

**Effect of callicrein on blood-sugar in man.** E. ALTENBURGER (Klin. Woch., 1933, 12, 789—791).—Callicrein (I), injected intramuscularly into normal men, produces a fall of blood-sugar from the fasting level, and diminishes the hyperglycaemia and increases the subsequent hypoglycaemia after carbohydrate feeding; sometimes hypoglycaemic symptoms are induced. NUTR. ABS. (m)

**Anterior pituitary extract and insulin resistance.** E. DI BENEDETTO (Compt. rend. Soc. Biol., 1933, 112, 499—501; Chem. Zentr., 1933, ii, 896).—Injection into dogs of alkali extracts of the anterior pituitary lobe increases the blood-sugar (I); injection of insulin then diminishes (I), but not to the normal low val. Insulin intoxication is not observed with animals which have received such extracts. After hypophysectomy resistance to insulin is considerably diminished. A. A. E.

**Pituitary and glycogen in the toad.** B. A. HOUSSAY, E. DI BENEDETTO, and P. MAZZOCCO (Compt. rend. Soc. Biol., 1933, 113, 465—467).—In the toad (I), either total hypophysectomy or removal of the pars glandularis results in a diminution of blood-sugar, a considerable decrease in liver-glycogen (II), and a less marked fall of muscle-glycogen (III); a restoration to normal vals. follows the injection of pituitary extracts. In normal and hypophysectomised (I), (II) and (III) formation from injected glucose is increased if extracts of pituitary are simultaneously administered. NUTR. ABS. (m)

**Rôle of the liver in the diabetes-producing action of the pituitary in the toad.** C. A. CAMPOS, J. L. CURUTCHET, and A. LANARI (Compt. rend. Soc. Biol., 1933, 113, 467—469).—The rise of blood-sugar (III), which follows implantation (I) of anterior pituitary gland (II) into a depancreatized hypophysectomised toad, appears after 7 hr., attains a max. in 24—30 hr., and disappears after 70 hr. (I) of (II) into a depancreatized hepatectomised toad does not result in a rise of (III), so that the presence of the liver is necessary for the production of diabetic symptoms by the secretion of the pituitary gland of the toad. NUTR. ABS. (m)

**Pituitary and pancreatic diabetes in batrachians and reptiles.** B. A. HOUSSAY and A. BIASOTTI (Compt. rend. Soc. Biol., 1933, 113, 469—471).—Extirpation of the pars glandularis of the pituitary gland hinders or prevents the appearance of diabetic symptoms (I) following pancreatectomy in the following batrachians (II): *Leptodactylus ocellatus*, *Ceratophrys ornata*, *Bufo d'Orbigny*, and in the serpent *Ophis merremii*; in (II) implantation (III) of anterior pituitary material causes appearance of the symptoms. The results of either hypophysectomy or (III) are unaffected by the absence of the following organs: lungs, kidneys, adrenal glands, testes or ovaries, thyroid gland, and the alimentary apparatus. Normal and diabetic urines contain an easily adsorbed substance which stimulates the appearance of (I) in the hypophysectomised depancreatized toad. NUTR. ABS. (m)

**Action of anterior pituitary extract on phloridzin diabetes.** B. A. HOUSSAY, A. BIASOTTI, E. DI BENEDETTO, and C. T. RIETTI (Compt. rend. Soc. Biol., 1933, 112, 497—499).—Removal of the pituitary glands reduces the glycosuria (I), diuresis (II), N excretion, and D/N ratio of the phloridzinised dog, and the animal dies of hypoglycaemia (III). The injection of anterior pituitary extract prevents (III) and increases (I), (II), and ketonuria, especially when accompanied by a diet of meat or sugar. NUTR. ABS. (b)

**Is the thyroid-stimulating hormone of the anterior pituitary excreted by the kidney?** M. KROGH and H. OKKELS (Compt. rend. Soc. Biol., 1933, 113, 635—641).—When a concentrate of the urines of cases of Graves' disease prepared by a process known to separate the thyrotropic factor from anterior pituitary extracts is injected intraperitoneally into adult male guinea-pigs there is no significant thyroid reaction and the basal metabolic rate is not affected. NUTR. ABS. (m)

**Effect of anterior pituitary extract on blood-iodine in dogs after removal of thyroid or pituitary.** B. A. HOUSSAY, A. BIASOTTI, and P. MAZZOCCO (Compt. rend. Soc. Biol., 1933, 113, 459—460).—The increase in blood-I in normal or hypophysectomised dogs after injection of anterior pituitary extracts (I) is due to the thyroid gland in the absence of which (I) usually cause a fall in blood-I. NUTR. ABS. (m)

**Metabolism and specific dynamic action in fasting and fed dogs after removal of the pituitary or damage of the tuber cinereum.** P. MAZZOCCO



(Compt. rend. Soc. Biol., 1933, 113, 456—459).—As regards the sp. dynamic action (I) of meat there is no difference between normal and hypophysectomised dogs, but (I) is slightly higher, especially after a three days' fast, in dogs with the pars tuberalis cauterised.

NUTR. ABS. (m)

Relation between anterior pituitary lobe and thyroid gland. W. HOHLWEG and K. JUNKMANN (Pflüger's Archiv, 1933, 232, 148—158; Chem. Zentr., 1933, ii, 562).—Injection of follicular hormone (progynon) into rats prevents anterior pituitary (I) changes due to castration (II), but not somewhat similar changes due to thyroidectomy (III); the latter are prevented by ingestion of thyroid or injection of thyroxine. In (II) the gonadotropic hormone of (I) is increased, but in (III) the thyreotropic hormone (IV) of (I) is normal. After (III) and injection of thyroxine, (IV) is diminished.

