

# BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

## A., I.—General, Physical, and Inorganic Chemistry

OCTOBER, 1938.

**Band spectrum of helium.** S. P. McCALLUM and M. S. WILLS (*Nature*, 1938, **142**, 252—253).—Band spectra of a discharge in He at 27.5 mm. pressure obtained under different excitation conditions indicate that He mols. formed in the discharge have a life  $\sim 1/600$  sec. or, more probably, that they are formed by the collision of metastable with neutral atoms after interruption of the discharge.

L. S. T.

**Band spectra of nitrogen forming a Rydberg series.** T. TAKAMINE, T. SUGA, and Y. TANAKA (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1938, **34**, 854—864).—The absorption bands of  $N_2$  forming a Rydberg series have been studied. An emission band, which is also visible, forms a Rydberg series converging to the same limit as that of the absorption bands, viz., 661.2  $\mu$ , corresponding with the  $A^{12}\Sigma^+$  state of  $N_2$ .

W. R. A.

**Identification of aurora radiations.** J. KAPLAN (*Z. Physik*, 1938, **108**, 744—749).—Certain auroral lines can be identified with single-headed members of the  $A^3\Sigma \rightarrow X^1\Sigma$  series (the so-called  $\epsilon$  system) of gaseous  $N_2$  within the limits of experimental error, whereas Vegard's identification of the lines with double-headed members of the  $\epsilon$  system of solid  $N_2$  is less precise and erroneously suggests the presence of solid  $N_2$  in the auroral region.

H. C. G.

**Excitation of the aurora spectrum in the laboratory.** J. KAPLAN (*Z. Physik*, 1938, **109**, 750—752).—See following abstract.

H. C. G.

**Auroral afterglows.** J. KAPLAN (*Physical Rev.*, 1938, [ii], **54**, 176—178).—The prep. of auroral afterglows in pure  $N_2$  is discussed in detail. A nomenclature for the five stages most frequently met in the prep. of these glows and normally occurring in the order  $O_3$ ,  $NO$ ,  $CN$ , Lewis-Rayleigh, and auroral stages is introduced.

N. M. B.

**Production of highly vibrating molecules.** J. KAPLAN (*Physical Rev.*, 1938, [ii], **54**, 230).—First positive  $N_2$  bands originating on very high vibrational levels and occurring in the spectrum of the auroral afterglow have been photographed in the spectrum of a new high-pressure afterglow. The enhancement of the bands is shown and contrasted with the Lewis-Rayleigh glow.

N. M. B.

**Colour of the nocturnal sky.** R. GRAND-MONTAGNE (*Compt. rend.*, 1938, **207**, 275—277).—The mean energy radiated by the nocturnal sky in the spectral bands 5800—6550, 6550—7000, and 7000—9000  $\mu$  is 6.50, 3.56, and 11.25 arbitrary units, respectively. The energy vals. undergo diurnal

and seasonal variations, but the spectral energy distribution remains approx. const.

A. J. E. W.

**Band spectrum of the ionised oxygen molecule.** L. BOZÓKY (*Math. nat. Anz. ung. Akad. Wiss.*, 1936, **54**, 557—585; *Chem. Zentr.*, 1936, ii, 1118).—The spectrum was photographed with an improved source and high dispersion. The following consts. were redetermined:  $A^2\Pi_B = 1.070$ ,  $\alpha = 0.022$ ;  $X^2\Pi_B = 1.668$ ,  $\alpha = 0.019$ .

H. J. E.

**Broadening and displacement of the higher series sodium lines through caesium vapour.** C. FÜCHTBAUER and G. HEIMANN (*Z. Physik*, 1938, **110**, 8—20).—The broadening of certain Na lines due to admixture of Cs with the emitting Na vapour is measured. The effect is large and comparable with the Cs/Cs broadening; it indicates an unusually great action cross-section for the Cs atom. The displacements are all towards the red and from them the action cross-section of Cs towards slow electrons is obtained as  $25.9 \times 10^3$  sq. cm. per c.c. at 1 mm. pressure.

L. G. G.

**Moments and abundances of the atomic nuclei  $^{171}\text{Yb}$  and  $^{173}\text{Yb}$ .** H. SCHÜLER and J. ROIG (*Naturwiss.*, 1938, **26**, 495).—The classification of the Yb lines in a term-scheme by Meggers *et al.* (*A.*, 1938, I, 108) makes it possible to determine the moments of  $^{171}\text{Yb}$  and  $^{173}\text{Yb}$  from the hyperfine structure of the lines. Transitions between the terms  $(4f^{14}6s^2)^1S_0$ ,  $(4f^{14}6s7s)^3S_1$ , and  $(4f^{14}6s6p)^3P_{0,1,2}$  were investigated. The mechanical moments of  $^{171}\text{Yb}$  and  $^{173}\text{Yb}$  are 1/2 and 5/2, respectively, this being the first example where the mechanical moments of two isotopes differ by two units. The abundance ratio  $^{173}\text{Yb}/^{171}\text{Yb}$  is 1.13 (cf. Aston, *A.*, 1934, 341). The magnetic moment of  $^{171}\text{Yb}$  is positive and about as large as that of  $^{180}\text{Hg}$ .  $^{173}\text{Yb}$  has a negative magnetic moment and a large positive quadrupole moment.

A. J. M.

**Spectrum of neutral iridium, Ir I.** W. ALBERTSON (*Physical Rev.*, 1938, [ii], **54**, 183—184).—From new data in the range 4627—2159  $\mu$ , intensities,  $\lambda\lambda$ , and classifications of the most intense lines are tabulated. The normal electron configuration of Ir I is  $5d^76s^2$  and the ionisation potential is  $\sim 9.2$  v.

N. M. B.

**Atom factor of thallium.** J. PALACIOS and J. LOSADA (*Congr. int. Quim. pura apl.*, 1934, **9**, II, 165—171; *Chem. Zentr.*, 1936, ii, 2293).—The atom factor is calc. from X-ray powder photographs of  $\text{TlCl}$ .

A. J. E. W.



**Extension of X-ray spectra towards optical radiation.** M. SIEGBAHN (Nuovo Cim., 1938, 15, 115—116).—A summary. O. J. W.

**Absolute wave-length determination of the Al  $K\alpha_{1,2}$  line with a concave grating.** F. TYRÉN (Z. Physik, 1938, 109, 722—727).—The  $\lambda$  of the Al  $K\alpha_{1,2}$  line measured with a concave-grating spectrograph at grazing incidence is  $8.3397 \pm 0.0003$  Å. Combining this with the lattice const. of calcite the val. of the electronic charge is  $4.803 \pm 0.004$  e.s.u. L. G. G.

**Rontgen lines of the M series of  $^{48}\text{Cd}$  to  $^{58}\text{Ce}$ .** H. KIESSIG (Z. Physik, 1938, 109, 671—684).—Lines of the M series for elements  $^{48}\text{Cd}$  to  $^{58}\text{Ce}$  were photographed with a plane-grating spectrometer and the data arranged in a Moseley diagram. Two new Moseley lines were found and ascribed to the transitions  $M_{IV}O_{II}$  and  $M_{VO_{III}}$ . An  $M\alpha\beta$  doublet was found with  $^{57}\text{La}$ . New energy level vals. are calc. Measurements of the half-width vals. of  $M\epsilon$  lines show a definite relationship with the periodic system. H. C. G.

**X-Ray spectra. II. Comparison of the spectra of tungsten and platinum in the first and second orders.** F. VIERHELLER and J. A. SARALEGUI (Strahlenther., 1934, 51, 704—713; Chem. Zentr., 1936, ii, 2088).—The relation between the first-order spectra is in accord with the at. nos. The line spectra become more complex in the second order. A classification of lines in the neighbourhood of the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -lines is attempted. A. J. E. W.

**Excitation of metastable atoms in a gas discharge.** V. FABRIKANT (Compt. rend. Acad. Sci. U.R.S.S., 1938, 19, 385—388).—In the discharges in Hg rectifiers the excited atoms constitute about 10% of the total and have a Boltzman distribution. At the initial moment (stationary discharge) the excited atoms are distributed over the discharge section according to Bessel's function and not uniformly (cf. Meissner and Graffunder, A., 1928, 212), and an exponential abatement in concn. occurs with time. F. J. L.

**Effect of magnetic field on mercury discharge radiation.** V. FABRIKANT and G. ROCHLIN (Compt. rend. Acad. Sci. U.R.S.S., 1938, 19, 393—396).—The effect of the magnetic field produced by two solenoids on the luminous discharge from a low-pressure,  $\text{H}_2\text{O}$ -cooled, liquid-cathode Hg lamp is investigated. The luminosity of the positive column is little affected by a longitudinal homogeneous field, but a non-homogeneous field increases the intensities of the lines  $\lambda\lambda$  5461, 5770—5791 Å. 6—7 times and of the resonance lines  $\lambda\lambda$  1850 and 2537 Å. 2—5 times. The magnetic field causes distortions of the electron paths and increases the no. of collisions between atoms and electrons. F. J. L.

**Influence of ultrasonic waves on the discharge potential of hydrogen.** R. PIONTELLI (Atti R. Accad. Lincei, 1938, [vi], 27, 357—363).—The influence of ultrasonic waves on the current-potential curves at smooth Pt cathodes in 0.1N-HCl, -KCl, and -NaOH has been studied at 25°. The ultrasonics bring about a strong depolarisation, which is about

0.8 v. at the lowest c.d. and decreases with increasing c.d. The bearing of the results on modern theories of overvoltage is discussed. O. J. W.

**Generalisation of the theory of electrical discharges.** J. S. TOWNSEND and E. W. B. GILL (Phil. Mag., 1938, [vii], 26, 290—311).—The theory is extended to cover discharges in gases at low pressure and under the influence of magnetic field. O. D. S.

**Excitation of radiating atoms in a gas discharge.** V. FABRIKANT (Compt. rend. Acad. Sci. U.R.S.S., 1938, 19, 389—392).—Theoretical calculations of the concns. of excited radiating atoms based on the analogy between the diffusion of quanta and atoms suggested by Compton (Physical Rev., 1922, 20, 283). F. J. L.

**Ionisation of air by X-rays of varying hardness and degree of homogeneity up to 400 kv. in cylindrical chambers with diameter up to 70 cm.** W. I. BLOCK (Ann. Physik, 1938, [v], 32, 701—733).—An extension of the investigation of Küstner (A., 1931, 994) for X-rays of higher energy. The variation in sharpness and intensity of X-ray beams of 220 and 400 kv. energy at various depths in  $\text{H}_2\text{O}$  have been investigated by means of a small chamber. O. D. S.

**Secondary emission of beryllium.** E. G. SCHNEIDER (Physical Rev., 1938, [ii], 54, 185—188; cf. A., 1938, I, 3).—As the deposition of Be film, by evaporation in vac., proceeds, the secondary emission ratio rises from that of the support metal to about 2.5 and then falls to  $<1$ , whilst the voltage of the primary electrons necessary to reach the max. drops to about 200 v. Heating the thick Be to bright redness for a few min. raises the emission to about 1.6 with the max. at a primary energy of about 630 v. Surface oxidation increases the emission to about 4.1. Explanations of these effects are discussed and evidence is given that the max. secondary emission ratio for pure bulk Be is 1.6. N. M. B.

**Emission of protons from hydrogenated palladium.** T. FRANZINI (Nuovo Cim., 1938, 15, 88—99).—The emission of positive and negative particles from Pd saturated with  $\text{H}_2$  has been studied for the temp. range 100—1250°. Expressions are given showing the variation with temp. of (a) the velocity of thermal emission of electrons from pure Pd, (b) the velocities of thermal emission of electrons and of protons from Pd saturated with  $\text{H}_2$ , and (c) the velocity of diffusion of  $\text{H}_2$  through Pd. The results show that the H emitted by Pd is partly in the form of protons. O. J. W.

**Determination of  $e/m$  for electrons.** A. E. SHAW (Physical Rev., 1938, [ii], 54, 193—209).—A new precision method utilising the good focussing properties of crossed electric and magnetic fields (cf. A., 1934, 233) is described. The final equation for  $e/m$  does not involve the velocity explicitly and focussing criteria eliminate the markedly error-inducing influence of electron velocity. The val. of  $e/m$  is  $(1.7571 \pm 0.0013) \times 10^7$  e.m.u. The limitations imposed by the design of the condenser are discussed. N. M. B.



**Atomic electron velocities in hydrogen.** A. L. HUGHES and (Miss) M. A. STARR (Physical Rev., 1938, [ii], 54, 189—193; cf. A., 1938, 109).—The relation of the inelastic scattering of fast electrons by gases to the distribution of velocities among the at. electrons is discussed. A beam of electrons of energy 1737—4040 v. was directed into  $H_2$  at low pressure and from measurements of the distribution of energies among those electrons scattered at  $34.2^\circ$  the distribution of component velocities among the at. electrons was found. The experimental curve is wider by about 11% at half-width than the curve computed by Hicks (cf. A., 1937, I, 590). In view of exact agreement for He, the theory in the case of  $H_2$  probably needs revision. N. M. B.

**Velocity distribution of elastically colliding electrons in a gas with molecules executing thermal movements.** R. LICHTENSTEIN (Physikal. Z., 1938, 39, 646—656).—Theoretical. The velocity distribution of electrons which suffer elastic collisions with the mols. of a gas executing thermal movements is calc. when the electrons are under the influence of a homogeneous electric field. The velocity distribution of rapid electrons is determined by the thermal movements of the mols. A. J. M.

**Electronic space charge with homogeneous initial electron velocity between plane electrodes.** M. J. O. STRUTT and A. VAN DER ZIEL (Physica, 1938, 5, 705—717). H. J. E.

**Spontaneous electron emission from electrodes and the field electron emission from thin layers of insulators as an after-effect of the discharge through gases.** H. PAETOW (Naturwiss., 1938, 26, 497).—When the discharge in a tube is switched off a stream of electrons continues to flow from the cathode, the val. of this current decreasing with time, and being  $\propto$  product of the time for which the discharge took place and the current strength up to a saturation val. The effect has its origin in surface and adsorption layers as it disappears if the electrodes are pure, or if they are preheated. Different gases exert different effects on the surface layers, e.g., only He and Ne could induce the effect in  $O_2$  layers, showing that in the discharge in He and Ne photons of greater energy than in other gases occur. By the addition of impurities, e.g., MgO, to the electrodes the after-current could be increased to  $10^{-9}$  amp. If the MgO or other insulator is separated from the metal electrode by a semi-conducting layer, electrons of energy  $>20$  e.v. are emitted. The excitation is caused by photons. With a homogeneous layer of  $Al_2O_3$  on Al, however, a greater excitation is produced by ions than by photons. A. J. M.

**Influence of adsorbed films on the liberation of electrons and the reflexion of ions from tungsten bombarded by positive caesium ions.** H. PAETOW and W. WALCHER (Z. Physik, 1938, 110, 69—83).—The no. of electrons liberated from W surfaces by bombardment with positive Cs ions is greatly increased by the presence of adsorbed films. Such films also have a considerable effect on the reflexion of ions. The mechanism of these pheno-

mena is discussed and the reflexion process compared with surface ionisation. H. C. G.

**Spin phenomena and limiting conditions.** F. MÖGLICH (Z. Physik, 1938, 110, 1—7).—Mathematical. The directional quantisation of an electron can be calc. without employing the matrix of Dirac and Pauli. H. C. G.

**Production of positrons in the passage of fast  $\beta$ -particles through matter.** H. STAUB (Helv. Phys. Acta, 1936, 9, 306—316; Chem. Zentr., 1936, ii, 933—934).—From Wilson chamber measurements the effective cross-section for such a process is  $<5 \times 10^{-24}$  sq. cm., as is required by theory. H. J. E.

**Production of positron-electron pairs during the passage of  $\beta$ -particles through matter.** N. FEATHER and J. V. DUNWORTH (Proc. Camb. Phil. Soc., 1938, 34, 435—441).—The production of positron-electron pairs by high-energy  $\beta$ -particles from a source of U-X in absorbers of Al, Pb, and brass is investigated by recording the simultaneous emission of the pairs of oppositely directed quanta which are produced when positrons, having already lost all their energy in ionisation, finally suffer annihilation. F. J. L.

**Slow positive rays.** A. ROSTAGNI (Nuovo Cim., 1938, 15, 117—120).—A summary of previous work. O. J. W.

**Anomalous scattering of  $\alpha$ -particles and long-range nuclear forces.** H. S. W. MASSEY and C. B. O. MASSEY (Proc. Camb. Phil. Soc., 1938, 34, 498—501).—The anomalous scattering of  $\alpha$ -particles in  $H_2$ ,  $D_2$ , and He revealing appreciable deviations from Coulomb's law cannot be explained by the electrostatic polarisation of the colliding nuclei due to their electric charges. F. J. L.

**Equilibrium state between large ions and ions produced in a gas by X-rays.** O. TE-TCHAO and (MLE.) A. M. MOULIN (Compt. rend., 1938, 206, 1464—1466).—The production by X-rays of large positive and negative ions in a current of air containing smoke particles has been investigated. The relation between the no. of ions produced and the ionisation intensity is discussed. A. J. E. W.

**Townsend ionisation number,  $\gamma$ , and its relation to field intensity.** R. SCHÖFER (Z. Physik, 1938, 110, 21—36).—Discharge initiation potentials in A with various electrodes under different conditions have been measured in order to determine  $\gamma$ , which was also calc. from the decrease in initiation potential resulting from incident radiation. The two methods give concordant results. H. C. G.

**Striated positive column. I. Pure hydrogen.** A. GÜNTHER-SCHULZE and H. MEINHARDT (Z. Physik, 1938, 110, 95—117; cf. A., 1938, 378).—The c.d. at which the non-striated discharge changes into the striated form can be measured accurately and is an exponential function of the pressure. The formation of discrete pairs of striæ and the various phases of the discharge are discussed. H. C. G.

**Influence of the Ramsauer effect on the potential gradient in a positive column.** B. KLARFELD (Compt. rend. Acad. Sci. U.R.S.S., 1938, 19, 471—



473; cf. Groos, A., 1934, 711).—In the pressure range 0.001–10 mm. Hg, potential gradient- $p$  curves have been recorded by a probe method for discharges in He, Ne, A, and Kr, and in K and Hg vapours. Where a Ramsauer effect exists (Kr, A, Ne, and possibly Hg) the curves show a min. Agreement with theory is qual. I. McA.

**Nuclear law of 4 and isotopy of the elements. Structure of the nucleus of atoms. III. G. ODDO** (Gazzetta, 1928, 68, 352–359; cf. A., 1933, 996).—For the 20 most abundant elements in the earth's crust the relative abundances of isotopic masses corresponding with  $4n$ ,  $4n+1$ ,  $4n+2$ , and  $4n+3$  are 82.23, 2.28, 1.81, and 12.17%, respectively. The five elements F, Na, Al, P, and Mn, which have no isotopes, all have at. wts. corresponding with  $4n+3$ . Isotopes of mass  $4n+2$  are apparently least stable. This rule holds also for the less abundant elements, although not so strikingly. O. J. W.

**Isotopes of potassium. A. K. BREWER** (Ind. Eng. Chem., 1938, 30, 893–896).—A type of Geiger counter suitable for the measurement of radioactivity of K, and a mass-spectrograph for the estimation of the no. and abundance of isotopes, are described. The approx. proportions are  $^{39}\text{K}$  8300,  $^{40}\text{K}$  1,  $^{41}\text{K}$  585. Ratios  $^{39}\text{K}/^{41}\text{K}$  for K from various sources are tabulated. In general plant tissues have the ratios for the soil in which they grow but kelp and seaweeds are exceptions. Animal tissues show marked selectivity. The only radioactive isotope is  $^{40}\text{K}$ . Its disintegration const. is computed. The combined disintegration steps are  $^{40}\text{K} \rightarrow ^{40}\text{Ca} + \beta$ ,  $^{40}\text{K} + e \rightarrow ^{40}\text{Ar} + \gamma$ . The relative rates of production of  $^{40}\text{Ca}$  to  $^{40}\text{Ar}$  should be equal to the ratio of  $\beta$ - to  $\gamma$ -rays or 100:1. This is about the ratio in the earth's crust. It seems probable that most if not all the  $^{40}\text{Ca}$  and  $^{40}\text{Ar}$  in the earth's crust results from  $^{40}\text{K}$  decay. C. I.

**Mass number of stable isotopes of elements 43, 61, 85, and 87. R. GRÉGOIRE** (Compt. rend., 1938, 206, 1477–1478).—The following mass nos. are deduced from a consideration of the stable isotopes of neighbouring elements: element 43, 97 and 99; element 61, 145, 147, and possibly 149; element 85, 213, 215, and possibly 217; element 87, 219 and 221. If elements 85 and 87 form part of a disintegration series commencing with U, the parent element must be a hitherto unknown isotope of mass no. 231, 233, or 237. A. J. E. W.

**Probable existence of element 93 in the natural state. H. HULUBER and (Mlle.) Y. CAUCHOIS** (Compt. rend., 1938, 207, 333–335).—X-Ray emission lines at 886, 696, 734, and 596 X, which are identified with the  $L\alpha_1$ ,  $\beta_1$ ,  $\beta_2$ , and  $\gamma_1$  lines of element 93, respectively, have been observed on examination of minerals containing U and Re. The intensity of the lines increases on chemical concn. of the Re, confirming the presence of an analogous element. A. J. E. W.

**Existence of hitherto unknown natural  $\alpha$ -radiation. J. SCHINTLMAYER** (Sitzungsber. Akad. Wiss. Wien, 1935, IIa, 144, 475–487; Chem. Zentr., 1936, ii, 1115).— $\alpha$ -Rays of range  $\sim 2.1$  cm. have been reported, but their source is unknown. They are always associated with Sm, Ga, Ge, In, Tl, Se, and P

were shown to be inactive, and the activity may be due to Tu or to element 61. H. J. E.

**Variation of ionisation with range of  $\alpha$ -particles, protons, deuterons, and  $^3\text{H}$  particles. J. C. BOWER** (Proc. Camb. Phil. Soc., 1938, 34, 450–458).—The positions of max. ionising efficiency for single  $\alpha$ -particles, protons, deuterons, and  $^3\text{H}$  particles have been determined by photometric measurement of the variation of density along photographs of expansion chamber tracks to be 2.78, 0.78, 1.47, and 2.39 mm., respectively. F. J. L.

**Method of determining the degree of dependence of the disintegrations of polonium atoms. M. FERBER** (Compt. rend., 1938, 207, 336–337).—A theoretical discussion of oscillographic records of  $\alpha$ -particle emission from Po. A. J. E. W.

**Radioactive recoil in the preparation of thorium-C'. V. MAJER** (Coll. Czech. Chem. Comm., 1938, 10, 236–241).—Examination by the Geiger-Müller counter of the decay of Th-C' (half-life 3.2 min.), obtained from the active deposit of Th by recoil, shows the presence of Th-C (60 min.), Th-B (10.6 hr.), and also 10% of Th-X (87.4 hr.); the observed effects are attributed to the formation of at. aggregates. K. W. P.

**$\beta$ -Rays from radium-E. B. T. WRIGHT and A. W. McREYNOLDS** (Physical Rev., 1938, [ii], 54, 231).—The emission of heavy electrons from Ra-E as reported by Jauncey (cf. A., 1938, I, 111) is investigated. When ebonite screens are placed between the condenser plates electrons scattered from the plates are eliminated as suggested by Compton (cf. *ibid.*, 224). N. M. B.

**Total energy of the  $\gamma$ -radiation emitted from the active deposit of actinium. (Miss) E. KARACHAILOVA** (Proc. Camb. Phil. Soc., 1938, 34, 429–434).—The total energy emitted in the form of  $\gamma$ -radiation from Ac-B + C is determined by measuring the ionisation produced relative to that of a Ra-C and Th-B + C  $\gamma$ -radiation after absorption in various thicknesses of Pb from 0 to 2 cm. F. J. L.

**$\beta$ -Rays of actinium-B and -C' partial spectra. B. W. SARGENT** (Physical Rev., 1938, [ii], 54, 232).—The end points of the  $\beta$ -rays of Ac-B and Ac-C', determined with increased precision by an absorption method, are 1.40 and 1.47 Me.v., and the ranges 0.64 and 0.68 g. per sq. cm. of Al, respectively. Intensities, constitutions, and transformations are discussed, and the relative importance of the use of max. instead of average energies is examined. N. M. B.

**Scattering of D-D neutrons. S. KIKUCHI and H. AOKI** (Sci. Papers Inst. Phys. Chem. Tokyo, 1938, 34, 865–872).—The scattering cross-sections ( $I$ ) of 21 elements for D-D neutrons have been measured by an apparatus which is described. The data obtained indicate that  $I$  is a regular function of the at. no. having max. and min. This is in contradiction to the conclusion of Dunning (A., 1935, 1186). W. R. A.

**Diffusion properties of slow neutrons. E. AMALDI and E. FERMI** (Ric. sci. Prog. tec., 1936, [ii], 7, I, 393–395; Chem. Zentr., 1936, ii, 2086).—The



mean free path for *D*- and *A*-group neutrons (cf. A., 1938, I, 427) is corr. to  $\sim 1.1$  cm.; the val. for the *C*-group, the determination of which is described, is 0.275 cm. The cross-sections for elastic collision with H and for capture are 4.8 and  $0.32 \times 10^{-24}$  sq. cm., respectively. The mean life period is  $1.6 \times 10^{-4}$  sec.

A. J. E. W.

#### Interaction of fast neutrons with atomic nuclei.

A. SOETAN (Nature, 1938, 142, 252).—Measurements of the absorption of neutrons (deuteron bombardment of Li) by various substances indicate that for heavy nuclei, at least, the sticking probability is  $< 1$ , i.e., a fast neutron may fall on a nucleus without sticking to it and without changing its direction to any great extent.

L. S. T.

**Distribution of resonance levels from the excitation of nitrogen by fast neutrons.** J. THIBAUD and P. COMPARAT (Compt. rend., 1938, 207, 226—228; cf. A., 1938, I, 427).—Resonance levels are observed with energies of 0.85, 1.02, 1.30, 1.60, 1.75, 2.05, 2.25, 2.55, 2.75, 3.05, and 3.30 Me.v.

H. J. E.

**Artificial  $\alpha$ -radioactivity.** R. DÖPEL (Verh. phys.-med. Ges. Würzburg, 1936, 59, 78—79; Chem. Zentr., 1936, ii, 2287—2288).—Artificial  $\alpha$ -radioactivity with a decay period of several min. has been observed in Ce, Cs, and In after neutron bombardment. This shows, in agreement with Gamow's theory, that no fundamental distinction exists between spontaneous and artificially excited  $\alpha$ -particle emission.

A. J. E. W.

**Detection of  $\alpha$ -rays during the irradiation of thorium and uranium with radium-beryllium neutrons.** G. F. VON DROSTE (Z. Physik, 1938, 110, 84—94).—An ionisation chamber is described which in combination with a valve amplifier can detect  $\alpha$ -particles in the presence of Ra,  $\gamma$ -rays being separated by means of a W filter. Within experimental error of the counter no (*n*,  $\alpha$ ) process occurs with Th or U.

L. G. G.

**Yield of  $\alpha$ -particles from beryllium bombarded by protons.** G. T. HATCH (Physical Rev., 1938, [ii], 54, 165—171; cf. A., 1938, I, 7).—Experiments to determine the excitation function of the reaction  ${}^9\text{Be}(p, \alpha){}^6\text{Li}$  for proton energies  $> 400$  kv. are described. The yield is of the order  $4 \times 10^{-6}$   $\alpha$ -particle per proton at 400 kv., but the derived thin target curve shows a marked flattening from the exponential form observed at lower voltages. Above 300 kv. the cross-section is nearly const. at about  $2.3 \times 10^{-25}$  sq. cm.

N. M. B.

**Energy change in the transmutation of beryllium into lithium by proton bombardment.** S. K. ALLISON, L. S. SKAGGS, and N. M. SMITH, jun. (Physical Rev., 1938, [ii], 54, 171—175; cf. preceding abstract).—Since the  $\alpha$ -particle yield from the reaction  ${}^9\text{Be}(p, \alpha){}^6\text{Li}$  is very high, energies were measured with high precision by deviating a beam of  $\alpha$ -particles through  $90^\circ$  by means of a steady source of high voltage which could be measured to 0.1% up to 40 kv. Be was bombarded by 320- and by 383-kv. protons. The energy distribution curves of the  $\alpha$ -particles show a sharp high-energy limit increasing with proton energy. The energy balance of the

reaction is  $2.152 \pm 0.04$  Me.v., corresponding with  $2.310 \pm 0.04 \times 10^{-3}$  at. wt. unit. The difference in mass of  ${}^9\text{Be}$  and  ${}^6\text{Li}$  is thus  $2.99804 \pm 0.00009$ . Assuming the val. 6.01686  $\pm 0.00020$  for  ${}^6\text{Li}$ , the mass of  ${}^9\text{Be}$  is  $9.01491 \pm 0.00025$ .

N. M. B.

**Beryllium isotope of mass 8.** O. LAAFF (Ann. Physik, 1938, [v], 32, 743—760).—An amplifying circuit is described for the quant. measurement of the ionising power of single fast nuclear fragments. The  ${}^8\text{Be}$  nucleus produced by the process  ${}^{11}\text{B}(p, \alpha){}^8\text{Be}$  disintegrates into two  $\alpha$ -particles detected by their simultaneous entry into the ionisation chamber. It is calc. that the energy of disintegration is  $< 0.2$  Me.v. Discrepancies from the theoretical vals. for the spatial distribution of the liberated  $\alpha$ -particles were observed.

O. D. S.

**Absorption and coincidence experiments on the radiations from radioactive sodium,  ${}^{24}\text{Na}$ .** N. FEATHER and J. V. DUNWORTH (Proc. Camb. Phil. Soc., 1938, 34, 442—449).—The energy spectrum of the  $\beta$ -particles from  ${}^{24}\text{Na}$  is simple and continuous with an upper limit at  $1.40 \times 10^6$  e.v., but many of the  $\beta$ -particles are not time-correlated with the  $\gamma$ -ray emission, although almost all  $\gamma$ -ray quanta occur "simultaneously" with  $\beta$ -emission.

F. J. L.

**Radiosilicon produced by bombardment of sulphur with fast neutrons.** J. CICHOCKI and A. SOETAN (Compt. rend., 1938, 207, 423—425).—Periods of 14.5 days (cf. A., 1937, I, 490) and  $\sim 2.6$  hr. are observed on bombardment of S with 13.5 Me.v. neutrons. The 2.6-hr. period is associated with Si in chemical separations, confirming that it is due to  ${}^{31}\text{Si}$ :  ${}^{32}\text{S} + {}^1_0\text{n} \rightarrow {}^{31}_{14}\text{Si} + {}^1_2\text{He}$ . The exact period ( $157.3 \pm 1.3$  min.) is in agreement with that of  ${}^{31}\text{Si}$  formed by a (*n*, *p*) reaction from  ${}^{31}\text{P}$  ( $156.9 \pm 1.6$  min.).  ${}^{30}\text{P}$  produced by a (*n*, 2*n*) reaction has a period of  $130.6 \pm 1.5$  sec.

A. J. E. W.

**Radioelement produced in cadmium under the action of fast neutrons.** M. DODÉ and B. PONTECORVO (Compt. rend., 1938, 207, 287—289).—A radioelement of period  $50 \pm 5$  min. has been produced by bombarding Cd with neutrons from a Rn-Be source. Its radiation is of high intensity but very low penetrating power. Chemical separations show that the element is probably a Cd isotope, possibly corresponding with a metastable state to which the atom returns after excitation without neutron capture;  $\gamma$ -rays or conversion electrons are emitted on reversion to the fundamental state.

A. J. E. W.

**Disintegration of boron with emission of deuterons.** I. ZŁOTOWSKI (Compt. rend., 1938, 207, 148—150).—In the disintegration of B with Po  $\alpha$ -particles 4  ${}^3\text{H}$  and 270  ${}^3\text{H}$  tracks were observed (A., 1938, I, 290). Repetition of the experiment with higher-energy  $\alpha$ -particles (5.15 instead of 4.8 Me.v.) gives 147  ${}^3\text{H}$  and 6  ${}^3\text{H}$  tracks. Of the 10  ${}^3\text{H}$  particles 8 have energies between 3.65 and 4.05 Me.v. and the other 2 between 4.81 and 5.20 Me.v. The probabilities of the occurrence of the alternative disintegrations  ${}^{10}\text{B} + {}^4\text{He} \rightarrow {}^{12}\text{C} + {}^3\text{H} + 1.39$  Me.v. (a) or  ${}^{10}\text{B} + {}^4\text{He} \rightarrow {}^{11}\text{B} + {}^3\text{H} + 4.30$  Me.v. (b) are discussed; (b) is 40 times as probable as (a).

W. R. A.



**Disintegration of nitrogen by neutrons.** G. KIRSCH and F. RIEDER (Sitzungsber. Akad. Wiss. Wien, IIa, 1935, 144, 383—392; Chem. Zentr., 1936, ii, 935).—The Wilson chamber photographic method was employed. Two processes are associated with the capture of neutrons. In one  $^{11}\text{B}$  is produced by emission of an  $\alpha$ -particle, and in the other, which is less frequent and mainly due to faster neutrons, a proton is emitted and  $^{14}\text{C}$  produced. The energy relationships lead to the expectation of a long life for the products. H. J. E.

**Disintegration of aluminium, examined by the photographic method.** E. STEPPAN (Sitzungsber. Akad. Wiss. Wien, IIa, 1935, 144, 455—474; Chem. Zentr., 1936, ii, 937).—Proton groups of range 17, 22, 25, 28, 41, 46, 50, and 56 cm. at  $15^\circ$  were detected. The energy relationships are discussed. H. J. E.

**Disintegration of elements from argon to manganese with polonium  $\alpha$ -rays.** J. SCHINTLMEISTER and E. FÖYN (Sitzungsber. Akad. Wiss. Wien, IIa, 1935, 144, 409—418; Chem. Zentr., 1936, ii, 935; cf. A., 1936, 1045).—Of the elements A, K, Ca, Sc, Ti, V, and Mn, only K gave an appreciable yield of H particles. The remainder gave  $>0.2$  H particle per  $10^6$  Po  $\alpha$ -particles. H. J. E.

**Nuclear photo-effect with  $\gamma$ -rays from  $^{11}\text{B}$  ( $p, \gamma$ ).** W. GENTNER and W. BOTHE (Naturwiss., 1938, 26, 497—498).—Artificial radioactive nuclei ( $^{13}\text{N}$ , 11 min.;  $^{34}\text{Cl}$ , 33 min.;  $^{39}\text{Ca}$ , 4.5 min.;  $^{62}\text{Cu}$ , 10.5 min.;  $^{63}\text{Zn}$ , 38 min.;  $^{106}\text{Ag}$ , 24 min.;  $^{108}\text{Ag}$ , 2.3 min.; Sb, 15 min.) have been produced by the nuclear photo-effect using  $\gamma$ -rays from  $^{11}\text{B}$  obtained by bombarding B with protons of 900—950 kv. energy. The relative efficiencies of the  $\gamma$ -rays from Li and B are compared. Except in the case of  $^{108}\text{Ag}$  there is little difference in the efficiencies. A. J. M.

**Zero effect of counter tubes.** H. OSTERWISCH (Physikal. Z., 1938, 39, 661—665).—The residual radiation of counter-tubes of various dimensions was determined in a rock-salt mine at 1000 m.  $\text{H}_2\text{O}$  equiv. The val. was const. over the normal working range of the tubes. A. J. M.

**Cause of abrupt changes in counter-tube discharges.** R. SCHADE (Naturwiss., 1938, 26, 546—547).—The sudden changes in counter-tube discharges are attributed to statistical variations in the subsequent emission of electrons, possibly a photo-electric emission from the cathode. A. J. M.

**Heavy electrons in cosmic rays.** V. VEKSLER and N. DOBROTIN (Compt. rend. Acad. Sci. U.R.S.S., 1938, 19, 479—482; cf. A., 1938, I, 114, 382, et al.).—The previous arrangement of proportional counters is now used at sea level to determine the dependence of the no. of coincidences on the thickness of an interposed Fe plate. Other causes being eliminated, the particles responsible are shown from range and ionisation to be heavy electrons of mass 50—300 $m$ ; these are of secondary origin. I. McA.

**Large cosmic showers of the atmosphere.** P. AUGER and R. MAZE (Compt. rend., 1938, 207, 228—230).—Data are recorded for coincidences in

the recording of counters at 2 m., 5 m., and 20 m. apart, and for the effect of screening. H. J. E.

**Hard cosmic-ray showers.** W. BOTHE (Indian J. Physics, 1938, 12, 155—161).—A lecture.

W. R. A.

**Angles between the components of a pair [of particles produced by  $\gamma$ -rays].** A. ALI-CHANIAN, B. DZELEPOV, and P. SPIVAK (Compt. rend. Acad. Sci. U.R.S.S., 1938, 19, 379—380).—The no. of particles produced by internal conversion of  $\gamma$ -rays from 20 mc. of Po deposited electrically on a thin foil (30  $\mu$ .) of Al-Be alloy (65% Be) were measured by the method of coincidences in two Geiger counters set at  $0^\circ$ ,  $30^\circ$ ,  $60^\circ$ ,  $90^\circ$ ,  $120^\circ$ ,  $150^\circ$ , and  $180^\circ$  to each other. The angles between the pairs created by  $\gamma$ -rays (Po and Be) in Pb were also investigated. A strong max. in the no. of coincidences occurs at  $45$ — $50^\circ$ . F. J. L.

**Ionisation in gases at high pressures by gamma radiation.** J. CLAY and M. KWIESER (Physica, 1938, 5, 725—736).—Measurements are recorded for Kr, Ar, and  $\text{N}_2$  at pressures up to 140 atm. and for fields up to 6000 v. per cm. Addition of small amounts of A has no effect on the results for  $\text{N}_2$ , and vice versa, but addition of a small amount of  $\text{O}_2$  to  $\text{N}_2$  or A made it more difficult to obtain saturation in these gases. The effect of screening with  $>10$  mm. of Pb on the ionisation produced in  $\text{N}_2$ , Ar, Kr, and Xe by the  $\gamma$ -rays from Ra was studied. H. J. E.

**Theory of natural and artificial radioactivity based on the constitution of atomic nuclei.** A. VÉRONNET (Compt. rend., 1938, 207, 121—123; cf. A., 1938, I, 429).—On the basis of the theory that all at. nuclei are built up from  $\text{D}^+$  and  $^3\text{H}^+$ , natural radioactivity arises from the spontaneous decomp. of  $^2\text{H} \rightarrow \alpha + \beta + \text{D}$ . Induced radioactivity is due to interaction between  $^3\text{H}$  particles and protons, deuterons, neutrons, and  $\alpha$ -particles. Schemes for these interactions are given.

W. R. A.

**Artificial transformation of a proton into a neutron.** M. FIERZ (Helv. Phys. Acta, 1936, 9, 245—264; Chem. Zentr., 1936, ii, 933).—Theoretical.

H. J. E.

**Theory of nuclear forces.** C. MÖLLER (Nature, 1938, 142, 290—291).

L. S. T.

**Theory of  $\beta$ -decay.** M. H. HEBB (Physica, 1938, 5, 701—704).—The method of Crane and Halpern for detecting the neutrino is discussed. For the validity of this method it is necessary that the  $\beta$ -disintegration be adiabatic. Theoretical arguments that this is so are advanced. H. J. E.

**Interaction between charged particles and radiation field.** H. A. KRAMERS (Nuovo Cim., 1938, 15, 108—114).—Mathematical. O. J. W.

**Interaction between elementary particles.** E. C. G. STUECKELBERG (Compt. rend., 1938, 207, 387—389).—Mathematical. A. J. E. W.

**Transformations of elements in the interior of stars.** II. C. F. VON WEIZSÄCKER (Physikal. Z., 1938, 39, 633—646).—The assumption that all the known elements are being formed in stars at present



is discarded on the grounds that the lower limit of the occurrence of He in stars based on it does not agree with experiment, the existence of U and Th cannot be satisfactorily explained, and the explanation of Harkins' rule given previously (A., 1937, I, 214) in this connexion is not correct. The sources of energy produced by stars are discussed. Such energy must depend alone on nuclear reactions involving light nuclei. The necessary physical conditions for the production of elements and for the production of all types of nuclei in comparable amounts are considered. A. J. M.

**Deviation of the nuclei  ${}^4\text{He}$  and  ${}^{16}\text{O}$  from the Hartree model.** B. O. GRÖNBLOM (Z. Physik, 1938, 110, 37—57).—A mathematical discussion of the correction arising from nuclear structure to be applied to the Hartree energy. The discussion is based on assumptions as to the nuclear forces involved. H. C. G.

**Fundamental physical concepts.** C. V. DRYSDALE (Nature, 1938, 142, 288—289).—Theoretical. L. S. T.

**Cosmological and atomic constants.** D. S. KOTHARI (Nature, 1938, 142, 354—355). L. S. T.

**Gravitational constant, specific charge, and ratio of mass of proton and electron.** H. ERTEL (Naturwiss., 1938, 26, 498—499).—Theoretical. A relationship between the gravitational const. ( $f$ ), the sp. charge ( $e$ ), the mass of the electron and proton ( $m$ ), Sommerfeld's fine structure const. ( $\alpha = 1/137$ ), and the no. of protons ( $N$  = no. of electrons for electrical neutrality of all matter in the universe) is derived, which gives a satisfactory val. for  $f$  when experimental vals. are substituted. A. J. M.

**Quantum mechanical-relativistic foundation of the connexion between the universal physical constants.** H. ERTEL (Naturwiss., 1938, 26, 499—500).—The relationship between the universal physical const.  $h$ ,  $c$ ,  $\pm e$  (electrical quantum),  $\pm m$  (mass of proton and electron),  $f$  (Newton's gravitational const.), and  $\lambda$  (cosmological const. of the relativistic field equations) has been derived by means of a modification of the theory of a static universe put forward by Sambursky *et al.* (Phys. Rev., 1938, 53, 256). A. J. M.

**Order of magnitude of probabilities of radioactive transition in the nucleus.** B. PONTECORVO (Compt. rend., 1938, 207, 230—232).—Theoretical. H. J. E.

**Powers of exchange between elementary particles and Fermi's  $\beta$ -disintegration theory as consequences of a possible field theory of matter.** E. C. G. STUECKELBERG (Helv. Phys. Acta, 1936, 9, 389—404; Chem. Zentr., 1936, ii, 2087).—A theory is considered in which the electron, neutrino, proton, and neutron are regarded as quantum states of a single elementary particle. A. J. E. W.

**Characteristic functions of the fundamental operators of the Dirac theory of the electron.** G. PETIAU (Compt. rend., 1938, 206, 1455—1457).—Mathematical. A. J. E. W.

**Charge-dependence of nuclear forces.** N. KEMMER (Proc. Camb. Phil. Soc., 1938, 34, 354—364).—The hypothesis that the forces between elementary nuclear particles are independent of the charges of the particular particles involved ("charge-independence hypothesis") is extended to explain the proton-proton interaction. F. J. L.

**Binding energies of the hydrogen isotopes.** A. H. WILSON (Proc. Camb. Phil. Soc., 1938, 34, 365—374).—Assuming that the potential energy of a proton and a neutron is of the form  $e^{-\lambda r}/r$ , the wave equation of the deuteron in its ground state is solved, and the binding energy of the isotope  ${}^3\text{H}$  is calc. F. J. L.

**Relativity correction for the ionisation energy of atoms with two electrons.** H. A. S. ERIKSSON (Z. Physik, 1938, 109, 762—773).—The general formula for the relativity correction of the ionisation energy of atoms with 2 electrons and any nuclear charge  $Z$  is shown to be an expansion of  $1/Z$ . The energies of dissociation thus corr. are shown for a no. of atoms to be in better agreement with experimental results than the non-relativistic vals., especially in the cases of He I and Li II. L. G. G.

**Energies associated with the two-centre problem. I. General features of the energy surface.** (MISS) E. MONROE (Proc. Camb. Phil. Soc., 1938, 34, 375—381).—Mathematical treatment of the quantal problem of one electron in the field of two unequal nuclei. F. J. L.

**Emission spectra of ozone in the ultra-violet.** J. JANIN (Compt. rend., 1938, 207, 145—146).—The emission spectrum of  $\text{O}_3$ , containing a trace of  $\text{N}_2$ , has been photographed from 3050 to 4530 Å. by an apparatus which is described. A continuous spectrum is obtained containing numerous emission bands the  $\lambda\lambda$  and relative intensities of which are given. Some of the observed bands approx. coincide with the principal max. of  $\text{O}_3$ . W. R. A.

**Gas temperature and population of atomic levels in a carbon arc at low pressure.** R. C. MASON (Physica, 1938, 5, 777—783).—Intensity measurements on the 3883 Å. CN band and on certain lines of Ba and Zn, added to the anode, were measured, and used in calculating the relative population of the excited states. With decreasing pressure the density of excited atoms exceeded that to be expected from the thermal equilibrium by increasing amounts. H. J. E.

**So-called boric acid continuum emitted from the auricle of the carbon arc.** W. FINKELNBURG and H. HESS (Physikal. Z., 1938, 39, 666—668).—The so-called  $\text{H}_3\text{BO}_3$  continuum obtained from a C arc impregnated with  $\text{H}_3\text{BO}_3$  and burning in  $\text{O}_2$  or a gas containing  $\text{O}_2$  can be ascribed to a B-O compound, the exact nature of which is unknown. A. J. M.

**Spectrum of rubidium hydride,  $\text{RbH}$ .** A. G. GAYDON and R. W. B. PEARSE (Nature, 1938, 142, 291).—The passage of a discharge through  $\text{Rb} + \text{H}_2$  gives a band spectrum of the many-line type extending from 4800 to 6500 Å. The bands are due to a



$^1\Sigma \rightarrow ^1\Sigma$  transition. Approx. positions of the heads and approx. vals. of the mol. consts. are recorded.

L. S. T.

**Band spectra of selenium, tellurium, and their oxides, in the ultra-violet.** C. S. PIOW (Ann. Physique, 1938, [xi], 10, 173—290).—The study of the band spectra of Se, Te, SeO, TeO, SeO<sub>2</sub>, and TeO<sub>2</sub> has been extended to the far ultra-violet. Several band systems (including some new systems) have been observed in the far ultra-violet for Te and Se, two systems for SeO and one for TeO in the ordinary ultra-violet, and a spectrum, rich in bands, for SeO<sub>2</sub> and TeO<sub>2</sub> in the ultra-violet and visible. The new band systems, due to diat. Se<sub>2</sub> and Te<sub>2</sub>, violate the Mecke-Birge rule, as also do those due to S<sub>2</sub> (cf. Wieland *et al.*, A., 1934, 1047). The new absorption bands of SeO<sub>2</sub> and TeO<sub>2</sub> have been studied qualitatively and quantitatively, and their vibrational structure has been partly analysed. SeO bands show resolution which does not exist in the spectra of O<sub>2</sub>, SO, and TeO, and this is attributed to two systems of different bands. The rotational structure of several bands of SeO and TeO has been partly analysed and the energies of dissociation of the excited and normal states of TeO have been determined. Comparison of the mol. consts. of the spectra of these elements with those of their oxides shows a regular variation of the spectroscopic properties for the mols. of the same group. The identity of the chemical bond in the oxides of the S group has been deduced from the recorded spectroscopic data. W. R. A.

**Sharp mitogenetic spectra.** G. DECKER (Protoplasma, 1936, 25, 515—527; Chem. Zentr., 1936, ii, 1003).—Resolution to 5 Å. was achieved with radiation from a yeast culture. H. J. E.

**Absorption spectrum of diacetyl between 1500 and 2000 Å.** V. R. ELLS (J. Amer. Chem. Soc., 1938, 60, 1864—1866).—Absorption regions in the vapour correspond generally with those of COMe<sub>2</sub> and COMeEt, although displaced in the direction of longer  $\lambda$ . The existence of other bands permits Ac<sub>2</sub> to be identified in presence of COMe<sub>2</sub> and COMeEt.

E. S. H.

**Ultra-violet spectrometry of *d*-araboascorbic and glucoheptoascorbic acid.**—See A., 1938, II, 347.

**Group resonators. XXIV. Predominance of musical intervals in simple spectral series and in the spectra of group resonators.** D. RĂDULESCU. **XXV. Intra-atomic group resonators and the ratios of frequencies of the absorption and luminescent bands of the rare earths. Absorption spectrum of NO<sub>2</sub>.** D. RĂDULESCU and A. CIOARĂ (Bul. Soc. Chim. România, 1937, 19, 3—20, 21—34).—XXIV.  $\nu$  of the spectral lines of the series for monat. elements, and the limits of the series, represent a succession of harmonics with musical intervals of the natural scale predominating. The narrow bands of the vapour spectrum, the groups of lines forming a band, and the  $\nu$  of the max. of the normal spectrum in solution are separated by the same musical intervals. The analogy between group oscillators and simple acoustic oscillators is developed. Several predictions are substantiated by reference to

the spectra of C<sub>10</sub>H<sub>8</sub>, C<sub>10</sub>H<sub>7</sub>Me, NH<sub>2</sub>Ph, NHPhAc, PhBr, C<sub>6</sub>H<sub>4</sub>Br<sub>2</sub>, and fluorene in C<sub>6</sub>H<sub>14</sub>.

**XXV. Elements with configurations sufficiently remote from that of a rare gas form group resonators, the valency electrons constituting a mobile system of coupled electrons. The cathodic luminescence spectrum of Pr and the absorption spectra of Nd and Pr do not present musical intervals as predicted. The prediction of musical intervals in the absorption spectrum of NO<sub>2</sub> is in accord with experimental data.**

W. R. A.

**Absorption spectrum and molecular structure.**

**II. Phenol and its derivatives. III. Derivatives of organic acids.** S. KATO and F. SOMENO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1938, 34, 905—911, 912—921; cf. A., 1937, I, 597).—II. The absorption spectra of PhOH, PhOMe, and Ph<sub>2</sub>O have been examined in the gaseous state and in solution in Et<sub>2</sub>O or conc. H<sub>2</sub>SO<sub>4</sub>. Each spectrum is divisible into two band systems, series (a) and (b), of unequal intensity. This type of absorption, similar to that of H<sub>2</sub>O and lower aliphatic alcohols, appears to be associated with the presence of a singly-linked trivalent O atom. The series (b) of gaseous PhOH and PhOMe and in Et<sub>2</sub>O solution, which is the strong band on the shorter- $\lambda$  side, is attributed to a transition to  $^1A$ , whilst the weak bands, series (a), are attributed to the transition between  $2p(x)$  and  $(3s)^3A$ . With Ph<sub>2</sub>O the intensities of the two absorptions are reversed, due probably to the influence of the strong field from the two Ph radicals on the O atom. The appearance of series (a) and (b) in the absorption of the compounds in H<sub>2</sub>SO<sub>4</sub> solution indicates that the pairing of  $2p(x)$  electrons of the O atom is not destroyed by the effect of strong interaction with H<sub>2</sub>SO<sub>4</sub>, thus differing from the aromatic amines (*loc. cit.*). The continuum, however, is displaced towards longer  $\lambda$ , and the intensities for H<sub>2</sub>SO<sub>4</sub> solutions are considerably stronger than those for the gas or Et<sub>2</sub>O solution, due to the effect of the strong mol. field of H<sub>2</sub>SO<sub>4</sub> close to the O.

**II. The absorption band near 3000 Å., found in all ketones and aldehydes, and characteristic of the C:O group, is not found for acids and several acetates. Comparison of the absorption bands due to the Ph radical for the compounds between PhOMe and PhOAc, and between CPhMe and MeOBz, and examination of the spectra in the far ultra-violet due to the C:O group and the O atom of these compounds, lead to the conclusion that the normal and excited orbits of the non-bending electron of the singly-linked O in the mol. are close to the C:O group, in which strong polarity causes the attractive interaction. Thus the reduction of the net charge confined in the O of the C:O group cannot give rise to the transition of the forbidden type,  $2p(y) \rightarrow (a-a)$ , which corresponds with the absorption near 3000 Å.** W. R. A.

**Absorption spectra by reflexion of organic substances in the solid state.** (MME.) T. GUILLMART (Compt. rend., 1938, 207, 289—291).—The technique of the method is outlined. The absorption spectra in the range 2470—2700 Å. of the solid amides Ph-[CH<sub>2</sub>]<sub>n</sub>-CO-NH<sub>2</sub> ( $n = 0-6$ ) have been studied. The narrow bands due to the Ph chromophore group



increase in intensity for  $n = 0-4$ , but decrease, with some displacement towards higher  $\lambda$ , for  $n = 5$  and 6. The intensity of the continuous absorption decreases up to  $n = 4$ , increasing for  $n = 5-6$ . These results confirm that buckling of the mol. occurs with  $n > 4$ .

A. J. E. W.

**Absorption spectra of organic substances in concentrated sulphuric acid. III. Substances with ethylenic linkings and carbonyl groups.** F. BANDY (Biochem. Z., 1938, 298, 81-100; cf. A., 1938, I, 227).—Lower aliphatic, unsaturated mono- and di-carboxylic acids in  $H_2SO_4$  absorb light of short  $\lambda$  only, the curve for crotonic acid exhibiting a max. at 2300 Å., whilst the higher members of the series (e.g., oleic acid) exhibit max. at 3050 Å. (3700 when diluted). Allyl alcohol and bromide, vinyl Et and vinyl Bu ether, simple unsaturated hydrocarbons and their Cl substitution products (e.g., chlorobutadiene), and aromatic compounds containing ethylenic linkings also have max. absorption in the region 2400-4400 Å. Results are somewhat different with  $H_3PO_4$  as solvent.

W. McC.

**Absorption and fluorescence of porphyrins.**—See A., 1938, II, 381.

**Phthalocyanines and associated compounds. XIII. Absorption spectra.** J. S. ANDERSON, E. F. BRADBROOK, A. H. COOK, and R. P. LINSTED (J.C.S., 1938, 1151-1156).—The absorption spectra of phthalocyanine (I), 15 of its metallic derivatives, and a no. of associated compounds containing the tetrazaporphin (porphyrazine) ring have been examined in the visible region. The spectrum of (I) is composed of < seven bands which can be placed in two groups, in each of which the intensity diminishes regularly with increasing  $\nu$ . Within each group the bands are separated by a const.  $\nu$  difference. Introduction of metals into (I) causes a shift in the spectrum to higher  $\nu$ , the displacement increasing with the at. no. of the central atom. The various spectra are compared and are correlated with the spectra of the porphyrins and azaporphyrins.

W. R. A.

**Absorption spectra of co-ordination compounds. III. Special bands of chromium complexes.** R. TSUCHIDA and M. KOBAYASHI (Bull. Chem. Soc. Japan, 1938, 13, 471-480).—The bands for aq. solutions of  $[Cr(H_2O)_6]Cl_3$ ,  $[Cr(NH_3)_6]Cl_3$ ,  $[Cr(NH_3)_5Cl]Cl_2$ ,  $[Cr(NH_3)_5NCS](NCS)_2$  (also prepared with  $H_2O$ ),  $[Cr(NH_3)_2(NCS)_4]NH_4.H_2O$ ,  $[Cr(NCS)_6]K_3.4H_2O$ , and  $[Co(NH_3)_5CrO_4]Cl$  are recorded. All these complexes contain first and second bands due to co-ordinated  $Cr^{+++}$ , the NCS group gives rise, when present, to a special band and when anions are present there is a third band attributed to *trans* pairing. The spectrochemical series of Cr is identical with that of Co complexes.  $K_2CrO_4$  has the second and third bands. The bands of the polynuclear compound are analysed into those of the component complex radicals.

F. R. G.

**Absorption spectra of *cis*- and *trans*-isomerides in the near infra-red.** Y. TA (Compt. rend., 1938, 207, 326-329).—The absorption spectra of *cis*- and *trans*- $CHCl:CHCl$  and  $-CHI:CHI$  (I) in the  $\nu$  range 6000-9320  $cm^{-1}$  have been studied. The existence

of combination  $\nu\nu$  giving replicas of the vibrational spectrum in the neighbourhood of the principal CH lines (cf. A., 1938, I, 434) is confirmed, and these spectra enable the *cis*- and *trans*-isomerides to be distinguished. New vibrational  $\nu\nu$  for (I) have been approx. determined. A combination  $\nu$  due to CH and the C:C vibration at 1580  $cm^{-1}$  is observed with both isomerides, although this vibration should be inactive with the *trans*-form. Harmonics of the fundamental CH  $\nu$  in  $CHX:CHX$  appear to have two components.

A. J. E. W.

**Kinetics of the OH radicals as determined by their absorption spectrum. III. Quantitative test for free OH; probabilities of transition.** O. OLDENBURG and F. F. RIEKE (J. Chem. Physics, 1938, 6, 439-447).—The abs. intensities of OH absorption lines in  $H_2O$  vapour thermally dissociated at 1473° have been investigated by photographic photometry and the transition probabilities ( $f$  vals.) computed. Comparison of these with known  $f$  vals. of other mols. indicates that the OH band belongs to a half-forbidden transition. The calc. lifetime of the excited state is approx.  $4 \times 10^{-6}$  sec.

W. R. A.

**Infra-red absorption of solutions of hydroxides and hydrolysing salts.** W. GORDY (J. Elisha Mitchell Sci. Soc., 1935, 51, 242-243).—Hydroxide mols. in solution have characteristic bands at 1.81, 2.60, 3.65, and 5.2  $\mu$ . The OH ion has a characteristic band at 2.30  $\mu$ . and hydrated acid mols. have a band at 5.6  $\mu$ . The bands at 2.30, 3.65, and 5.2  $\mu$ . are fundamentals, the others being harmonics. CH. Abs. (e)

**Intra- and inter-molecular "hydrogen bond" and absorption spectra in the near infra-red.** R. FREYMAN (J. Chem. Physics, 1938, 6, 497-498).—Attention is directed to publications by the author, since 1932, in this field. The main results are summarised.

W. R. A.

**Vapour-liquid-solution displacements in vibration absorption bands.** J. W. ELLIS and E. L. KINSEY (J. Chem. Physics, 1938, 6, 497).—The displacements from the vapour positions of certain sharp infra-red CH and OH bands of pure liquids and of solutions in  $CCl_4$  and  $CS_2$  are considered. CH bands are influenced by the surrounding medium < OH bands. The extent of the shift depends on the magnitude of the frequency. Shifts in non-polar solvents are > those in pure liquids.  $CS_2$  solutions give shifts > those in  $CCl_4$  solutions.

W. R. A.

**Absorption of infra-red radiation by thin layers of air.** G. FALCKENBERG (Meteorol. Z., 1936, 53, 172-175; Chem. Zentr., 1936, ii, 2118).—The variation of the absorption of air layers 110-1020 cm. thick with the  $H_2O$  v.p. and the temp. of the source has been investigated.

A. J. E. W.

**Infra-red absorption and Raman spectra of liquefied hydrogen chloride.** B. VODAR, R. FREYMAN, and Y. TA (J. Phys. Radium, 1938, [vii], 9, 282-286).—The infra-red absorption spectrum of gaseous and liquid HCl has been examined from 0.8 to 2.1  $\mu$ .; the third harmonic, anticipated to lie between 0.9 and 1.1  $\mu$ . could not be detected, nor could any Raman displacement, corresponding with its funda-



mental, be observed in the spectrum of liquid HCl at  $-80^\circ$ . In the second harmonic a new band at  $1.29 \mu$ . appears in addition to the band at  $1.23 \mu$ .; the former disappears gradually as the temp. increases and characterises associated HCl mols., whilst the latter is due to single mols. The extent of association is small. The difference in location of band max. in gaseous and liquid HCl is discussed. W. R. A.

**Absorption of carbon dioxide in the region of the band  $\lambda = 4.3 \mu$ . between  $300^\circ$  and  $1000^\circ \text{K}$ ., and the radiation of furnace gases and its practical calculation.** O. BRONDER (Physikal. Z., 1938, 39, 620—621).—Remarks on papers by Tingwaldt (A., 1938, I, 117) and Schack (Z. tech. Physik, 1924, 5, 267). The latter, in deriving the formula for the total emission of a band, overlooked the variation with temp. of the indices in Beer's law. When this temp. effect is taken into account the results of Tingwaldt agree with the formula. A. J. M.

**Absorption spectrum of pyrrole, thiophen, and furan in the middle infra-red.** R. MANZONI-ANSIDEI and M. ROLLA (Atti R. Accad. Lincei, 1938, [vi], 27, 410—413).—Measurements in the range  $600$ — $1500 \text{ cm}^{-1}$  are recorded. O. J. W.

**Comparison of the infra-red absorption spectra of heterocyclic compounds and homocyclic hydrocarbons.** J. LECOMTE (Compt. rend., 1938, 207, 395—398).—Absorption max. and Raman  $\nu$  ( $500$ — $1350 \text{ cm}^{-1}$ ) for  $\text{C}_6\text{H}_6$ , PhMe, cyclohexane,  $\text{C}_{10}\text{H}_8$ , and related heterocyclic compounds are compared and discussed with reference to the symmetry of the mols. A. J. E. W.

**Infra-red absorption spectrum of hydrogen peroxide.** C. R. BAILEY and R. R. GORDON (Trans. Faraday Soc., 1938, 34, 1133—1138).—Measurements with liquid and gaseous  $\text{H}_2\text{O}_2$  are reported. The results coupled with Raman data support the structure proposed by Penney and Sutherland (A., 1934, 1158). E. S. H.

**Assignment of the fundamental frequencies and computation of the potential function of tetrachloroethylene.** J. DUCHESNE (Nature, 1938, 142, 256).—A re-investigation of the spectrum of  $\text{C}_2\text{Cl}_4$  using a potential function of the type employed by Manneback and Verleysen (A., 1937, I, 223) gives for the C—C force const. a val. of  $8 \times 10^5$  instead of  $6.25 \times 10^5$  dynes per cm. (cf. *ibid.*, 224). Earlier conclusions regarding the existence of resonance in this mol. may be premature, since the frequencies can now be correlated with a force field in which the C—C const. has its normal double-bond val. L. S. T.

**Inner rotation and normal vibrations of ethane. III. Statistic calculation of the heat of rotation and entropy of ethane.** K. SCHÄFER. **IV. Raman spectrum of liquid ethane.** J. GOUBEAU and J. KARWEIL. **V. Co-ordination of infra-red and Raman lines with normal vibrations.** J. KARWEIL and K. SCHÄFER (Z. physikal. Chem., 1938, B, 40, 357—375, 376—381, 382—390).—III. Mathematical. The mol. is regarded as spinning symmetrically but with hindered rotation. Application of the theoretical conclusions to recorded data

indicates that the hindered rotation is equiv. to  $3 \text{ kg.-cal. per mol.}$

**IV.** Two new lines at  $786$  and  $1491 \text{ cm}^{-1}$  have been observed.

**V.** From the Raman and infra-red data (cf. A., 1938, I, 295) the 12 fundamental frequencies are assigned. C. R. H.

**Diffuse fluorescence spectrum of rare earth ions in solution and in crystals.** P. C. MUKERJI (Z. Physik, 1938, 109, 573—585).—La, Ce, Pr, and Nd ions in solution give rise to fluorescence bands in the near ultra-violet when excited by shorter-wave radiation. La ions in the crystal do not give a fluorescence band, but Ce ions in the crystal give rise to bands the no. of which varies with the anion. The extent of continuous absorption of dissolved La ions is also studied. L. G. G.

**Fluorescence in a layer of thickness comparable with the wave-length. II. Fluorescence polarisation.** F. S. BARISHANSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1938, 19, 465—468; cf. A., 1938, I, 62).—Fluorescence polarisation of films of fluorescein ( $10^{-4}$ — $10^{-2} \text{ g. per c.c. in H}_2\text{O or glycerol}$ ) has been studied in relation to orientation of the incident polarised light, film thickness, and concn. The technique permits high concn. and avoids absorption corrections. Results of Vavilov (*ibid.*) are confirmed. I. MoA.

**Fluorescence of dyes.** S. B. SEN-GUPTA (J. Indian Chem. Soc., 1938, 15, 263—300).—Absorption spectra and fluorescence intensities for carefully cryst. fluorescein, eosin (I), rhodamine 6G (II), rhodulin-orange, Magdala-red (III), rhodamine B (IV), acriflavine (V), benzoflavine, phloxine, and phosphine 2G in EtOH are recorded. The fluorescence yields, opposite to, normal to, and in the line of the incident light, and also the mol. extinction coeff. at  $365 \text{ m}\mu$ ., are recorded. The yields are shown to be independent of cell thickness, but except at low concn. the yields fall very rapidly with increase in concn., whilst the max. of the fluorescence bands are shifted towards the red. The yields  $\propto \lambda$  of the exciting light. Mol. conductivities at  $29$ — $30^\circ$  for (I)—(V) are recorded. Quenching of fluorescence is considered to be due to formation of micelles which break up on dilution (cf. Moilliet *et al.*, A., 1935, 299) as there is a break in the conductivity/ $\sqrt{\text{concn.}}$  curve corresponding with the concn. at which rapid quenching of the fluorescence begins. F. R. G.

**Photochemical studies. XXVI. Fluorescence of acetone vapour and its relation to the photochemical decomposition.** M. S. MATHESON and W. A. NOYES, jun. (J. Amer. Chem. Soc., 1938, 60, 1857—1864).—The ratio of intensities of absorbed to fluorescent light is a function of incident light intensity and of time of exposure. The Stern-Volmer equation is obeyed only at very low intensities. The fluorescence spectra of  $\text{COMe}_2$  and  $\text{Ac}_2$  are identical at  $\lambda\lambda > 5000 \text{ \AA}$ . The fluorescence of  $\text{COMe}_2$  is increased greatly by small amounts of  $\text{Ac}_2$ . The mechanism is discussed and an explanation advanced, based on the deactivation of excited  $\text{COMe}_2$  mols. by  $\text{Ac}_2$ , the excited  $\text{Ac}_2$  being responsible for the fluorescence.



An apparatus for study of fluorescence of gases is described. E. S. H.

**Fluorescent ion of chromium in ruby.** B. V. THOSAR (Phil. Mag., 1938, [vii], 26, 380—389).—The Zeeman pattern of the red fluorescence doublet of ruby at  $-180^\circ$  is explained by the hypothesis that the spin-moment of the  $3d$  electrons of the  $\text{Cr}^{+++}$  ion responds only to the external magnetic field, the orbital moment of the ion being unaffected. This entails that the fluorescent  $\text{Cr}^{+++}$  ion substitutes for  $\text{Al}^{+++}$  ions in the  $\text{Al}_2\text{O}_3$  lattice. The hypothesis is in agreement with the theory of paramagnetism of the ions of the transition series. The calc. Zeeman interval is of the same order of magnitude as the observed, but numerically different. A possible explanation of this difference and also of the asymmetry of the Zeeman pattern is offered. The difference in intensity of the red doublet for ruby and sapphire, and in their colour, is discussed, and the intensity of this forbidden doublet is explained.

W. R. A.

**Distribution of fluorescence excitation of bivalent europium in calcium fluoride and of bivalent samarium in calcium sulphate.** H. P. ECKSTEIN (Nature, 1938, 142, 256—257).—Max. of excitation  $\lambda\lambda$  for the blue and red fluorescences, respectively, are recorded. L. S. T.

**Chemiluminescence of the chlorophylls and other porphyrin metal complex salts.** P. ROTHEMUND (J. Amer. Chem. Soc., 1938, 60, 2005).—Red chemiluminescence is exhibited when solutions of chlorophyll in tetrahydronaphthalene (I) are heated at  $125$ — $190^\circ$ . Mg and Zn complex salts of porphyrin and of  $\alpha\beta\gamma\delta$ -tetraphenylporphyrin show the same phenomenon in (I), xylene, *p*-cymene, and bromocyclohexane. E. S. H.

**Non-adiabatic reactions. Chemiluminescence.** M. G. EVANS, H. EYRING, and J. F. KINCAID (J. Chem. Physics, 1938, 6, 349—358).—Theoretical. Chemiluminescent reactions are non-adiabatic because emission of radiation can occur only by transition from a higher to a lower potential energy surface. The second law of thermodynamics places an upper limit on the efficiency of excitation by radiationless transitions and on the no. of quanta of energy emitted. Upper potential energies are reached by activation by black-body radiation at the temp. of the surface or by "crossing" of potential energy surfaces. The experimental data of Audubert (A., 1937, I, 164) on chemiluminescent reactions occurring during the thermal decomp. of metallic azides are interpreted in the light of the theory. W. R. A.

**Cathode[ray] luminescence of aluminium oxide.** E. IWASE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1938, 34, 761—774; cf. A., 1932, 1076; 1933, 446).—Japanese rubies give a cathode-ray luminescence identical with, although weaker than, that of N. Carolina rubies. Synthetic  $\text{Al}_2\text{O}_3$  when calcined at  $1000$ — $1200^\circ$  with small additions of Sm salts gave an orange luminescence; Mn produced an orange-green colour, whilst Cr gave a red luminescence under all conditions. R. C. M.

**Photochemical investigations of metal sulphides. I. Crystal structure and luminescence of sulphide phosphors.** S. MAKISHIMA (J. Soc. Chem. Ind., Japan, 1938, 41, 202—205 B).—ZnS and CaS phosphors are cryst. The effect of temp. and the influence of crystal structure (*e.g.*, Zn blende or wurtzite types of ZnS) on the luminescence are discussed. W. R. A.

**Properties of zinc sulphide phosphors.** F. SEITZ (J. Chem. Physics, 1938, 6, 454—461).—The properties of pure and Cu-activated ZnS phosphors are interpreted by a method similar to that used for alkali halide phosphors activated by Tl (A., 1938, I, 230). Ordinary luminescent varieties of ZnS are assumed to have the high-temp. hexagonal (wurtzite) structure. The combination of photoconductivity and the bimol. decay law of phosphorescence implies that excitation of ZnS phosphors is accompanied by an ionisation process, phosphorescence being the result of the recombination of ionised centres and electrons. Application of the quantum theory of solids shows that the ionisation process does not involve the  $\text{Zn}^{++}$  and  $\text{S}^{--}$  ions of the lattice. The pure ZnS phosphor probably contains neutral interstitial Zn atoms and these may be responsible for luminescence and photoconductivity, whilst in the Cu-activated phosphor interstitial Cu atoms are responsible. A study of the relative stability of interstitial and substitutional Cu ions according to the Schottky-Wagner theory of deviations from stoichiometrical proportions indicates that the interstitial Cu atoms are probably in a metastable condition.

W. R. A.

**Luminescence efficiency of zinc silicate phosphors in the gas discharge.** A. RÜTTENAUER (Z. tech. Physik, 1938, 19, 148—150).—The efficiency of Zn silicate phosphors activated with Mn for the detection of ultra-violet radiation has been investigated. The luminescence radiation shows three different max. according to the [Mn] with exciting radiation of different  $\lambda$ . Phosphors containing 0.4% Mn give a max. emission for excitation of  $\lambda$  736—744 Å., those containing 1.5% Mn for excitation of  $\lambda$  1850—2537 Å., and those containing 5% Mn for excitation of  $\lambda$  3650 Å. The higher is the [Mn] the longer is the  $\lambda$  of the exciting light for max. emission. With a phosphor containing 1.5% Mn radiation of  $\lambda$  2537 Å. (Hg discharge) was converted into emission of  $\lambda$  5350 Å. with a quantum efficiency of 0.8.

A. J. M.

**Charging potential of phosphorescent masses on irradiation with electrons.** H. BEY (Physikal. Z., 1938, 39, 605—611).—An insulated phosphorescent screen behaves like an insulated metal screen on irradiation with electrons. With increasing anode potential it becomes positively charged. From a certain point it follows the anode potential, but much more slowly, differing in this respect from a metal screen. The relationship between the intensity of the emitted light and the anode potential was investigated.

A. J. M.

**Raman spectra of ammonia and the ammonium ion.** G. COSTEANU (Compt. rend., 1938, 207, 285—286).—Weak Raman lines 3460 and 3545  $\text{cm}^{-1}$ ,



corresponding with lines in the absorption spectrum (A., 1935, 563), have been observed with the three principal  $\text{NH}_3$  frequencies in liquid  $\text{NH}_3$  at  $-40^\circ$ . These lines also occur, at higher  $\nu$ , in conc. aq.  $\text{NH}_3$  and in solutions of  $\text{NH}_4\text{CNS}$  and  $\text{NH}_4\text{NO}_3$  in  $\text{NH}_3$ . These solutions and aq.  $\text{NH}_4\text{NO}_3$  also give Raman  $\nu$  at  $\sim 1387$ , 1456 (due to  $\text{NH}_4^+$  or  $\text{NO}_3^-$ ), 1655, and  $1687 \text{ cm}^{-1}$  (due to  $\text{NH}_4^+$ ). A. J. E. W.

**Raman spectra of hydrogen and deuterium sulphides in the gas, liquid, and solid states.** G. M. MURPHY and J. E. VANCE (J. Chem. Physics, 1938, 6, 426—429).—In gaseous and liquid  $\text{H}_2\text{S}$  and  $\text{D}_2\text{S}$  only one Raman displacement was observed; in the solid state both compounds give one single line and a close doublet. The differences  $\nu_{\text{gas}} - \nu_{\text{liq.}}$  is 1.4% and  $\nu_{\text{liq.}} - \nu_{\text{solid}}$  is 1.3%. Available spectroscopic data do not permit calculation of isotope effect, force consts., anharmonicity, or angle; the angle is not  $90^\circ$ . W. R. A.

**Raman spectrum of gaseous boron trifluoride.** D. M. YOST, D. DE VAULT, T. F. ANDERSON, and E. N. LASSETTRE (J. Chem. Physics, 1938, 6, 424—425; cf. A., 1937, I, 10).— $\text{BF}_3$  was prepared by thermal decomp. of benzenediazonium fluoborate,  $\text{PhN}_2\text{BF}_4$ . The Raman spectrum excited by the 2537 Å. Hg line is recorded. From it and infra-red data, frequencies have been assigned to fundamental modes of vibration in complete agreement with the assignment of Bailey *et al.* (*ibid.*, 548). W. R. A.

**Raman spectra of the  $\text{ClO}'$ ,  $\text{ClO}_2'$ , and  $\text{BO}_3'''$  ions.** T. G. KUJUMZELIS (Physikal. Z., 1938, 39, 665—666).—The Raman spectrum of a saturated solution of  $\text{NaOCl}$  gives, in addition to the  $\text{H}_2\text{O}$  bands, a sharp line at  $713 \pm 3 \text{ cm}^{-1}$ , corresponding with the simple vibration  $\text{Cl} \leftrightarrow \text{O}$ , and agreeing with the  $\text{Cl} \leftrightarrow \text{Me}$  line in the Raman spectrum of  $\text{MeCl}$ . A solution of  $\text{ClO}_2$  gives only one sharp line at  $935 \pm 8 \text{ cm}^{-1}$  which is due to the  $\text{ClO}_2$  mol.  $\text{ClO}_2'$  gives a line at  $802 \text{ cm}^{-1}$ .  $\text{H}_3\text{BO}_3$  (5% solution) gives a strong continuum with a line of moderate strength at  $878 \text{ cm}^{-1}$  and traces of lines at 400—500 and  $1400 \text{ cm}^{-1}$ . A. J. M.

**Vibrations and structure of the  $\text{XO}_3$  ions.** T. G. KUJUMZELIS (Z. Physik, 1938, 109, 586—597).—Several new Raman lines were observed with conc. solutions of carbonates, nitrates, chlorates, bromates, and iodates. From a consideration of the vibrations theoretically possible combined with the available data, it is concluded that the  $\text{CO}_3$  ion has a plane configuration, the  $\text{NO}_3$  ion has an easily deformable plane structure, whilst the  $\text{ClO}_3$ ,  $\text{BrO}_3$ , and  $\text{IO}_3$  ions are pyramidal. H. C. G.

**Raman spectra of crystalline powders. Hydrates.** E. CANALS and P. PEYROT (Compt. rend., 1938, 207, 224—226).—Vals. are given for the bands due to  $\text{H}_2\text{O}$  observed in  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ,  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , and ice. Even in similarly constituted mols. with the same  $\text{H}_2\text{O}$  of crystallisation (e.g., for  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), the bands are quite distinct in structure. H. J. E.