A. A. E.

Anterior pituitary hormone in endocrine deficiency. II. Determination of sexual (anterior pituitary and follicular) hormone in health and in mental and neural disease. W. OESTERREICHER (Klin. Woch., 1933, 12, 896—899; Chem. Zentr., 1933, ii, 234).—In endocrine deficiency the amounts of pituitary sexual hormones in the blood, urine, and pituitary are increased except in cases of pituitary injury.

A. A. E.

Influence of the anterior pituitary hormone on the genital system of male mammals. B. ZAVADOVSKI, M. G. GRIGOREVA, and V. SARAFANOV (J. Physiol. U.S.S.R., 1933, 15, 518—633).—A method based on the measurement of the seminal vesicles is proposed for the standardisation of the anterior pituitary hormone and applied to the diagnosis of pregnancy.

A. L.

Function, assay, and preparation of galactin, a lactation-stimulating hormone of the anterior pituitary. Factors controlling normal lactation. W. V. GARDNER and C. W. TURNER (Missouri Agric. Exp. Sta. Res. Bull., 1933, No. 196, 61 pp.).—The extraction, properties, and biological assay of galactin (I) are described. (I) retains its activity after storage for 6 months. Factors influencing the control of lactation by (I) are examined.

A. G. P.

Separation of the pressor and oxytocic substances from the posterior lobe of the pituitary gland. R. L. STEHLE (J. Biol. Chem., 1933, 102, 573—590).—The material is treated with 0.5% aq. AcOH, and inert substances in the conc. filtrate are removed by pptn. first with EtOH, and then with Ba(OH)<sub>2</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, and colloidal Fe. The concentrate obtained is then dissolved in aq. EtOH and fractionally pptd. with EtOAc, when the pressor fraction is pptd. first. Further purification is obtained by utilising the different distribution of the substances between the two phases of a H<sub>2</sub>O—EtOH—EtOAc system, the pressor substance being found in the aq., the oxytocic in the EtOAc, phase. Some chemical properties and pharmacological actions of the fractions are described.

A. L.

Secretion of the posterior lobe of the pituitary after administration of drugs. A. SIMON (J.

Pharm. Exp. Ther., 1933, 49, 375—386).—Administration of insulin to unanæsthetised dogs failed to produce in the cerebrospinal fluid a definite increase of vasopressin, whilst diuretics (urea or novasurol) did not increase the oxytocic potency of the fluid.

W. O. K.

Influence of pituitary gland on parturition. II. Metabolism during injection of posterior pituitary extracts. III. Posterior pituitary and the water balance. S. MORRIS (J. Obstet. Gynaecol., 1933, 40, 580—597, 598—605).—II. Small doses of pituitrin cause antidiuresis (I) and decrease (25%) in urinary N; large doses cause (I) followed by diuresis. Urea-N is decreased; NH<sub>3</sub>- and NH<sub>2</sub>-acid-N are increased. Anterior pituitary extracts sensitise the body towards pituitrin.

III. Posterior pituitary extracts convert blood-org. Cl into -Cl', increasing the osmotic pressure and causing retention of H<sub>2</sub>O.

CH. ABS.

Anterior pituitary sexual hormone from urine of pregnancy. F. HAUROWITZ, M. REISS, and J. BALINT (Z. physiol. Chem., 1933, 222, 44—49).—The activity of the crude urinary hormone (I) is greatly increased (100—300-fold) by adsorption on BzOH, also to some extent on keeping the aq. solution at 38°. Purified (I) is pptd. by EtOH, COMe<sub>2</sub>, and phosphotungstic acid and gives an opalescence with Esbach's reagent, sulphosalicylic acid, or tannin, but is not pptd. by CCl<sub>3</sub>·CO<sub>2</sub>H or on boiling. It is salted out by (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. It contains about 7% of sugar and gives the biuret, Sakaguchi, Millon, and Pauly reactions. Only a single hormone is postulated, since both follicular ripening and luteinisation are produced together by all preps.

J. H. B.

Excretion of prolan in the urine of aged women. C. HAMBURGER (Klin. Woch., 1933, 12, 934—935; Chem. Zentr., 1933, ii, 233).—In 75% of the cases examined (59—85 years) there was increased excretion of prolan, the quantities (100—300 mouse units per litre) being approx. those observed after castration.

A. A. E.

Relationship of the (œstrus) dose of follicular hormone (menoformone) in rats and mice. S. E. DE JONGH and E. LAQUEUR (Acta Brev. néerl. Physiol., 1933, 3, 33—35; Chem. Zentr., 1933, ii, 561).—A rat unit=9 mouse units (approx.).

A. A. E.

Conjugation in *Rhizopus* inhibited by female sex hormone. G. W. PLUMB and L. W. DURRELL (Science, 1933, 78, 386).—œstrin inhibits zygospore formation in *R. nigricans*.

L. S. T.

Humoral excitation of the nesting instincts in rabbits. E. B. TIETZ (Science, 1933, 78, 316).—Loosening of hair in the rabbit parallels the involution of the corpus luteum; an additional factor is necessary for excitation of the nesting instinct, which, in absence of pregnancy, can be induced by the injection of the urine of pregnant women.

L. S. T.

Occurrence of male sexual hormone in the urine of newly born infants and in the placenta. Antagonistic action of sexual hormone. H. GOECKE, P. WIRZ, and H. DANERS (Arch. Gynaekol., 1933, 153, 233—243; Chem. Zentr., 1933, ii, 233).—



Male sexual hormone is present in the urine of newly born boys and girls, and in the placenta in the latter, but not in the former, case. A. A. E.

**Hormone and vitamin actions and their mutual relationships.** E. ABDERHALDEN (Med. Klinik, 1933, 29, 523—525; Chem. Zentr., 1933, ii, 893—894).—A discussion. A. A. E.

**Vitamins and the prevention of abortion in sheep.** H. DRYERRE (Nature, 1933, 132, 751).—Feeding with a concentrate of vitamins-A, -D, and -E appears to reduce abortion in ewes. L. S. T.

**Occurrence of vitamin-A in the oil of West Indian sharks.** C. F. ASENJO (Science, 1933, 78, 479). L. S. T.

**Vitamin-A content of barley.** E. H. HUGHES (J. Agric. Res., 1933, 47, 487—494).—Diets containing barley as the sole source of vitamin-A (I) failed to produce normal growth in rats. The (I) of barley was > that of white maize, but approx. one sixth of that of yellow maize. A. G. P.

**Carotene and vitamin-A in the human organism.** F. KAUFFMANN and W. VON DRIGALSKI (Klin. Woch., 1933, 12, 306—308).—The carotene (I) content of human blood is usually < 0.01 mg. per 100 c.c. (max. 0.27 mg.). When carrot juice, eggs, or (I) are administered to cases previously giving negative tests, a latent period (II) occurs before an increase can be detected, probably due to absorption of (I) by the organs. There is no (II) in cases already showing (I) in the blood. The max. val. obtainable on diets rich in (I) varies from 0.11 to 0.27 mg. per 100 c.c. in different individuals. Slight xanthosis results from feeding (I), the intensity depending on the (I) val. Carotenæmia cannot be prevented by exposure of the subject to insolation. Urine, bile, gallstones, cerebrospinal fluid, non-hæmorrhagic ascitic fluid, and sweat are free from (I) and vitamin-A, which are, however, found in the faeces of rats receiving them in excess. Except during lactation, loss of vitamin-A reserve in man can take place only through normal utilisation or decomp. NUTR. ABS. (m)

**Vitamin-A content of rat's liver after feeding with  $\alpha$ -,  $\beta$ -, and  $\gamma$ -carotene, and the antimony trichloride reaction of vitamin-A preparations.** H. BROCKMANN and M. L. TECKLENBURG (Z. physiol. Chem., 1933, 221, 117—128).—Rats receiving  $\alpha$ -,  $\beta$ -, or  $\gamma$ -carotene stored vitamin-A (determined by  $\text{SbCl}_3$  reaction) in the liver.  $\beta$ -Carotene gave much the best yield. Lutein, zeaxanthin, and lycopene were inactive. Rat-liver oils before and after saponification show the absorption band 620  $\mu$ , unsaponified fish oils, 608—609  $\mu$ , shifting to 620  $\mu$  on saponification which removes an impurity present. A band at 573  $\mu$  is due to oxidation products. J. H. B.

**Growth-promoting action of carotenes and xanthophylls.** R. KUHN and H. BROCKMANN [with A. SCHEUNERT and M. SCHIEBLICH] (Z. physiol. Chem., 1933, 221, 129—136).— $\alpha$ -,  $\beta$ -, and  $\gamma$ -Carotene restore growth and cure xerophthalmia in rats, the limiting doses being 5, 2.5, and  $5 \times 10^{-6}$  g., respectively. The accepted constitutions by which  $\beta$ -carotene affords 2 mols. and  $\alpha$ - and  $\gamma$ -carotene each one mol. of vitamin-

A, respectively, are thus confirmed. Lutein, zeaxanthin, violaxanthin, azafrin Me ester, dihydrocrocin, and chlorophyll were inactive. J. H. B.

**Vitamin-A and lipin metabolism.** H. J. JUSATZ (Naturwiss., 1933, 21, 800).—The serum-cholesterol of rabbits receiving daily 0.5—1.5 c.c. of a vitamin-A prep. (40,000 units per c.c.) for a period of 1 month is increased by approx. 80% (cf. A., 1933, 645). F. O. H.

**Vitamin-A deficiency in normal and depancreatized dogs.** E. P. RALLI, A. PARIENTE, G. FLAUM, and A. WATERHOUSE (Amer. J. Physiol., 1933, 103, 458—467).—Depancreatized dogs showed symptoms claimed to resemble those of vitamin-A (I) deficiency, which were not cured by feeding carotene, nor (in one dog) by (I). The (I) content of the livers of depancreatized dogs was low. Failure to utilise (I) may be related to a disturbance in fat metabolism. NUTR. ABS. (b)

**Toxicity of vitamin-A.** W. VON DRIGALSKI (Klin. Woch., 1933, 12, 308—309).—Large daily doses (20,000—40,000 rat units) of vitamin-A cause loss of wt., disease, and death (in 5—19 days) in rats. NUTR. ABS. (m)

**Relationship between the antimony trichloride blue value of cod-liver oils and that of their unsaponifiable fractions.** F. J. DYER (Quart. J. Pharm., 1933, 6, 338—346).—The  $\text{SbCl}_3$  blue vals. of 39 cod-liver oils and of their unsaponifiable fractions are recorded, the average ratio being 1:1.65. Distribution of the results (1.163—2.055) is statistically normal. R. S. C.