**Raman spectra of hydrocarbons containing tertiary C—D linkings.**—See A., 1938, II, 401.

**Raman effect in tetradeutero- $\alpha\beta$ -dibromomethane.** S. MIZUSHIMA, Y. MORINO, and S. SUGIURA (Proc. Imp. Acad. Tokyo, 1938, 14, 250—251).— $\text{CD}_2\text{Br} \cdot \text{CD}_2\text{Br}$  was prepared by the following reactions: (i)  $\text{CaC}_2 + 2\text{D}_2\text{O} = \text{C}_2\text{D}_2 + \text{Ca}(\text{OD})_2$ ; (ii)  $4\text{D}_2\text{O} + 5\text{Br} + \text{P} = \text{D}_3\text{PO}_4 + 5\text{DBr}$ ; (iii)  $\text{C}_2\text{D}_2 + 2\text{DBr} = (\text{CD}_2\text{Br})_2$ .  $(\text{CH}_2\text{Br})_2$  was prepared by a similar method. The Raman spectra have been measured and are compared. The calc. Teller-Redlich product ratio for vibrations of the same symmetry class for two isotopic analogues agrees with the experimental val. The results support previous conclusions (cf. A., 1938, I, 233) regarding the mol. structure of  $(\text{CH}_2\text{Br})_2$ . W. R. A.

**Raman effect in the diagnosis of the constituents of a mixture of isomeric dihalogenated benzene derivatives.**—See A., 1938, II, 401.

**Molecular association of acetic acid.** P. KOTESWARAM (Z. Physik, 1938, 110, 118—133).—Raman lines for pure  $\text{AcOH}$  and its solutions in  $\text{H}_2\text{O}$ ,  $\text{CCl}_4$ , and  $\text{C}_6\text{H}_6$  are photographed. Increase in temp. of the pure acid, or its dilution with  $\text{H}_2\text{O}$ , shifts the lines to higher frequencies, indicating depolymerisation.  $\text{CCl}_4$  and  $\text{C}_6\text{H}_6$  as solvents do not reduce the association. There is no direct evidence for the existence of hydrates. L. G. G.

**Structure of associated molecules of organic acids on the basis of Raman spectra.** V. TSCHELINEV (Compt. rend. Acad. Sci. U.R.S.S., 1938, 19, 489—491; cf. A., 1937, I, 502).—On a review mainly of Raman spectra evidence, the form

$\text{CR} \begin{smallmatrix} \text{O} \cdots (\text{H}) \cdots \text{O} \\ \text{O} \cdots (\text{H}) \cdots \text{O} \end{smallmatrix} \text{CR}$ , based on the author's work on keto-phenolic systems, is preferred for dimerides formed by  $-\text{CO}_2\text{H}$  association. A like occurrence of quadrivalent ketonic O is suggested in salicylaldehyde and the enol form of diketones (where Raman  $-\text{OH}$   $\nu$  are absent), and accounts for acid salts of monobasic acids. I. McA.

**Molecular diffusion of light by liquids. Variation of diffused intensity with wave-length.** A. ROUSSET and R. GARNIER (Compt. rend., 1938, 207, 142—145).—Comparison of the variation of the intensity of the light diffused by  $\text{C}_6\text{H}_6$  with that of  $\text{CCl}_4$ ,  $\text{AcOH}$ , and  $\text{EtOH}$  by the method of photographic photometry shows that, in the spectral range 3650 to  $5460 \text{ Å}$ ,  $\text{C}_6\text{H}_6$  follows the Vessot-King rule. The ratio of existing abs. vals. of the intensity of light diffused by  $\text{Et}_2\text{O}$  and by  $\text{C}_6\text{H}_6$  agrees with that of the vals. calc. from this rule and also shows that  $\text{C}_6\text{H}_6$  obeys it. W. R. A.

**Sparking potential in benzene vapour.** E. BADAREU and L. CONSTANTINESCO (Compt. rend., 1938, 207, 217—220).—Vals. of the sparking potential were determined with plane Al electrodes at 0.1—1.8 mm. Hg. The relationship between the sparking potential ( $V$ ) and the product of the pressure and the distance between the electrodes ( $pd$ ) passed through a min. at  $V = 489 \pm 1 \text{ v.}$  and  $pd = 0.24 \pm 0.01$ . H. J. E.



**Breakdown potential in benzene vapour.** E. BADAREU (Compt. rend., 1938, 207, 279—281).—A theoretical discussion of previous work (preceding abstract). Ionisation of the  $C_6H_6$  mol. requires an electron of min. energy  $\sim 120$  e.v., a val.  $\gg$  that for other gases. A. J. E. W.

**Investigations of photochemical processes in crystals and measurements by electrical means.** R. HILSCH and R. W. POHL (Trans. Faraday Soc., 1938, 34, 883—888).—When crystals of KBr, containing  $10^{-6}$  of KH in solid solution, are allowed to absorb ultra-violet light, "Farbzentren" are developed and the KH is photochemically decomposed. The photochemical process is accompanied by thermal oscillations of the lattice and an experiment to illustrate this is described. At low temp. no decomp. occurs. Preliminary results for KD are discussed; the dependence of its photochemical yield on temp. is different from that for KH. The absorption spectrum of RbH is given and interpreted as due to electron transitions from the anion to the cation. The magnitude of the binding energy of "Farbzentren" in the lattice of alkali salts is discussed and a method of measuring it electrically is outlined. W. R. A.

**Photo-electric primary current in alkali halide crystals as a function of temperature and the concentration of colour centres.** G. GLASER and W. LEHFELDT (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., II, 1936, 2, 91—108; Chem. Zentr., 1936, ii, 754).—Measurements are recorded for NaCl, KCl, and KBr at  $-250^\circ$  to  $250^\circ$ . H. J. E.

**Mechanism of photosensitisation by solids.** C. F. GOODEVE and J. A. KITCHENER (Trans. Faraday Soc., 1938, 34, 902—908).—The mechanism of photosensitisation by solids, which is closely allied to the inner photosensitisation by liquids, depends on the nature and action of the absorbed quantum or "exciton" which determines the type of chemical change which takes place. The enhancing power of glycerol and glucose on the activity of solid photosensitisers is probably due to a second stage with a chemical mechanism. Different mechanisms for the fluorescence of phosphors are considered, the "exciton" being generally regarded as a free electron. Detailed photochemical study of the bleaching of chlorazol-sky-blue FF on  $TiO_2$  in the dry state (A., 1938, I, 261) shows that  $TiO_2$  acts as a true photosensitiser. The photographic process is considered to involve both direct and sensitised photo-reactions. The degradation of excitons to heat is discussed. W. R. A.

**Photo-electric effect in membranes. II.** L. BRAUNER and M. BRAUNER (Rev. Fac. Sci. Istanbul, 1938, 3, 189—254).—The photo-electric effect with parchment-paper sensitised by graphite has been investigated. There is an optimum thickness for the max. effect. The variation of the effect with the intensity of the light shows a similar curve with a max. Of added substances examined KOH gave the greatest and HCl the weakest photo-effect. A method for the sensitisation of parchment-paper membranes with some vegetable pigments (chlorophyll, lycopene, carotene) is described; of these, chlorophyll

gave the greatest effect. Experiments were also carried out to determine the photo-electric effect obtainable with living tissues. The leaves of *Helodea densa* show a definite cross-sectional polarity, the upper side being more photo-sensitive than the under side. A. J. M.

**New "positive" barrier plane photo-electric effect and the new barrier plane photocell.** B. KOLOMIEZ (Compt. rend. Acad. Sci. U.R.S.S., 1938, 19, 383—384).—The sensitivity of Tl sulphide photo-cells, in which the electrons pass from the metal to the semi-conductor (positive photo-electric effect), is 10 times that of Se cells under the same conditions of illumination. The e.m.f. is 0.3 v., and the spectral sensitivity is the same as that of the "thallofids." F. J. L.

**Photo-electric effect in natural single crystals of red copper ore.** R. DEAGLIO (Atti R. Accad. Sci. Torino [Cl. Sci. fis.], 1935, 70, I, 52—61; Chem. Zentr., 1936, ii, 951; cf. A., 1935, 430).

H. J. E.

**Relation between electrolytic conduction in solids and crystal structure.** J. A. A. KETELAAR (Trans. Faraday Soc., 1938, 34, 874—881).—The mechanism of conduction in good ionic conductors is discussed.  $Ag_2HgI_4$  is considered in detail in connexion with the Bragg-Williams theory of order-disorder transformations, and the relation between the energy difference and the degree of order is derived experimentally. The difference between true averaged structures and multiple twin structures is indicated; only the former show a high ionic conductivity. W. R. A.

**Electrical conductivities and dielectric constants of quartz and certain other crystals.** N. G. RAHIMI (J. Phys. Radium, 1938, [vii], 9, 291—296).—The electrical conductivity of quartz is reduced after keeping at  $700^\circ$  for a period of time, more particularly if the crystals have been maintained under strain. This treatment also causes the disappearance of anomalous dielectric properties of quartz and, therefore, appears to produce in quartz a well-defined state. W. R. A.

**Dielectric constants of glycerides.** B. V. BHIDE and R. D. BHIDE (Current Sci., 1938, 7, 16).—The dielectric consts. of monomyristin (I) and  $COPh_2$  have been determined at radio frequencies. The curve of dielectric const. against temp. shows distinct breaks at the transition temp. of these substances. The m.p. of the different forms of (I) given by Malkin *et al.* (A., 1937, I, 17) were confirmed, but a sudden break was also found at  $27^\circ$  instead of at  $24^\circ$  as given by the above workers. A. J. M.

**Variation of dielectric constant on solidification of homopolar liquids.** R. GUILLIEN (Compt. rend., 1938, 207, 393—395; cf. A., 1938, I, 297).— $\epsilon$  for PhMe, *m*-xylene,  $CCl_4$ , and liquid  $N_2$  increases on solidification. Data are given for  $\epsilon$  and the mol. polarisation of  $N_2$  at  $63$ — $78^\circ$  K. A. J. E. W.

**Dielectric-constant measurements with pure organic liquids.** R. J. W. LE FÈVRE (Trans. Faraday Soc., 1938, 34, 1127—1132).—Apparatus and technique are described. Results for 21 liquids



over different ranges of temp. are reported. All the liquids appear to have approx. the same dielectric const. at their crit. points. E. S. H.

**Dipole moments of anthracene derivatives and the stereochemical mechanism of additive and fission reactions in the anthracene series.**—See A., 1938, II, 407.

**Dipole moments of vapours. VII. Calculation of valency angles in chloroform and methylene chloride.** L. G. GROVES (J.C.S., 1938, 1195—1196; cf. A., 1938, I, 64).—Using vals. for the moments of the C-Cl and C-H links obtained from the recorded moment of MeCl, the Cl-C-Cl intercovalency angle, after allowing for induction components, is found to be approx. tetrahedral in both  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$ , and agrees with electron diffraction data. W. R. A.

**Molecular volumes and parachors of mercuric halides and their group relationships.** E. B. R. PRIDEAUX and J. R. JARRATT (J.C.S., 1938, 1203—1205).—The mol. vols. of liquid  $\text{HgCl}_2$  and  $\text{HgBr}_2$  are > the sums of the at. vols. of their constituents under corresponding conditions. The differences are attributed to differences in covols., which are controlled by internal pressures identified with van der Waals mol. attractions. These pressures are increased in heteropolar mols. containing polar or semipolar bonds. The physical properties dependent on covol. and internal pressure, reviewed for  $\text{Hg}^{++}$ , Cd, and Zn halides, are thus affected by the electronic systems of the mols. The parachors of  $\text{HgCl}_2$  and  $\text{HgBr}_2$ , determined by the max. bubble pressure method, are < the sums of the parachors of their at. constituents, but a correction for semi-polar bonds brings the vals. into closer agreement. W. R. A.

**Refraction of simple organic isomerides.** J. M. STEVELS (Rev. trav. chim., 1938, 57, 921—928).—The theory previously developed (A., 1937, I, 601; 1938, I, 232) is extended to  $\text{C}_2\text{H}_6$  and  $\text{C}_2\text{H}_4$  derivatives. F. L. U.

**Effect of a longitudinal magnetic field on the conductivity and refractive index of ionised air.** B. N. SINGH (Phil. Mag., 1938, [vii], 26, 244—252).—Measurements of the conductivity and refractive index of ionised air in the presence of applied longitudinal magnetic field have been made, using waves of frequency  $8.1 \times 10^7$  cycles per sec. Vals. are in agreement with those calc. without approximation from magneto-ionic theory. Vals. do not approach  $\infty$  at the gyro frequency of the incident wave as the magnetic field is increased. O. D. S.

**Magnetic rotatory power of imperfect complexes.** F. GALLAIS (J. Chim. phys., 1938, 35, 212—222).—The magnetic rotatory power of the mercuri-iodides and other complexes of Hg, Bi, Cd, and Ag has been investigated. The formation of  $[\text{HgI}_4]^{--}$  ions is accompanied by a considerable increase in the magnetic rotation, but the investigation of the other complexes shows that the effect is not general, nor is it confined to any particular type of complex. A. J. M.

**Periodicity law. Break in continuity in values of molecular rotatory power in optically active homologous series.** P. PETRENKO-KRITSCHENKO and J. EKSTER (Compt. rend. Acad. Sci. U.R.S.S., 1938, 19, 493—496; cf. A., 1938, II, 167).—Available data for  $[\text{M}]_D$  (those of Pickard and Kenyon are not cited) refute rules of its monotonic variation with chain length. Anomalous vals. are really max. or min. as  $[\text{M}]_D$  in a series is claimed to be of periodic wave form. Similarly,  $[\text{M}]_D$  increases, then falls, in the succession  $\text{C}\cdot\text{C} \rightarrow \text{C}:\text{C} \rightarrow \text{C}:\text{C}$ . I. McA.

**Rotatory power of quartz in the far ultra-violet and the Schumann region.** R. SERVANT (Compt. rend., 1938, 207, 283—285).—Vals. of the rotatory power ( $\alpha$ ) at 1950—1525 Å. are recorded. Above 1850 Å. the results are in agreement with those of Duclaux and Jeantet (A., 1926, 886).  $\alpha$  increases rapidly in the Schumann region, and the observed vals. are not in accord with the Lowry-Coode-Adams or Bradshaw-Livens formulæ (A., 1927, 813; 1929, 242). A. J. E. W.

**Paramagnetic rotatory power of hydrated neodymium ethyl sulphate in the direction of the optic axis.** J. BECQUEREL, W. J. DE HAAS, and J. VAN DEN HANDEL (Physica, 1938, 5, 753—762; cf. A., 1936, 1056).—Measurements at 1.480—4.256 $\mu$ , 14.16—20.42 $\mu$ , and 63.50—77.47 $\mu$  k. are recorded. Vals. of the Verdet const. are calc. Results for the Et sulphate and normal sulphate are compared. H. J. E.

**Crystal twins of normal  $\text{C}_{24}\text{H}_{50}$  and the influence of phase transitions on their orientation.** G. C. H. KOLVOORT (J. Inst. Petroleum Tech., 1938, 24, 338—347).—The twin-structure of  $\text{C}_{24}\text{H}_{50}$ , m.p. 50.5—50.9°, has been studied. The (110) and (310) planes act as twinning planes.  $\text{C}_{24}\text{H}_{50}$  is biaxial, the birefringence being positive; the angle between the optic axes is about 45° and is less for red light than for blue. At 41° and at 46° new solid phases are formed. J. S. G. T.

**Deformation of valency angles. Structure and absorption of derivatives of oximes.**—See A., 1938, II, 367.

**Structure of the aldol of acetaldehyde.**—See A., 1938, II, 392.

**Inertness and chemical activity of the rare gases. I. Theory of zero valency. General problem of the chemical activation of the rare gases. II. Stable compounds from the interaction of helium and platinum, activated by cathodic evaporation. III. Comparison of the properties of helium-platinum compounds with those of the hydrogen-platinum system and of compounds of oxygen and nitrogen with the same metal.** H. DAMIANOVICH (Bull. Soc. chim., 1938, [v], 5, 1085—1091, 1092—1106, 1106—1120).—I. A general review of early work on the reactivity of the rare gases.

II. Various methods for preparing He-Pt compounds are described. Two such compounds decompose endothermically at 92.5° and 310°, the calc. heats of reaction being 11,805 and 18,831 g.-cal., respectively.

III. The author's collected researches are sum-



marised and the following conclusions are reached. Only theories of chemical reactions which result in stable compounds can satisfactorily explain the data; the theory of zero valency is unsound as it is based on negative evidence; inertness is a state which can be eliminated under suitable conditions. C. R. H.

**Classification of the rare earths.** (A) W. KLEMM. (B) W. NODDACK and A. BRUKL (*Angew. Chem.*, 1938, **51**, 575—581).—A discussion in which the former upholds his classification into two groups, whilst the two latter propose three groups.

K. W. P.

**Primary processes in photodecomposition.** M. BURTON and G. K. ROLLEFSON (*J. Chem. Physics*, 1938, **6**, 416—423).—A simple rupture process is defined as one in which decomp. occurs at the locus of absorption within one vibration period after the creation of the excited state. The term "predissociation" covers all other photodecomp. processes. In diat. mols. the only mechanisms of predissociation possible are by rupture as a result of either spontaneous or induced adiabatic transition from an attractive to a repulsive or "weakly attractive" level. In polyat. mols., spontaneous or induced shifts of energy, or rearrangement of groups, resulting in decomp., may also occur. The various processes are illustrated by reference to  $S_2$ ,  $I_2$ ,  $O_3$ , and aldehydes. Two different types of predissociation are indicated for  $CH_2O$ , one in a single potential hypersurface and the other a spontaneous transition between two hypersurfaces.

W. R. A.

**Summation of state for dissociation processes.** K. H. RIEWE (*Z. Physik.*, 1938, **109**, 753—757).—Mathematical. The summation of state for a mol. in a partly dissociated gas is calc. on the basis of a method previously employed by Planck in the case of a partly ionised gas consisting of H atoms.

H. C. G.

**An assumption in the theory of co-operative phenomena.** G. S. RUSHBROOKE (*Proc. Camb. Phil. Soc.*, 1938, **34**, 424—428).—The effect of the assumption, "that the term in the partition function for the excited states of a mol. is not affected, owing to intermol. forces, by the environment of the mol.," on the results of the approx. methods of Bragg and Williams used in theoretical work on co-operative phenomena is deduced.

F. J. L.

**Molecular forces and imperfect gases.** W. WEN-PO (*Phil. Mag.*, 1938, [vii], **26**, 225—244).—Theoretical.

O. D. S.

**Spectroscopy and valency. VI. Periodicity of bonding energies of hydride di-atoms.** R. W. BERRIMAN and C. H. D. CLARK (*Proc. Leeds Phil. Soc.*, 1938, **3**, 465—476; cf. A., 1936, 782).—The periodicity of spectroscopic nos. is extended to include bonding energy (heat of dissociation) of hydride di-atoms, and the principle is used to "weight" the vals. recorded by various authors. New vals. of bonding energies calc. by thermal methods are: Si-H 3.27, S-H 3.80, As-H 2.06, Se-H 3.18, Te-H 2.70, and Sb-H 1.6 e.v. Spectroscopic and thermochemical bonding energies are compared and discussed, an anomalous C-H val. is explained, and the C-C val. is examined in relation to the stability of long chains in *n*-paraffins. The

II (A., I.)

departure from additivity increases regularly in the CH—FH series of thermal vals. with increasing polar opposition of the two atoms concerned. N. M. B.

**Deformation of molecules and their vibration spectra in the condensed state.** E. BAUER and M. MAGAT (*Physica*, 1938, **5**, 718—724).—It is shown that it is possible to account quantitatively for changes in the Raman and infra-red frequencies associated with groups such as OH and NH, in passing from the vapour to the condensed phase, by a theory of electrostatic interaction. It is unnecessary to postulate more complex phenomena, such as H bond formation.

H. J. E.

**Calculation of the polarisability of a molecule.** M. M. BIEDERMANN (*Physica*, 1938, **5**, 689—692).—It is shown that the additional polarisation of one atom by the electric dipole induced in another can be described by using the perturbed wave function in the second-order approximation.

H. J. E.

**Energy levels in real and ideal crystals.** N. F. MOTT (*Trans. Faraday Soc.*, 1938, **34**, 822—827).—The conditions under which crystals conduct an electronic current are discussed. The removal of an electron from one ion leaves a "positive hole" which can be filled by an electron from a neighbouring ion, a process which can continue throughout the whole crystal. An electron can be introduced from outside or it can be raised photoelectrically from an inner energy of one ion to "conduction band" levels. Electrons in the conduction band can be trapped in metastable positions. Trapping can occur not only at various lattice imperfections but also in a perfect lattice.

W. R. A.

**Excited energy levels of insulating crystals.** J. C. SLATER (*Trans. Faraday Soc.*, 1938, **34**, 828—832).—A comparison and discussion of existing theories on the excited states of insulating crystals.

W. R. A.

**Energies of disorder in ionic crystals.** W. JOST (*Trans. Faraday Soc.*, 1938, **34**, 860—867).—Theoretical. The magnitude and significance of the energies of disorder for different salts are discussed. These can be  $\ll$  lattice energies. Energies from different types of disorder are compared and methods for evaluating the energy barrier, which migrating ions must surmount, are considered.

W. R. A.

**Mechanism of the movement of ions and electrons in solids and the interpretation of reactions between solids.** C. WAGNER (*Trans. Faraday Soc.*, 1938, **34**, 851—859).—In solid ionic compounds, deviations from the strict order of the ideal crystal lattice lead to electrical conductivity by the movement of ions and electrons. Typical examples are discussed and the disorder of the ions is indicated qualitatively. The degree of disorder in AgCl can be calc. from the electrical conductivity of pure AgCl and of solutions containing  $CdCl_2$  or  $PbCl_2$  in AgCl. The reactions between solids are regarded as caused by the diffusion of ions and electrons through the reaction products formed between the phases of the initial state. In simple cases the rate of chemical change may be calc. from electrical data. This is illustrated by reference



to, *inter alia*,  $2\text{Ag} + \text{S} = \alpha\text{-Ag}_2\text{S}$ ;  $2\text{AgI} + \text{HgI}_2 = \text{Ag}_2\text{HgI}_4$ ;  $6\text{Li} + \text{N}_2 = 2\text{Li}_3\text{N}$ ;  $\text{Cu} + \text{AgCl} = \text{Ag} + \text{CuCl}$ ;  $\text{AgCl} + \text{NaI} = \text{AgI} + \text{NaCl}$ .

W. R. A.

**Lattice energies of some alkali halides and the electron affinity of iodine.** A. N. TANDON (Proc. Nat. Acad. Sci. India, 1937, 7, 102—110; cf. A., 1934, 719; 1935, 273; 1937, I, 170, 398).—Previous theory, experimental methods, and results are reviewed. With the thermal ionisation technique used for the bromides, vals. determined for the lattice energies of NaI and KI, and for the electron affinity of I, are 166.4, 150.6, and 72.4 kg.-cal., respectively, confirming available data.

I. McA.

**Effect of temperature on the atomic distribution in liquid potassium.** C. D. THOMAS and N. S. GINGRICH (J. Chem. Physics, 1938, 6, 411—415).—Using Mo  $K\alpha$  radiation, the X-ray diffraction patterns of liquid K at 70°, 200°, 295°, and 395° have been obtained. The intensity curves show three peaks becoming less pronounced with rising temp. The at. distributions for 70° and 395° have been determined by Fourier analysis. A rise of temp. causes a shift in the peak positions in the distribution curve to greater distances and the high-temp. curve is more highly damped.

W. R. A.

**Scattering of X-rays by a crystal.** J. LAVAL (Compt. rend., 1938, 207, 169—170).—The scattering of X-rays by crystals of calcite and single crystals of sylvine is discussed.

W. R. A.

**X-Ray surface reflexion fields and their application to absorption corrections and to background patterns.** M. J. BUERGER (Z. Krist., 1938, 99, 189—204; cf. Hendershot, A., 1937, I, 581).—For zero- and  $n$ -layer photographs, both the normal beam and equi-inclination (*ibid.*, 49) techniques being considered, the nature and position of the areas in Weissenberg X-radiograms characterised by surface and transmitted reflexions are calc. for typical crystal habits. Absorption corrections in crystal analysis are simplified by charting of these areas, which may be experimentally realised as a background pattern of use where optical goniometry is unsuitable.

I. McA.

**Reflecting power of crystals with an ideal mosaic.** V. DOLEJEK, M. JAHODA, J. JEZEK, and M. ROZSÍVAL (Nature, 1938, 142, 253).—Photographic investigation of the relationship between the magnitude of the mosaic structure of crystals and the intensity of X-ray reflexion shows that with specially-selected crystals of gypsum, rock-salt (I), and sphalerite (II) the product of the exposure and the magnitude of the ideal mosaic is const. With quartz, where the mosaic is insignificant, the results fluctuate. Under the influence of a direct electric field  $\sim 10^4$  v. per cm. the mosaic diminishes for (II) but not (I).

L. S. T.

**Comparison of the rotary crystal method and the powder method.** M. STRAUMANIS and A. LEVIŠ (Z. Physik, 1938, 109, 728—743).—The lattice consts. of rock-salt from 5 sources, determined on single crystals and on the powder, are in good agreement, and are respectively  $5.62735 \pm 0.00002$  and

$5.62747 \pm 0.000003$  Å. Measurements on  $\text{Co}[\text{Hg}(\text{CNS})_4]$  show that the lattice consts. vary slightly for individual crystals and lie in the ranges  $a_{25}$  11.08944—11.09756 and  $c_{25}$  4.36465—4.36524 Å. L. G. G.

**Interpretation of Laue photographs in terms of the reciprocal lattice.** C. C. MURDOCK (Z. Krist., 1938, 99, 205—216).—Crystallomathematical.

I. McA.

**Crystal structure models.** W. A. WOOSTER and G. KNOTT (Nature, 1938, 142, 251).—Models are constructed from table tennis balls and celluloid rod which can be firmly joined together after treatment with  $\text{COMe}_2$ . Mol. packing can be illustrated with balls from which spherical caps have been cut. Photographs of models illustrating the interat. distances and mol. packing of  $\text{C}_{10}\text{H}_8$  are reproduced.

L. S. T.

**Nature of twinning in potassium and rubidium dithionates.** W. H. BARNES and A. V. WENDLING (Amer. Min., 1938, 23, 391—398).

L. S. T.

**Structure of rubidium dithionate,  $\text{Rb}_2\text{S}_2\text{O}_6$ .** W. H. BARNES and A. V. WENDLING (Z. Krist., 1938, 99, 153—180).—Optical activity in untwinned crystals is confirmed. X-Ray analysis gives a hexagonal (rhombohedral) cell,  $a$  10.02,  $c$  6.35 Å.;  $\rho$  2.86; 3 mols. per cell; space-group  $D_3^2$ ; these confirm available data. An extensive analysis based on relative intensities yields parameters almost identical (save for 2 O vals.) with Huggins' vals. (A., 1934, 16) for the isomorphous  $\text{K}_2\text{S}_2\text{O}_6$ . The  $\text{S}_2\text{O}_6^{2-}$  ion consists of 2 apex-linked  $\text{SO}_3$  tetrahedra with trigonal axes collinear with the central S-S bond. S—S, S—O, and O—O are 2.08, 1.50, and 2.51 Å., respectively.

I. McA.

**Rate of crystallisation of aluminium of 99.992% purity.** J. CZOCHRALSKI and J. MIKOŁAJCZYK (Wiadom. Inst. Met., 1936, 3, 106—107; Chem. Zentr., 1936, ii, 3059).—A single crystal of 99.992% pure Al could be drawn from the melt at the crystallisation temp. at a max. speed of 160 mm. per min. The impurities influence the no. of crystallisation centres, but not the rate of crystallisation.

H. J. E.

**Crystal structure of some bromocupric complexes.** A. SILBERSTEIN (Compt. rend., 1938, 206, 1490—1492).—The compounds  $(\text{NH}_4)_2[\text{CuBr}_4 \cdot 2\text{A}]$  ( $\text{A} = o$ - or  $m$ - $\text{C}_6\text{H}_4\text{Me} \cdot \text{NH}_2$ ) are similar in structure to  $(\text{NH}_4)_2[\text{CuBr}_4 \cdot 2\text{H}_2\text{O}]$ , having  $a$  and  $b$  7.88,  $c$  17.43 and 17.64 Å., respectively. Supposed compounds having  $\text{A} = \text{C}_5\text{H}_5\text{N}$ ,  $\text{NH}_2\text{Me}$ , or  $p$ - $\text{C}_6\text{H}_4\text{Me} \cdot \text{NH}_2$  are of doubtful individuality, as they give X-ray powder diagrams identical with those due to mixtures of  $\text{NH}_4\text{Br}$  and  $\text{CuBr}_2 \cdot 2\text{A}$ . A structure proposed for  $(\text{NH}_4)_2[\text{CuBr}_4 \cdot 2\text{NH}_3]$  (A., 1938, I, 91) is corr.; the spatial arrangement of N and Br in  $\text{NH}_4\text{Br}$  is preserved, the Cu atoms occupying two out of 24 possible positions at face centres of the  $\text{NH}_4\text{Br}$  unit cell.

A. J. E. W.

**Crystal structure of ammonium, potassium, rubidium, and caesium chloro- and bromopalladates.** J. A. A. KETELAAR and J. F. VAN WALSEM (Rec. trav. chim., 1938, 57, 964—966).—The compounds all belong to the  $\text{K}_2\text{PtCl}_6$  type. Vals. of  $a$  ( $\pm 0.01$  Å.) for the unit cell and calc.  $d$  for



the K,  $\text{NH}_4$ , Rb, and Cs salts, respectively, are as follows:  $\text{M}_2\text{PdCl}_6$  9.74, 2.83; 9.81, 2.48; 9.99, 3.25; 10.16, 3.68;  $\text{M}_2\text{PdBr}_6$  9.92, 4.49; 9.95, 4.17; 10.25, 4.68; 10.64, 4.38. F. L. U.

**Crystal structure of caesium aurous auric chloride,  $\text{Cs}_2\text{AuAuCl}_6$ , and caesium argentous auric chloride,  $\text{Cs}_2\text{AgAuCl}_6$ .** N. ELLIOTT and L. PAULING (J. Amer. Chem. Soc., 1938, 60, 1846—1851).— $\text{Cs}_2\text{AuAuCl}_6$ , tetragonal, has a body-centred unit, with  $a_0$   $7.49 \pm 0.02$  and  $c_0$   $10.87 \pm 0.02$  Å., containing 2 mols.; space-group  $D_{2h}^{17}$ — $I4/mmm$ . The positions of the atoms have been determined.  $\text{Cs}_2\text{AgAuCl}_6$  has a similar unit and at. arrangement, with  $a_0$   $7.38 \pm 0.02$  and  $c_0$   $11.01 \pm 0.02$  Å. The crystals contain linear  $[\text{AgCl}_2]'$  and  $[\text{AuCl}_2]'$  ions and square co-planar  $[\text{AuCl}_4]'$  ions. A metastable modification of  $\text{Cs}_2\text{AgAuCl}_6$  is described; the unit is cubic, with  $a_0$   $5.28 \pm 0.01$  Å., and contains 0.5 mol.

E. S. H.

**Polymorphism of MnSe.** A. BARONI (Z. Krist., 1938, 99, 336—339; cf. A., 1936, 669).—Three polymorphs (preps. described) are characterised by electron diffraction as similar to the MnS forms (Schnaase, A., 1933, 341).  $\alpha$ -MnSe with  $a$  5.44 Å. has the cubic NaCl structure. The unstable ( $\rightarrow \alpha$ )  $\beta$ -MnSe has the cubic Zn blende structure with  $a$  5.82 Å.  $\gamma$ -MnSe is hexagonal, like wurtzite, with  $a$  4.12,  $c$  6.72 Å.

I. McA.

**Molecular structure of arsenious oxide,  $\text{As}_4\text{O}_6$ , phosphorus trioxide,  $\text{P}_4\text{O}_6$ , phosphorus pentoxide,  $\text{P}_4\text{O}_{10}$ , and hexamethylenetetramine,  $(\text{CH}_2)_6\text{N}_4$ , by electron diffraction.** G. C. HAMPSON and A. J. STOSICK (J. Amer. Chem. Soc., 1938, 60, 1814—1822).—Interat. distances (in Å.) and angles recorded are:  $\text{As}_4\text{O}_6$ , As—O  $1.80 \pm 0.02$ ,  $\angle \text{OAsO}$   $100 \pm 1.5^\circ$ ,  $\angle \text{AsOAs}$   $126 \pm 3^\circ$ ;  $\text{P}_4\text{O}_6$ , P—O  $1.65 \pm 0.02$ ,  $\angle \text{OPO}$   $99 \pm 1^\circ$ ,  $\angle \text{POP}$   $127.5 \pm 1^\circ$ ;  $(\text{CH}_2)_6\text{N}_4$ , C—N  $1.47 \pm 0.02$ ,  $\angle \text{CNC}$   $109.5^\circ$ ,  $\angle \text{NCN}$   $109.5^\circ$ ;  $\text{P}_4\text{O}_{10}$ , P—O  $1.62 \pm 0.02$ , P—O'  $1.39 \pm 0.02$ ,  $\angle \text{OPO}$   $101.5 \pm 1^\circ$ ,  $\angle \text{POP}$   $123.5 \pm 1^\circ$ ,  $\angle \text{OPO}'$   $116.5 \pm 1^\circ$ . The shortening of the distances in  $\text{As}_4\text{O}_6$ ,  $\text{P}_4\text{O}_6$ , and  $\text{P}_4\text{O}_{10}$  below the theoretical single-linking vals. is ascribed to single-linking double-linking resonance. The abnormally low val. for P—O' is ascribed to the polar character of the linking. E. S. H.

**Crystal structure of  $\text{Cu}_3\text{As}$  and  $\text{Cu}_3\text{P}$ .** B. STEENBERG (Arkiv Kemi, Min., Geol., 1938, 12, A, No. 26, 1—15).—Three phases of formula  $\text{Cu}_3\text{As}$  have been investigated. "Artificial domeykite" is hexagonal with  $a$  7.088,  $c$  7.232 Å.; 6 mols. per cell; space-group  $C3c$ . Each As is surrounded by 12 Cu; at. radius of Cu = 1.24 Å., and of As = 1.12 Å. Natural domeykite is cubic,  $a$  9.592 Å.; 16 mols. per cell; space-group  $I43d$ ; at. radii Cu = 1.28, As = 1.35 Å. The mineral algodonite has been synthesised and studied.  $\text{Cu}_3\text{P}$  is isomorphous with "artificial domeykite,"  $a$  7.070,  $c$  7.135 Å. T. H. G.

**X-Ray studies on bismuth trioxide.** L. G. SILLÉN (Arkiv Kemi, Min., Geol., 1938, 12, A, No. 18, 1—15).—Four varieties of  $\text{Bi}_2\text{O}_3$  have been obtained.  $\alpha$ - $\text{Bi}_2\text{O}_3$  is a pure form stable at room temp. with a monoclinic pseudo-orthorhombic structure as deduced from Laue and powder photographs;  $a$  5.83,  $b$  8.14,  $c$  7.48 Å.,  $\beta$   $67.07^\circ$ ; 4 mols. per cell;

space-group uncertain.  $\beta$ - $\text{Bi}_2\text{O}_3$  is also pure but is tetragonal pseudo-cubic;  $a$  10.93,  $c$  5.62 Å.; 8 mols. per cell; space-group  $C42n$ . A complete structure is suggested with 6 O around each Bi, Bi—O = 2.37 Å. A third phase is cubic but is contaminated with Si;  $a$  5.525 Å.; 2 mols. per cell; space-group  $Pn3m$ . A structure is proposed in which every Bi is surrounded by 6 O at 2.40 Å.; it resembles  $\text{As}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_3$  somewhat but the formation of mols. is not pronounced. It is isomorphous with  $\text{Mg}_3\text{P}_2$ . The fourth phase contained a slight amount of  $\text{Al}_2\text{O}_3$  or  $\text{Fe}_2\text{O}_3$ ; it is body-centred cubic,  $a$  10.08 Å.; 12 mols. per cell; space-group  $I23$ . Alternative structures are proposed. T. H. G.

**Variations in the crystalline parameter of cadmium oxide by insertion of cadmium atoms into its lattice.** R. FAIVRE and A. MICHEL (Compt. rend., 1938, 207, 159—161).—Solid solutions of CdO and Cd can be produced by heating a mixture of CdO and Cd in a sealed tube or by heating CdO in vac. In the latter case dissociation is followed by the insertion of free Cd atoms in the CdO lattice. The progress has been studied by X-ray crystal analysis. W. R. A.

**Structure of the true antimony tetroxide and of the isomorphous stibio-tantalite,  $\text{SbTaO}_4$ .** K. DIHLSTRÖM (Z. anorg. Chem., 1938, 239, 57—64).—On prolonged ignition at  $900^\circ$  of hydrated  $\text{Sb}_2\text{O}_5$ , the  $\text{Sb}_2\text{O}_5\text{OH}$  which is first formed (cf. A., 1938, I, 68) is changed to  $\text{Sb}_2\text{O}_4$ . This also results on prolonged ignition of  $\text{Sb}_2\text{O}_3$  in air. It is isomorphous with stibio-tantalite,  $\text{SbTaO}_4$ . They are rhombic,  $a$  4.804,  $b$  5.424,  $c$  11.76 Å. for  $\text{Sb}_2\text{O}_4$ , and  $a$  4.916,  $b$  5.542,  $c$  11.78 Å. for  $\text{SbTaO}_4$ . The unit cell contains 4 mols. and the space-group is  $C_{2v}^2$ . At. parameters and a structure diagram are given.

F. J. G.

**Crystal structure of  $\text{Ni}_3\text{S}_2$ .** A. WESTGREN (Z. anorg. Chem., 1938, 239, 82—84).— $\text{Ni}_3\text{S}_2$  is rhombohedral with  $a$  4.041 Å.,  $\alpha$   $90.3^\circ$ . The unit cell contains 1 mol. and the space-group is  $D_{3d}^5$ . At. parameters and a structure diagram are given. F. J. G.

**Structure of libethenite,  $\text{Cu}_2(\text{OH})(\text{PO}_4)$ .** H. HERITSCH (Naturwiss., 1938, 26, 529).—Similarities between the structure of andalusite and olivenite indicate that the two horizontal axes should be interchanged. Investigation of the structure of libethenite shows that the horizontal axes should be interchanged in this case also. A. J. M.