**Vitamin-D potency of sun-irradiated, dried yeast.** K. H. COWARD (Lancet, 1933, 225, 920).—Dried yeast may be activated antirachitically by exposure to strong sunlight. L. S. T.

**Clinical tests of the antirachitic activity of calciferol.** J. C. SPENCE (Lancet, 1933, 225, 911—915).—Calciferol (I) acted as effectively as cod-liver oil or irradiated ergosterol in 12 cases of human rickets. 1 c.c. of (I) solution (3000 units) daily produced a max. curative effect. L. S. T.

**Substances which affect the residual nitrogen increase in cats brought about by vitamin-D.** S. HERMANN and M. ZENTNER (Biochem. Z., 1933, 266, 418—421).—Vigantol is able to increase the blood-residual N (I) in cats by 100%, the effect being completely inhibited if Kombuchal (II) is fed together with vigantol. Gluconic acid, one constituent of (II), inhibits the increase of (I) only in 40% of cases, whilst citric acid is inactive. P. W. C.

**Effect of overdoses of irradiated ergosterol, administered for approximately two months, on the composition and structure of the bones of rats.** J. H. JONES and G. M. ROBSON (Amer. J. Physiol., 1933, 103, 338—350).—Of three similarly constituted groups of rats, on a diet low in Ca, group *a* was killed after a week, and *b* and *c* after 7—9 weeks; *c* had received in addition large daily doses of irradiated ergosterol (I). The ash content and X-ray density of the bone were the same in groups *a* and *b*, but markedly lowered in *c*. The histology of the bones in *c* also showed marked changes. In another similar



series, on a slightly different diet also low in Ca, the rats receiving no addition of (I) showed a lowering of ash and of serum-Ca, whilst in rats receiving moderate, non-toxic doses of (I), the lowering of ash was less and the serum-Ca was normal. NUTR. ABS. (b)

**Avitaminosis. XIV. Effect of vitamin-A deficiency on concentration of blood-lipins of the albino rat. XV. Effect of vitamin-D deficiency on concentration of lipins of the blood of the albino rat.** B. SURE, M. C. KIR, and A. E. CHURCH (Proc. Soc. Exp. Biol. Med., 1933, 30, 620—621; 621—622).—XIV. The vals. for the content of fatty acids (I), phospholipins (II), and cholesterol (III) in the blood of rats deprived of vitamin-A were normal.

XV. Vitamin-D deficiency did not affect the (I), (II), or (III) content of the blood. NUTR. ABS. (b)

**Fresh and dried yeast as sources of vitamin-B<sub>1</sub>.** R. WALKER and E. M. NELSON (Amer. J. Physiol., 1933, 103, 25—29).—The vitamin-B<sub>1</sub> obtained by rats (growth criterion) from yeast cakes when fed fresh was approx. half that obtained from the same cakes if dried before feeding. This is ascribed to the fact that viable yeast cells pass unaltered through the digestive tract. The dried yeast cakes were found to be half as active as a commercial dried yeast, possibly owing to the freedom of the latter from starch.

NUTR. ABS. (b)

**Effects of variations in the amounts of vitamin-B and protein in the ration.** A. G. GOGAN and R. W. PILCHER (Missouri Agric. Exp. Sta. Res. Bull., 1933, No. 195, 46 pp.).—Additions of vitamin-B to a basal diet for rats increased the food intake (I) and growth rate. Raising the protein level increased the growth rate without affecting the gross intake of food. When the two changes were made simultaneously (I) was greatly increased and the growth was still further accelerated. No inter-relationships were apparent between the level of protein intake and the vitamin-B requirement. A. G. P.

**Dietary requirements for fertility and lactation. XXV. Does the amount of fat in diet influence vitamin-B requirements for lactation?** B. SURE (Proc. Soc. Exp. Biol. Med., 1933, 30, 622—623).—Rats deprived of vitamin-B<sub>1</sub> were no more successful in rearing their young when the diet contained 20% or 30% of lard than when it contained 10%. NUTR. ABS. (b)

**Quantitative relationships between vitamin or hormone requirement and nutrient substances involved in metabolism.** E. ABDERHALDEN [with WERTHEIMER] (Münch. med. Woch., 1933, 80, 722; Chem. Zentr., 1933, ii, 894).—The relation between vitamin-B<sub>1</sub> and carbohydrate metabolism, which has been confirmed, is discussed.

A. A. E.

**Rôle of vitamin-B in the utilisation of sugars by the pigeon. Comparative effect of hexoses and disaccharides in diets containing 66% of sugar.** R. LECOQ (Compt. rend., 1933, 197, 1155—1157).—The presence in the diet of 66% of galactose or lactose leads to alimentary unbalance; addition of large amounts of vitamin-B (I) (dry brewer's yeast) has no effect on the time of survival. The action of

fructose (and sucrose) is similar but not so marked. Glucose and maltose require the same amount of (I) to prevent death; the min. dose is twice that required for a diet containing 35% of the sugar (A., 1933, 541). H. B.

**Hydrogen-ion concentration in the organs of pigeons fed on polyneuritis-producing diets.** R. McCARRISON, G. SANKARAN, and K. B. MADHAVA (Indian J. Med. Res., 1933, 20, 739—756).—*p<sub>H</sub>* determinations on the organs of pigeons killed at the onset of polyneuritis gave evidence of increased acidity of the pons, optic lobes, cerebellum, and cerebrum, decreased acidity of skeletal muscles and liver, and an increase in the difference in reaction between auricle and ventricle as compared with normal controls. NUTR. ABS. (b)

**Ascorbic acid (vitamin-C).** M. BACHSTETZ (Giorn. Chim. Ind. Appl., 1933, 15, 510—511).—Ascorbic acid has been isolated from *Capsicum annuum* (Voghiera variety). T. H. P.

**Vitamin-C in the adrenal gland of the human foetus and the physical state of the vitamin in the gland cell.** G. BOURNE (Nature, 1933, 132, 859—860).—The cytological method previously described (A., 1933, 372) has been applied to the adrenal glands of a 55-cm. human foetus. The whole of the gland blackened, the cortex (I) > the medulla. The outer portions of (I) reacted < the deeper, whilst the "foetal cortex" showed a strong reaction. The nuclear aggregation of the stained granules was strong enough to obscure the nuclei in many cases. The physical condition of the vitamin in the gland cell is discussed. L. S. T.

**Determination of vitamin-C.** L. K. WOLFF, M. VAN EEKELLEN, and A. EMMERIE (Acta Brev. néerl. Physiol., 1933, 3, 44—45; Chem. Zentr., 1933, ii, 571).—After trituration of the tissue with sand and extraction with 5% aq. CCl<sub>3</sub>·CO<sub>2</sub>H (5—10 c.c. per g.) the following vals. (c.c.) were obtained on titration with 0.02% aq. 2:6-dichlorophenol-indophenol: ascorbic acid (1 mg.) 16.4, lemon juice (1 c.c.) 5.5, rabbit's liver (1 g.) 1.1, rabbit's adrenal (1 g.) 23.9, pig's spleen (1 g.) 2.8, pig's kidney (1 g.) 1.7, pig's adrenal (1 g.) 37.6, pig's pancreas (1 g.) 1.9, tuberculous human liver (1 g.) 0.5, human adrenal (1 g.) 1.2. Adrenaline does not reduce. Small quantities of glutathione and Fe do not interfere. A. A. E.

**Influence of temperature and light density on photosynthesis and respiration and an explanation of "solarisation" and "compensation point."** N. R. DHAR (J. Indian Chem. Soc., 1933, 10, 541—561).—The non-applicability of the Arrhenius equation to photosynthesis and many other phenomena in plant life are explained by assuming the reversible equilibrium  $n\text{CO}_2 + n\text{H}_2\text{O} \rightleftharpoons \text{C}_n\text{H}_{2n}\text{O}_n + n\text{O}_2$ , in which the direct action (photosynthesis) is opposed by the reverse action (respiration).

E. S. H.

**Relationship between physiological phenomena and pigment formation in plants. V. Anthocyanins and transpiration.** H. KOSAKA (J. Dept. Agric. Kyushu Imp. Univ., 1933, 4, 95—126).—The total transpiration and the daily variation are increased



in those plants which contain large amounts of anthocyanin pigments (*Oryza sativa*, *Perilla nankinensis*, etc.) in the leaves and stems. Lack of sunlight has an inhibiting effect. P. G. M.

**Changes in composition of Florida avocados in relation to maturity.** A. L. STAHL (Florida Agric. Exp. Sta. Bull., 1933, No. 859, 61 pp.).—Chemical and physical changes with advancing growth are recorded. Of these, the increase in oil and fat content (I) in the immature fruit is most marked. An inverse relationship is established between (I) and the *d* of the fruits. Firm fruit, stored until soft, showed an increase in (I) and hydrolysable sugars and a decrease in *d*,  $H_2O$ , free reducing and total sugar contents. A. G. P.

**Biochemistry of seed germination, especially of *Zea mays*.** R. C. MALHOTRA (J. Biochem. Japan, 1933, 18, 173—197).—During the germination (I) of peas (II), maize (III), and wheat, starches (IV), hemicelluloses (V), and, to a smaller extent, fats are utilised; proteins are catabolised only with (II). Sugars are formed during (I), but the calorific energy of the seeds decreases. The wt. of the seedlings is always < the initial wt. of their seeds. With (III), fats and heat energy diminish more rapidly in the embryo (VI) than in the endosperm (VII) where (IV) and (V) are mostly used. The N content remains approx. const. in both parts of the seed. Isolated (VI) of (III) during (I) show changes similar to those of the intact (VI), whilst isolated (VII) kept under conditions suitable for (I) exhibit changes only in sugars and (IV). The mechanism of these changes is discussed. F. O. H.

**Biochemistry of the wheat plant.** R. C. MALHOTRA (J. Biochem. Japan, 1933, 18, 199—205).—During the growth of wheat, the  $H_2O$  content attains min. vals. during the early and late stages, whilst the content is highest at maturity (I). Both sugars and hemicelluloses gradually increase until just before (I) when they diminish. The total N content remains const. until three months before (I) when it slowly increases. Starch is completely utilised during the first three months for the development of the grain. F. O. H.

**Cause of the chemical variation of chickpea seeds.** N. N. IVANOV (Bull. Appl. Bot., Leningrad, 1933, [iii], No. 1, 3—11).—The protein content (12.3—31.5%) is related to soil and locality. Low vals. are associated with absence of sp. bacteria, and the plant then assimilates combined N from the soil. CH. ABS.

**Carbohydrate metabolism of the soya-bean during germination.** S. SASAKI (J. Agric. Chem. Soc. Japan, 1933, 9, 693—696).—Reducing sugar, produced after germination in the dark, decreased after one week; sucrose and stachyose decreased gradually. Dextrin and starch were found in the germinated seeds and increased considerably. During germination araban and cellulose increased, whilst galactan decreased. CH. ABS.