**Crystallographic and optical investigation of some new rare earth tartrates with antimonyl and potassium chloride.** C. MINGUZZI (Period. Min., 1936, 7, 77—97; Chem. Zentr., 1936, ii, 776).—Isomorphous crystals of compounds of the type  $\text{MK}(\text{SbO})_2(\text{C}_4\text{H}_4\text{O}_6)_2 \cdot 6.5\text{H}_2\text{O}$  were prepared (M = La, Ce, Pr, or Nd). The crystallographic consts. were: La compound,  $a:b:c = 0.9642:1:1.0190$ ,  $\beta$   $93^\circ 09'$ ; Ce compound,  $a:b:c = 0.9602:1:1.0095$ ,  $\beta$   $92^\circ 45'$ ; Pr compound,  $a:b:c = 0.9714:1:1.0132$ ,  $\beta$   $92^\circ 08'$ ; Nd compound,  $a:b:c = 0.9694:1:1.0117$ ,  $\beta$   $92^\circ 44'$ . H. J. E.

**Crystal structure of  $\text{EuS}$ .** W. NOWACKI (Z. Krist., 1938, 99, 339—341).—Powder X-radiograms



yield a face-centred cubic cell with  $a$   $5.957 \pm 0.002$  Å.;  $\rho_{\text{pyk}}$  5.884; 4 mols. per cell. Photometred intensities indicate a NaCl structure. The ionic radius for  $\text{Eu}^{2+}$ , calc. by comparison with the isomorphous  $\text{SrS}$  and  $\text{BaS}$ , is  $\sim 1.19$  Å. in accord with Pauling's val. (1.17 Å.) from the isomorphous sulphates. I. MCA.

**Precision determination of the lattice constants of non-cubic substances (Bi, Mg, Sn) by the asymmetric method.** A. IEVINŠ, M. STRAUMANIS, and K. KARLSONS (Z. physikal. Chem., 1938, B, 40, 347—356).—Vals. for the lattice const. have been obtained with an average accuracy of 0.001%. The vals. agree best with those of Jette and Foote (cf. A., 1936, 45). C. R. H.

**Deformation and lattice constants.** A. PHILLIPS and R. M. BRICK (Metallwirts., 1936, 15, 541—542; Chem. Zentr., 1936, ii, 754).—Data are recorded for the changes in lattice const. of Au-Ag (76 at.-% Au) and Al-Cu (5% Cu) alloys on extension of a wire specimen. H. J. E.

**X-Ray diffraction study of soda-boric oxide glass.** J. BISCOE and B. E. WARREN (J. Amer. Ceram. Soc., 1938, 21, 287—293).—Glasses containing the mol. quantities 0.114, 0.225, and 0.333 of  $\text{Na}_2\text{O}$  were examined using  $\text{Mo K}\alpha$ . The changes in interat. distance and in the no. of O atoms surrounding each B atom are continuous and indicate that the B atoms are partly in triangular and partly in tetrahedral co-ordination, the proportion of the latter increasing with  $\text{Na}_2\text{O}$  content. Each Na is surrounded by 6 O at 2.4 Å. and each O by 5—6 O at 2.4 Å. This arrangement is equiv. to a random network of B atoms bonded to 3—4 O with Na in the spaces. Max. and min. in the property-composition curves (e.g., the marked min. thermal expansion at 16%  $\text{Na}_2\text{O}$ ) is explained by the ability of the B atom to change to tetrahedral co-ordination when the  $\text{Na}_2\text{O}$  is present to supply the necessary O. J. A. S.

**Supra-molecular structure of fibrous materials.** O. KRATKY and H. MARK (Papier-Fabr., 1938, 36, 345—348).—The cellulose mol. chains have varying plasticity on which depend such factors as the settling rate and  $\eta$  of cellulose solutions. The mechanism of the crystallisation of cellulose is discussed in various stages and a parallel drawn in the case of rubber in that a network of chain mols. is formed in each instance with parallel methods of linking between the chains. D. A. C.

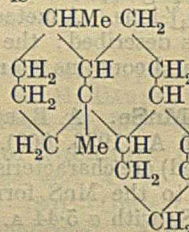
**Symbolic representation of crystalline form.** H. BUTTGENBACH (Bull. Acad. roy. Belg., 1938, [v], 24, 259—284).—In view of the present chaotic state of crystallographic expression, proposals for a unified scheme based on definite rules are defined in detail for the various crystal systems and their application to various typical crystals is given. N. M. B.

**Structure of the insulin molecule.** (MRS.) D. M. WRINCH (J. Amer. Chem. Soc., 1938, 60, 2005—2006).—The author's cyclol structure (A., 1937, I, 604) for insulin is in line with X-ray data (A., 1938, I, 300). R. S. C.

**Structure of triterpenes and related substances. II.** G. GIACOMELLO (Gazzetta, 1938, 68,

363—376).—Analysis of X-ray data shows that the hydrocarbon  $\text{C}_{24}\text{H}_{38}$  obtained by dehydrogenation of triterpenes has a structure analogous to that of the triterpenes themselves. The structure of related substances is discussed. O. J. W.

**Mol. wt. of fichtelite.** (MISS) D. CROWFOOT (J.C.S., 1938, 1241—1242).—Crystals of fichtelite on optical and X-ray evidence show close similarity to certain types of sterol crystal. From X-ray determination the dimensions of the unit cell are  $a$  10.69,  $b$  7.45,  $c$  13.10 Å.,  $\beta$   $127^\circ 5'$ ,  $c \sin \beta$  10.45 Å.; space-group  $P2_1$ ,  $n = 2$ ;  $\rho$  1.045. Assuming 2 mols. per unit cell the mol. wt. is  $264 \pm 4$ , in good agreement with 262 the formula wt. of  $\text{C}_{19}\text{H}_{34}$ . The probable mol. structure is



W. R. A.

**Crystal structure of cyclohexane and of some of its simpler derivatives.** O. HASSEL and A. M. SOMMERFELDT (Z. physikal. Chem., 1938, B, 40, 391—395).—In the neighbourhood of the m.p. the mols. in cubic crystals of cyclohexane, -hexanol, -hexanone, and chlorocyclohexane possess considerable rotational freedom. The lattice const. are 8.76, 8.83, 8.61, and 9.05 Å., respectively. C. R. H.

**X-Ray analysis of the structure of anthraquinone.** B. C. GUHA (Phil. Mag., 1938, [vii], 26, 213—223; cf. A., 1937, I, 401).—The C atoms of anthraquinone lie in one plane tilted from the (001) plane by  $6^\circ$  about each of the  $a$ ,  $b$ , and  $c$  axes. The side rings of the mol. have internal angles  $120^\circ$  and side lengths 1.35 Å. for the C-C and 1.46 Å. for the C-C bonds. The middle ring has angles  $109^\circ$  between two single bonds, and  $125^\circ$  between a double and a single bond, with lengths of sides as in the outer rings. The O atoms are inclined unsymmetrically to the C plane. The C—O distances are 1.13 Å. O. D. S.

**Crystal structure of thianthren and selenanthren.** J. E. CRACKSTON and R. G. WOOD (Nature, 1938, 142, 257).—Thianthren,  $a : b : c$  2.37 : 1 : 1.95,  $\beta$   $110^\circ 0'$ ,  $a_0$  14.3,  $b_0$  6.09,  $c_0$  11.8 Å., and selenanthren,  $a : b : c$  2.36 : 1 : 1.97,  $\beta$   $110^\circ 20'$ ,  $a_0$  14.5,  $b$  6.21,  $c$  12.1 Å., both have space-group  $C_{2h}^2$  and are isomorphous (cf. A., 1937, I, 448; 1938, II, 118). L. S. T.

**Space group of creatinine.** K. BANERJEE and A. HAQUE (Indian J. Physics, 1938, 12, 183—194).—The space-group is  $C_{2h}^2/P2m$ ; 8 mols. per unit cell; and  $a$  14.86,  $b$  13.14,  $c$  5.85 Å.,  $\beta$   $110^\circ 30'$ . W. R. A.

**Crystal structure of condensed ring compounds. VI. 1:2-Benzanthracene, 5-methyl-1:2-benzanthracene, and 3-methyl-1:2-benzanthraquinone.** J. IBALL (Z. Krist., 1938, 99, 230—237; cf. A., 1936, 1451).—X-Ray analysis yields for the respective monoclinic cells:  $a$  7.91,



8.21, 7.52,  $b$  6.43, 6.53, 16.81,  $c$  23.96, 48.4, 11.63 Å,  $\beta$  99°, 90°, 118.9°; mols. per cell 4, 8, 4;  $\rho$  1.245, 1.231, 1.393; probable space-group  $C_2^2-P2$ ,  $C_{2h}^2-P2/c$ ,  $C_{2h}^2-P2_1/a$ . Assuming plane C skeleton mols., orientations are discussed on the basis of estimated intensities, optical data, and general considerations.

I. McA.

**Crystal structure of cyanuric acid, (CHON)<sub>3</sub>.** E. H. WIEBENGA and N. F. MOERMAN (Z. Krist., 1938, 99, 217—229; cf. A., 1938, I, 125).—The pseudorhombic monoclinic cell has  $a$  7.90,  $b$  6.74,  $c$  9.04 Å,  $\beta$  ~90°; 4 (CHON)<sub>3</sub> per cell; space-group  $C_{2h}^2-C2/c$ . From X-ray intensities, cleavage, and twinning, layers parallel to (101) consist of plane triangle-cum-ring (OC·NH)<sub>3</sub> mols. lacking the trigonal symmetry and CN link distinctions of cyanuric triazide (A., 1935, 1194). Interat. distances (C—N 1.36—1.37 Å, C—O 1.24—1.31 Å) indicate resonance. Adjacent mols. in a layer are linked (O to N) by H bonds.

I. McA.

**Electron diffraction and surface structure.** G. I. FINCH (J.C.S., 1938, 1137—1146).—A lecture.

W. R. A.

**Structure of polished metal surfaces.** E. PLESSING (Physikal. Z., 1938, 39, 618—620).—The results of Dobinski (A., 1937, I, 227) for the structure of surfaces of Au and Ag under C<sub>6</sub>H<sub>6</sub> determined by electron diffraction have been confirmed, but the data for Ni, Cu, and Fe do not agree with Dobinski's but with Raether's results (A., 1933, 1222). The effect of mechanical treatment on Au was investigated.

A. J. M.

**Photographic intensity measurements of electron-diffraction patterns.** L. S. ORNSTEIN, H. BRINKMAN, A. HAUSER, and T. TOL (Physica, 1938, 5, 693—700).—The relation between intensity and the resulting photographic density was determined for each observation for the same exposure time and electron velocity as was used for the diffraction photographs. Data for Ag and Cu films are described. The at. factor for electron diffraction shows a dependence on the angle of scattering different from that found by previous investigators.

H. J. E.

**Electron-diffraction investigation of aluminium chloride, bromide, and iodide.** K. J. PALMER and N. ELLIOTT (J. Amer. Chem. Soc., 1938, 60, 1852—1857).—In the gaseous state the dimeric mols. consist of two tetrahedra sharing an edge with six halogen atoms at the corners, each tetrahedron containing one Al. Interat. distances are recorded for the three compounds.

E. S. H.

**Electron-diffraction investigation of the molecular structures of (1) phosphorus oxytrichloride, oxydichlorofluoride, oxychlorodifluoride, oxytrifluoride, fluorodichloride, pentafluoride, and trifluorodichloride, and of (2) disilane, trichlorosilane, and hexachlorodisilane.** L. O. BROCKWAY and J. Y. BEACH (J. Amer. Chem. Soc., 1938, 60, 1836—1846).—Interat. distances (in Å) and angles recorded are: PF<sub>3</sub>, P—F 1.52±0.04,  $\angle$ FPF 104±4°; PCl<sub>3</sub>, P—Cl 2.00±0.02,  $\angle$ ClPCl 101±2°; PFCl<sub>2</sub>, P—F 1.55±0.05, P—Cl 2.02±0.03,  $\angle$ ClPCl 102±3°; POCl<sub>2</sub>, P—F 1.52±0.02, P—O 1.56±0.03,  $\angle$ FPF 107±2°; POCl<sub>3</sub>, P—Cl 2.02±0.03, P—O

(1.58),  $\angle$ ClPCl 106±1°; POCl<sub>2</sub>, P—F 1.51±0.03, P—Cl 2.01±0.04, P—O 1.55±0.03,  $\angle$ FPF 106±3°; POCl<sub>2</sub>, P—F 1.50±0.03, P—Cl 1.99±0.04, P—O 1.54±0.03,  $\angle$ ClPCl 106±3°; PF<sub>5</sub>, P—F 1.57±0.02,  $\angle$ FPF 90°, 120°, 180°; PF<sub>3</sub>Cl<sub>2</sub>, P—F 1.59±0.03, P—Cl 2.05±0.03,  $\angle$ FPF 120°,  $\angle$ ClPCl 180°; Si<sub>2</sub>H<sub>6</sub>, Si—Si 2.32±0.03, Si—H 1.47±0.03; SiHCl<sub>3</sub>, Si—Cl 2.10±0.03, Cl—Cl 3.29±0.03,  $\angle$ ClSiCl 101±1°; Si<sub>2</sub>Cl<sub>6</sub>, Si—Si 2.32±0.06, Si—Cl 2.00±0.05.

E. S. H.

**Electron diffraction of dihalogen derivatives of cyclohexane.** J. G. GUDMUNDSEN and O. HASSEL (Z. physikal. Chem., 1938, B, 40, 326—332).—Data for the vapours of six derivatives are recorded.

C. R. H.

**Electron-diffraction examination of linear high polymerides.** K. H. STORKS (J. Amer. Chem. Soc., 1938, 60, 1753—1761).—Thin films of polyethylene succinate, adipate, and sebacate (I) and of natural gutta-percha (II) have been examined. Stretched films show diffraction patterns, characteristic of sharply oriented crystals, giving measurements in good agreement with existing X-ray data. Unstretched films of (II) are composed of relatively large crystallites, oriented with their fibre axis directions normal to the film surface. Unstretched films of (I) consist of relatively small crystals, apparently oriented with their fibre axis directions approx. in the plane of the film, but with limited rotation around the fibre axis directions.

E. S. H.

**Diffuse scattering of X-rays from piezo-electrically oscillating quartz.** G. E. M. JAUNCEY and W. A. BRUCE (Physical Rev., 1938, [ii], 54, 163—165).—Different modes and types of vibration have no effect on the intensity of the diffuse scattering, and since the latter cannot be affected by secondary extinction it is concluded that the change of intensity of the Laue spots (cf. A., 1936, 273) is due to a decrease of secondary extinction in the body of the crystal.

N. M. B.

**Paramagnetism of electrons in a rectangular band.** L. NÉEL (Compt. rend., 1938, 206, 1471—1473).—Theoretical. The magnetic properties of metals of the Fe group are discussed.

A. J. E. W.

**Magnetic after-effect.** S. KOCH (Naturwiss., 1938, 26, 493—494).—A theory of the magnetic after-effect which takes into account the connexion with the mechanical after-effect is put forward.

A. J. M.

**Ferromagnetic Curie point as a phase transition of the second kind.** J. DE BOER and A. MICHELS (Physica, 1938, 5, 775—776).—Data for Ni, although insufficient for a definite conclusion, are of the right order of magnitude.

H. J. E.

**Break in the magnetisation curve of iron single crystals in weak magnetic fields.** K. HONDA and T. NISHINA (Z. Physik, 1938, 109, 758—761).—The magnetisation curves for Fe single crystals along the 3 principal axes are determined with a high-sensitivity astatic magnetometer. The curves are collinear up to a crit. field strength at which point they diverge, the susceptibility then changing for each orientation. The results are explained in the light of the Honda-Okubo theory of paramagnetic substances.

L. G. G.



**Resistance, spontaneous magnetisation, and Curie point of nickel.** W. GERLACH, H. BITTEL, and S. VELAYOS (Sitzungsber. bayr. Akad. Wiss., 1936, 81—136; Chem. Zentr., 1936, ii, 2309).—The  $R$ - $\theta$  curves for impure samples of Ni can be obtained by the application of Matthiessen's additive rule to the corresponding curve for pure Ni. This conclusion is confirmed by measurements on pure and impure specimens of Ni at  $-200^\circ$  to  $600^\circ$ . The results are discussed in relation to anomalies in  $R$  and spontaneous magnetisation; the work of Borelius (cf. A., 1931, 552) is also discussed. Spontaneous magnetisation occurs considerably above the temp. regarded as the Curie point of Ni. A. J. E. W.

**Determination of elasto-optical constants with supersonic waves.** H. MUELLER (Z. Krist., 1938, 99, 122—141; cf. A., 1937, I, 505; 1938, I, 129; Bergmann and Fues, B., 1936, 1093).—The mathematical theory of the optical effects of ultrasonics in cubic crystals and amorphous solids is further reviewed with reference to the dependence of intensity and polarisation of the diffracted beam pattern on the elastic and elasto-optical consts. of the medium. On this basis, the intensity and polarisation for NaCl, KCl, and  $\text{CaF}_2$  crystals are calc. from measurements (Voigt, Pockels) of the consts.; three experimental methods are discussed for the (general) converse problem. I. McA.

**Optical observation of the Debye heat waves in crystals.** (Sir) C. V. RAMAN and C. S. VENKATESWARAN (Nature, 1938, 142, 250).—Photographs showing the interference pattern of the 4046 Å. radiation of a  $\text{H}_2\text{O}$ -cooled Hg lamp scattered by thermal agitation in a crystal of gypsum, and demonstrating the physical reality of the Debye heat waves in crystals, are submitted. The displacements of the three components into which the incident radiation is split correspond with acoustic wave velocities of 3350, 2050, and 1100 m. per sec., respectively. L. S. T.

**Recrystallisation diagram of cadmium.** J. CZOCHRALESKI and T. MIAZGA (Wiadom. Inst. Met., 1935, 2, 3—5; Chem. Zentr., 1936, ii, 433—434).—A diagram is constructed from grain-size measurements for compressively deformed Cd which was allowed to recrystallise for 30 min. at  $20^\circ$ ,  $50^\circ$ ,  $100^\circ$ ,  $150^\circ$ ,  $200^\circ$ ,  $250^\circ$ ,  $300^\circ$ , and  $310^\circ$ . H. J. E.

**Elastic constants of transparent isotropic solids by a new method.** K. H. HOESCH (Z. Physik, 1938, 109, 606—624).—Elastic waves are generated in glass blocks by affixing the latter to vibrating quartz crystal, suitable apparatus for the excitation of which is described in detail. Polarised light passed through the glass blocks is examined microscopically and the mean distance between the resultant striations is determined. Hence the velocity of propagation of the waves in the glass is calc., and the moduli of elasticity and torsion are obtained to an accuracy of 0.6% and the Poisson const. to 1.4%. L. G. G.

**Effect of pressure on elastic parameters of isotropic solids.** F. BIRCH (J. Appl. Physics, 1938, 9, 279—288).—Murnaghan's theory (Amer. J. Math.,

1937, 59, 235) of finite strain is applied to determine the effect of hydrostatic pressure on the elastic coeffs. of an isotropic body for further applied strains of small magnitude. The stress-strain relations are the same as those of the classical theory, but with elastic parameters which depend on the pressure. The observed pressure coeffs. are in agreement with the calc. vals. J. A. D.

**X-Ray diffraction study of sulphur allotropes.** S. R. DAS (Indian J. Physics, 1938, 12, 163—181).—The structures of various S allotropes have been investigated by Hull's diffraction method between  $-183^\circ$  and  $130^\circ$ . Roll S, flowers of S, milk of S, and the gummy deposits of colloidal S are cryst. and similar in structure to  $S_8$  (orthorhombic S). Freshly-prepared plastic S is amorphous but is readily transformed into a hard, solid,  $\text{CS}_2$ -insol. substance (I) of structure similar to  $S_8$ . When (I) is kept at about  $60^\circ$ , or treated with aq.  $\text{NH}_3$ , it becomes sol. in  $\text{CS}_2$ . White S, from hydrolysis of  $\text{S}_2\text{Cl}_2$ , gives a well-defined pattern, quite different from that of  $S_8$ ; it is insol. in  $\text{CS}_2$  but, when heated for some time at  $88^\circ$ , is changed completely into  $S_8$ . Data on  $S_8$  (monoclinic) could not be obtained but patterns of liquid S for  $114^\circ$ ,  $119^\circ$ , and  $128^\circ$  are given. At low temp. (to  $-183^\circ$ ) no change in structure of solid S is found. The solubility of the various forms in  $\text{CS}_2$  is discussed. For each insol. variety  $\text{SO}_2$  always takes part in the reaction involved and it is suggested that  $\text{SO}_2$  forms a protective layer on the surface of the crystals. W. R. A.

**Mol. wts. of globular proteins.** (Mrs.) D. M. WRINCH (Phil. Mag., 1938, [vii], 26, 313—332).—The predictions and general point of view of the cyclol theory agree well with the data of Svedberg. A consideration of the shape of the  $C_\alpha$  cyclols and the nature of the cyclol network indicates that compound cyclols may exist. The actual nos. given by Svedberg for 14 different mol. wt. classes may all be represented by simple or compound cyclols, assuming that the corresponding apparent residue wts. lie between 121 and 128. A simple interpretation of the reversible dissociation, characteristic of many proteins, has been suggested which explains in particular the effect of dilution and changes in  $p_H$  on the mol. wts. of such proteins. For virus proteins and other heavy proteins, a cage-colony structure has been proposed. W. R. A.

**Electrical conductivity of lead crystals at low temperatures in strong transverse magnetic fields.** E. JUSTI and H. SCHEFFERS (Physikal. Z., 1938, 39, 591—597).—The resistance of two Pb crystals with the 100 and 111 axes approx. parallel has been determined at  $1.8$ — $20^\circ$  K. under the action of a strong transverse magnetic field (31,000 gauss). The increase of resistance at  $14$ — $20^\circ$  K. on applying the field is comparatively small and isotropic in agreement with the low characteristic temp., but at the temp. of boiling He it increases considerably and shows increasing anisotropy with greater field strength. The residual resistance, defined as the difference between the measured and the ideal resistance, decreases considerably with falling temp. even before the onset of superconductivity. The mean relative



increase in resistance is a function of the ratio of the field strength to the resistance without the field.

A. J. M.

**Co-existence of normal and superconductive regions.** K. MENDELSSOHN and J. G. DAUNT (Phil. Mag., 1938, [vii], 26, 376—380).—Experimental proof is given for an isothermal co-existence of superconductive and normal material in the same specimen. The time effects in superconductors are discussed with regard to such a co-existence.

W. R. A.

**"Overshoot phenomenon" in superconductivity.** A. D. MISENER (Proc. Camb. Phil. Soc., 1938, 34, 465—469).—Transition curves are obtained for a sample of Ta wire (length 6 cm., diameter  $7.5 \times 10^{-3}$  cm.) at const. temp. and zero external magnetic field by increasing the current, and also by increasing the external field with const. current. Resistance becomes unsteady after  $\sim 10\%$  of the resistance of the specimen had been restored. This unsteadiness and the "overshoots" observed with coiled specimens occur in the same regions of the transition curve and are probably due to a secondary effect in the transition from the superconducting to the nonsuperconducting state.

F. J. L.

**Method of least squares and the thermo-electric power of rhodium.** H. T. WENSEL and L. B. TUCKERMAN (Rev. Sci. Instr., 1938, 9, 237—241).—Polemical. Proper application of the method of least squares to the data of Booth and Dixon (A., 1937, I, 606) indicates that their conclusions are not justified; this is supported by other evidence. Other reported irregularities in the behaviour of Rh near  $1100^\circ$  can be ascribed to the formation and decomp. of a surface film of  $\text{Rh}_2\text{O}_3$ . (Cf. following abstract.)

W. R. A.

**Discontinuity in the thermo-electric power of rhodium.** E. T. BOOTH and E. M. DIXON (Rev. Sci. Instr., 1938, 9, 242—243).—A reply to criticism. (Cf. preceding abstract.)

W. R. A.

**Thermomagnetic anomaly shown at room temperatures by microcrystalline ferromagnetic substances.** A. MICHEL and (Mlle.) M. GALLISSOT (Compt. rend., 1938, 207, 140—142).—A relationship between the magnetism-temp. curve and the microcryst. nature of the specimen has been indicated (A., 1938, I, 421). Microcryst. ferrites of Ni, Cu, and  $\text{MgO}$  have been investigated. There is no single definite Curie point for a substance; instead the Curie temp. extends over a small range. Both chemical and physical heterogeneity cause changes in the curvature of the magnetism-temp. curve.

W. R. A.

**Cause of the [magnetic] anomaly in magnetite at low temperatures.** R. FORRER (Compt. rend., 1938, 207, 281—283).—Natural  $\text{Fe}_3\text{O}_4$  gives an anomalous increase in  $\chi$  with increasing temp. between  $-138^\circ$  and  $-118^\circ$ , which is ascribed to the breaking at low temp. of linkings between pairs of Fe atoms in the lattice. A second form of  $\text{Fe}_3\text{O}_4$  (cf. Hilpert, A., 1937, I, 421) which reacts readily with  $\text{Cl}_2$  does not give this anomaly, indicating the absence of Fe-Fe linkings. Ferrites (in which such linkings cannot occur) give no anomaly.

A. J. E. W.

**Ferromagnetic and electrical properties. VIII. Longitudinal and transverse thermomagnetic effects of nickel.** P. WAGNER (Ann. Physik, 1938, [v], 32, 665—682; cf. A., 1932, 900).—The saturation val.  $E_\infty$  of the thermomagnetic e.m.f. of a Ni wire, when one end is at temp.  $> \Theta$ , the Curie temp., and the other at temp.  $T < \Theta$ , is given by  $E_\infty = C(\Theta - T)^2$ , where  $C$  is a const. dependent on the purity of the Ni. The transverse e.m.f.,  $E_\perp$ , has opposite sign to the longitudinal,  $E_\parallel$ , but is of equal magnitude. By the application of longitudinal stress  $E_\parallel$  is increased to a saturation val.,  $2E_\parallel$ , while  $E_\perp$  decreases towards zero. At high field strengths both  $E_\parallel$  and  $E_\perp$  decrease with increasing field. At small temp. difference and under stress  $E \propto I^2$ , where  $I$  is the magnetisation.

O. D. S.

**Magneto-resistance change of ferromagnetics in an alternating magnetic field.** S. SHARAN (Indian J. Physics, 1938, 12, 203—210).—The effects produced on the resistance of Ni and of Ni-Fe permalloy by an alternating magnetic field and by an alternating and direct field simultaneously have been investigated.

W. R. A.

**Mechanical and magnetic secondary effect of carbonyl iron.** G. RICHTER (Ann. Physik, 1938, [v], 32, 683—700).—A torsional secondary effect has been observed in wires of carbonyl iron with temp. variation similar to that of the magnetic secondary effect previously described (B., 1937, 1059). It is suggested that both are due to thermal fluctuations in the crystal lattice and the activation energy is calc., from the temp. coeff. of the velocity of establishment of the effect, to be 20 kg.-cal. per mol.

O. D. S.

**Paramagnetic relaxation.** P. DEBYE (Physikal. Z., 1938, 39, 616—618).—Theoretical.

A. J. M.

**Paramagnetic dispersion in chromium alum and its interpretation.** C. J. GORTER, P. TEUNISSEN, and F. BRONS (Physica, 1938, 5, 657—662).—Measurements at  $77^\circ$  and  $90^\circ$  K., and with field strengths of 800, 1600, 2400, and 3200 oersted, are recorded. The results are discussed in terms of the theories of Casimir and of Kronig.

H. J. E.

**Magnetic properties and structure of manganese and cobaltous dipyridine chlorides.** D. P. MELLOR and C. D. CORYELL (J. Amer. Chem. Soc., 1938, 60, 1786—1787).—Magnetic measurements indicate that the Mn and Co atoms in the above compounds form ionic rather than covalent  $d_{sp}^2$  linkings. It is suggested that an octahedral ionic type of structure occurs in the Mn and  $\alpha$ -Co compounds and a tetrahedral ionic type in the  $\beta$ -Co compound.

E. S. H.

**Magnetic susceptibilities of certain inorganic complex compounds.** J. H. FRAZER and N. O. LONG (J. Chem. Physics, 1938, 6, 462—465).—The method employed for determining gyromagnetic effect has been adapted to measure the magnetic susceptibilities ( $\chi$ ) of some inorg. substances at  $27^\circ$  in a weak field (approx. 300 oersted) using 0.5 g. of material. Constructional and operational details are given.  $\text{NaNO}$ , prepared by passing dry NO into a solution of Na in liquid  $\text{NH}_3$  and evaporating  $\text{NH}_3$ , is diamagnetic. *Na nitrosopentanitrocobaltate dihydrate*,



$\text{Na}_3[\text{Co}(\text{NO})(\text{NO}_2)_5] \cdot 2\text{H}_2\text{O}$  (I), and *nitrosopentammine* *Co dichloride*,  $[\text{Co}(\text{NO})(\text{NH}_3)_5]\text{Cl}_2 \cdot 5\text{H}_2\text{O}$  (II), have been investigated. (II) is paramagnetic; (I) is diamagnetic in weak fields but becomes paramagnetic as the field strength is raised. A tentative explanation of the  $\chi$  of the three compounds is given. W. R. A.

**Magnetic properties of ferric hydroxide.** R. CHEVALLIER and (MLLE.) S. MATHIEU (Compt. rend., 1938, 206, 1469—1471).—The val. of  $\chi$  for the hydroxide pptd. by KOH from  $\text{Fe}_2(\text{SO}_4)_3$  solutions and washed and dried under fixed conditions shows large variations with the initial concns. used, and with the ratio of KOH to Fe on pptn. The  $\text{Fe}_2\text{O}_3$  obtained on heating gives a const. val. of  $\chi$ . A. J. E. W.

**Paramagnetic magneton numbers of the ferromagnetic metals.** E. C. STONER (Proc. Leeds Phil. Soc., 1938, 3, 457—464).—The results of Sucksmith (cf. A., 1938, I, 71) for Fe, Co, and Ni are discussed in the light of a collective electron treatment of ferromagnetism using Fermi-Dirac statistics. The general character of the  $1/\psi$ - $T$  curves is in agreement with this treatment. Estimates of the ratio of the interchange interaction energy to the Fermi energy can be made from the results, and the Fermi energy so obtained for Ni is in good agreement with the val. deduced from the electronic sp. heat at low temp. N. M. B.

**Change of thermal energy with adiabatic change of magnetisation in iron, nickel, and carbon steel.** T. C. HARDY and S. L. QUIMBY (Physical Rev., 1938, [ii], 54, 217—223).—The change in thermal energy which occurs when the magnetisation is altered adiabatically is traced for each material, through a complete half-cycle of magnetisation which starts with the max. val. of the intensity of magnetisation. The external work done by the specimen at each stage is evaluated. The decrease in thermal energy on demagnetisation is < the external work done by the specimen in Fe and steel, and greater in unannealed Ni; in annealed Ni it is greater when magnetisation is continuous and less when it is discontinuous. N. M. B.

**Time effects in magnetisation.** J. L. SNOEK (Physica, 1938, 5, 663—688).—A theory is developed which accounts for the phenomena of magnetic viscosity and the reversible decrease of permeability with time. Confirmatory measurements on carbonyl Fe are described. H. J. E.

**Raman and Nath's theory of the diffraction of light by ultrasonic waves.** R. BÄR (Helv. Phys. Acta, 1936, 9, 265—284; Chem. Zentr., 1936, ii, 931—932).—The theory was verified for xylene with a frequency of 1500 kHz. and using a Hg lamp as light source. It was qualitatively applicable at a frequency of 7500 kHz. H. J. E.

**Mathematical theory of diffraction of light by ultrasonic waves.** G. WANNIER and R. EXTERMANN (Helv. Phys. Acta, 1936, 9, 337—339; Chem. Zentr., 1936, ii, 2284—2285).—The frequency of the diffracted light is given by  $\omega_n = \omega_0 + n\nu$  ( $\nu$  = sound frequency). Intensities of diffracted light are calc. and compared with Raman and Nath's theory. A. J. E. W.

**Diffraction of light by ultrasonic waves in air.** R. BÄR (Helv. Phys. Acta, 1936, 9, 367—371; Chem. Zentr., 1936, ii, 2285).—First- and second-order diffracted spectra have been obtained. Variations in  $n$  of  $\pm 1.3 \times 10^{-6}$ , corresponding with a pressure variation of  $4.8 \times 10^{-3}$  atm., are recorded. Ultrasonic velocities in gases may be determined by the method used (cf. A., 1937, I, 174). A. J. E. W.

**Interference of two plane ultrasonic waves. Application of this phenomenon in a new method of measuring the velocity of sound.** J. P. CANCE (J. Phys. Radium, 1938, [vii], 9, 308—312).—Details of the method (cf. A., 1938, I, 239) are given. The velocities of sound in PhMe and Hg are 1314 and 1442 m. per sec., in agreement with recorded data. W. R. A.

**Sound velocity in heavy water and compressibility.** K. YOSIOKA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1938, 34, 843—853).—The sound velocity,  $V$ , in  $\text{H}_2\text{O}$  and in  $\text{D}_2\text{O}$  has been determined at temp. between  $25^\circ$  and  $90^\circ$  at a frequency of 4900 kc., by an optical method utilising the diffraction of light caused by a train of supersonic waves. The max. val. of  $V$  is reached at a temp. in  $\text{D}_2\text{O} >$  in  $\text{H}_2\text{O}$ , whilst the adiabatic compressibility ( $\kappa$ ), calc. in both cases from  $V$  and  $d$ , reaches a min. val. at a temp. in  $\text{D}_2\text{O} >$  in  $\text{H}_2\text{O}$ . By extrapolation the following data have been found for pure  $\text{D}_2\text{O}$  at  $25^\circ$ :  $V$ , 1398.6 m. per sec.;  $\kappa$ ,  $46.27 \times 10^{-12}$  dyne $^{-1}$ , and isothermal compressibility,  $46.49 \times 10^{-12}$  dyne $^{-1}$ . W. R. A.

**Velocity of sound in liquid oxygen.** H. W. LIEPMANN (Helv. Phys. Acta, 1936, 9, 507—510; Chem. Zentr., 1936, ii, 3051).—Measurements for a frequency of 7500 kHz. are recorded. The velocity at  $-183.6^\circ$  was 903 m. per sec. and at  $-209.5^\circ$ , 1111 m. per sec. The adiabatic compressibility was calc. The piezo-electric properties of the quartz used persisted to  $-212^\circ$ . H. J. E.

**Ultrasonic radiation field of a quartz disc radiating into liquid media.** F. E. FOX and G. D. ROCK (Physical Rev., 1938, [ii], 54, 223—228).—The radiation pressure of sound waves on a spherical obstacle is used to determine the distribution of intensity in the sound field of a quartz disc radiating into  $\text{H}_2\text{O}$ . Results are in agreement with theory. N. M. B.

**Refractive index of air in the visible and photographic infra-red.** D. BENDER (Physical Rev., 1938, [ii], 54, 179—183).—Measurements of  $n$  for dry air free from  $\text{CO}_2$  were made from 5300—11,177 Å., and a dispersion formula for  $0^\circ$  and 760 mm. is given. A calculation indicates that the  $\text{O}_2$  absorption band at 7600 Å. has no measurable effect on the dispersion of air. N. M. B.

**Specific heats of beryllium, phosphorus, and titanium nitrides.** S. SATOH (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1938, 34, 888—896).—Using the ice calorimeter and Al as standard the sp. heats of  $\text{Be}_3\text{N}_2$  ( $0-95^\circ$ ,  $0-303^\circ$ ,  $0-500^\circ$ ),  $\text{P}_3\text{N}_5$  ( $0-99.6^\circ$ ,  $0-305^\circ$ ), and  $\text{TiN}$  (as  $\text{P}_3\text{N}_5$  and  $0-500^\circ$ ) are respectively  $0.2726 + 7.884 \times 10^{-4}t - 5.163 \times 10^{-7}t^2$ ;  $0.2027 + 6.252 \times 10^{-4}t$ ; and  $0.1410 + 1.918 \times 10^{-4}t - 1.127 \times 10^{-7}t^2$ . W. R. A.



**Atomic heats of nitrogen in various nitrides.**

I. S. SATOH (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1938, **34**, 751—760).—The at. heats of N in B, Al, Si, Ca, V, Mo, and Ta nitrides at 25°, 100°, 300°, and 500° have been calc. from measurements of the mol. heats of the nitrides, and the at. heats of the elements concerned. The mean val. of the at. heat for the range 0—100° was about 2.4 for the nitrides of the elements of low at. no., B, Al, Si, whilst for these of higher at. no. it varied from 3.26 for VN to 4.49 for  $\text{Ca}_3\text{N}_2$ . The temp. coeff. for the first group was low, the at. heat increase from 25° to 500° being about 1.85 units, whereas in the other group the increase was 3.257 for TaN, 3.963 for VN, and 4.766 for  $\text{Mo}_2\text{N}$ ,  $\text{Ca}_3\text{N}_2$  with 1.76 being exceptional. The mean val. for 0—100° is a periodic function of the at. no. of the elements. R. C. M.

**Heat capacity and entropy of barium fluoride, caesium perchlorate, and lead phosphate.** K. S. PITZER, W. V. SMITH, and W. M. LATIMER (J. Amer. Chem. Soc., 1938, **60**, 1826—1828).—Heat capacity data for the range 15—300° K. are recorded. The calc. mol. entropies at 298.1° K. are:  $\text{BaF}_2$  23.03±0.1,  $\text{Pb}_3(\text{PO}_4)_2$  84.45±0.4,  $\text{CsClO}_4$  41.89±0.2 g.-cal. per degree. E. S. H.

**Entropy of ethyl alcohol from molecular data and the equilibrium in the hydration of ethylene.** S. C. SCHUMANN and J. G. ASTON (J. Chem. Physics, 1938, **6**, 480—484).—The entropy and free energy of EtOH gas have been calc. from mol. data at several temp. on the basis of both free internal and restricted rotation. For restricted rotation hindering potentials of 3000 g.-cal. about the C-C bond and 10,000 g.-cal. about the C-O bond were assumed. The vals. for restricted rotation agree well with those obtained from the third law and from the equilibrium data on the hydration of  $\text{C}_2\text{H}_4$ . W. R. A.

**Entropy of acetone and isopropyl alcohol from molecular data. Equilibrium in the dehydrogenation of isopropyl alcohol.** S. C. SCHUMANN and J. G. ASTON (J. Chem. Physics, 1938, **6**, 485—488).—The discrepancies between the entropy vals. of  $\text{COMe}_2$  and of  $\text{Pr}^i\text{OH}$  gases, obtained by calculation from the third law of thermodynamics and from mol. data, can be explained by assuming restricted rotation in the mols. using the following restricting potentials:  $\text{COMe}_2$ , about the C-C bond 1000 g.-cal.;  $\text{Pr}^i\text{OH}$ , about the C-C 3400 and about C-O 5000 g.-cal. W. R. A.

**Communal entropy and the theory of fusion.** O. K. RICE (J. Chem. Physics, 1938, **6**, 476—479).—The concept of "communal" entropy (A., 1938, I, 73) is discussed. Theoretically and empirically the entropy of fusion of simple solids is not primarily concerned with the excitation of communal entropy as suggested by Eyring *et al.* (*loc. cit.*). The nature of the communal entropy and its manner of excitation are discussed. W. R. A.

**Depression of the m.p. by mixed structure of molecules of crystalline solid and crystalline liquid substances.** D. VORLÄNDER [with K. OST] (Ber., 1938, **71**, [B], 1688—1710).—The following points are treated experimentally and theoretically;

depressions of the m.p. by transition from solid crystals to the amorphous melt; anomalies of the depression of the f.p. in the cryoscopic determination of mol. wt.; comparison of the eutectic with the isotectic in the transition from the solid crystal to the amorphous melt; behaviours of mixtures of "children" in the transition from solid crystals to cryst. liquids and to amorphous melts (cryst. liquid *Pl*-form of the type of *p*-azoxyphenol ethers; cryst. liquid *Bz* form of the type of *Et p*-azoxybenzoate; cryst. liquid mixtures and "children" from *Pl* and *Bz* forms; m.p. diagrams of cryst. mixtures in connexion with the structural relationships between "parents" and "children." The original should be consulted for details. The following are described incidentally: *p*-phenetoleazo-*p*-anisole, m.p. 135—136°; *Et p*-phenetole-*p*-azobenzoate, m.p. 119°, and the corresponding acid, m.p. 215—217° and 254—257°; *p*-ethoxybenzylidene-*p'*-phenetidine, m.p. 148—149°; *p*-anisylidene-*p'*-phenetidine, m.p. 128—129°; *p*-ethoxybenzylidene-*p'*-anisidine, m.p. 122—123°. H. W.

**M.p. of paraffins and fatty acids.** E. B. MOULLIN (Proc. Camb. Phil. Soc., 1938, **34**, 459—464).—The relationships between the no. (*N*) of C atoms in paraffin and fatty acid chains and their m.p. (θ) are shown to be (a) for paraffins,  $\log(N-2) = 1.065 + 5.290/10^3$ , (b) for fatty acids, *N* odd,  $\log(2N-2) = 1.14 + 5.80/10^3$ , (c) *N* even,  $\log(2N-2) = 1.02 + 7.20/10^3$ . F. J. L.

**Thermal hysteresis of the methane transition at 20.4° K.** A. EUCKEN and E. BARTHOLOMÉ (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., II, 1936, **2**, 51—64; Chem. Zentr., 1936, ii, 773—774).—Heuse's observation of a hysteresis effect (A., 1930, 677) was confirmed. The hysteresis effect is reduced by a temporary interruption of the cooling process above the transition point. The max. sp. heat at the transition point is 120 g.-cal. per mol. The cause of the hysteresis is discussed. H. J. E.

**Vaporisation experiments in vacuum with polonium, radium-D, and radium-E.** M. HOFFER (Sitzungsber. Akad. Wiss. Wien, IIa, 1935, **144**, 393—396; Chem. Zentr., 1936, ii, 1691; cf. A., 1937, I, 99).—Po vaporises at a temp. 300° < that for Ra-D and 250° < for Ra-E. H. J. E.

**Vaporisation experiments with polonium in oxygen and nitrogen.** E. RONA and M. HOFFER (Sitzungsber. Akad. Wiss. Wien, IIa, 1935, **144**, 397—402; Chem. Zentr., 1936, ii, 1691).—Po vaporises at a lower temp. in  $\text{N}_2$  than in  $\text{O}_2$ . H. J. E.

**Solid-liquid equilibrium in argon.** O. K. RICE (J. Chem. Physics, 1938, **6**, 472—475).—The internal equilibrium between the solid and liquid phases of A is investigated by the method applied to  $\text{N}_2$  and  $\text{O}_2$  (A., 1937, I, 398). The intersection of the curves for the thermodynamic quantities  $T(\partial S/\partial V)_T$  and  $(\partial E/\partial V)_T + P$ , plotted as functions of the vol., determine the conditions of equilibrium of the system. The functions  $(\partial S/\partial V)_T$  and  $(\partial E/\partial V)_T$ , assumed dependent on vol. but independent of temp., are plotted against vol. and give curves which reproduce approx. most of the melting parameters of A



at high pressures. The significance of these curves is discussed. W. R. A.

**Nernst heat theorem and irreversible processes at low temperatures.** A. R. UBBELOHDE (Phil. Mag., 1938, [vii], 26, 260—268; cf. A., 1937, I, 571).—It is suggested that for systems obeying the Nernst heat theorem the probability of spontaneous change in the system will decrease rapidly on approaching 0° K. The application of this extension of the theorem to electrical resistance, thermal conductivity, and viscosity is discussed.

O. D. S.

**Relations between Stefan's radiation law, Nernst's heat theorem, and Maxwell's formula for the radiation pressure.** E. GUTH and A. E. HAAS (Proc. Nat. Acad. Sci., 1938, 24, 224—227).—Theoretical.

E. S. H.

**Modernised version of Gibbs' use of the grand canonical ensemble.** R. H. FOWLER (Proc. Camb. Phil. Soc., 1938, 34, 382—391).

F. J. L.

**Avogadro number with absolute significance and a derived equation of state for perfect gases.** L. LABOCCA (Ric. Sci. Progr. tecn., 1936, [ii], 7, I, 50—51; Chem. Zentr., 1936, ii, 759).—Theoretical.

H. J. E.

**Corresponding-states equation of practical interest for general physico-chemical computations.** F. G. KEYES (J. Amer. Chem. Soc., 1938, 60, 1761—1764).—Fugacity-pressure ratio charts for const. reduced temp. against reduced pressures lead at low pressures to a simple reduced equation of state. The consts. of this equation have been evaluated and show differences between polar and non-polar gases. The equation has been applied to certain equilibria and the results indicate that it is useful for making approx. physico-chemical calculations involving gases under pressure.

E. S. H.

**Pressure coefficient of thermal conductivity of metals.** C. STARR (Physical Rev., 1938, [ii], 54, 210—216).—Determinations were made for Cu, Ag, and Au by means of an improved longitudinal heat flow method. Results indicate that the Wiedemann-Franz ratio over a pressure range of 12,000 kg. per sq. cm. has a small positive coeff. of approx. 1% in 10,000 kg. per sq. cm., disagreeing with Bridgman, who found that the coeff. may be negative or positive. Experiments show that these negative coeffs. were due to a systematic convection error. The positive coeff. is attributed to the non-electronic part of the thermal conductivity.

N. M. B.

**Thermal conductivity of metals.** R. E. B. MAKINSON (Proc. Camb. Phil. Soc., 1938, 34, 474—497).—Theoretical. Formulae for the heat currents transported by the electrons ( $\kappa_e$ ) and by the lattice ( $\kappa_l$ ) are derived.  $\kappa_l$  is unimportant at any temp. in univalent metals, but plays a major part in Bi at low temp. The scattering of lattice waves at the boundaries of single crystals (including insulators) at low temp. is also considered.

F. J. L.

**Temperature coefficient of compressibility and the kinetics of liquids.** F. E. YENICAY (Rev. Fac. Sci. Istanbul, 1938, 3, 255—262).—Mathematical. Liquids are in an intermediate, transition state

between the stable, structurally well-defined solid and gaseous states. They possess different structures at each different temp.

T. H. G.

**Viscosity of liquid helium.** W. H. KEESOM and G. E. MACWOOD (Physica, 1938, 5, 737—744).—Apparatus of the oscillating-disc type for the measurement of  $\eta$  of liquid gases, interchangeably, is described. Measurements with He at 1.2—4.0° K. are recorded. There was no evidence that He II shows slip.  $\eta$  goes to zero as  $T$  approaches 0° K.

H. J. E.

**Viscosity of liquid hydrogen.** W. H. KEESOM and G. E. MACWOOD (Physica, 1938, 5, 745—748).—Measurements by the oscillating-disc method at 14.8—20.0° K. gave 215.0 to 138.8  $\mu$ -poise.

H. J. E.

**Viscosity of hydrogen vapour.** W. H. KEESOM and G. E. MACWOOD (Physica, 1938, 5, 749—752).—Measurements of the  $\eta$  of the saturated vapour of  $H_2$  at 14.5—20.3° K. are recorded.

H. J. E.

**Reaction rate theory of viscosity.** R. H. EWELL (J. Appl. Physics, 1938, 9, 252—269).—A theory of chemical reaction rates, based on the physical conception of potential energy barriers, is applied to evaluate the coeffs. of viscosity, plasticity, and diffusion of liquids, resins, and glasses. The relation between viscosity and v.p., and the effect of external pressure on viscosity, are considered. The theory can be applied to all flow phenomena including creep in metals, diffusion in crystals, and the electrical conductivity of glasses, liquids, and ionic solutions.

J. A. D.

**Viscosities of hydrocarbons. IV—VI.** E. B. EVANS (J. Inst. Petroleum Tech., 1938, 24, 321—337; cf. A., 1938, I, 305).—Vals. of the abs. and kinematical viscosities at 0—100° are tabulated for isoparaffins, monocyclic naphthenes including cyclopentane and -hexane and derivatives containing 5—32 C, acyclic and cyclic olefins. Details are given of the prep. and physical properties of the cyclopentane and -hexane hydrocarbons.

J. S. G. T.

**Thermal diffusion of colour centres in potassium chloride crystals at various concentrations.** O. STASIW (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., II [N.F.], 1936, 2, 131—137; Chem. Zentr., 1936, ii, 3058—3059).—Diffusion measurements are recorded. The vals. at low temp. are > the vals. expected from an extrapolation of high-temp. data.

H. J. E.

**Self-diffusion in solids.** G. HEVESY (Trans. Faraday Soc., 1938, 34, 841—845).—The use of radioactive isotopes as indicators is extended to experiments on diffusion in solids. The view that the diffusion rate in solids is dependent on the distribution of the electrical forces around the atoms explains the observed low diffusion coeffs. of Pb and accounts for the high diffusion rate of Au in solid Pb. Similar methods determine the self-diffusion rate of  $Pb^{++}$  in solid  $PbCl_2$  and  $PbI_2$ . Results permit the accurate calculation of the transference no. of  $Pb^{++}$ .

W. R. A.

**Self-diffusion coefficient of gold.** H. A. C. MCKAY (Trans. Faraday Soc., 1938, 34, 845—849).—The self-diffusion coeffs. ( $D$ ) of Au have been measured



for the temp. range 721—966° by two methods which are described. The vals. from both methods do not agree; these, and their differences, are discussed.

W. R. A.

**System sulphuric acid-ethers. II. System sulphuric acid-propyl ether.** S. K. K. JATKAR and N. G. GAJENDRAGAD (J. Indian Inst. Sci., 1938, 21A, 77—87).—The val. of  $\eta$  shows a pronounced max. at  $\text{H}_2\text{SO}_4\text{-Pr}_2\text{O}$  (cf. A., 1938, I, 141). Deviations of the fluidity from additivity show max. at  $\text{H}_2\text{SO}_4\text{-2R}_2\text{O}$  (R = Me, Et, Pr<sup>a</sup>). Vals. of sp. conductivity (which shows a max. at 92.6%  $\text{H}_2\text{SO}_4$ ) and of  $d$  are recorded for  $\text{H}_2\text{SO}_4\text{-Pr}_2\text{O}$  mixtures.

F. R. G.

**Diamagnetic susceptibility of formic acid-water mixtures.** S. R. RAO and S. SRIRAMAN (J. Annamalia Univ., 1938, 7, 187—193).—The susceptibilities ( $\chi$ ) of aq. solutions of  $\text{HCO}_2\text{H}$  containing 29—79 wt.-%  $\text{HCO}_2\text{H}$  have been measured by a Curie balance at 26°. Pure  $\text{HCO}_2\text{H}$  has  $\chi = 0.4464$ . The results show a deviation (>5%) from the additivity law and this may indicate the formation of a monohydrate. Alternately, the deviation may be due to partial association of  $\text{HCO}_2\text{H}$  mols.

W. R. A.

**Indium-lead system.** S. VALENTINER and A. HABERSTROH (Naturwiss., 1938, 26, 517).—Thermal analysis indicates the formation of a cryst. phase represented by  $\text{Pb}_6\text{In}_{26}$ . This is confirmed by X-ray analysis. Pure In or In with >10 at.-% Pb has a face-centred tetragonal lattice with  $c/a$  1.08, but at about 10 at.-% Pb a second face-centred tetragonal lattice with  $c/a$  0.94 makes its appearance, and is the only phase at 20 at.-% Pb. At 27 at.-% Pb the Pb lattice appears with const. 2% < those of pure Pb.

A. J. M.

**Theory of the thermoelectric properties of alloys.** T. MUTO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1938, 34, 741—750).—Mathematical.

R. C. M.

**Decomposition of the solid solution of copper in aluminium as a result of plastic deformation with subsequent annealing.** S. KONOBEJEWSKY and M. SACHAROSA (Metallwirts., 1936, 15, 412—417; Chem. Zentr., 1936, ii, 1681).—X-Ray measurements on mixed crystals with 5, 4, and 2% of Cu are recorded which show the influence of temp. and time of annealing on the decomp.

H. J. E.

**State of the nickel atom in the  $\gamma$ -phase of the Ni-Zn system.** J. DORFMAN and S. SIDEROV (Compt. rend. Acad. Sci. U.R.S.S., 1938, 19, 381—382).—The magnetic moment of the Ni atom in the  $\gamma$ -phase of the Ni-Zn alloy (16.1—20.25 at.-% Ni) is zero, indicating that the atom is neutral and in the  $^1S_0$  state. This is in agreement with the Hume-Rothery rule.

F. J. L.

**Effect of uniform pressure on the Curie temperature.** H. EBERT and A. KUSSMANN (Physikal. Z., 1938, 39, 598—605).—The variation of the ferromagnetic magnetisation of Ni-Cu, Ni-Al, and Ni-Fe alloys with pressure (up to 4000 kg. per sq. cm.) and temp. has been studied. At low temp. the influence of pressure on the magnetisation diminishes. The influence of pressure on the Curie point increases with rising temp., the effect being the more marked the

nearer the Curie point is approached. It is not possible to eliminate the ferromagnetism by the application of any finite pressure.

A. J. M.

**Difficulties in the preparation of mixed crystals with silver chloride.** V. CAGLIOTI (Congr. int. Quim. pura apl., 1934, 9, II, 471—482; Chem. Zentr., 1936, ii, 2301).—Drawn AgCl fibres show fibrous structure parallel to [100] and [111], the former alone remaining after recrystallisation at 320°. Working the fibres lowers the temp. at which they must be heated to restore the original hardness of the AgCl. Small additions of other halides (e.g., 0.01% CuCl,  $\text{CaCl}_2$ , or  $\text{MgCl}_2$ ; 0.04% RbCl) render the AgCl unworkable.

A. J. E. W.

**Singular elements of the region of stratification of ternary systems.** K. I. MOTSCHALOV (J. Gen. Chem. Russ., 1938, 8, 529—537).—Phase diagrams for the system  $\text{Ac}_2\text{O-H}_2\text{O-CS}_2$  are given for 0°, 18°, and 24°, and the surface tensions at the various phase interfaces are recorded.

R. T.

**Stable equilibria of liquid phases in the quaternary system glycerol-acetone-water-acetic anhydride.** K. K. PONOMAREV (J. Gen. Chem. Russ., 1938, 8, 544—551).—Equilibrium relations have been studied at 20°.

R. T.

**Perchlorates and the lyotropic series. II.** J. DUCLAUX and A. DURAND-GESSELIN (J. Chim. phys., 1938, 35, 189—192).—Metallic perchlorates affect considerably the solubility of many org. compounds in  $\text{H}_2\text{O}$ .  $\text{Mg}(\text{ClO}_4)_2$  causes increases in the solubilities of  $\text{CO}(\text{NH}_2)_2$ , glycine, leucine, glutamic acid, asparagine,  $\text{CS}(\text{NH}_2)_2$ , alloxan, succinimide, and allantoin, which were determined, and in those of other compounds which were not determined. The effect seems to be limited to ketones, alcohols, amides, and amines. The effect of 17 metallic perchlorates on the solubility of  $\text{COMeEt}$  in  $\text{H}_2\text{O}$  was investigated. In every case the solubility was increased, but the effect was due to  $\text{ClO}_4^-$ , depending to only a very slight extent on the cation. The specificity of the lyotropic action is not clearly marked in this case where complexes were not formed.  $\text{Mg}(\text{ClO}_4)_2$  gives solid complexes with some of the above compounds.

A. J. M.

**Adsorption.** P. HARTECK (Z. Elektrochem., 1938, 44, 468—473).—A lecture. Recent investigations are discussed in relation to modern theories.

C. R. H.

**Interfacial phenomena.** P. A. THIESSEN (Z. Elektrochem., 1938, 44, 458—459).—Introduction to a symposium.

C. R. H.

**Unimolecular layers.** R. BRILL (Z. Elektrochem., 1938, 44, 459—468).—A lecture. The prep. of unimol. layers and the determination of their state of aggregation are among the subjects considered.

C. R. H.

**Chemical methods of investigating interfacial relations.** R. SCHENCK (Z. Elektrochem., 1938, 44, 523—524).—Possible methods are discussed.

C. R. H.

**Investigation of interfacial phenomena by radioactive methods.** O. HAHN (Z. Elektrochem.,



1938, 44, 497—498).—Possible applications of the methods are enumerated. C. R. H.

**Fine structure of interfaces.** T. SCHOON (Z. Elektrochem., 1938, 44, 498—507).—Methods of investigating structure, especially the electron diffraction method, are discussed. The application of the latter method to the determination of the variations in lattice consts. in the interface, and to the examination of ZnS, MgO,  $\text{Al}_2\text{O}_3$ , graphite, and fatty acids and their salts, is described. C. R. H.

**Movement in interfaces.** K. NEUMANN (Z. Elektrochem., 1938, 44, 474—478).—A lecture. Vol. diffusion, grain boundary migration, and surface diffusion are discussed. C. R. H.

**Electron transference in external interfaces.** R. SUHRMANN (Z. Elektrochem., 1938, 44, 478—488).—A general survey. C. R. H.

**Energy exchange at interfaces.** J. H. DE BOER (Z. Elektrochem., 1938, 44, 488—497).—A general survey. C. R. H.

**Exchange of substances in interfaces.** C. WAGNER (Z. Elektrochem., 1938, 44, 507—512).—A general survey. C. R. H.

**Equilibria and reaction velocities in the solid state.** K. FISCHBECK (Z. Elektrochem., 1938, 44, 517).—Theoretical. C. R. H.

**Catalysis at interfaces.** G. M. SCHWAB (Z. Elektrochem., 1938, 44, 517—523).—A lecture. C. R. H.

**Adsorption of nitrogen and oxygen by tungsten.** A. B. VAN CLEAVE (Trans. Faraday Soc., 1938, 34, 1174—1177).—The adsorption has been studied using the accommodation coeff. of Ne. Rapid adsorption of  $\text{N}_2$  at room temp. has been confirmed. Properties of the second  $\text{O}_2$  film, which is formed in addition to the well-known stable film, have been investigated. E. S. H.

**Adsorption of deuterium on reduced nickel.** S. IJIMA (Bull. Inst. Phys. Chem. Res. Japan, 1938, 17, 540—546, and Rev. Phys. Chem. Japan, 1938, 12, 83—89).—Rates of adsorption of  $\text{D}_2$  and  $\text{H}_2$  on reduced Ni at  $-45^\circ$ ,  $-78^\circ$ , and  $-121^\circ$  have been determined. The equation for the adsorption velocity of  $\text{H}_2$  and  $\text{D}_2$  is the same but the velocity coeff. for  $\text{D}_2$  is  $<$  that for  $\text{H}_2$ , as is also the heat of activation. W. R. A.

**Primary and secondary adsorption of metal ions on metal surfaces.** O. ERBACHER (Z. physikal. Chem., 1938, 182, 243—255).—The adsorption of  $\text{Pb}^{++}$  on Ag and Ni surfaces from solutions in 0.1N- and 12N-HCl has been studied by using Th-B as radioactive indicator, comparison being made with measurements of the adsorption of  $\text{Ag}^{++}$  on Au surfaces (Euler, A., 1923, ii, 13). The results can be explained on the assumption that the phenomenon comprises primary adsorption of cations, which carry anions with them into the adsorption layer. In 0.1N-HCl the extent of adsorption is independent of temp. and almost independent of the metal of the surface, so long as the concn. of metal ions is sufficient for the adsorption layer to cover  $>$  half the surface. At lower cation concn. variations with temp. and surface are observed. Secondary adsorption of Pb

is observed in 12N-HCl, where Pb exists almost entirely as  $\text{PbCl}_4^{--}$  and the metal is adsorbed only in anions accompanying the primarily adsorbed  $\text{H}^+$ . J. W. S.

**Adsorption of ions on polar adsorbents as a function of the reaction medium. I. Isolated adsorption of some multivalent anions on ferric hydroxide as a function of alkali concentration.** G. BALĂNEȘCU and V. T. IONESCU (Bul. Soc. Chim. România, 1937, 19, 93—131).—Adsorption of solids from solution, non-polar and polar, are discussed and the characteristics of each type indicated. Polar adsorption, which is greatly influenced by the reaction medium, presents the sp. characters of ordinary chemical reactions. The isolated adsorption of  $\text{AsO}_4^{--}$ , citric,  $\text{SO}_4^{--}$ , and  $\text{C}_2\text{O}_4^{--}$  anions on  $\text{Fe}(\text{OH})_3$ , in presence of various amounts of aq.  $\text{NH}_3$  and KOH, has been studied by a method which is described. The influence of the medium and of change in the ratio,  $[\text{Fe}^{+++}]/[\text{anion}]$ , is indicated. W. R. A.

**Direct displacement of equilibrium owing to adsorption of metal ions on platinum. Magnitude of the active spots on inert metals.** O. ERBACHER (Z. physikal. Chem., 1938, 182, 256—264).—In the adsorption of Pb from 12N-HCl solution on a Pt surface the adsorptive force is so great as to displace the equilibrium between  $\text{PbCl}_4^{--}$  and  $\text{Pb}^{++}$ , and cause considerable primary adsorption of  $\text{Pb}^{++}$ , although its equilibrium concn. in such solution is only  $10^{-7}$ . When the Pt is roughened with emery the effect is still further increased and a greater fraction of the surface seems to be covered with active spots, which, it is concluded, are of at. dimensions. J. W. S.

**Activation and clarifying properties of fuller's earth. IV. Equilibrium in the ionic exchanges in fuller's earth.** B. S. KULKARNI and S. K. K. JATKAR (J. Indian Inst. Sci., 1938, 21A, 1—7; cf. B., 1938, 682).—The equilibrium const. for the replacement of  $\text{H}^+$  by  $\text{Na}^+$  in fuller's earth has been measured by potentiometric methods in conc. NaCl solutions, and by conductivity methods in dil. solutions. Owing to the limit of exchangeability a certain amount of colour remains in safflower oil treated with the earth. F. R. G.

**Some properties of mobile and immobile adsorbed films.** J. K. ROBERTS (Proc. Camb. Phil. Soc., 1938, 34, 399—411).—The adsorption of a diat. gas mol., which dissociates on adsorption to fill two neighbouring vacant places on a solid surface, is investigated. When there is interaction between the adsorbed particles, the rate of formation of the film changes rapidly when  $\theta$  (fraction of sites occupied) is 0.5—0.6, and for mobile films this is accompanied by a change in the heat of adsorption or evaporation. For an immobile film the behaviour indicates no interaction. The relation of the true to the apparent heat of evaporation for a mobile film, and the kinetics of formation of an immobile film, are discussed. F. J. L.

**Statistical theory of adsorption. I. Elementary theory of adsorption in a first and second layer.** F. CERNUSCHI (Proc. Camb. Phil. Soc., 1938, 34, 392—398).—When mols. in the first layer do not



interact with one another, they may give rise to the adsorption of a mol. into the second layer which is bound more tightly than the mols. in the first layer are to the surface of the adsorber; such conditions are shown to give rise to crit. phenomena.

F. J. L.

**Films on freshly-abraded copper surfaces.** W. E. CAMPBELL and U. B. THOMAS (Nature, 1938, 142, 253—254; cf. A., 1937, I, 227).—Films of approx. equal thickness, giving similar cathode potential-time curves at const. current, are present on Cu freshly abraded in air or under  $C_6H_6$ . The thicknesses of the films, calc. as  $Cu_2O$ , are in air 47, under  $C_6H_6$  41, and under  $H_2O$  33 Å. Combination of the Cu with  $O_2$  dissolved in the  $C_6H_6$  or in the  $H_2O$  at the high local temp. developed explains the results obtained.

L. S. T.

**Liquid helium II.** A. K. KIKOIN and B. G. LASAREW (Nature, 1938, 142, 289—290; cf. A., 1938, I, 397).—A method for determining the thickness of a film of liquid He II on a surface in contact with it is described. The film is  $2-3 \times 10^{-6}$  cm. thick, and its  $\eta$  is  $\gg$  that found by Kapitza (*ibid.*, 131). Heat transfer in the film is high, but may depend on surface evaporation.

L. S. T.

**Kinetics of adsorption with long-range interaction between adsorbed particles.** J. S. WANG (Proc. Camb. Phil. Soc., 1938, 34, 412—423).—The rates of condensation and evaporation when there is long-range interaction between the adsorbed particles are considered for adsorption (a) without dissociation, (b) with dissociation. The formulæ in (a) are compared with the experimental vals. for the rate of evaporation of Na between 850° and 1250° K., and the variation of the dipole moment with  $\theta$  (the fraction of sites occupied) is discussed. The formulæ in (a) and (b) are applied to the diffusion of gases through metals.

F. J. L.

**Kinetics of wetting and selective linear corrosion of metals in polyphase systems: metal-liquid-liquid and metal-liquid-gas.** V. D. I. MIRLIS (Compt. rend. Acad. Sci. U.R.S.S., 1938, 19, 483—488; cf. A., 1938, I, 87).—With varied texture and activation of the metal surface, the corrosion of Al has been studied by previous methods (A., 1936, 1335) in the equilibrium systems Al-aq.  $R\cdot CO_2H$ - $C_6H_6$  ( $R = H, Me, Et, Pr^a$ ), Al-aq.  $Pr^aCO_2H$ -air, and Al- $H_2O$ - $C_6H_6$ . Corrosion, varying with  $R$ , is most marked at the three-phase boundary though negligible in  $C_6H_6$  solutions of  $R\cdot CO_2H$ . The function of the oxide and acid adsorption films is discussed in relation to comparable results for Fe. Increase in the no. of phases favours selective corrosion.

I. McA.

**Ageing of surface of solutions. III. Activated accumulation of dissolved molecules at the surface of benzopurpurin 10B solutions.** K. S. G. DOSS (Kolloid-Z., 1938, 84, 138—143; cf. A., 1936, 1335).—The rate of accumulation of mols. of benzopurpurin 10B at the surface of solutions at room temp. has been measured in relation to concn.,  $p_H$ , and the presence of dissolved non-electrolytes. The rate increases with concn. and with acidity, and is lowered by capillary-active non-electrolytes (EtOH,

$C_6H_{11}\cdot OH$ ). The results support the theory of activated accumulation.

F. L. U.

**Dependence on temperature of [ionic] exchange in alumina.** H. VON WARTENBERG and G. WEHNER (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., III, 1936, 1, 157—159; Chem. Zentr., 1936, ii, 2079).—Exchange of  $Cr^{+++}$  for  $Al^{+++}$  in  $Al_2O_3$ - $Cr_2O_3$  mixtures has been studied by observing the rate of colour change at different temp. If  $k$  is the velocity coeff. for the exchange,  $\log k = -146,000/4.57T + 15.6$ . At 1500—1800°,  $k$  is doubled by a temp. rise of 30°. Increase of the particle size from 5—10  $\mu$ . to 40—60  $\mu$ . decreases  $k$  to one third of its previous val., the temp. coeff. remaining unchanged.

A. J. E. W.

**Reactions between silica and calcium oxide in aqueous solutions and their relation to puzzuolanic action.** A. E. BETTLICH (J. Amer. Chem. Soc., 1938, 60, 1832—1836).—Electrical conductivity measurements at 30° show that  $SiO_2$  adsorbs CaO in dil. solutions in accordance with the Freundlich isotherm. When the ratio  $CaO/SiO_2 = 0.30-0.60$ , chemical combination occurs, and in the reaction product  $CaO : SiO_2 = 1 : 2$ . This product is stable in solutions containing 1.5 milli-equiv. of CaO per l. When the initial ratio is 0.60—0.90, adsorption occurs again and the product has  $CaO : SiO_2$  4 : 5. This product is stable in solutions containing up to 10 m.-equiv. of CaO per l. A third range of adsorption reactions takes place when the initial ratio is 1.3—3.75 and the  $CaO/SiO_2$  ratio in the product approaches 2 : 1, indicating the probable existence of  $2CaO\cdot SiO_2$  in saturated aq. CaO.

E. S. H.

**Dependence of stabilisation and wetting of particles suspended in oil medium on the quantity of surface-active substance adsorbed.** P. CHOMKOVSKI and P. REHBINDER (Compt. rend. Acad. Sci. U.R.S.S., 1938, 18, 575—578).—The effects of oleic acid on suspensions of pigment particles in PhMe have been investigated. The max. of stabilisation coincides with the min. of wetting by water and with saturation of the surface by adsorbed oleic acid.

F. J. G.

**Surface films of gliadin.** G. I. JENKINS and T. W. J. TAYLOR (Nature, 1938, 142, 291—292).—Data for the spreading of dil. solutions of gliadin in 70% alcohol on 0.01N- $H_2SO_4$  or -HCl substrates for a time interval from 3—1065 min. show no evidence of a transition point such as that reported by Mitchell (A., 1937, I, 511) at 1—2 dynes per cm. Equilibrium is reached in 5 min. For a time interval of 5—70 min. the extrapolated  $\rho$  of the film is fairly const. at  $1.22 \times 10^{-7}$  g. per sq. cm. The fall in  $\rho$  with time is due not to slow spreading but to accidental contamination of the film.

L. S. T.

**Hygroscopicity and hysteresis of mercerised cellulose.** F. I. BOGOLAVLENSKI (Utschen. Zap. Univ. Kazan, 1938, 97, 83—93).—Mercerised cotton wool absorbs  $H_2O$  vapour more readily than untreated cotton wool; its hygroscopicity rises with the alkali concn. and reaches a limit at 4N-NaOH and 6N-KOH, where it is 1.6—1.7 times that for untreated cotton wool. At the same concn. the hysteresis shows a max.

J. J. B.



**Heats of adsorption of alkalis by standard cellulose.** J. L. MORRISON, W. B. CAMPBELL, and O. MAASS (Canad. J. Res., 1938, B, 16, 195—202).—Heats of adsorption have been measured for aq. solutions of LiOH, NaOH, KOH, NaCl, and  $K_2CO_3$  and for a solution containing NaCl and NaOH. The results suggest that the adsorption of alkali depends on the availability of  $H^+$  from the cellulose which, in the presence of a strong base, acts as a weak acid. The  $OH^-$  ion of the base neutralises the  $H^+$  ion and the alkali cation attaches itself to the O of the cellulose very much as in salt formation. The cellulose is very readily hydrolysed. The heats of adsorption agree with this hypothesis. A. J. M.

**Measurement of diffusion coefficients in liquid systems.** S. PLESNIEWICZ (Congr. int. Chim. pura apl., 1934, 9, II, 237—248; Chem. Zentr., 1936, ii, 2317; cf. A., 1936, 1071).—Data for aq.  $CdCl_2$ ,  $K_2Cr_2O_7$ ,  $K_3Fe(CN)_6$ , and  $K_4Fe(CN)_6$  are recorded. A. J. E. W.

**Diffusion of non-electrolytes in organic liquids.** O. LAMM (Trans. Faraday Soc., 1938, 34, 1152—1158).—A crit. discussion of published work. E. S. H.

**Diffusion of water in glycerol.** O. LAMM and G. SJÖSTEDT (Trans. Faraday Soc., 1938, 34, 1158—1163).—The rate of diffusion, measured by a refractometric method, is abnormally high, indicating that the  $H_2O$  mols. are not bound to glycerol mols., and that the diffusibility of  $H_2O$  is not determined simply by the  $\eta$  of glycerol. E. S. H.

**Diffusion of electrolyte solutions.** K. SITE and V. DANIEL (Z. physikal. Chem., 1938, 182, 295—318).—The diffusion of electrolytes is treated theoretically, and it is inferred that in the limiting case of very dil. solutions it should follow a law  $D = D_0(1 + A\sqrt{c})$ , where  $D$  and  $D_0$  are the diffusion coeffs. at concn.  $c$  and at infinite dilution, respectively, and  $A$  is a const. The diffusion of LiCl, LiBr, NaCl, NaBr, NaI, KCl, KBr, and KI in aq. solution has been measured by Zuber's micro-method. At very low concn. the ideal law holds, but even at 0.05M the diffusion const. is  $>$  the theoretical val., and the divergences increase with concn. This behaviour is attributed to ionic association and reciprocal action with the  $H_2O$  dipoles. The diffusion coeffs. of LiCl in MeOH and EtOH and of NaI in EtOH are  $\gg$  the vals. predicted theoretically. The movement of ions in these solvents can be explained on the basis of interionic force and of forces between particles and dipoles of the solvent. It is unnecessary to assume sp. forces in  $H_2O$  or in the alcohols. J. W. S.

**Osmosis.** E. ERNST and J. KOCZKÁS (Z. Physik, 1938, 109, 625—641).—It is shown theoretically and experimentally that osmosis is not explainable in terms of the kinetics of the solute, but by the relations between the v.p. of the solvent on opposite sides of the membrane, such that when solutions of the same concn. and different temp. are separated by a membrane, solvent flows from the solution at the highest temp. L. G. G.

**Partial molal volumes of lithium chloride and of sodium nitrate in liquid monomethylamine.**

E. A. KELSO [with W. A. FELSING] (J. Amer. Chem. Soc., 1938, 60, 1949—1951).—The  $d$  of the solutions have been determined at 0—25° and recorded as functions of concn.; the apparent and partial mol. vols. have been calc. In LiCl solutions the apparent mol. vol. decreases as the dielectric const. of the solvent decreases in the order  $H_2O$ , MeOH, EtOH,  $NH_2Me$ . E. S. H.

**Densities, viscosities, and conductivities of alcoholic solutions of magnesium chloride.** F. OLMER (Bull. Soc. chim., 1938, [v], 5, 1178—1184).—Data for seven alcohols at 17° are graphically presented. The hexahydrate is more sol. than the anhyd. salt in primary alcohols. C. R. H.

**Viscosity and density of aqueous solutions of weak electrolytes at 35°.** M. K. SRINIVASAN and B. PRASAD (Trans. Faraday Soc., 1938, 34, 1139—1141).—For weak electrolytes the Jones and Dole equation assumes the form  $\eta/\eta_0 = 1 + A\sqrt{zc} + \beta(1 - \alpha)c$ , where  $A$  has the customary meaning. Vals. determined for  $A$  are: AcOH 0.020, salicylic acid 0.03, succinic acid 0.02, BzOH 0.00. The calc. val. for AcOH is 0.0031, and those for the other acids should be of the same order. In each case  $d$  varies linearly with concn. for dil. solutions. E. S. H.

**Optical properties of turbid liquids observed by reflexion; influence of dilution.** L. AMY (Compt. rend., 1938, 207, 329—331).—The colour of typical suspensions is found to be independent of the dilution. A. J. E. W.

**Aqueous solutions of acids of high mol. wt. and their salts.** W. KERN (Angew. Chem., 1938, 51, 566—569).—Although the conductivity of such solutions does not depend on the degree of polymerisation of the anion, acids of high mol. wt. act as cation buffers in osmotic pressure measurements. The expression for the dissociation of such polybasic acids resembles the Michaelis equation for monobasic acids. K. W. P.

**Highly-polymerised compounds. CXCVIII. Dependence on temperature of osmotic pressure, heat of dilution, and entropy of dilution of high-molecular solutions.** G. V. SCHULZ (Z. physikal. Chem., 1938, B, 40, 319—325).—Equations are derived and successfully applied to earlier data (cf. A., 1937, I, 563). C. R. H.

**Conductivity anomalies (field and frequency effects) in molecularly and colloiddally disperse solutions.** K. HOFFMANN (Kolloid-Z., 1938, 84, 344—357).—A review.

**Gas colloids.** R. HAUL (Chem.-Ztg., 1938, 62, 581—584).—A general discussion of aerosols. F. L. U.

**Pure silver iodide sols.** H. DE BRUYN and J. T. G. OVERBEEK (Kolloid-Z., 1938, 84, 186—191).—AgI sols, after prolonged purification by electro-dialysis and electrodecantation, show departures from the behaviour of strong acids when submitted to electrometric titration. The observed deviations have been traced to the presence of  $Zn^{++}$  and  $Cu^{++}$  in the wash  $H_2O$ . The use of doubly distilled  $H_2O$  affords sols in which  $>98\%$  of the "gegenions" consist of  $H^+$ . F. L. U.



**Magnetic birefringence of colloidal solutions of iron oxide.** J. ERRERA, W. OOSTVEEN, and H. SACK (Rec. trav. chim., 1938, 57, 850).—An error in a previous paper (A., 1938, I, 194) is corr. F. L. U.