**Brassica japonica**, Sieb., var. **Sugukina Makino** (*B. hipposinica*, Bailey). I. Chemical changes during growth. H. KOJIMA (J. Agric.

Chem. Soc. Japan, 1933, 9, 664—671).—The reducing sugar increased, and polysaccharide decreased, with growth. CH. ABS.

**Composition of the seeds of the pine and the acorns of the oak of different geographical origins.** V. A. VINOGRADOV (Bull. Appl. Bot., Leningrad, 1933, [iii] No. 1, 183—193).—The total ash of the pine, and the total ash, fat, and  $H_2O$  extractives of acorns of *Quercus robur pedunculata* are independent of geographical location, but various parts of the seeds contain different amounts of ash. CH. ABS.

**Cucurbita.** V. V. ARASIMOVICH (Bull. Appl. Bot., Leningrad, 1933, [iii], No. 1, 73—99).—In *C. maxima*, *C. pepo*, and *C. mixta* the sugar content does not increase proportionately to the maturation of the fruit. Glucose is > fructose; sucrose is sometimes absent. Invertase is active only during the first two weeks of maturation. The oil and protein of the seeds accumulate at the expense of the sugars. The I val. of the oil increases, whilst the acid val. and enzymic activity of the seeds decrease, with maturation. CH. ABS.

**Physiologically balanced culture solutions with stable hydrogen-ion concentration.** S. F. TRELEASE and H. M. TRELEASE (Science, 1933, 78, 438—439).—With a suitable ratio of  $NO_3/NH_4$  wheat cultures could be maintained at a  $p_H$  which remained approx. const. during the 8-day period between solution renewals. L. S. T.

**Growth-promotion experiments with living orchid pollen.** F. LAIBACH (Ber. Deut. bot. Ges., 1933, 51, 336—340).—Living pollen from tropical orchids when placed on cut surfaces of leaf stems, epicotyls of seedlings, etc. promotes growth activity in neighbouring tissue. A. G. P.

**Occurrence of growth substance in marine algæ.** H. G. VAN DER WEIJ (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 759—760).—Of several kinds of marine algæ examined, only young, rapidly growing specimens of *Valonia macrophysa* contained growth substance. Extraction of the cell wall with  $Et_2O$  indicated its presence there in a concn. < 20 times that in the sap. R. K. C.

**Growth substance in *Elæagnus angustifolius*.** H. G. VAN DER WEIJ (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 760—761).—Growth substance (I) was transmitted to agar by young leaves or the base portions of young stem, but the tops of the latter or vegetation tips (the upper 3—4 mm. of a young shoot), did not yield (I). R. K. C.

**Evaporation, transpiration, and oxygen consumption by roots.** W. A. CANNON, D. DEMAREE, and E. A. PURER (Science, 1933, 78, 388—389).—The rate of  $O_2$  consumption (I) by the root of the willow is indirectly affected by light relations of the shoot, and may be directly affected by the temp. of the culture solution. There is no apparent positive relation between transpiration rate and that of  $O_2$  absorption by the root, but there may be a direct relation between the evaporating power of the air and (I). L. S. T.



**Relation of moisture to respiration and heating in stored oats.** A. L. BAKKE and N. L. NOECKER (Iowa Agric. Exp. Sta. Res. Bull., 1933, No. 165, 319—336).—The  $O_2$  consumption of stored oats increases with their  $H_2O$  content. No relationships between  $H_2O$  content and temp. attained are apparent. Mould growth reached a max. at 30—35° and with a  $H_2O$  content of 24—40% according to aeration. When the  $H_2O$  content was < 15% all heat evolved was radiated. A. G. P.

**Iodocolorimetry of cellulose dextrins and determination of cellulose.** L. PALOHEIMO and V. VALAVAARA (Biochem. Z., 1933, 266, 301—322).—The cellulose dextrins (I) obtained by the action of 70%  $H_2SO_4$  give a strong colour with I in KI, which can be used for the photometric determination of cellulose. The influence of temp., age of solution, duration of hydrolysis, I and (I) concns. on the light absorption of (I) after adding I are investigated. P. W. C.

**Bog moss. II. Composition of *Sphagnum fimbriatum*.** Wils. M. WATANABE (J. Agric. Chem. Soc. Japan, 1933, 9, 649—654).—Part of the cellulose, obtained by chlorination, is insol. in cuprammonium solution. On hydrolysis with  $H_2SO_4$  it afforded a low yield of glucose. CH. ABS.

**Metabolism of calcareous algæ. I.** P. HAAS and T. G. HILL (Biochem. J., 1933, 27, 1801—1804).—Extraction of *Corallina officinalis* with hot  $H_2O$  and of the conc. solution with EtOH yielded hexa-acetyl-floridoside, m.p. 100—101°,  $[\alpha]_D + 108.5^\circ$ , deacetylated to floridoside. A polypeptide of aspartic acid was pptd. from the aq. extract with  $Hg(OAc)_2$ . H. D.

**Floridoside, present in *Florideæ*.** H. COLIN and E. GUÉGUEN (Compt. rend., 1933, 197, 1688—1690).—The presence of floridoside (I) (A., 1930, 835, 1324) in the EtOH extracts of a large variety of species of *Florideæ* is established by high dextrorotation and non-reducing properties, no sucrose, glucose, or fructose being detected. (I) is isolated from *Furcellaria fastigiata* extract after purification with phosphotungstic acid and removal of mineral matter with a zeolite. J. W. B.