**Stability of colloidal solutions.** J. DUCLAUX (J. Chim. phys., 1938, 35, 185—188).—The stability of a colloidal solution, defined as the osmotic work required to separate the micelles and the intermicellar liquid, varies considerably from one colloidal solution to another. It is greater for dil. solutions than for more conc. ones, and varies, within a certain limit, with log concn. The stability is also governed by the mol. wt. of the colloid and its degree of ionisation. There is no direct relationship between the electrokinetic potential or the hydration and the stability of the colloidal solution, although these are indirectly connected with it. A. J. M.

**Dispersion of solids in liquids by ultrasonic waves.** K. SÖLLNER (Trans. Faraday Soc., 1938, 34, 1170—1174).—Solids of low cohesion (e.g., mica, gypsum, graphite, S) are dispersed in liquids by the action of ultrasonic waves. The dispersions contain particles of colloidal size; the dispersed particles are further disintegrated when irradiated with ultrasonic waves of high energy. E. S. H.

**Thixotropy.** C. W. KORRENS and H. G. F. WINKLER (Naturwiss., 1938, 26, 517).—Colloidal particles which are flat or rod-shaped (kaolin, halloysite, meta-halloysite, muscovite, glauconite, graphite, Mo glance, tremolite) show thixotropy in  $H_2O$ . Approx. isometric sols, e.g., powdered quartz, feldspar, and fluor spar, do not show thixotropy. The thixotropy is the greater the smaller is the size of the particle, and for small particle size the relationship is linear. Electrolytes are unnecessary. Their effect varies and does not follow the coagulation series. Thixotropy also occurs in all org. liquids investigated, and may be greater here than in  $H_2O$ . It is possible to make quartz, feldspar, and fluor spar particles of diameter 1—6  $\mu$ , show thixotropy in  $C_6H_6$ . It is inferred that all substances will show the phenomenon in a suitable liquid if the particle size is small enough. A. J. M.

**Electrochemistry of Congo dye sols.** W. PAULI and P. SZARVAS (Kolloid-Z., 1938, 84, 179—186).—In Congo-blue sols (obtained by electrodialysis of Congo-red) the H-ion activity calc. from conductivity measurements is < that determined potentiometrically, and the inequality persists at the highest dilution used ( $3 \times 10^{-5}M$ ). Potentiometric titration with NaOH indicates, in the region  $p_H$  10—12, additional alkali fixation up to a limit of 4 NaOH:1 mol. dye. These results are interpreted in relation to the chemical constitution of the dye. F. L. U.

**Lyotropic series in swelling.** XIII. Effect of salts of alkylamines.—See A., 1938, III, 842.

**Influence of colloids on cathodic polarisation. Electrodeposition of silver in presence of Paal's mixture.** G. S. VOZDVISHENSKI (Utschen. Zap. Univ. Kazan, 1937, 97, No. 8, 51—54; cf. B., 1937, 146).—Paal's mixture increases the cathodic polarisation of Ag in  $AgNO_3$  solutions. J. J. B.

**Structural viscosity and properties of cellulose esters.** IV. Change in viscosity of concentrated solutions of cellulose nitrates. Z. ROGOVIN and S. GLAZMAN (J. Gen. Chem. Russ., 1938, 8, 498—506; cf. B., 1938, 357).—The  $\eta$  of 12% solutions of cellulose nitrate (I) in a series of solvents falls with time to an extent which diminishes in the series  $COMe_2 > EtOH-Et_2O > MeOH > EtOAc$ . The effect is not due to elimination of  $HNO_3$ , but appears to be associated with change in the shape of the (I) mols. R. T.

**Variations in viscosity of cellulose nitrate sols.** III. Cellulose nitrate of lowered viscosity. A. A. MOROZOV, A. V. PAMFILOV, and A. G. SCHICHER (J. Gen. Chem. Russ., 1938, 8, 572—577; cf. A., 1938, I, 311).—The gradual fall in  $\eta$  of sols of cellulose acetate or nitrate in various solvents is ascribed to the slowness of the dissolution process. R. T.

**Optical properties of cellulose dispersed in cuprammonium hydroxide solution.** J. COMPTON (J. Amer. Chem. Soc., 1938, 60, 1807—1812).— $[\alpha]$  for cellulose-cuprammonium hydroxide dispersions (A) is unchanged by pre-treatment of the cellulose with HCl, NaOCl, or  $H_2O_2$ ; the reduction in  $\eta$  caused thereby is due to destruction of the "cementing" material and not to any effect on the crystallites. (A) are not true solutions, for the no. of crystallites present may be counted under high magnification using the slit ultramicroscope; this no. is that theoretically expected for crystallites  $1.1 \times 1.5 \mu$ . The crystallites have all the properties of Hess' micelles, excepting the shape and size. Evidence is adduced to show that cellulose-Cu complex formation precedes dispersion in cuprammonium hydroxide solution.  $[\alpha]$  vals. for cellodextrin-cuprammonium hydroxide dispersions are < those for (A); the cellodextrin particles therein are too small to be made visible by the ultramicroscope. R. S. C.

**Lyophilic properties of cellulose and its derivatives.** XVI. Absorption of the vapours of various liquids. K. KANAMARU and J. CHAO (J. Soc. Chem. Ind. Japan, 1938, 41, 171—182B).—Determinations have been made of the absorption isotherms at 30° of the vapours of  $H_2O$ , MeOH, EtOH,  $Pr^oOH$ ,  $Bu^oOH$ ,  $Et_2O$ ,  $COMe_2$ ,  $C_6H_6$ , AcOH, and  $CHCl_3$  on cellulose (I) in various forms, including regenerated (I), and on (I) acetates and nitrates of various degrees of esterification and in various mechanical forms. Comparisons are made of the absorptions at 20 and 90% relative v.p. Regenerated (I) has a higher hygroscopicity than ordinary (I), but absorbs smaller amounts of org. liquids, particularly at low v.p. At a low v.p. the absorption of an org. vapour by a material in film form is generally lower than that by the same material in the fibrous condition, but this tendency is reversed at a high v.p. There is no simple relation between the solubility of a (I) ester in an org. liquid and the absorption of the corresponding vapour. Calculations are made for each system of two quantities stated to be  $\propto \zeta$ -potential (A., 1938, I, 396, 456). Comparison of these quantities with the mol. % absorptions supports the view that the lyophilic properties of (I) and its derivatives depend on the  $\zeta$ -potential. W. A. R.



**Mechanism of action of neutral salts on collagen.** S. A. PAVLOV (J. Gen. Chem. Russ., 1938, 8, 456—459).—The peptising action on collagen of bivalent is  $>$  that of univalent cations. The  $\text{NH}_2\text{-N}$  of the solutions as determined by Van Slyke's method differs considerably from that derived from Sørensen titration of  $\text{CO}_2\text{H}$  groups. The action of neutral salts is supposed to consist in the removal of polypeptide fragments, and possibly in their cyclisation.

R. T.

**Charge-reversing concentrations of alkali and alkaline-earth chlorides for tri- and hexahydroxystearate at varying  $p_{\text{H}}$ .** P. H. TEUNISSEN, S. ROSENTHAL, and W. H. ZAAIJER (Rev. trav. chim., 1938, 57, 929—940).—Electrophoretic measurements with  $\text{SiO}_2$  particles coated with tri- (I) or hexa- (II) hydroxystearate in presence of alkali or alkaline-earth ions show a tendency for the order of the lyotropic series to be reversed with increasing OH content of the acid, the tendency being weak at  $p_{\text{H}}$  10 and pronounced at  $p_{\text{H}}$  6. In this respect (I) and (II) form a transition between oleic and arabic acids; thus in an acid medium the order is for oleate  $\text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$ , for (I)  $\text{Ca} < \text{Mg} < \text{Sr} < \text{Ba}$ , for (II)  $\text{Ba} < \text{Ca} < \text{Sr} < \text{Mg}$ , and for arabate  $\text{Ba} < \text{Sr} < \text{Ca} < \text{Mg}$ . It is inferred that the polarisability of the  $\text{CO}_2\text{H}$  is diminished by introduction of OH.

F. L. U.

**Physical chemistry of amino-acids, peptides, and related substances. XI. Solubility of cysteine in presence of ions and another dipolar ion.** E. V. COHN, T. L. McMECKIN, and M. M. BLANCHARD (J. Gen. Physiol., 1938, 21, 651—663).—Both glycine (I) and neutral salts increase the solubility of cysteine (II) at all concns. The interaction between (II) and ions is diminished by (I); increase in ionic strength diminishes the interaction of (I) and (II).  $\text{Na}_2\text{SO}_4$  increases the solubility of (II), but above 1 mol. per l. it has a salting-out effect, enhanced by (I). These interactions are analysed mathematically and discussed in detail.

A. E. W.

**Adsorption of proteins of oil-water interfaces and artificial proteins-lipin membranes.** I. LANGMUIR and D. F. WAUGH (J. Gen. Physiol., 1938, 21, 745—755).—Experiments of Devaux (A., 1935, 819, 1071) on the formation of insol. protein fibres at air- $\text{H}_2\text{O}$  and oil- $\text{H}_2\text{O}$  interfaces are repeated and confirmed. Attempts were made, with some success, to build up pure protein membranes on Pt-wire loops passed through a protein film adsorbed at an oil- $\text{H}_2\text{O}$  interface. The most durable membranes were obtained when the protein films were pre-stretched, and when lecithin was present. A mixture of  $\text{C}_6\text{H}_6$  and  $\text{CCl}_4$  in  $\text{H}_2\text{O}$  forms a stable suspension when it is shaken with a few drops of 1% albumin solution. The large drops of hydrocarbon are almost motionless in the aq. phase, and are not uniformly spherical (i.e., the surface tension is zero). In many instances a droplet of  $\text{H}_2\text{O}$  is seen inside the hydrocarbon drops. It is suggested that perfusion of such double drops with  $\text{H}_2\text{O}$  would dissolve out the hydrocarbons, leaving a double shell of protein rather like a cell wall. Further biological applications of these experiments are suggested.

A. E. W.

**Electrokinetic phenomena. XIII. Comparison of isoelectric points of dissolved and crystalline amino-acids.** H. A. ABRAMSON and L. S. MOYER (J. Gen. Physiol., 1938, 21, 729—744).—The isoelectric points of the surfaces of cryst. tyrosine (I), cystine (II), and aspartic acid all lie near  $p_{\text{H}}$  2.3, although the isoelectric points of the dissolved substances differ widely. Crystals of (I) and (II) adsorb gelatin (III), the surface attained being identical with (III)-coated quartz or colloidion particles. Al ions reduce the electric mobility of (I) crystals to zero in a manner analogous to their effect on other surfaces. The relations of these results to the concept and general definition of the isoelectric points is discussed.

A. E. W.

**Application of cryolysis to humus complexes.** C. ANTONIANI (Naturwiss., 1938, 26, 479).—Changes occurring in the degree of dispersion of colloidal humus complexes on freezing have been investigated by determining the velocity of electrophoretic migration before and after freezing. Freezing causes an increase in the velocity of migration and hence increases the dispersion of the colloidal particles.

A. J. M.

**Vapour retention capacity of active gels.** F. KRCZIL, F. SCHÄTZLER, and E. BRIKEL (Kolloid-Z., 1938, 84, 144—149).—The amount of  $\text{C}_6\text{H}_6$  vapour retained by active  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  gels after passage of a stream of air is ultimately independent of the initial vapour-charge. As with active C (A., 1934, 358) differences are observed only in the early stages of desorption.

F. L. U.

**Quantitative study of rhythmic precipitation.** K. NEUMANN and V. COSTEANU (Kolloid-Z., 1938, 84, 130—138).—The time of formation and linear separation of the rings formed by  $\text{AgNO}_3$  diffusing into capillary tubes containing  $\text{K}_2\text{CrO}_4$ -gelatin have been measured for different concns. of the reactants and at different temp. The results are in harmony with the supersaturation theory. The empirical relation between time, separation, and ordinal no. of the rings found by Lakhani and Mathur (A., 1934, 488) is derived theoretically.

F. L. U.

**Interference patterns with Liesegang rings.** (Sir) C. V. RAMAN and K. SUBBARAMIAH (Nature, 1938, 142, 355).—Liesegang rings of  $\text{AgCl}$  or  $\text{Ag}_2\text{CrO}_4$  in gelatin show an interference pattern with characteristic discontinuity of phase on either side of a line of zero disturbance.

L. S. T.

(A) **Silver chromate banding in silicic acid gel.**  
(B) **Calcium phosphate banding in silicic acid gel.**  
T. ISEMURA (Bull. Chem. Soc. Japan, 1938, 13, 489—493, 493—504).—(A) Rhythmic ppts. are formed by adding  $\text{AgNO}_3$  to  $\text{Na}_2\text{SiO}_3$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  in presence of 0.6—0.7N- $\text{HNO}_3$  (cf. Hatschek, A., 1926, 349). At lower acid concn. there is no banding, and gelatinisation does not occur at higher concn. Other acids may be used.

(B) Two methods are described for preparing rhythmic ppts. from  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Na}_2\text{HPO}_4$ , 0.75N- $\text{AcOH}$ , and  $\text{Na}_2\text{SiO}_3$ . The bands are not obtained with higher or lower acid concn. but either  $\text{Ca}(\text{NO}_3)_2$  or  $\text{Na}_2\text{HPO}_4$  may be used as inner electrolyte. The



varying appearance of the bands with varying concn. of inner electrolyte and gel, and with addition of sucrose, glucose,  $\text{CO}(\text{NH}_2)_2$ , KBr, and NaCl, are recorded. Ageing of the gel produces no effect.

F. R. G.

**Colloid-chemical investigation of Chistopol floridin clays.** G. S. VOZDVISHENSKI and A. F. GERASIMOV (Utschen. Zap. Univ. Kazan, 1937, 97, No. 8, 33—50).—The rate of sedimentation is measured and the particle sizes are calc. The rate is strongly increased by dialysis. It is increased by salts according to the series  $\text{HCl} > \text{H}_2\text{SO}_4 > \text{K}_2\text{SO}_4 > \text{KCl} > \text{KH}_2\text{PO}_4 > \text{NaCl} > \text{Na}_2\text{SO}_4 > \text{Li}_2\text{SO}_4$ , is little affected by gelatin and agar, and decreased by  $\text{NH}_3$ , LiOH, NaOH, and KOH.

J. J. B.

**Micellar structure of hydrous cellulose gels.** P. H. HERMANS (Kolloid-Z., 1938, 84, 168; cf. A., 1938, I, 79).—An acknowledgment of a paper by Gerngross and others (A., 1932, 1088).

F. L. U.

**Micellar structure and deformation processes in fibrous materials.** V. Theory of structural network. O. KRATKY (Kolloid-Z., 1938, 84, 149—168; cf. A., 1937, I, 515).—The behaviour of a fibrous network during swelling and mechanical deformation is discussed theoretically.

F. L. U.

**Space model of viscosity function of disperse systems.** F. FRIMBERGER and J. REHME (Kolloid-Z., 1938, 84, 196—199).—Three-dimensional models showing the relations between total  $\eta$ ,  $\eta$  of the dispersion medium, and vol. of disperse phase are described. Their use is illustrated by reference to suspensions of red blood corpuscles in gum arabic solutions.

F. L. U.

**Structure mechanics of viscous-elastic continua. II. Wave-mechanical theorem of turbulence.** H. UMSTÄTTER (Kolloid-Z., 1938, 84, 168—179; cf. A., 1936, 795).—Mathematical.

F. L. U.

**Dissociation coefficient of hypobromous acid.** E. A. SCHILOV and J. N. GLADTSCHIKOVA (J. Gen. Chem. Russ., 1938, 8, 448—451).— $K$  is  $2.06 \times 10^{-9}$ , at  $20^\circ$ .

R. T.

**Dissociation constants of deutero-acids by e.m.f. measurements.** C. K. RULE and V. K. LA MER (J. Amer. Chem. Soc., 1938, 60, 1974—1981).—The cells investigated by Korman and La Mer (A., 1936, 1202) have been re-examined. The ratio of dissociation consts. in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  has been determined for  $\text{BzOH}$ ,  $\text{H}_2\text{PO}_4'$ , and quinol and compared with published data for  $\text{AcOH}$  and  $\text{CH}_2\text{Cl-CO}_2\text{H}$ . The ratio decreases as the strength of the acid increases and may become unity for acids as strong as  $\text{H}_3\text{O}^+$ .

E. S. H.

**Acid dissociation constants in dioxan-water mixtures. Correction of dissociation constant of benzoic acid.** C. C. LYNCH and V. K. LA MER (J. Amer. Chem. Soc., 1938, 60, 2000).—A correction (cf. A., 1938, I, 358).

E. S. H.

**Electrometric and ultra-violet spectrographic investigation of some  $\alpha$ -ketonic ene-diols.** G. E. CARPÉNI (J. Chim. phys., 1938, 35, 193—211; cf. A., 1938, I, 399; II, 347).—The dissociation consts. and

K K (A., I.)

the ultra-violet absorption spectra of *l*-ascorbic, *d*-arabo-ascorbic, *d*-gluco-ascorbic acids, reductone, reductinic, croconic, and rhodizonic acids have been determined. The first dissociation consts. of the products obtained by oxidising the first six of these with I have also been obtained. The order of magnitude of the second dissociation consts. was obtained from a study of the ultra-violet absorption of their solutions. The characteristic absorption bands for the ene-diols vary with  $p_H$ , the effect being due to variation in the absorption due to the undissociated mols., the univalent ions, and the bivalent ions.

A. J. M.

**Electrolytic dissociation of cadmium iodide.** Y. DOUCET (Compt. rend., 1938, 207, 362—364).—Results of cryoscopic measurements for solutions of  $\text{CdI}_2$  in  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  are recorded. The vals. of  $f$  are confirmed by e.m.f. measurements. The data suggest the presence of two ions for  $c = 0.12$ — $0.30$  mol. per l., and up to six ions for more dil. solutions; a similar result is obtained with solutions of  $\text{CdI}_2$  in  $\text{KNO}_3$ — $\text{H}_2\text{O}$  eutectic. The results suggest the existence of  $\text{Cd}[\text{CdI}_4]$  in conc. solutions, the complex  $\text{CdI}_4$  dissociating at high dilutions.

A. J. E. W.

**Activity coefficient of cobalt chloride in aqueous solution at  $25^\circ$ .** R. A. ROBINSON (Trans. Faraday Soc., 1938, 34, 1142—1143).—Data determined by the isopiestic v.p. method for 0.05—2M. solutions are recorded. The results appear to indicate complete dissociation.

E. S. H.

**Application of the Raman effect to the study of complexes existing in solutions containing mercuric iodide and an alkali iodide.** (Mlle.) M. L. DELWAULLE, F. FRANÇOIS, and J. WIEMANN (Compt. rend., 1938, 207, 340—342).—Raman  $\nu$  attributed to  $\text{HgI}_4''$  and  $\text{HgI}_3'$  are exhibited by solutions containing both  $\text{HgI}_2$  and LiI in  $\text{H}_2\text{O}$ , alcohols, and  $\text{COMe}_2$ . The  $\text{HgI}_3'$   $\nu$  is also shown by cryst.  $\text{KI} \cdot \text{HgI}_2 \cdot \text{H}_2\text{O}$ , suggesting that this ion may also contain a solvent mol.  $\text{HgI}_4''$  probably has a tetrahedral structure.

A. J. E. W.

**Polyiodides and polyiodide ions. Cæsium polyiodides.** G. VENTURELLO (Gazzetta, 1938, 68, 394—404).—Vals. of  $d$  and of  $\eta$  at  $25^\circ$  for solutions of  $\text{CsI} + \text{I}_2$  in aq. alcohol (57.9 vol.-% EtOH) are recorded. These indicate the presence of  $\text{I}_3'$ ,  $\text{I}_5'$ , and  $\text{I}_7'$  ions, but not of  $\text{I}_4'$  or  $\text{I}_9'$ . The viscosity of  $\text{CsI}$  solutions in the above solvent decreases with increasing concn.

O. J. W.

**Equilibria in chromic acid and dichromate solutions.** E. ENDRÉDY (Math. nat. Anz. ung. Akad. Wiss., 1936, 54, 459—493; Chem. Zentr., 1936, ii, 1684).—In aq. solutions of  $\text{CrO}_3$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  an equilibrium between  $\text{Cr}_2\text{O}_7''$  and  $\text{HCrO}_4'$  ions is established, the const. for which varies only slightly with the temp. The concn.-dependence of the conductivity, of the mol. vol., and of the absorption spectrum is explained in terms of this equilibrium. The vals. of the ionic mobility of  $\text{HCrO}_4'$  and  $\text{Cr}_2\text{O}_7''$  at  $20^\circ$  are 49.5 and 62—63, respectively.

H. J. E.

**Constitution of double-shelled complex compounds.** Á. VON KRSS and D. VON CZEGLÉDY (Z. anorg. Chem., 1938, 239, 27—38).—Extinction curves



from 200 to 700  $\mu\mu$ . for the  $[\text{Co}(\text{NH}_3)_6]^{+++}$ ,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{++}$ ,  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{++}$ ,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{++}$ , and  $[\text{Co}(\text{NH}_3)_4\text{CO}_3]^{+}$  ions in  $4\text{N}-(\text{NH}_4)_2\text{SO}_4$ ,  $3\text{N}-\text{K}_2\text{HPO}_4$ ,  $3\text{N}-\text{K}_2\text{C}_2\text{O}_4$ ,  $4\text{N}-\text{NaCl}$ , and  $3\text{N}-\text{Na}_2\text{S}_2\text{O}_3$  have been determined and compared with those in  $\text{H}_2\text{O}$ . The curves resemble those in  $\text{H}_2\text{O}$  for all five complex ions in  $(\text{NH}_4)_2\text{SO}_4$ , for the  $[\text{Co}(\text{NH}_3)_6]^{+++}$  and  $[\text{Co}(\text{NH}_3)_4\text{CO}_3]^{+}$  ions in  $\text{NaCl}$  and  $\text{K}_2\text{HPO}_4$ , and for the  $[\text{Co}(\text{NH}_3)_4\text{CO}_3]^{+}$  ion in  $\text{K}_2\text{C}_2\text{O}_4$ . In other instances more or less pronounced changes are found. The bearing of these results on the nature of the complex ion in solution is discussed. Where the curves are unchanged a heteropolar double-shelled complex anion is formed. In the other instances the changes are not attributed to a homopolar character of the double-shelled complex, but to changes in the cobalt-ammine unit, such as the replacement of chloro- or aquo-groups by hydroxo- or oxalato-groups, followed by formation of a heteropolar double-shelled complex involving the new cobaltammine unit. F. J. G.

**Water as an admixture in liquid sulphur dioxide.** K. WICKERT (Z. anorg. Chem., 1938, **239**, 89–94).—The equilibrium between liquid  $\text{SO}_2$  and  $\text{H}_2\text{O}$ , and the behaviour of solutions of  $\text{H}_2\text{O}$  in liquid  $\text{SO}_2$ , have been investigated. At  $22^\circ$  the liquid layers contain 2.3 g. of  $\text{H}_2\text{O}$  per 100 g. of  $\text{SO}_2$ , and 49.1 g. of  $\text{SO}_2$  per 100 g. of  $\text{H}_2\text{O}$ , respectively. On evaporation at  $0^\circ$  of liquid  $\text{SO}_2$  saturated with  $\text{H}_2\text{O}$  crystals remain of the compound  $\text{SO}_2\cdot\text{H}_2\text{O}$ , which decomposes at  $12^\circ$ . Anhyd.  $\text{SO}_2$  has  $\chi = 0.1 \times 10^{-6} \omega^{-1}$  independently of temp. from  $-20^\circ$  to  $30^\circ$ ; solutions of  $\text{H}_2\text{O}$  in  $\text{SO}_2$  have a greater  $\chi$  which increases with rising temp. When the solutions are electrolysed, gas is evolved at the anode and S is deposited at the cathode. These results are interpreted by regarding  $\text{SO}_2\cdot\text{H}_2\text{O}$  as thionyl hydroxide,  $\text{SO}(\text{OH})_2$ , ionising to  $\text{SO}^{2+} + 2\text{OH}^-$ , which are discharged on electrolysis as follows:  $2\text{SO}^{2+} + 2\ominus = \text{SO}_2 + \text{S}$ ;  $2\text{OH}^- + 2\oplus = \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$ . When a sealed tube containing  $\text{SO}_2$ ,  $\text{KBr}$ , and  $\text{H}_2\text{O}$  is left for some weeks  $\text{KHSO}_3$  is pptd. in accordance with:  $\text{SO}(\text{OH})_2 + 2\text{KBr} = \text{SOBr}_2 + 2\text{KOH}$  and  $\text{KOH} + \text{SO}_2 = \text{KHSO}_3$ . F. J. G.

**Volatility of boric acid in presence of various salts. Borophosphates and boroarsenates.** V. G. R. LEVI and R. CURTI (Gazzetta, 1938, **68**, 376–380; cf. A., 1938, I, 354).—The volatility of  $\text{H}_3\text{BO}_3$  from aq. solution at the b.p. is increased by those salts which diminish the solubility, and vice versa. Substances which can form complexes with  $\text{H}_3\text{BO}_3$  lower its volatility. In presence of Na salts of  $\text{H}_3\text{PO}_4$  and of  $\text{H}_3\text{AsO}_4$  it is found that borophosphoric and boroarsinic acids can be detected in sufficiently conc. solutions even at the b.p. O. J. W.

**Selenious acid.** F. ISHIKAWA and H. ABE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1938, **34**, 775–786; cf. A., 1913, ii, 948; 1922, ii, 283).—Tensimetric measurements show that the dissociation pressure (mm.) of  $\text{H}_2\text{SeO}_3$  can be expressed below  $70^\circ$  by  $\log p = -3516.94/T + 11.9024$  and above  $70^\circ$  by  $\log p = -188615/T + 7.1520$ . Above  $71^\circ$ ,  $\text{H}_2\text{SeO}_3$  is unstable with respect to  $\text{SeO}_2$ ; this is indicated by a break in the  $\log p-1/T$  plot, and supported by analysis of the solid phase produced when  $\text{H}_2\text{SeO}_3$  is heated with a small quantity of  $\text{H}_2\text{O}$  for

48 hr. at  $80^\circ$ . Measurements of the solubility of  $\text{H}_2\text{SeO}_3$ , and of the v.p. of its saturated solutions, have been made; the results are considered to be more accurate than those in the literature since great care was taken to ensure equilibrium conditions.

R. C. M.

**Properties of osmium tetroxide in carbon tetrachloride solutions. Thermodynamic constants of osmium tetroxide.** L. H. ANDERSON and D. M. YOST (J. Amer. Chem. Soc., 1938, **60**, 1822–1825).—The distribution ratios of  $\text{OsO}_4$  between  $\text{CCl}_4$  and  $\text{H}_2\text{O}$  at  $25^\circ$  have been determined at different concns. up to the saturated solutions. V.p. of  $\text{CCl}_4$  over solutions containing  $\text{OsO}_4$  have been determined at  $25^\circ$ ; the results are not in accordance with Raoult's equation. The free energies of formation of solid, gaseous, and aq.  $\text{OsO}_4$ , calc. from electron-diffraction, spectroscopic, and thermal data, are:  $-70,900$ ,  $-28,000$ , and  $-68,788$  g.-cal. E. S. H.

**Transition temperature of magnesium bromide.** F. H. GETMAN (Rec. trav. chim., 1938, **57**, 847–849).—The transition temp. corresponding with  $\text{MgBr}_2\cdot 10\text{H}_2\text{O} \rightleftharpoons \text{MgBr}_2\cdot 6\text{H}_2\text{O} + 4\text{H}_2\text{O}$ , determined thermometrically, is  $10.84^\circ$ . The temp. previously deduced (A., 1936, 30) from solubility data is incorrect.

F. L. U.

**System Cr-P.** H. NOWOTNY and E. HENGLEIN (Z. anorg. Chem., 1938, **239**, 14–16).—The system has been analysed by the X-ray method from 0 to 50 at.-% P. In addition to CrP (cf. A., 1987, ii, 265; 1931, 809) there is a compound  $\text{Cr}_3\text{P}$ . It is a light grey powder, very faintly ferromagnetic, and isomorphous with  $\text{Fe}_3\text{P}$ , i.e., space-group  $S_6^2$ , with 8 mols. in the unit cell and  $a$  9.126,  $c$  4.560 Å. CrP is dark grey, non-ferromagnetic, and isomorphous with MnP, having space-group  $D_{2d}^{10}$  with 4 mols. in the unit cell and  $a$  5.93,  $b$  5.35,  $c$  3.12 Å. F. J. G.

**X-Ray investigation of the system Co-S.** D. LUNDQVIST and A. WESTGREN (Z. anorg. Chem., 1938, **239**, 85–88).—The only compound phases in the temp. interval  $500$ – $650^\circ$  are  $\text{Co}_9\text{S}_8$ ,  $\text{CoS}$ ,  $\text{Co}_3\text{S}_4$ , and  $\text{CoS}_2$ .  $\text{Co}_9\text{S}_8$  has  $a$  9.907 Å., whether formed in presence of excess of Co or of CoS, and irrespective of its thermal history. CoS when tempered at  $650^\circ$  has  $a$  3.367,  $c$  5.177 Å. if saturated with Co, and  $a$  3.361,  $c$  5.160 Å. when saturated with S, the homogeneous region extending from 51 to 53 at.-% S. On prolonged tempering at  $200^\circ$  it changes over from the NiAs structure to a complicated structure which has not been analysed. The existence of  $\text{Co}_3\text{S}_4$  (cf. A., 1927, 502; 1935, 1335) is confirmed; it is face-centred cubic with  $a$  9.382 Å., space-group  $O_7^4$ , 8 mols. in the unit cell. The structure found for  $\text{CoS}_2$  agrees with that given by de Jong and Willems (A., 1927, 328) but the val. found for  $a$  is 5.524 Å. instead of 5.64 Å. F. J. G.

**Carbide studies by the methane method. II. [System Mn-C.]** R. SCHENCK and K. MEYER (Z. anorg. Chem., 1938, **239**, 161–179).—The system Mn-C has been investigated by measurements of the  $\text{CH}_4$ - $\text{H}_2$  equilibrium over it at  $700$ – $970^\circ$ .  $\text{Mn}_3\text{C}$  exists as a stable phase above  $750^\circ$ , and forms solid solutions with its constituents. Below  $750^\circ$   $\text{Mn}_4\text{C}$



appears as a metastable phase. An equilibrium diagram is given. F. J. G.

**Cyanic acid. III. Melting system cyanic acid-water.** M. LINHARD (Z. anorg. Chem., 1938, 239, 155—160; cf. A., 1938, II, 352).—HCNO and H<sub>2</sub>O form a simple eutectiferous system; HCNO melts at  $-86.8^\circ$ , and the cryohydric point corresponds with  $-102^\circ$  and 67 mol.-% of HCNO. There are no indications of the formation of hydrates or of NH<sub>2</sub>·CO<sub>2</sub>H. F. J. G.

**System KCl-KHCO<sub>3</sub>-H<sub>2</sub>O between  $10^\circ$  and  $40^\circ$ .** R. PARIS and P. MONDAIN-MONVAL (Bull. Soc. chim., 1938, [v], 5, 1142—1147).—Data obtained at four temp. are recorded. Only KCl and KHCO<sub>3</sub> are present as solid phases. C. R. H.

**Equilibrium and formation of complexes in the system H<sub>2</sub>O-NH<sub>4</sub>NO<sub>3</sub>-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.** V. A. SOKOLOV (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 123—135).—Solubility data have been obtained from  $70^\circ$  to  $-22.4^\circ$ . The existence of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·3NH<sub>4</sub>NO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·2NH<sub>4</sub>NO<sub>3</sub>, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·NH<sub>4</sub>NO<sub>3</sub> is confirmed by thermal and X-ray analysis. The regions of stability of the double salts have been determined. E. S. H.

**Solubility curves of secondary and tertiary potassium orthophosphate in water.** M. I. RAVITSCH (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 137—146).—The data show that the stable phases are: K<sub>2</sub>HPO<sub>4</sub>·6H<sub>2</sub>O ( $-13.5^\circ$  to  $14.3^\circ$ ), K<sub>2</sub>HPO<sub>4</sub>·3H<sub>2</sub>O ( $14.3$ — $48^\circ$  approx.), K<sub>2</sub>HPO<sub>4</sub> ( $> 48^\circ$ ), K<sub>3</sub>PO<sub>4</sub>·9H<sub>2</sub>O ( $-24^\circ$  to  $-15^\circ$ ), K<sub>3</sub>PO<sub>4</sub>·7H<sub>2</sub>O ( $-15^\circ$  to  $45.4^\circ$ ), K<sub>3</sub>PO<sub>4</sub>·3H<sub>2</sub>O ( $> 45.4^\circ$ ). E. S. H.

**Crystallographic study of solid phases of the system K<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub>-H<sub>2</sub>O.** G. B. BOKI and E. E. BUROVAJA (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 185—194).—Crystallographic data are recorded for K<sub>3</sub>PO<sub>4</sub>·3H<sub>2</sub>O, K<sub>3</sub>PO<sub>4</sub>·7H<sub>2</sub>O, K<sub>3</sub>PO<sub>4</sub>·9H<sub>2</sub>O, K<sub>2</sub>HPO<sub>4</sub>·K<sub>3</sub>PO<sub>4</sub>·3H<sub>2</sub>O, K<sub>2</sub>HPO<sub>4</sub>·6H<sub>2</sub>O, K<sub>2</sub>HPO<sub>4</sub>, and KH<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub>. E. S. H.

**Solid solutions in the system KH<sub>2</sub>PO<sub>4</sub>-NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>-H<sub>2</sub>O.** A. J. ZVORIKIN and V. G. KUZNETZOV (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 195—201).—Solubility data for  $0^\circ$ ,  $25^\circ$ , and  $50^\circ$  are recorded. Well-formed mixed crystals are obtainable when either salt is present in considerable excess. X-Ray investigation shows that solid solutions are formed within the ranges 0—41.65% KH<sub>2</sub>PO<sub>4</sub> and 0—33.48% NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>. The lattice const. for KH<sub>2</sub>PO<sub>4</sub> increase as the proportion of NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> in solid solution increases. E. S. H.

**Solubility isotherm of the ternary system K<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub>-H<sub>2</sub>O at  $50^\circ$ .** L. G. BERG (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 161—166).—The isotherm consists of ten curves, corresponding with the solid phases: KOH·H<sub>2</sub>O, KOH·2H<sub>2</sub>O, K<sub>3</sub>PO<sub>4</sub>·3H<sub>2</sub>O, K<sub>3</sub>PO<sub>4</sub>·7H<sub>2</sub>O, K<sub>2</sub>HPO<sub>4</sub>·K<sub>3</sub>PO<sub>4</sub>·3H<sub>2</sub>O, K<sub>2</sub>HPO<sub>4</sub>·KH<sub>2</sub>PO<sub>4</sub>·3H<sub>2</sub>O, KH<sub>2</sub>PO<sub>4</sub>, KH<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub>, and 2H<sub>3</sub>PO<sub>4</sub>·H<sub>2</sub>O. Microscopic, chemical, and crystallographic methods have been used in the examination of these phases. No evidence of K<sub>3</sub>PO<sub>4</sub> or K<sub>3</sub>PO<sub>4</sub>·8H<sub>2</sub>O has been obtained. The existence of 2K<sub>2</sub>HPO<sub>4</sub>·KH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O and 3K<sub>2</sub>HPO<sub>4</sub>·2H<sub>2</sub>O is confirmed and that of 5K<sub>2</sub>HPO<sub>4</sub>·KH<sub>2</sub>PO<sub>4</sub>·2(?)H<sub>2</sub>O,

3K<sub>2</sub>HPO<sub>4</sub>·KH<sub>2</sub>PO<sub>4</sub>·3H<sub>2</sub>O, and K<sub>2</sub>HPO<sub>4</sub>·KH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O reported. E. S. H.

**Solubility isotherm of the ternary system K<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub>-H<sub>2</sub>O at  $0^\circ$ .** M. I. RAVITSCH (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 167—176).—The isothermal curve exhibits 9 branches, corresponding with the solid phases observed at  $50^\circ$  (cf. preceding abstract) with KOH·H<sub>2</sub>O excepted. Most of the branches can be followed into the metastable region, and those for K<sub>3</sub>PO<sub>4</sub>·3H<sub>2</sub>O, K<sub>3</sub>PO<sub>4</sub>·9H<sub>2</sub>O, and K<sub>2</sub>HPO<sub>4</sub>·3H<sub>2</sub>O lie entirely in the metastable region. Solubility data for stable and metastable phases at the same temp. are compared. E. S. H.

**Solubility in the system NH<sub>3</sub>-H<sub>3</sub>PO<sub>4</sub>-H<sub>2</sub>O.** B. A. MUROMTSEV and L. A. NAZAROVA (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 177—184).—Data for  $0^\circ$ ,  $25^\circ$ , and  $50^\circ$  are recorded. The phases identified are: (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>·3H<sub>2</sub>O, (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, NH<sub>4</sub>H<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, and 2H<sub>3</sub>PO<sub>4</sub>·H<sub>2</sub>O. E. S. H.

**Equilibrium in aqueous potassium and ammonium nitrates, dihydrogen phosphates, and chlorides.** A. G. BERGMANN (Bull. Acad. Sci., U.R.S.S., 1938, Sér. Chim., 229—235).—A review of published work. E. S. H.

**Equilibrium in aqueous potassium and ammonium nitrates, dihydrogen phosphates, and chlorides.** A. G. BERGMANN and P. F. BOTSCHKAREV (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 237—266).—Data are recorded for the temp. ranges from complete solidity to  $30^\circ$ . No evidence of hydrate formation has been obtained. Eutectics are formed at  $-3.8^\circ$  (KNO<sub>3</sub> 7, KH<sub>2</sub>PO<sub>4</sub> 9.3, H<sub>2</sub>O 83.7%),  $-16.8^\circ$  (NH<sub>4</sub>NO<sub>3</sub> 41.5, NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> 2, H<sub>2</sub>O 56.5%), and  $-6.3^\circ$  (NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> 13.2, KNO<sub>3</sub> 9.6, H<sub>2</sub>O 77.2%). E. S. H.

**Equilibrium in ammonium and potassium chlorides and nitrates.** A. G. BERGMANN (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 203—216).—Data for the range  $-20^\circ$  to  $30^\circ$  are recorded. E. S. H.

**Equilibrium in magnesium and potassium chlorides and nitrates.** A. G. BERGMANN and G. I. NAGORNI (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 217—228).—Data for the range  $-33.2^\circ$  to  $30^\circ$  are recorded. Max. conversion of Mg(NO<sub>3</sub>)<sub>2</sub> is attained at  $-23.2^\circ$ , giving 96% of KNO<sub>3</sub>. E. S. H.

**Potassium sulphate systems and solid solutions of the glaserite type.** S. Z. MAKAROV (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 111—122).—A brief summary of work relating to systems containing K, Na, Mg, Ca, SO<sub>4</sub>, Cl, and H<sub>2</sub>O. The investigations have reference to the economic utilisation of the Ural-Emba K deposits and equilibrium conditions have been determined over a wide temp. range. It is claimed that the individuality of glaserite has been definitely established. E. S. H.

**Relationship of beryllium to the vitriol-forming group and to the alkaline-earth metals. II. Double-sulphate formation between sodium and beryllium sulphates in comparison with the vitriols. I. Polytherms of the ternary system BeSO<sub>4</sub>-Na<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O between  $0^\circ$  and  $100^\circ$ .** W. SCHRÖDER [with J. HAHNRATH and E. KEHREN] (Z.



anorg. Chem., 1938, 239, 39—56).—The 0°, 16.5°, 25°, 50°, and 60° isotherms of the system have been determined. No double salts are indicated.

F. J. G.

**System ammonium selenate-magnesium selenate-water at 30°.** R. W. LAWRENCE and G. B. KING (J. Amer. Chem. Soc., 1938, 60, 1987—1989).—Equilibrium data at 30° are recorded. The system is analogous to the corresponding sulphate system.

E. S. H.

**Decomposition of zinc carbonate and the action of carbon dioxide on zinc oxide. Mechanism of reactions of the type  $A_{\text{solid}} = B_{\text{solid}} + C_{\text{gas}}$ .** J. ZAWADZKI and (MLLE.) A. ULINSKA (Bull. Acad. Polonaise, 1938, A, 62—97).—The dissociation pressure of  $\text{ZnCO}_3$  is > previously reported, but the actual vals. observed are not concordant, depending on the degree of decomp., previous history, nuclear size, and nature of the specimen. At low temp. the rate of dissociation is very slow. The assumption that irregularities are due to formation of solid solutions of  $\text{ZnO}$  and  $\text{ZnCO}_3$  (A., 1930, 699) is not in accord with the behaviour of the system or with X-ray observations.  $\text{ZnO}$  does not combine with  $\text{CO}_2$ , but some gas is adsorbed. At room temp. some  $\text{CO}_2$  is adsorbed rapidly by  $\text{ZnO}$ , this being desorbed again at higher temp. There is also a strong activated adsorption at higher temp., equilibrium being reached after a definite amount of gas has been adsorbed. The solid so saturated with  $\text{CO}_2$  can adsorb further amounts of gas to an extent which depends on the pressure, and gives a reversible equilibrium pressure. The results are attributed to the difficulty of formation of nuclei of a new phase.

J. W. S.

**Equilibrium between metals, sulphides, and silicates in a melt. VI. Equilibrium between aluminium and sodium with their chlorides and fluorides in a melt.** W. JANDER and H. HERRMANN (Z. anorg. Chem., 1938, 239, 65—81).—With a view of studying in a simple case the conditions of equilibrium in melts, the systems  $3\text{Na} + \text{AlCl}_3 \rightleftharpoons \text{Al} + 3\text{NaCl}$  and  $3\text{Na} + \text{AlF}_3 \rightleftharpoons \text{Al} + 3\text{NaF}$  have been investigated. Details are given of a procedure by which 0.002% of Na in Al may be determined with an accuracy of 10%. In the chloride system the equilibrium lies so far over on the Al-NaCl side that the metal contains only 0.002—0.005% Na and the melt only 0.003—0.02% Al. The mass-action law is approx. obeyed, the const.  $[\text{Na}^3]/[\text{Al}^{**}]$  being  $5.2 \times 10^{-10}$  at 825° and  $5.8 \times 10^{-10}$  at 900°. The very small temp. coeff. cannot be reconciled with the heats of formation. In the fluoride system, with small percentages of Al in the melt the equilibrium lies nearer to the Na- $\text{AlF}_3$  side, and at 1090° the const.  $[\text{Na}^3]/[\text{Al}^{**}]/[\text{Na}]^3$  is  $\sim 2.0 \times 10^{-9}$ , for > 12.8% Al in the melt. Beyond this composition (which corresponds with  $\text{Na}_3\text{AlF}_6$ ) [Na] in the metal falls abruptly to  $\sim 0.004\%$  as found in technical Al, and the corresponding val. for the "const." is  $\sim 0.1 \times 10^{-9}$ . From the vals. for the "const." above and below the crit. composition the degree of dissociation of the  $\text{AlF}_6^{3-}$  ion in fused  $\text{Na}_3\text{AlF}_6$  is found to be > 2%.

F. J. G.

**Phase-rule studies of soap systems. I. Applicability of the phase rule.** J. W. MCBAIN, R. D. VOLD, and M. J. VOLD. II. **System sodium laurate-sodium chloride-water.** J. W. MCBAIN, G. C. BROCK, R. D. VOLD, and M. J. VOLD (J. Amer. Chem. Soc., 1938, 60, 1866—1869, 1870—1876).—I. A discussion of principles justifying the application of the phase rule to thermodynamically stable colloid systems in true equilibrium, and to soap systems in particular. The phases present in soap systems are defined.

II. Phase-equilibrium data for the systems Na laurate- $\text{H}_2\text{O}$  and Na laurate- $\text{NaCl-H}_2\text{O}$  at 60—310° have been determined. True reversible equilibrium, independent of time, is reached, and is defined exactly by the phase rule.

E. S. H.

**System mercuric iodide-mercuric bromide-absolute alcohol; characterisation of a mercuric bromiodide by the Raman effect.** F. FRANÇOIS (Compt. rend., 1938, 207, 425—427).—A ternary diagram for the system at 50° is given; the solid phases are mixed  $\text{HgBr}_2\text{-HgI}_2$  crystals of three types. The solutions and the solids obtained on evaporation give Raman  $\nu$  at 205 ( $\text{HgBr}_2$ ), 150 ( $\text{HgI}_2$ ), 233, and 168  $\text{cm}^{-1}$  (attributed respectively to  $\text{Hg-Br}$  and  $\text{Hg-I}$  linkings in  $\text{HgBrI}$ ). A. J. E. W.

**Equilibrium in the reduction of stannic oxide by hydrogen and deuterium.** F. ISHIKAWA and S. ANDO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1938, 34, 873—887).—Equilibria in the systems,  $\text{SnO}_2(s) + 2\text{H}_2(g) \rightleftharpoons \text{Sn}(l) + 2\text{H}_2\text{O}(g)$  (I), and  $\text{SnO}_2(s) + 2\text{D}_2(g) \rightleftharpoons \text{Sn}(l) + 2\text{D}_2\text{O}(g)$  (II), have been studied by an apparatus which is described. The equilibrium const.,  $K_1$ , of (I), for the temp. range 650—759°, can be expressed by  $\log K_1^{\frac{1}{2}} = -2295.8/0 + 2.68297$ ; and for (II), for the temp. range 652—723°,  $\log K_2^{\frac{1}{2}} = -1928.6/0 + 2.4323$ . The equilibrium const.,  $K_w$ , of the water-gas system  $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$  is computed by combining  $K_1^{\frac{1}{2}}$  and recorded vals. of  $K_3$  of the reaction  $\frac{1}{2}\text{Sn} + \text{CO}_2 \rightleftharpoons \frac{1}{2}\text{SnO}_2 + \text{CO}$ ;  $K_w = K_1^{\frac{1}{2}}K_3$ . The vals. of  $K_4$  of the exchange reaction  $\text{H}_2\text{O}(g) + \text{D}_2(g) \rightleftharpoons \text{H}_2(g) + \text{D}_2\text{O}(g)$  at 600—800°, computed from  $K_4 = K_2^{\frac{1}{2}}/K_1^{\frac{1}{2}}$ , agree well with those calc. from the equilibrium consts. given by Farkas (A., 1935, 33) for  $\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD}$ ,  $\text{H}_2\text{O} + \text{D}_2\text{O} \rightleftharpoons 2\text{HDO}$ , and  $\text{H}_2\text{O} + \text{HD} \rightleftharpoons \text{HDO} + \text{H}_2$ . Employing the observed vals. of  $K_1$ , the following relations are found for the reaction  $\text{SnO}_2(s) + 2\text{H}_2(g, 1 \text{ atm.}) \rightleftharpoons \text{Sn}(l) + 2\text{H}_2\text{O}(g, 1 \text{ atm.})$ :  $\Delta H = 27619 - 4.40T - 0.003758T^2 + 0.00000165T^3 - 252000/T$ ;  $\Delta G^\circ = 27619 + 4.40T \ln T + 0.003758T^2 - 0.000000825T^3 - 126000/T - 64.375T$ ; and  $\log K_1^{\frac{1}{2}} = -3019.3/T - 1.077 \log T - 0.0004108T + 0.00000009T^2 + 13774/T^2 + 7.0374$ . The vals. of  $K_1^{\frac{1}{2}}$  and  $\Delta G^\circ$  thus calc. agree well with the observed vals.,  $\Delta S^\circ$  decreases slightly with increasing temp. From these results  $\Delta H$  and  $\Delta G^\circ$  for the formation of  $\text{SnO}_2$  are computed ( $\Delta H_{298.1}^\circ$ , -139,019 g.-cal.,  $\Delta G_{298.1}^\circ$ , -124,087 g.-cal.) and are in moderate agreement with previous vals.

W. R. A.

**Relations between the chemical constitution of substituted phenols and of ascorbic acid and the size of their solubility products with antipyrine and pyridine.** R. LABES and H. BERGSTER-



MANN (Arch. exp. Path. Pharm., 1937, 187, 389—408).—For the conditions under which a base (A) ( $C_5H_5N$  at  $p_H$  7.5 or antipyrine at  $p_H$  5.3) and a phenol (B) [ $PhOH$ ,  $C_6H_4(OH)_2$ , cresol,  $C_6H_4Cl-OH$ ,  $C_6H_2Cl_3-OH$ , picric acid] just fail to give a ppt.,  $[A]^x[B]$  is const.  $x$  is 1—3, usually 2, being so chosen as to make the product const. This product is termed the solubility product. Its size is held to indicate the combining tendency of the components. Combination (*i.e.*, low solubility product) is depressed by hydrophilic (OH) groups and increased by hydrophobic groups ( $NO_2 > Cl > Me$ ); it is also influenced by electric forces, as indicated by dipole moments, for with polar substituents (particularly OH and  $NO_2$ ) the order of efficacy is  $p > m > o$ . The ppts. are usually oils, but occasionally cryst. (in some cases only with limited ratios of the components). Owing to its many hydrophilic groups, ascorbic acid gives no ppt.;  $p_H$  measurements indicate, however, that antipyrine may bind 0.25 mol. of the acid. The solubility products are so high that combination of these or similar components in the body is an improbable cause of pharmacological effects.

R. S. C.

Thermal dissociation of some chlorides ( $CuCl_2$ ,  $PdCl_2$ , and  $PtCl_4$ ). J. KRUSTINSONS (Z. Elektrochem., 1938, 44, 537—539).—The dissociation pressures at various temp. are recorded. The calc. heats of dissociation are respectively 29,000, 37,500, and 24,000 g.-cal. The dissociation of  $PtCl_4$  into  $PtCl_2$  occurs above  $382^\circ$ ; the heat of dissociation of  $PtCl_2$  is 29,400 g.-cal.

C. R. H.

Heats of dissolution of caesium perchlorate, rubidium perchlorate, rubidium chlorate, and lead phosphate. K. S. PITZER (J. Amer. Chem. Soc., 1938, 60, 1828—1829).—Data recorded for infinite dilution and  $25^\circ$  are:  $CsClO_4$   $13,260 \pm 100$ ,  $RbClO_4$   $13,570 \pm 60$ ,  $RbClO_3$   $11,410 \pm 60$ ,  $Pb_3(PO_4)_2$   $7860 \pm 1000$  g.-cal. per mol.

E. S. H.

Heat of dissolution of anhydrous aluminium chloride. W. A. ROTH and E. BÖRGER (Z. Elektrochem., 1938, 44, 540).—The data obtained lead to an average val. 79.43 kg.-cal., which is  $>$  vals. hitherto recorded.

C. R. H.

Heats and entropy changes accompanying the dissolution of ions in water. D. D. ELEY and M. G. EVANS (Trans. Faraday Soc., 1938, 34, 1093—1112).—Mathematical. The entropy change accompanying the dissolution of a gaseous ion in  $H_2O$  is discussed. A qual. connexion exists between the entropy and the heat of hydration.

W. R. A.

Entropies of aqueous ions. W. M. LATIMER, K. S. PITZER, and W. V. SMITH (J. Amer. Chem. Soc., 1938, 60, 1829—1831).—Vals. calc. from published data have been revised and extended to include 11 additional ions.

E. S. H.

Heat of autodiffusion. J. A. M. VAN LIEMPT (Rec. trav. chim., 1938, 57, 891—892).—Cichocki's formula (A., 1938, I, 346) and the author's (A., 1935, 1310) are interconvertible.

F. L. U.

Thermochemical and X-ray investigation of the Hedvall effect. R. FRICKE, W. DÜRR, and E. GWINNER (Naturwiss., 1938, 26, 500).—The

Hedvall effect, *i.e.*, the passage of solid substances through an activated state in the course of allotropic transformations and reactions, has been investigated by thermochemical and X-ray methods in the case of  $ZnO-Fe_2O_3$  mixtures. An active  $ZnO$  was mixed with various samples of  $Fe(OH)_3$  and  $Fe_2O_3$  in the ratio  $ZnO : Fe_2O_3$ , heated for 1 hr. at various high temp., and suddenly cooled. The heats of dissolution, and the width, position, and intensity of lines in the X-ray spectra of the products, were compared. At the lower temp. there was an increase in heat of dissolution owing to dehydration of  $Fe(OH)_3$  and its conversion into the active form. On further heating the heat of dissolution decreased owing to more perfect formation of the crystal lattice. Shortly before the X-ray diagrams indicated spinel formation the decrease in heat of dissolution with rising temp. was  $<$  normal and when spinel formation was well advanced it decreased rapidly again. This is due to the strongly deformed lattice of the spinel when first formed, and this is held to be the reason for the existence of the Hedvall effect.

A. J. M.

Thermometric study of the neutralisation of weak acids and bases. P. MONDAIN-MONVAL and R. PÂRIS (Compt. rend., 1938, 207, 338—339).—End-points are indicated by a max. on the curve obtained by plotting rise of temp. against the vol. of the added solutions; these are sharply defined even with weak acids and bases. Typical curves for the titration of  $H_3BO_3$  and  $H_3AsO_3$  with  $NaOH$ , and of aq.  $NH_3$  with  $AcOH$ , are given.

A. J. E. W.

Electrical conductivity of fused mixtures of sodium, potassium, and magnesium chlorides. K. P. BATASCHOV (Metallurg, 1935, 10, No. 7, 100—113).—Binary and ternary systems have been studied at  $650-1000^\circ$ .

CH. ABS. (e)

Concentration-conductivity relationship of multivalent electrolytes in aqueous solution. J. P. VAN DER HAMMEN (Rec. trav. chim., 1938, 57, 851—862).—From the theories of Onsager and Bjerrum a formula expressing the influence of ionic association on the conductivity of multivalent electrolytes is derived. The conductivity of aq.  $[Co en_3][Fe(CN)_6]$  over the concn. range  $0.5-3 \times 10^{-4}M$  is in agreement with the theory. Measurements of light absorption by the solutions indicate no appreciable mutual deformation of the ions. The small ionisation const. ( $0.643-0.406$ ) is therefore accounted for by powerful Coulomb forces between the highly charged ions.

F. L. U.

Thermodynamic dissociation constant of  $\alpha$ -benzenesulphonylpropionic acid. I. HEDLUND (Arkiv Kemi, Min., Geol., 1938, 12, A, No. 41, 1—5).—The equiv. conductivity of the hypothetical, completely dissociated acid was determined from measured vals. for the K salt and vals. for  $HCl$  and  $KCl$ . The relation between conductivity and concn. was then found by multiplying by the concn. and hence from the observed conductivities the concn. of the dissociated acid was deduced. This led first to the "concn. const." and then by the Debye-Hückel theory to the thermodynamic const.,  $k_0$ .  $k_0 = 2.79 \times 10^{-3}$ .

T. H. G.



**Behaviour of substances in solution.** K. WICKERT (Naturwiss., 1938, 26, 500—501).—Solutions of HCl gas in liquids which are not proton acceptors (e.g.,  $\text{Et}_2\text{O}$ ,  $\text{C}_6\text{H}_6$ ,  $\text{SO}_2$ ) conduct only when a definite quantity of a proton acceptor (e.g.,  $\text{EtOH}$ ) has been added. The effect of addition of  $\text{EtOH}$  on the conductivity of a solution of  $\text{HCl}$  in  $\text{C}_6\text{H}_6$  has been investigated. Three solution states are differentiated: (1) the solution is conducting, and the solute enters into ionic reactions; this occurs when there is a definite min. no. ( $n$ ) of  $\text{EtOH}$  mols. to each  $\text{HCl}$  mol.  $n$  can be determined by conductivity measurements. (2) The solution does not conduct, but the solute can still enter into ionic reactions; the  $\text{HCl}$  mols. are in an excited state. This occurs when the no. of  $\text{EtOH}$  mols. to each  $\text{HCl}$  mol. is  $< n$ . (3) The solution does not conduct and the solute does not enter into ionic reactions; this is the case when there are no  $\text{EtOH}$  mols. present. The following cells give potentials only if  $\text{EtOH}$  is present:  $\text{Hg}|\text{HgCl}(\text{C}_6\text{H}_6, \text{HCl})|\text{H}$  ( $\sim 0.07$  v.),  $\text{Hg}|\text{HgCl}(\text{Et}_2\text{O}, \text{HCl})|\text{H}$  ( $\sim 0.05$  v.).

A. J. M.

**Cd/Cd<sup>++</sup> potential in very dilute solution.** F. MÜLLER and W. DÜRICHEN (Z. physikal. Chem., 1938, 182, 233—242).—Using Cd electrodes produced by distillation of the metal in a high vac., it has been shown that the potential of a  $\text{Cd}|\text{Cd}^{++}$  electrode changes with  $[\text{Cd}^{++}]$  to a concn.  $\ll$  that at which McAulay and Spooner observed a min. val. (A., 1933, 28). During the first hr. the potential drifts towards less negative vals., but the change is then reversed and after about 20 hr. the full potential corresponding with the theoretical val. is attained. The changes occurring with time are probably due to attainment of adsorption and distribution equilibria. With electrodes not prepared in a high vac. the variations of potential with time are reversed. During the first hr. it passes towards more negative vals., and then a reverse change occurs, the final val. attained being approx. that observed by McAulay and Spooner. These changes are attributed to desorption of  $\text{O}_2$  from the metal and to formation of  $\text{Cd}(\text{OH})_2$ , respectively.

J. W. S.

**Potential of the antimony electrode.** H. VOGELS (Congr. Chim. ind. Bruxelles, 1935, 15, II, 1068—1073; Chem. Zentr., 1936, ii, 2105).—The  $E_{\text{Sb}}-p_{\text{H}}$  curve is discontinuous, consisting of three successive parallel straight lines corresponding with successive oxidation of  $\text{Sb}$  to  $\text{SbO}^+$ ,  $\text{Sb}^{+++}$ , and  $\text{Sb}^{++++}$ . Decomp. potential measurements confirm that oxidation to  $\text{SbO}^+$  may be the primary stage of the process.

A. J. E. W.

**Electrode potential of iron and platinum in nitric, hydrochloric, and sulphuric acids.** Y. YAMAMOTO (Bull. Inst. Phys. Chem. Res. Japan, 1938, 17, 517—539).—The single electrode potentials,  $e$ , of Fe and of Pt in  $\text{HNO}_3$ ,  $\text{HCl}$ , and  $\text{H}_2\text{SO}_4$  have been measured relative to a standard calomel electrode. The relation between  $e$  and acid has been investigated. No exact relation exists between  $e$  and the rate of corrosion of Fe.

W. R. A.

**Normal Volta potential,  $V_0$ , of electrochemical two-phase systems.** Temporal changes in surface structure in highly concentrated electro-

lyte solutions. O. KLEIN and E. LANGE (Z. Elektrochem., 1938, 44, 562—568).—Vals. of  $V_0$  have been calc. from the data for electron work functions (cf. following abstract). Three of the systems examined afford data in agreement with calculation. For conc. solutions the surface potential decreases with time. The data are discussed.

C. R. H.

**Electron work functions of metals.** O. KLEIN and E. LANGE (Z. Elektrochem., 1938, 44, 542—562).—Theoretical. Present knowledge and theories are reviewed and discussed. Volta potentials, determined for 45 metals against Hg, lead to a val. 4.52 v. for the work function of Hg. The formation of an oxide film increases the potential, and the removal of this film by rubbing leaves the metal surface in an unstable condition. Further potential changes take place as the metal surface changes to a polycryst. state. Comparison is made between the work function of ions and the corresponding ionisation potential.

C. R. H.

**Influence of oxygen on the potential of local cathodes.** M. STRAUMANIS [with A. LUGGE and E. ENCE] (Korros. u. Metallschutz, 1936, 12, 148—154; Chem. Zentr., 1936, ii, 2220).—In the absence of  $\text{O}_2$ , the local cells formed with Pt, Ni, and Fe cathodes are characterised by a low e.m.f.; the e.m.f. and the rate of corrosion increase as soon as  $\text{O}_2$  is admitted. The effect is attributed to change in the cathode potential owing to reduction of the  $[\text{H}^+]$  at its surface by catalysed combination with  $\text{O}_2$ . The same effect probably occurs with cathodes of Pb, Sb, Bi, and other metals.

A. J. E. W.

**Polarographic studies with the dropping mercury electrode. VII. Temperature coefficient of the diffusion currents.** D. ILKOVIĆ (Coll. Czech. Chem. Comm., 1938, 10, 249—252).—The temp. coeff. of such currents has been deduced theoretically and evaluated for  $\text{H}^+$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{Zn}^{++}$ . The val. for most ions should be about 1.63% per  $1^\circ$ .

K. W. P.

**Effects of solvents on polarographic wave heights.** E. S. PERACCHIO and V. W. MELOCHE (J. Amer. Chem. Soc., 1938, 60, 1770—1775).—The wave heights exhibited in aq. solutions are lowered by adding  $\text{MeOH}$ ,  $\text{EtOH}$ , or  $\text{PrOH}$ . Differences in the wave heights for equiv. concns. of alkali chlorides are lessened by addition of the alcohols and eliminated by addition of dioxan.  $(\text{CH}_2\text{OH})_2$ , trimethylene glycol, and glycerol also lower the wave heights in aq. alkali chlorides, but with the more viscous solutions the curves obtained are poorly defined. Equiv. concns. of  $\text{CdCl}_2$ ,  $\text{BiCl}_3$ , and  $\text{PbCl}_2$  do not give equal wave heights.

E. S. H.

**Polarisation in the discharge of ammonium ions and their alkylated derivatives at a mercury cathode.** M. LOSCHKAREV and O. ESSIN (J. Gen. Chem. Russ., 1938, 8, 510—518).—The cathode potential in the electrolysis of aq.  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_3\text{MeCl}$ , or  $\text{NH}_2\text{Me}_2\text{Cl}$  (dropping Hg cathode) is expressed by  $K - (RT \log i)/F - Ri$ , where  $K$  is const., and  $i$  is the c.d.

R. T.

**Optical investigation of the passivity of iron in nitric and chromic acids.** C. W. BORGMANN (J.



Elisha Mitchell Sci. Soc., 1935, 51, 248).—Passivity in  $\text{HNO}_3$  is due to formation of an impermeable film of  $\text{Fe}_2\text{O}_3$  the thickness of which is 25–35 Å. on polished Fe, 10 Å. on stainless steel, and 80–100 Å. on ordinary steel. In  $\text{H}_2\text{CrO}_4$  it is due to a film of partly hydrated oxide. CH. ABS. (e)

**Theory of passivity. XXXII. Anodic passivity of magnesium in alkaline solutions.** W. J. MÜLLER and E. NACHTIGALL (Korros. u. Metallschutz, 1938, 14, 198–205).—The anodic behaviour of Mg in N-NaOH has been studied, and the observation of Baworevsky (J. Elektrochem., 1905, 465) that there are two different passive conditions is confirmed. Below 6 v. the passive Mg has relatively good conductivity, considerable gas is evolved, and little Mg goes into solution. Above 6 v. the conductivity is low, the metal is practically insol., and very little gas is evolved. In each case there is a considerable and rapid fall in c.d. when the potential is first applied to the Mg anode, and this is more slowly followed by a large or small increase. The gas evolved is mainly  $\text{O}_2$ , with a few % of  $\text{H}_2$ . The attainment of good conductivity at low voltages is tentatively explained by assuming a change in the structure of the  $\text{MgO}$  film, and the slight increase in conductivity at high voltages by a widening of the pores. The freshly abraded Mg has an air-formed film  $10^{-4}$  cm. thick, containing pores amounting to 10–50% of its area. C. E. H.

**Mechanism of electrolytic processes. V. Adsorption and desorption of hydrogen at platinum electrodes.** J. D. PEARSON and J. A. V. BUTLER (Trans. Faraday Soc., 1938, 34, 1163–1170).—Changes of potential of Pt electrodes in aq.  $\text{H}_2\text{SO}_4$ ,  $\text{NaOH}$ , and  $\text{HCl}$  on anodic and cathodic polarisation have been investigated at high c.d., using a cathode-ray oscillograph. At active electrodes an adsorbed film of at. H is formed before liberation of  $\text{H}_2$  at the cathode, and is removed by anodic treatment at potentials more positive than the reversible H potential. E. S. H.

**Electrochemical processes and their value for the absolute definition of metal surfaces.** O. ERBACHER (Chem.-Ztg., 1938, 62, 601–604).—A general review (cf. A., 1937, I, 84, 625; 1938, I, 510).

W. R. A.

**Semiquinone radicals in the indamine and indophenol groups.** G. SCHWARZENBACH and L. MICHAELIS (J. Amer. Chem. Soc., 1938, 60, 1667–1678).—Potentiometric titration of Bindschedler's green and of phenol-blue with reduced rosinduline GG or  $\text{TiCl}_3$ , and of the reduced dyes with  $\text{Br-H}_2\text{O}$  or  $\text{K}_3\text{Fe}(\text{CN})_6$ , furnishes curves the slopes of which indicate the intermediate formation of semiquinone radicals. Ionisation consts. for the reduced, oxidised, and half-oxidised forms have been determined and checked by spectrophotometric measurements. Electronic formulæ are given for the possible states of ionisation of the three forms of the above dyes and of phenol-indophenol. F. L. U.

**Free acetyl.**—See A., 1938, II, 390.

**Reaction velocity.** P. VAN RYSELBERGHE (Bull. Acad. roy. Belg., 1938, [v], 24, 353–356).—Mathematical. N. M. B.

**Proof of De Donder's fundamental hypothesis when the reaction velocity is a function of the state of the system.** R. DEFAY (Bull. Acad. roy. Belg., 1938, [v], 24, 347–352).—Mathematical. N. M. B.

**Evaluation of specific reaction rates in chain reactions.** G. K. ROLLEFSON (J. Physical Chem., 1938, 42, 773–781).—A review. Uncertainties in the evaluation of the efficiencies of chain-starting and chain-terminating reactions and the determination of rate consts. for chain-continuing reactions are discussed. J. W. S.

**Theory of explosive reactions.** H. MURAOUR (Trans. Faraday Soc., 1938, 34, 989–992).—A résumé of the theory (A., 1932, 233) is given and the conclusions reached from it as to the action of a vac. on the propagation of explosive reactions are supported by experimental data. W. R. A.

**Energy and entropy of activation of the reaction between nitric oxide and chlorine.** I. WELINSKY and H. A. TAYLOR (J. Chem. Physics, 1938, 6, 466–472).—The concept of entropy of activation,  $S$ , and methods for its calculation are discussed. Details are given for the experimental determination of the energy of activation,  $E$ , of the formation of  $\text{NOCl}$  from  $\text{NO}$  and  $\text{Cl}_2$ ;  $E$  increases with temp. and from it  $S$  may be evaluated. Previous work is criticised. W. R. A.

**Reaction of oxygen atoms with methane.**—See A., 1938, II, 387.

**Kinetics of pyrolysis of isobutyl iodide.** J. L. JONES (J. Amer. Chem. Soc., 1938, 60, 1877–1882).—The rate at 550–600° K. is given by  $-d[\text{Bu}^i\text{I}]/dt = k[\text{Bu}^i\text{I}][\text{I}_2]^{\frac{1}{2}}$ . A mechanism consistent with the experimental data is proposed. E. S. H.

**Explosiveness of mixtures of methyl chloride, methyl bromide, and air.** C. RANDACCIO and T. GIARRINI (Annali Chim. Appl., 1938, 28, 254–258).—The most explosive mixture of  $\text{MeCl}$  and air (viz.,  $\text{MeCl}$  11.5, air 82.2 vol.-%) is rendered safe (to electric sparking of a described type) by addition of 1.3 vol.-% of  $\text{MeBr}$ . F. O. H.

**Detection of radicals in the chemical decomposition of alkyl iodides.**—See A., 1938, II, 387.

**Electrical ignition of mixtures of ether vapour, air, and oxygen.** W. M. THORNTON (J. Inst. Elect. Eng., 1938, 83, 145–155).—The conditions of ignition of various  $\text{Et}_2\text{O}$ -air and  $\text{Et}_2\text{O-O}_2$  mixtures by coil, circuit break, and single jump sparks, and by hot and fused wires have been investigated. Mixtures containing 3–80% of  $\text{Et}_2\text{O}$  in  $\text{O}_2$  can be ignited by hot wires, but the limits of composition for ignition by sparks are narrower. "Fizzling" sparks between tufts of fine wire, such as are produced at breaks in flex lines, readily cause ignition, especially when a.c. is used. Electrical circuits in operating theatres should be loaded with such resistance that the possible current passing is  $\geq$  a certain val. J. W. S.

**Risk of explosion due to electrification in operating theatres of hospitals.**—See A., 1938, III, 840.



**Salt effect in the paramagnetic conversion of para-hydrogen.** M. CALVIN (J. Amer. Chem. Soc., 1938, 60, 2003).—The rate consts. for the conversion by solutions of diamagnetic salts are independent of the concn. of the salt if the change in solubility of  $H_2$  is allowed for. E. S. H.

**Polymerisation and condensation of formaldehyde in heavy water.**—See A., 1938, II, 392.

**Hydrolysis of methyl iodide.** R. A. OGG, jun. (J. Amer. Chem. Soc., 1938, 60, 2000—2001).—The reaction in 50 vol.-% MeOH- $H_2O$  is of the first order with respect to MeI, but is complicated in the later stages by formation of a considerable amount of I in accordance with  $MeI + H_3O^+ + I^- \rightarrow CH_4 + 2I + H_2O$ . The rate coeffs. at 55° and 100° have been calc. and compared with those for the reaction in  $H_2O$ . E. S. H.

**Kinetics of hydrolysis of ethyl orthoformate in deuterium oxide-water mixtures.** F. BRESCIA and V. K. LA MER (J. Amer. Chem. Soc., 1938, 60, 1962—1967).—The rate has been studied in 0—100%  $H_2O$ - $D_2O$  in presence of NaOAc-AcOH buffers at 25° by a dilatometric method. The sp. catalytic const. for  $D_3O^+$  is 2.35 times that for  $H_3O^+$ . The greater val. for  $D_3O^+$  is explained as a shift in the equilibrium  $S + H^+ \rightleftharpoons SH^+$  (where  $S$  = substrate) in favour of the  $D^+$  complex. E. S. H.

**Kinetic study of acidolysis phenomena.** H. GAULT and A. CHABLAY (Compt. rend., 1938, 207, 293—295; cf. A., 1937, II, 4).—The reversible reactions between Me palmitate and the acids  $R-CO_2H$  ( $R$  = Me, Et,  $Pr^a$ ,  $Bu^a$ , or  $n-C_5H_{11}$ ) have been studied. The mass-action law is obeyed,  $K$  at 175° being  $\sim 1$  in each case;  $K$  is probably independent of temp. A. J. E. W.

**Fission of esters of phosphoric acid.**—See A., 1938, II, 399.

**Kinetics of decarboxylation of certain organic acids.** R. A. FAIRCLOUGH (J.C.S., 1938, 1186—1190).—The decarboxylation of aq. solutions of the Na salts of  $CCl_3\cdot CO_2H$ ,  $CBBr_3\cdot CO_2H$ ,  $CPh_3\cdot CO_2H$ , and  $CH_2(CO_2H)_2$ , measured over a range of temp., is in each case kinetically of the first order. Qual. observations are recorded on the behaviour of  $p$ -nitro- and 2:4-dinitro-phenylacetic, dibromogallic acid, and  $Cl_3\cdot CO_2H$ . A mechanism is proposed for the monobasic acids in which the rate-determining step is the rupture of the C-C bond. This yields a simple explanation of the correlation between  $E$  and  $\log PZ$  which is observed for these acids. It is probable that a different mechanism is operative for the dibasic acids. H. J. E.

**Benzilic acid rearrangement.**—See A., 1938, II, 408.

**Velocity of the hydrogen atom exchange of acetone in dilute aqueous sodium hydroxide.** W. D. WALTERS and K. F. BONHOEFFER (Z. physikal. Chem., 1938, 182, 265—274).—The velocity of introduction of D into  $COMe_2$  in aq. NaOH  $\propto$  the  $[OH^-]$  and increases rapidly with increasing  $[D_2O]$ . The velocity of the reaction in pure  $D_2O$  is deduced. The

exchange is attributed to the equilibrium  $COMe_2 + OH^- \rightleftharpoons COMe\cdot CH_2^- + H_2O$ , and the results are compared with those for the action of I on  $COMe_2$  in alkaline solution (A., 1928, 1101). J. W. S.

**Thermal rearrangement of N-chloroacetanilide in aqueous solution.**—See A., 1938, II, 404.

**Kinetic reinvestigation of isomerisation of camphene hydrochloride.**—See A., 1938, II, 371.

**Nuclear formation in the thermal decomposition of solids.** W. E. GARNER (Trans. Faraday Soc., 1938, 34, 940—946).—Decomp. of solids is associated with the formation of nuclei at places where the lattice structure has been disorganised by impurities or mechanical damage. The shape of the nuclei is determined by the rate of growth in different directions, in turn depending on the structure of the crystal, of its product, and of the interface. The growth of the no. of crystals does not follow any simple law, there being definite evidence that there is a variable activation energy of nuclear formation. Unscratched crystals show a period of induction ( $t$ ) before the nuclei become visible. During  $t$  very small nuclei are probably growing at a rate  $<$  the linear rate found to hold for large nuclei.  $t$  can be accounted for by two alternative explanations which can be expressed by the same mathematical formulation. Experimental evidence is advanced in support of the view that in certain cases of exothermic solid decomp. nuclei grow according to a chain mechanism, and must, therefore, in the early stages of their growth, possess a diffuse structure. W. R. A.

**Absolute rates of heterogeneous reactions. I. General theory of adsorption.** G. E. KIMBALL (J. Chem. Physics, 1938, 6, 447—453).—The statistical theory of reaction rates, developed for homogeneous reactions by Eyring (A., 1935, 586, 1205), is extended to heterogeneous reactions. The derived expressions for the rates of adsorption and desorption have the same forms as the rates of homogeneous reactions, provided that for the activated state a "superpartition" function, formed by the addition of the partition functions for all the active spots, is used. The application of the pseudo-thermodynamical form of the rate const. to various mechanisms of adsorption is discussed. W. R. A.

**Detonation or explosion arising out of thermal decomposition.** W. E. GARNER (Trans. Faraday Soc., 1938, 34, 985—989).—The hypothesis that the detonation arising out of the thermal decomp. of explosives is due to simultaneous decomp. of a small no. of neighbouring mols. in the solid is examined critically by reference to available data. W. R. A.

**Decomposition of nitrogen iodide.** F. R. MELDRUM (Trans. Faraday Soc., 1938, 34, 947—950).—When  $NI_3\cdot NH_3$  is dried over  $P_2O_5$  at  $2 \times 10^{-3}$  cm. the thermal decomp. proceeds slowly, then accelerates, and finally stops; further pumping re-starts the decomp. The suggested explanation for these data was that  $I_2$  was the retarding agent (cf. A., 1936, 439).  $I_2$  vapour at various pressures has been added to the reaction vessel but no retardation is exhibited. Analyses of the decomp. products show that



$N_2:NH_3:I_2 = 1:2:3$  and thus, at low pressures, the reaction which occurs is  $2NH_3.NI_3 = N_2 + 2NH_3 + 3I_2$ . The mechanism involves initial removal of  $NH_3$ , leaving  $NI_3$  which then decomposes. The retarding agent is  $NH_3$  which is adsorbed on the surface, probably with formation of compounds containing 1, 2, 3, and 12 mols. of  $NH_3$ . On the other hand, nuclei of  $NI_3$  may be present on the crystal surface and be "active" in the decomp. when  $NH_3$  is absent; in presence of  $NH_3$  their no. is so reduced that the reaction is slowed down or stopped. The decomp. is a chain reaction with chains (of infinite length) which are broken by  $NH_3$ .  $H_2O$  vapour also retards the decomp. and probably acts as a chain breaker. The adsorbed layer of  $NH_3$  is very stable at  $<0^\circ$  and the reaction can be started only with difficulty when such a layer exists. W. R. A.

**Autoxidation of *n*-hexadecane.** G. ARDITTI (Compt. rend., 1938, 207, 155—157).—The autoxidation of  $n-C_{16}H_{34}$  in a heterogeneous system shows an induction period (A., 1935, 1208). The influence of temp. on the reaction velocity has been studied. For any temp. a period of const. reaction velocity ( $V$ ) is found beyond this period of induction, and  $\log V$  for different temp. is a linear function of temp. Reaction velocities and energies of activation show that, of all the reactions which can take place in the autoxidation, that of min. speed is the same at all temp. studied ( $100$ — $152^\circ$ ). W. R. A.