**Optical activity of phytol.** T. WAGNER-JAUREGG (Z. physiol. Chem., 1933, 222, 21—23).—The optical activity of crude phytol is completely accounted for by that of the residue after distillation. The natural substance is probably inactive. J. H. B.

**Fluorescence spectra of hypericin and mycoporphyrin.** C. DHÉRE (Compt. rend., 1933, 197, 948—950).—In  $C_5H_5N$ , hypericin (I), the pigment of *Hypericum perforatum*, shows fluorescence spectral bands at 657—648, 626—619, and 610—599  $m\mu$ , and an absorption band at 606—596  $m\mu$ , which coincide with the bands for mycoporphyrin (II) (*Penicillioopsis clavariae formis*). There is similar agreement in EtOH solution. (I) and (II) are probably identical. A. C.

**Pigment of *Carica papaya*, L.** I. R. YAMAMOTO and S. TIN (J. Agric. Chem. Soc. Japan, 1933, 9, 752—757).—In addition to violaxanthin, caricaxanthin, m.p. 166°, containing two OH groups, is present. CH. ABS.

**Mandarin pigment. I.** L. ZECHMEISTER and P. TUZSON (Z. physiol. Chem., 1933, 221, 278—280).— $\beta$ -Carotene was isolated from the flesh and rind of the mandarin (*Citrus madurensis*). Violaxanthin and other xanthophylls were also present. J. H. B.

**Pinene from the Lauraceæ. *Nectandra olæophora*, Bar. Rod.** N. B. GONSALVES (Arch. Pharm., 1933, 271, 461—462).—The oil from this tree contains much  $\alpha$ -pinene, some  $\beta$ -pinene and camphene. R. S. C.

**Distribution of saponins in plants.** T. SOLACOLU and E. WELLES (Arch. Pharm., 1933, 271, 470—477).—The approx. saponin content of different parts of many plants is estimated by the blood-gelatin method. R. S. C.

***Toddalia aculeata* (Pers.). I.** Two alkaloids and a neutral crystalline substance from its root-walls.—See this vol., 88.

**Exudation and volatilisation of alkaloids from plants.** J. CHAZE (Compt. rend., 1933, 197, 1148—1150).—An alkaloidal exudate is detected histochemically (by  $KI_2$ ) on the leaves, stems, and flowers of the hemlock. In warm sunlight, exudation is followed by rapid volatilisation. H. B.

**Indian medicinal plants. III. Leaves of *Erythrina indica*.** S. N. CHAKRAVARTI, M. L. SITARAMAN, and A. VENKATASUBBAN (J. Annamalai Univ., 1933, 2, 238—242).—The leaves contain a N-free substance, m.p. 83°, extractable by boiling  $Et_2O$ , EtOH, or light petroleum, which does not give glucoside or phytosterol reactions, and an alkaloid, m.p. 117°, pptd. from the 1% HCl extract by  $KBiI_4$ . H. A. P.

**Proteins and non-protein nitrogenous substances in the juice of "erba medica."** G. BARBERA (Annali Chim. Appl., 1933, 23, 462—470).—The apical parts of "erba medica" are very rich in non-proteins, mostly  $NH_2$ -acids and amido-compounds, these containing about 50% of the total N compounds of the fresh juice. The remaining 50% is largely protein precipitable by EtOH and sol. in KOH. T. H. P.

**"Manna-grass" (*Glyceria spectabilis*), a species of high hydrocyanic acid content.** H. MINNSEN (Landw. Versuchs-Stat., 1933, 117, 279—312).—The relatively large proportion of HCN in manna-grass probably occurs as an easily decomposable compound other than a glucoside. Ensilage of the material reduces the HCN content. The liberation of HCN is accelerated by treatment of leaves with 1% tartaric acid solution. Small amounts of HCN also occur in the female inflorescence of maize. A. G. P.

**Comparative zinc content of green and etiolated leaves.** G. BERTRAND and M. ANDREITCHIEVA (Compt. rend., 1933, 197, 1374—1376).—Determination of the Zn present in a large variety of green and either artificially etiolated or inner, yellow, leaves (cabbage, lettuce) confirms the previous conclusion (A., 1929, 362) that the Zn content is the greater the greater is the chlorophyll content of the leaf. J. W. B.



Changes in the cell contents of wood (xylem parenchyma) and their relationships to the respiration of wood and its resistance to *Lyctus* attack and to fungal invasion. S. E. WILSON (Ann. Appl. Biol., 1933, 20, 661—690).—Starch present in the xylem parenchyma of the sap wood of trees when felled disappears during delayed drying, e.g., when stored in log form. This is attributable to the continued activity of sapwood cells. Kiln-drying or steaming kills the cells and starch remains, thus rendering wood more liable to infestation by *Lyctus* beetles, of which starch forms the principal food. A. G. P.

Nature of the sheath material in the feeding punctures produced by the potato leaf hopper and the three-cornered lucerne hopper. F. F. SMITH (J. Agric. Res., 1933, 47, 475—485).—The sheathing substance is mainly of insect origin and gives positive tests for pectin, protein, and, probably, chitin. Colour tests differentiating sheath material from plant tissue are given. A. G. P.

Exanthema in pears and its relation to copper deficiency. J. OSERKOWSKY and H. E. THOMAS (Science, 1933, 78, 315—316).—Exanthema in pears appears to be due to a deficiency of Cu. Spraying with Bordeaux mixture or the introduction of sol. Cu salts into the trunks of trees effects a marked improvement in diseased trees (I). The Cu content of leaves of (I) is always < that of leaves from disease-free localities. L. S. T.

Qualitative analysis of protein solutions. A. SCHMITZ (Z. physiol. Chem., 1933, 221, 197—201).—A nephelometric method employing fractional pptn. with  $(\text{NH}_4)_2\text{SO}_4$  is described. When the content of saturated  $(\text{NH}_4)_2\text{SO}_4$  solution is plotted against turbidity, various proteins give characteristic curves. J. H. B.

Biuret reaction in medicine and the chemistry of foodstuffs. H. KÜHL (Pharm. Zentr., 1933, 74, 751—754).—A summary of earlier results of the application of the biuret reaction in urine testing and cereal analysis. Physico-chemical differences in composition of flours can be detected by its use. P. G. M.

Deproteinisation with iodine. A. BAUDOUIN and J. LEWIN (Compt. rend. Soc. Biol., 1933, 113, 155—157; Chem. Zentr., 1933, i, 96).—When wet decomp. is effected with  $\text{H}_2\text{SO}_4$  in presence of oxalate, pptn. with  $\text{CCl}_3\text{CO}_2\text{H}$  or I gives concordant vals. for non-protein-N in the filtrate (e.g., from blood). A. A. E.

Determination of ethyl iodide by the katharometer in determinations of cardiac output in man. J. S. DONAL, jun., and C. J. GAMBLE (Amer. J. Med. Sci., 1933, 185, 744).—A sample of respired air is freed from  $\text{CO}_2$  and  $\text{H}_2\text{O}$  by exposure to ascarite and  $\text{P}_2\text{O}_5$ ; the thermal conductivity is determined before and after removal of  $\text{EtI}$  with liquid air. The average error is 0.00055 vol.-%. CH. ABS.

Determination of ketonic substances by means of the step photometer. W. NEUWEILER (Klin. Woch., 1933, 12, 869—870).—The method is based

on the colour reaction of  $\text{COMe}_2$  with salicylaldehyde in presence of KOH. Pulfrich's instrument is used for comparing the absorption with that of a standard solution. 5 c.c. of blood are required.

NUTR. ABS. (m)

Carbohydrates. I. Micro-determination of menthol-, borneol-, and  $\beta$ -naphthol-glycuronic acid in blood. II. Colorimetric micro-determination of free and conjugated menthol in blood and tissue. H. MASAMUNE (J. Biochem. Japan, 1933, 18, 259—276, 277—283).—I. The method of Quick (A., 1924, ii, 876) for urine is applied to blood (1 c.c.). The mol. reducing power of glycuronic acid (I) = that of glucose. The hydrolysis consts. of menthol-,  $\beta$ -naphthol-, Na borneol-, and phenol-glycuronic acid are 0.1495, 0.0288, 0.2154, and 0.0203, respectively. Data for the blood content of (I) (calc. as phenolglycuronic acid) for various animals are given.

II. The tissue (1 g.) or blood (1 c.c.) is deproteinised with  $\text{EtOH}$ , free menthol distilled with the solvent, the distillate treated with  $p\text{-NMe}_2\text{-C}_6\text{H}_4\text{-CHO}$ , and the red colour produced compared with suitable standards. The residue is treated with aq. NaOH followed by aq.  $\text{CdSO}_4$  and filtered, the filtrate being tested as above. F. O. H.

Micro-determination of glycogen. S. SIMONOVITS (Biochem. Z., 1933, 265, 437—443).—Glycogen (I) determinations by Sahyun's method (A., 1932, 77) gave much lower results than by Pflüger's macro-method, some (I) being lost by adsorption on the charcoal. A method which gives reasonably accurate results with 0.6 mg. of (I) is described. P. W. C.

Micro-determination of cholesterol. G. MONASTERIO (Biochem. Z., 1933, 265, 444—447).—Cholesterol (I) is pptd. with digitonin, the digitonide oxidised with  $\text{CrO}_3$ , and the excess of the latter determined by micro-iodometric titration. The method is used for determination of free and combined (I). P. W. C.

Micro-incineration of tissues. R. F. MACLENNAN (Science, 1933, 78, 367).

Determination of iron in biological material. R. F. HANZAL (Proc. Soc. Exp. Biol. Med., 1933, 30, 846—848).—A colorimetric method is based on the reaction between Fe salts and  $\text{SH}\cdot\text{CH}_2\text{CO}_2\text{H}$  in alkaline solution. NUTR. ABS. (m)

Semi-micro-determination of sulphur in finger nails. R. C. NEALE and W. A. PEABODY (J. Lab. Clin. Med., 1933, 18, 1178—1181).—The material (25 mg.) is fused with  $\text{Na}_2\text{O}_2$ ; S is pptd. as  $\text{BaSO}_4$  with  $\text{BaCl}_2$ , excess of which is titrated with  $\text{K}_2\text{Cr}_2\text{O}_7$  (phenol-red indicator). CH. ABS.

Separation and determination of bismuth and arsenic in biological material. E. H. MAECHLING (J. Lab. Clin. Med., 1933, 18, 1058—1061).—The sample (5 c.c.) is digested with  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ ; the product is treated with  $\text{N}_2\text{H}_4$ ,  $\text{H}_2\text{SO}_4$  and distilled. The distillate is oxidised with  $\text{Br-H}_2\text{O}$  and  $\text{As}^v$  determined volumetrically or colorimetrically. Bi in the residue is determined by Leonard's method. CH. ABS.