**Part played by surface oxides in the oxidation of carbon.** R. F. STRICKLAND-CONSTABLE (Trans. Faraday Soc., 1938, 34, 1074—1080).—The structure of C, as elucidated by X-ray analysis, indicates the presence of very strong free valencies at the edge of the crystal which should be capable of forming very stable compounds. The high m.p. of C supports this view. All properties of the surface oxide complex (I) can then be explained by assuming it to consist of a no. of distinct covalent compounds. The decomp. of (I) over a wide temp. range is accounted for by the different thermal stability limits of these compounds. The kinetics of the oxidation of C at moderate temp. is explained by assuming the formation of a distinct intermediate compound, which is less stable than (I) and thus more reactive towards a further mol. of oxidising gas coming from the gas phase, giving  $CO_2$  in a first-order reaction. The interaction between  $N_2O$  and CO in the presence of C is explained as a first-order reaction between CO and the intermediate. W. R. A.

**Mechanism of reactions of the type: solid = solid + gas.** J. ZAWADZKI and S. BRETSZNAJDER (Trans. Faraday Soc., 1938, 34, 951—959).—In the thermal decomp. of coarsely-ground calcite, in the dissociation of  $CdCO_3$ , and in the formation of  $CdCO_3$  from  $CdO$  and  $CO_2$  spurious equilibria are established in which a variation in pressure ensues for the least change in temp. The velocity of the reactions diminishes almost to zero at a certain distance from equilibrium. These spurious equilibria are caused by sorption and slow rates of crystallisation. The equilibria relating to the dissociation and formation of  $CaCO_3$ ,  $CdCO_3$ , and  $ZnCO_3$  are discussed. W. R. A.

**Surface state and oxidisability of cobalt.** (MME.) G. CHAUVENET (Compt. rend., 1938, 207, 360—362).—The rate of absorption of  $O_2$  by Co at  $1200$ — $1350^\circ K.$  decreases on keeping at room temp. for 2—12 months, the activation energy of the absorption remaining const. With fresh surfaces the wt. of  $O_2$  absorbed is not  $\propto t^{\frac{1}{2}}$  (cf. A., 1937, I, 571), owing to the rates of reaction ( $v_r$ ) and of diffusion through the surface layer ( $v_d$ ) being of the same order of magnitude. On keeping  $v_d$  is decreased by progressive formation of a protective film. Expressions giving  $v_r$  and  $v_d$  are derived. A. J. E. W.

**Influence of the radius of curvature on the velocity of oxidation of cobalt.** (MME.) G. CHAUVENET (Compt. rend., 1938, 207, 398—400).—Expressions for the rate of oxidation of wire and spherules, confirmed previously for Ni (cf. A., 1935, 1466; 1936, 434), also apply to the oxidation of Co at  $850$ — $1100^\circ$ . A. J. E. W.

**Effect of annealing temperature on corrosion of magnesium alloys.**—See B., 1938, 1055.

**Rate of dissolution of wollastonite in sodium silicates in relation to temperature.** O. K. BOTVINKIN and A. A. GUREVITCH (Monograph on Phys. and Phys. Chem. of Glass, Moscow, 1933, 34).—The times of dissolution (in min.) of 3-g. samples of wollastonite ground in an agate mortar in 20 g. of the  $Na_2Si_2O_5 + 0.7SiO_2$  eutectic were at  $1035^\circ$ , 1440;  $1125^\circ$ , 600;  $1162^\circ$ , 300;  $1210^\circ$ , 120;  $1240^\circ$ , 60;  $1260^\circ$ , 30 min. CH. ABS. (e)

**Effects of argon and helium on explosions of carbon monoxide and oxygen.** E. F. FLOCK and C. H. ROEDER (Nat. Advisory Comm. Aeronautics, 1936, Rept. No. 553, 1—10; cf. A., 1937, I, 86).—Addition of Ar or He, except possibly in the case of small additions of the latter gas, reduces both the flame speed and the expansion ratio for mixtures of CO,  $O_2$ , and  $H_2O$ . The effect is independent of the ratio of CO to  $O_2$ . CH. ABS. (e)

**Polymerisation of isobutene.** E. W. R. STEACIE and G. SHANE (Cand. J. Res., 1938, 16, B, 210—212).—Polymerisation of mixed isobutenes at  $400$ — $468^\circ/600$  mm. is markedly autocatalytic.  $O_2$  is also a catalyst. The initial reaction rate indicates a second-order reaction with an activation energy  $43.4 \pm 4$  kg.-cal. and a collision efficiency  $4 \times 10^{-4}$  (i.e., normal for this type of reaction; cf. Bawn, A., 1936, 296). R. S. C.

**Catalytic effects in the bromination of toluene.**—See A., 1938, II, 401.

**Temperature coefficients of the base-catalysed decomposition of nitramide in deuterium oxide.** S. LIOTTA and V. K. LA MER (J. Amer. Chem. Soc., 1938, 60, 1967—1974).—The velocity of anion catalysis decreases approx. 2.3-fold at  $15^\circ$  and 2.0-fold at  $25^\circ$  for  $OAc^-$ ,  $OBz^-$ , and salicylate ions on passing from  $H_2O$  to 91.5%  $D_2O$ . The Brönsted equation  $G = kK_A^\alpha$  relating velocity and dissociation consts. holds accurately in  $D_2O$ ;  $\alpha$  is not affected by temp. or isotopic substitution. The difference in the free energy of activation between H and D forms is practically const. for the anion catalysts at  $25^\circ$ , but the corresponding entropy and energy differences do



not remain const. For a given solvent the entropy factor mainly determines the rate for a series of anions, whilst for the same anion catalyst the energy of activation is the more important factor in D substitution. The influence of temp. and D substitution suggests that the spontaneous  $H_2O$  reaction has a mechanism different from the anion-catalysed process.

E. S. H.

**Kinetics of co-ordination reactions in the cobaltamine series. II. Effects of nitrate and sulphate ions on the rate of aquotisation of the chloropentamine ion.** F. J. GARRICK (Trans. Faraday Soc., 1938, **34**, 1088—1093).—The rate of liberation of  $Cl^-$  ions by  $H_2O$  from  $[Co(NH_3)_5Cl]^{2+}$  is increased by electrolytes (A., 1937, I, 248). The acceleration is sp. for anions but independent of the cation. The influence of sulphates and nitrates and their mixtures on the rate has been investigated at 25°. Sulphates have a much greater influence than nitrates; the acceleration by sulphates of univalent cations is > that for bivalent cations. Relationships between rate and ionic strength are given.

W. R. A.

**Kinetics of the reaction between formates and iodine.** E. JOZEFOWICZ (Congr. int. Quim. pura apl., 1934, **9**, II, 268—275; Chem. Zentr., 1936, ii, 3774—3775; cf. A., 1929, 771).—Reaction between  $HCO_2H$  (Na, K, and Ca salts) at 30°, 40°, and 50° and  $I_2$  is more complicated than that between  $HCO_2H$  and Br and is affected by  $[H^+]$  and  $[I_3^-]$ , as is shown by results obtained with only slight excess of KI. At lower temp.  $k$  is const. (after an induction period) but increases during the reaction at higher temp. and  $[I]$ , suggesting reaction between  $I_3^-$  and  $HCO_2H$ . Temp. coeffs. are  $k^{40}/k^{30} = 3.3$ ;  $k^{50}/k^{40} = 3.0$ ;  $k^{60}/k^{50} = 3.2$ ; activation energy = 23 kg.-cal.  $KNO_3$ ,  $Na_2SO_4$ , and  $K_2SO_4$  accelerate, whereas Li, Na, K, Ca, Sr, and Ba bromides, Na, Mg, Ca, and Sr nitrates, and Li, Na, and Mg sulphates inhibit reaction. Br is the most effective anion and bivalent are more effective than univalent cations (cf. A., 1926, 474).  $K$ , the dissociation const. of  $HCO_2H$ , and  $[I_2][I^-]/[I_3^-]$  are correlated but no connexion between the temp. coeff. of  $k$  and the salt effect was found.

A. H. C.

**Catalytic decarboxylation of  $\beta$ -keto-acids.**—See A., 1938, II, 392.

**Dehydrogenating autoxidation and biological oxidation. I.** A. SZENT-GYÖRGYI. **II.** Iron and copper complexes. I. BANGA. **III.** Oxidation-reduction potential of the iron-pyrocatechol complex. **IV.** Inhibition by carbon monoxide and cyanides of the oxidation of ferro-pyrocatechol complex. K. LAKI and G. PAPP. **V.** Autoxidation of sulphite. M. GERENDÁS. **VI.** Oxidation-reduction of ascorbic acid and methylene-blue. F. B. STRAUB. **VII.** Inhibition of the action of dehydrogenases and of polyphenol-oxidase by substances which yield copper complexes. I. BANGA and E. PORGES. **VIII.** Existence of ascorbic acid oxidase. F. B. STRAUB (Z. physiol. Chem., 1938, **254**, 147—164, 165—175, 175—176, 177—184, 184—192, 192—199,

200—204, 205—206).—I (cf. A., 1934, 992). The evidence presented in parts II—VIII supports the view that the autoxidation of the substances considered is a special case of oxidation-reduction and that many dehydrogenases are metal-protein compounds. In the cells no free metallic oxide is produced since it is the metal complexes which undergo autoxidation. The specificity of the complexes accounts for that of the dehydrogenases and oxidases.

II (cf. Wieland and Binder, A., 1912, i, 445). Pyrocatechol (I) combines with  $Fe^{II}$  in absence of  $O_2$  yielding a colourless complex which is reversibly oxidised by atm.  $O_2$  at  $p_H$  5—7.5 to a very stable violet complex of  $Fe^{III}$  which is reduced by  $Na_2S_2O_4$  (but not by cysteine or ascorbic acid) to the colourless complex. Oxidation, accompanied by slow uptake of  $O_2$ , of (I) by  $Fe^{III}$  is checked because equilibrium is very rapidly attained in the system  $Fe^{II}-Fe^{III}$ -ferrous complex-ferric complex-quinone-quinone complex. Substances which form Fe complexes reversibly compete with (I) for Fe and the degree of decolorisation of the violet complex is a measure of the relative complex-forming powers. In the production of Fe-CN complexes the irreversible formation of ferro- and ferri-cyanide seems to be preceded by reversible formation of intermediate products. Fe seems to form mixed complexes, e.g., containing CN and other residues, and CN sometimes increases the catalytic power of Fe (as in the oxidation of  $Na_2S_2O_3$ ).  $Cu^{II}$  behaves like  $Fe^{III}$  but has greater affinity for  $:CO$ ,  $:N$ , and  $:NH_2$  and yields a violet complex with  $(CH_2:NH_2)_2$ . Fe and Cu accelerate the autoxidation of *o*-diphenols and *o*-phenylenediamines (production of 5-membered rings) and Cu (but not Fe) accelerates that of the corresponding *p*-compounds (production of 7-membered rings). Most substances which yield Fe complexes accelerate the oxidation of  $Fe^{II}$  to  $Fe^{III}$  and some substances accelerate the oxidation without yielding complexes (with  $Fe^{III}$  at least). Ascorbic acid also yields a colourless  $Fe^{II}$  complex and a  $Fe^{III}$  complex (compound with  $NH_3$ ,  $C_{11}H_{19}O_{12}NFe$ ) of low stability, violet at  $p_H$  6—9. The equilibrium in the  $Fe^{III}$ -ascorbic acid system checks oxidation of the acid by  $Fe^{III}$ .

III. At  $p_H$  5 the  $Fe^{II}$ - and  $Fe^{III}$ -(I) complexes form a reversible oxidation-reduction system having  $E_0 = +0.293$  v.

IV. Photometric measurements show that the oxidation of the  $Fe^{II}$ - to the  $Fe^{III}$ -(I) complex is a unimol. reaction, the rate of which is proportional to the  $O_2$  tension. The rate increases exponentially as the  $p_H$  increases.  $CN^-$  competes with (I) but not with  $O_2$  for Fe but inhibits the oxidation only when in excess.  $CO$  also inhibits the oxidation, competing with  $O_2$  but not with (I) for Fe.  $CO$  inhibits the oxidation of the  $Fe^{II}$ - to the  $Fe^{III}$ -citrate complex but not the autoxidation of (I) catalysed by Fe.

V. The autoxidation of  $NaHSO_3$ , which depends greatly on  $p_H$ , is catalysed by metals present as impurities; some of these inhibit, whilst others, especially  $Cu^I$ ,  $Cu^{II}$ ,  $Fe^{II}$ , or  $Fe^{III}$ , activate, the process. When Fe is the catalyst the autoxidation is limited above  $p_H$  5.2 by the reduction of the Fe ( $Fe^{III}$  complex) and below  $p_H$  5.2 by oxidation of the Fe ( $Fe^{II}$  complex), the equilibrium of the system being dependent



on  $p_H$ . The autoxidation is inhibited by most substances which form complex with Fe but accelerated by others, especially KCN,  $(CH_3)_2NH$ , and  $C_5H_5N$ . Many substances which form complexes with Cu accelerate the autoxidation.

VI (cf. Ball, A., 1937, I, 246). The spontaneous reduction of methylene-blue by ascorbic acid is not dependent on the presence of metals, is accelerated by light, and is dependent on  $p_H$  (1–4.5), being most pronounced at  $p_H$  approx. 2. Reduction catalysed by Cu is less affected by light but is affected by  $p_H$  in almost the same way. At  $p_H > 4.5$  Cu yields a complex with methylene-blue and inhibits the acceleration by light. CO or very low concns. of HCN, HCNS, or  $H_2S_2O_3$  inhibit the reduction catalysed by Cu but have no effect on the spontaneous reduction.

VII. Org. substances, approx.  $\propto$  the readiness with which they yield complexes with Cu, inhibit the action of succinic dehydrogenase and of the other dehydrogenases of muscle. With inorg. substances the parallelism is less pronounced, some which have poor complex-forming power being powerful inhibitors. Most substances which yield Cu complexes have no effect on the action of polyphenol oxidase.

VIII (cf. Stotz *et al.*, A., 1937, III, 352). Cucumber juice, crude or partly purified by centrifuging, accelerates the autoxidation of ascorbic acid 5 to 10 times as much as does the solution obtained by evaporating the juice to dryness, igniting the residue, evaporating the ash with  $HNO_3$ , and dissolving in  $H_2O$ . Hence if Cu is the activator of the autoxidation, it acts in combination with protein, the compound being ascorbic acid oxidase. W. McC.

Comparative rates of amylase action on starches.—See A., III, 845.

Sucrose inversion by baker's yeast as a function of temperature.—See A., 1938, III, 846.

Reaction between hydrogen and oxygen on metallic palladium. T. TUCHOLSKI (Z. physikal. Chem., 1938, B, 40, 333–346).—The order of the reaction depends on whether  $O_2$  or  $H_2$  is admitted first to the reaction vessel. The reaction is of the first order or of zero order according to whether a Pd–O or a Pd–H surface is formed on the Pd. Substituting  $D_2$  for  $H_2$  leads to a lower reaction velocity in the case of the first-order reaction, but no difference is observed in the velocity of the zero-order reaction. Possible mechanisms are discussed. C. R. H.

Catalytic properties of defined, active oxides. G. M. SCHWAB and H. NAKAMURA (Ber., 1938, 71, [B], 1755–1762).—The rate of decomp. of  $N_2O$  at active specimens of MgO and CuO characterised with regard to the cause of their difference in energy by Fricke (A., 1938, I, 529) has been investigated. In the case of MgO the damage by heat to the catalytic activity is caused by increase in the heat of activation with simultaneous but inadequate increase of the action const. The increase is attributed to the disappearance of lattice deformations. In the case of CuO the diminution of catalytic activity by heat is consequent on a great decrease of action const. with simultaneous but inadequate depression of the heat

of activation. The great heat of activation of the more active, finely-divided specimens is probably due to the enclosure of the cryst. surfaces in amorphous material +  $H_2O$ ; the high action const. are due to an increased capacity of adsorption. H. W.

Amorphous and crystallised oxide hydrates and oxides. XLV. Oxidation of aqueous solutions of organic dyes by hydrogen peroxide in presence of röntgenographically amorphous ferric hydroxide as catalyst in a heterogeneous system. A. KRAUSE and A. POLAŃSKI (Ber., 1938, 71, [B], 1763–1765).—Oxidation of many dyes, particularly indigo-carmin, is readily effected by  $H_2O_2$  in presence of orthoferric hydroxide. The change is  $O \leftarrow \begin{smallmatrix} \text{Fe-OH} \\ \text{Fe-OH} \end{smallmatrix} \text{ (I)} + H_2O_2 = O \leftarrow \begin{smallmatrix} \text{Fe-O} \\ \text{Fe-O} \end{smallmatrix} \text{ (II)} + 2H_2O$  and  $(II) + \text{indigotin} \rightarrow (I) + \text{isatin}$ . Oxidations can be repeated as desired with the same sample of catalyst whereas finality is soon reached with acidified  $FeSO_4$  as inductor. H. W.

Fission of esters of phosphoric acid in presence of lanthanum hydroxide.—See A., 1938, II, 399.

Reactions in the solid state at high temperatures. XIX. Intermediate states arising in the formation of a spinel from magnesium oxide and alumina. W. JANDER and H. PFISTER (Z. anorg. Chem., 1938, 239, 95–112).—The intermediate states have been studied by following the variation in the properties of equimol. mixtures of MgO and  $Al_2O_3$  after heating to various temp. The properties studied were the catalytic activity for gas reactions, the adsorptive power for  $H_2O$  vapour and for dissolved dyes, and the X-ray diagram. Two clearly-marked stages occur at  $800^\circ$  and  $920^\circ$ . The first, characterised by max. of catalytic power and hygroscopicity, corresponds with the max. of disorder in the reaction zone, and the second, at which the catalytic and adsorptive powers begin to decrease rapidly and the lines of the spinel structure appear, corresponds with the beginning of crystallisation of the product. Other less definitely-marked stages occur at  $400$ – $500^\circ$  and  $500$ – $600^\circ$ . F. J. G.

Catalytic interaction of hydrogen and deuterium with ethylene and deuterioethylenes on copper. G. JORIS, H. S. TAYLOR, and J. C. JUNGERS (J. Amer. Chem. Soc., 1938, 60, 1982–1986).—Rates of addition of  $H_2$  and  $D_2$  to  $C_2H_4$ ,  $C_2H_2D_2$ , and  $C_2D_4$  on active Cu catalysts at  $-20^\circ$  to  $40^\circ$  have been determined. In each case the rate of addition of  $D_2$  is  $\sim 50\%$  of that of  $H_2$ . No differences are observed in the initial rates of hydrogenation of the several ethylenes on catalysts of high activity, but small differences appear as the catalyst slowly deteriorates, the D-rich mols. reacting more rapidly. Collision rates of  $H_2$  and  $D_2$  with the surface are inadequate to account for the relative rates of addition; zero-point energy differences are also involved. The apparent activation energies of the reactions are about 11.5 kg.-cal. E. S. H.

Hydrogenation of ethylene and partly deuterated ethylene on catalytic metal surfaces. G. G. JONES and J. C. JUNGERS (J. Amer. Chem. Soc., 1938, 60, 1999–2000).—The times of half-reaction for hydro-



genation of  $C_2H_4$  and  $C_2H_2D_2$  in presence of Ni at  $64^\circ$ , Pt at  $-21^\circ$ , and Co at  $0^\circ$  are 28 and 13, 18 and 12, and 3.5 and 2.8 min., respectively (cf. preceding abstract). R. S. C.

**Effect of certain metals on the oxidation process of carbon.** J. D. LAMBERT (Trans. Faraday Soc., 1938, 34, 1080—1082).—Atoms of Fe and Mn, when adsorbed on the active parts of a C surface, appear to catalyse the decomp. of the surface oxide complex, which is otherwise stable at the temp. employed ( $250$ — $500^\circ$ ), and actually block the surface available for oxidation by the first-order reaction  $C + O_2 = CO_2$ , which takes place at a clean C surface. The catalytic activity of C for the reaction between CO and  $O_2$  is also greatly diminished by the presence of adsorbed Fe and Mn. W. R. A.

**Water content of some oxides and their catalytic action in the decomposition of alcohols.** P. SPINOGLIO (Atti Mem. R. Accad. Padova, 1935, 51, 25—35; Chem. Zentr., 1936, ii, 930).— $Al(OH)_3$  gel dried for a definite time at  $150$ — $300^\circ$  in a stream of  $N_2$  had a lower  $H_2O$  content than that dried in  $C_2H_4$ . Vals. for air and  $H_2$  were intermediate. With decreasing  $H_2O$  content in the gel, the quantity of  $C_2H_4$  produced in the dehydration of EtOH increases, and that of  $H_2$  decreases. Similarly with  $Cr_2O_3$  [from  $Cr(OH)_3$  gel] and  $PrOH$ , decrease in  $H_2O$  in the oxide increased the  $C_2H_6$  and decreased the  $H_2$ . H. J. E.

**Influence of irradiation on solid catalysts in gas reactions.** G. COHN and J. A. HEDVALL (Z. anorg. Chem., 1938, 239, 114—125).—The catalytic activity for gas reactions of a no. of phosphorescent and other solid substances, when irradiated with visible and ultra-violet light, has been investigated. In only one instance ( $N_2O$  and  $H_2$  on a BN phosphor) was a very small increase in activity observed. F. J. G.

**Selective hydrogenation of ethylenic compounds in presence of palladium and platinum catalysts.** II. N. K. JURASCHEVSKI (J. Gen. Chem. Russ., 1938, 8, 438—444).—The relative velocities of hydrogenation of ethylenic compounds in presence of Pd or Pt catalysts cannot be predicted from the structure of the compounds, nor can the rate of hydrogenation of constituents of mixtures be deduced from the hydrogenation curves. It is suggested that more trustworthy information is given by heat of hydrogenation data. Pd catalysts differ from Pt in their greater activity in the hydrogenation of phenylated ethylenes. R. T.

**Catalytic formation of methane from carbon monoxide and hydrogen.** V. Promoter effect on nickel catalyst. K. M. CHAKRAVARTY (J. Indian Chem. Soc., 1938, 15, 245—248).—Reduction of pure  $Ni(OAc)_2$  with  $H_2$  is more thorough in presence of a little  $Ce(NO_3)_3$  with  $V_2O_5$  or, better,  $Ce(NO_3)_3$  with  $Cr(OAc)_3$ . The greater efficiency of the catalysts, deposited on pumice, is exemplified by the reaction of CO with  $H_2$  at  $300^\circ$ , but the possibility of direct influence of the promoters on the reaction is not elucidated. F. R. G.

**Combination of bromine with vinyl bromide at glass surfaces.** G. WILLIAMS (Trans. Faraday Soc., 1938, 34, 1144—1152).—Kinetic investigations show that the reaction in a gaseous system, forming  $CH_2Br \cdot CHBr_2$ , is a surface reaction in the dark between  $0^\circ$  and  $50^\circ$ . The rate falls sharply with rising temp., and is given by  $dx/dt = k_3[CH_2 \cdot CHBr][Br]^2$ . When  $CH_2 \cdot CHBr$  is in excess, a single val. of  $k_3$  covers the reaction, but under other conditions an initial rapid reaction is damped and succeeded by a third-order reaction with a reduced velocity coeff. The damping is connected with the condensation of the reaction product. On certain inert surfaces the reaction agrees with  $dx/dt = k_2[CH_2 \cdot CHBr][Br]$ ; the presence of  $H_2O$  vapour accelerates the reaction and restores third-order kinetics. The mechanism is discussed. E. S. H.

**Importance of surface on course of chemical reactions.** R. HAUL (Z. Ver. deut. Ing., 1938, 82, 1021—1024).—A lecture. R. B. C.

**Reactions in concentrated sulphuric acid.** IV. Carbon oxysulphide. J. MILBAUER [with J. MÝLA] (Chem. Obzor, 1936, 11, 65—68; Chem. Zentr., 1936, ii, 2701; cf. A., 1938, I, 406).—COS begins to react with  $H_2SO_4$  at  $150^\circ$  (in presence of Pd at  $90^\circ$ ; other catalysts in order of decreasing efficiency are Se, Pt, Ag, Cu, V, Hg, Pb, Te, Sn, Bi, Cd, Si, Sb, Zn, Fe, As, Mo, W, and a limit to the efficiency of increasing quantities was noted), the reaction rate increasing rapidly with temp. The thermal decomp. of COS into CO, S,  $CO_2$ , and  $CS_2$  is accelerated by  $H_2SO_4$ , and CO and  $CS_2$  are further oxidised to  $CO_2$ ,  $SO_2$ , and S. A. H. C.

**Sulphuric acid manufacture.** Vanadium oxide catalyst.—See B., 1938, 1032.

**Catalytic hydrogenation of carbon disulphide.**—See B., 1938, 1012.

**Catalytic hydrogenation of octenes to octanes.**—See B., 1938, 1008.

**Promoter effect on a nickel catalyst.**—See B., 1938, 1005.

**Catalytic gas reactions.**—See B., 1938, 994.

**Nickel-copper [fat-hardening] catalysts from the pyridine complex salts of the formates.**—See B., 1938, 1065.

**Catalysts in phenol-formaldehyde condensations.**—See B., 1938, 1072.

**Fractionation of lithium and potassium [and nitrogen] isotopes by chemical exchange with zeolites.** T. I. TAYLOR and H. C. UREY (J. Chem. Physics, 1938, 6, 429—438).—A 38% LiCl solution was electrolysed at  $36^\circ$  in the cell previously described (A., 1937, I, 470) with a flowing Hg cathode and a graphite anode. After 450 g. of solution had been electrolysed to 5 g. the ratio  $^7Li : ^6Li$  was 13.8 and the fractionation factor 1.039. A mass spectrometer for analysing isotopic abundance ratios is described. The normal abundance ratios,  $^7Li : ^6Li = 11.71 \pm 0.14$  and  $^{39}K : ^{41}K = 14.10 \pm 0.09$ , have been determined. Fractionation of Li isotopes has also been effected by chemical exchange with zeolites, either by



shaking with numerous batches of zeolite, or by using a long column packed with zeolite.  $^7\text{Li}^+$  is more readily removed from zeolite than  $^6\text{Li}^+$  but  $^6\text{Li}^+$  is preferentially taken up by the zeolite. The ratio for Li increases or decreases (from 11.7) according to experimental conditions. The fractionation factor with Na zeolite is 1.022. Similar exchange reactions for  $^{39}\text{K}$  and  $^{41}\text{K}$  and for  $^{14}\text{N}$  and  $^{15}\text{N}$  give 10% change. The exchange for K isotopes was carried out with Na, K, and Ca zeolites, and for N isotopes with Na and H zeolites. For both these atoms the heavier isotope is more readily taken up by the zeolite. An equilibrium process is responsible for the fractionation.

W. R. A.

**Active aluminium obtained by high-temperature electrolysis.** A. CHRÉTIEN and J. BISCH (Compt. rend., 1938, 207, 237–239).—A fused 2 : 1 mol. mixture of  $\text{AlBr}_3$  and  $\text{KBr}$  was electrolysed at  $500^\circ$  in an atm. of  $\text{N}_2$  under pressure, using an Al anode and a Hg cathode (50 c.c.) in a steel bomb. The solubility of Al in Hg increases with temp. (20.4 g.-mols. of Al per 100 g.-mols. of Hg at  $510^\circ$ ). A current of 2 amp. at 30 v. was employed. Active Al separates from the Hg on cooling. H. J. E.

**Oxidation of carbon in electrolytes at normal temperature.** H. THIELE (Trans. Faraday Soc., 1938, 34, 1033–1039).—The behaviour of graphite electrodes, immersed in various types of electrolytes, has been investigated when a current is passed. The electrolytes have ranged from alkalis to conc. acids, and the graphite of the electrodes has been varied from cryst. graphite to amorphous C. In alkalis  $\text{O}_2$  is evolved briskly at the anode; the anode is coloured brown and deposits the discoloration into the solution. Amorphous C, which is attacked to a greater extent than graphite, is oxidised to  $\text{CO}_2$  and to humic acid. In  $\text{N-H}_3\text{PO}_4$  no  $\text{O}_2$  is evolved but a primary oxide is formed which, after a time, yields graphite and  $\text{O}_2$ . The primary oxide possesses oxidising properties, liberating free halogens from halides, and in contact with alkalis  $\text{O}_2$  is evolved almost violently. Under similar conditions graphite in  $\text{H}_2\text{SO}_4$  takes up more  $\text{O}_2$  than in  $\text{H}_3\text{PO}_4$  of equal concn. The behaviour in  $\text{HNO}_3$ ,  $\text{HClO}_3$ ,  $\text{HClO}_4$ , and  $\text{HF}$  resembles that of  $\text{H}_2\text{SO}_4$ , whilst  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{AcOH}$ ,  $\text{CH}_2\text{Cl-CO}_2\text{H}$ , and chromic acids are similar to  $\text{H}_3\text{PO}_4$ . In conc.  $\text{H}_2\text{SO}_4$  practically no  $\text{O}_2$  is evolved; most of the  $\text{O}_2$  enters spaces between crystal planes, causing the anode to swell and become lamellated. Cryst. graphite undergoes cleavage, amorphous C becomes swollen, and retort or arc C is split into fragments with crackling. For each concn. of all acids similar in behaviour to  $\text{H}_2\text{SO}_4$ , and for their salts, swelling takes place after a time above a crit. c.d. No swelling occurs for "phosphoric-like" acids. When anhyd.  $\text{H}_2\text{SO}_4$  is used the swollen anode becomes a lustrous deep blue colour. The amount of  $\text{O}_2$  bound in the anode has been determined and formation of graphitic salts is not supported (cf. Hofmann and Rüdorff, A., 1938, I, 531). Distension of graphite, as distinct from swelling, is considered. The properties of graphite oxide and graphitic acid are discussed. W. R. A.

**Electrochemical interpretation of Wagner's theory of tarnishing reactions.** T. P. HOAR and

L. E. PRICE (Trans. Faraday Soc., 1938, 34, 867–872).—Theoretical. The process of tarnishing a metallic surface, with the production of a compact film of oxide, sulphide, etc., is regarded as the action of a cell with the metal-film and the film-attacking substance interfaces as anode and cathode respectively; the film acts as both external circuit and electrolyte. Using this conception, an expression for the rate of tarnishing, similar to that obtained by Wagner (A., 1933, 564), is deduced. A similar expression for the more complicated case, where the conductivity of the tarnished film varies with the pressure of the attacking gas, is derived. The theory offers a logical explanation of tarnish-resistant metals and alloys.

W. R. A.

**Electrodeposition of silver from solutions of silver nitrate in presence of addition agents.**—See B., 1938, 1057.

**Dissolution of rhodium by alternating current electrolysis.**—See B., 1938, 1052.

**Nature of the primary process in photochemical reactions.** G. K. ROLLEFSON (J. Physical Chem., 1938, 42, 733–737).—A review. Predissociation is discussed from the viewpoint of the uncertainty principle, and examples illustrating various types of primary process are given.

J. W. S.

**Comparisons between photochemical processes in gases and solutions.** R. G. DICKINSON (J. Physical Chem., 1938, 42, 739–748).—A review. Fundamental differences between reactions in gases and in the liquid state are discussed, with particular reference to the increased possibility of recombination of the primary dissociation products when reaction occurs in the liquid phase.

J. W. S.

**Quantum yields in experimental photochemistry.** F. DANIELS (J. Physical Chem., 1938, 42, 713–732).—The quantum yields of about 120 reactions, under various conditions of temp. and  $\lambda$ , are tabulated.

J. W. S.

**Experimental technique in photochemistry.** F. DANIELS (J. Physical Chem., 1938, 42, 701–711).—Recent advances in technique are summarised, with particular reference to light sources, filters, and monochromators, measurement of radiation, reaction cells, microanalysis of reaction products, and measurement of absorption spectra.

J. W. S.

**Secondary processes in the photo-chlorination of carbon monoxide and hydrogen.** H. S. TAYLOR (J. Physical Chem., 1938, 42, 789–794).—A review. The mechanism of the photochemical reactions between  $\text{CO}$  and  $\text{Cl}_2$  and  $\text{H}_2$  and  $\text{Cl}_2$  are discussed with particular reference to recent results of Bodenstein and his collaborators.

J. W. S.

**Secondary processes in the photo-decomposition of ammonia and hydrazine.** H. S. TAYLOR (J. Physical Chem., 1938, 42, 783–788).—A review. Various mechanisms suggested for the photo-decomp. of  $\text{NH}_3$  and  $\text{N}_2\text{H}_4$  are discussed critically.

J. W. S.

**Mechanism of aldehyde and ketone photolysis.** P. A. LEIGHTON (J. Physical Chem., 1938, 42, 749–761).—A review of the various types of



primary process and secondary reactions and of polymerisation processes encountered in the photochemical decomp. of aldehydes and ketones.

J. W. S.

**Hydrocarbon free radicals in photo-processes.** H. S. TAYLOR (J. Physical Chem., 1938, 42, 763—772).—A review. The primary and secondary processes and quantum yields in the photolysis of alkyl iodides and metal alkyls, the Hg-sensitised hydrogenation of unsaturated hydrocarbons, and the Hg-sensitised decomp. of saturated hydrocarbons, in each case with production of free hydrocarbon radicals, are discussed.

J. W. S.

**Photochemical primary process of ions in aqueous solution.** A. FARKAS and L. FARKAS (Trans. Faraday Soc., 1938, 34, 1113—1120).—Theoretical. The process occurring in the absorption of light is considered to be the transfer of an electron from the ion to the  $H_2O$  mol. in the hydration layer. The electron can then return to its initial state (no photochemical change), or can pass over to the final state (chemical reaction). In the reaction of negative ions the final state is reached by the transfer of the electron to a positive ion. The mechanism is formulated for  $I^-$ ,  $SO_3^{2-}$ , and  $Fe^{3+}$ .

E. S. H.

**Separation of hydrogen isotopes in the photochemical liberation of hydrogen from aqueous solutions.** A. FARKAS and L. FARKAS (Trans. Faraday Soc., 1938, 34, 1120—1127).—Separation factors for solutions of  $NaI + HCl$ ,  $Na_2SO_3$ , and  $FeSO_4 + H_2SO_4$  in 15—78%  $D_2O$  are 3.7—6.5, 10.6, and 3.8—4.8, respectively. Separation is considered to occur in the photochemical process, H having about 4 times as great a probability of being formed as D.

E. S. H.

**Photochemical deamination of amino-acids in water.** II. C. WEIZMANN, Y. HIRSBERG, and E. BERGMANN (J. Amer. Chem. Soc., 1938, 60, 1799—1801; cf. A., 1936, 1349).—The photochemical change,  $NH_2 \cdot CHR \cdot CO_2H \rightarrow OH \cdot CHR \cdot CO_2H$ , in  $H_2O$  is faster for phenylalanine and alanylglycine than for alanine, but the concn. affects the numerical ratios. This change is the only possible biochemical method of hydrolysis of amino-acids. The quantum yield for glycine, alanine, and betaine is 0.1, 0.087, and 0.064, respectively.

R. S. C.

**Spectral sensitivity of photographic layers.** J. EGGERT and M. BILTZ (Trans. Faraday Soc., 1938, 34, 892—901).—The sensitivity of photographic AgBr layers has been measured as a function of  $\lambda$ ; the AgI content, the state of ripening, and the sensitisation have been varied. Quant. relationships between AgBr and dye content, AgBr and light quanta absorbed, and AgBr and developed density have been established for a layer sensitised optimally for the green. The mechanism of the photographic process is considered. The sensitivity of AgBr is due to *Störstellen* in the crystal lattice. When energy is supplied, the *Störstellen* undergo photolysis with production of new *Störstellen* in the hitherto undisturbed AgBr lattice. At  $\lambda > 5000$  Å. the *Störstellen* alone determine the sensitivity of an unsensitised layer. From 5000 Å. to shorter  $\lambda$  AgBr acts as an energy carrier. Sensitisers, such as AgI

or dyes, act as energy carriers and give up absorbed light to the *Störstellen*.

W. R. A.

**Adsorption theory of photographic development.** A. J. RABINOVITCH (Trans. Faraday Soc., 1938, 34, 920—926).—The supersaturation and catalytic theories of development are reviewed and an adsorption theory is formulated, in which adsorption of the org. developers takes place on colloidal Ag particles forming the nuclei of the latent image and not on the surface of AgBr, as proposed by Shepard (Phot. Korr., 1922, 76). Experimental evidence supports this theory. An apparatus by which the development of a single grain of a AgBr emulsion can be photographed is described. From an invisible nucleus, situated usually on the edge of the grain, darkening spreads in circular zones with the radius increasing linearly with the time of development, as predicted by the theory. The effects of changing the conditions of development are discussed.

W. R. A.

**New time phenomenon in photographic emulsions.** F. WEIGERT (Trans. Faraday Soc., 1938, 34, 927—930).—The production of photodichroism on an oblique film of AgCl-gelatin by the combined action of natural blue and red light is described. When plotted against the spectrum, the photodichroism was the more positive as the time interval between a blue and a red exposure was increased, but a dark interval following a red exposure had no appreciable effect. This is probably due to the production, by the blue light, of a sensitiser for red which slowly loses its activity. This phenomenon confirms the mechanisms of sensitising and auto-sensitising actions previously suggested (A., 1935, 311).

W. R. A.

**Generalisation of the theory of photodichroism.** S. NIKITINE (Compt. rend., 1938, 207, 331—333; cf. A., 1938, I, 318).

A. J. E. W.

**Photographic sensitivity.** LÜPPO-CRAMER (Trans. Faraday Soc., 1938, 34, 930—935).—The contradictory opinions as to the photographic sensitivity of pure dry Ag halides are reviewed. Principally the sensitivity of ordinary photographic plates is due to the germs. With layers quite free from binding material the sensitivity decreases with increasing size of the grain, the smaller grain being more easily reduced by the developer. The reverse is true with AgBr-gelatin, as the protective action of the colloid is more effective with the small grains. Optically determinable light absorption cannot measure light-sensitivity. The latent image formed by X-ray irradiation of AgBr films is chiefly conc. on the grain surface, as is shown by the action of oxidising agents and desensitising dyes. Other reversible phenomena in photographic layers are discussed.

W. R. A.

**Action of various elements and compounds on photographic plates.** II. S. AOYAMA and T. FUKUROI (Sci. Rep. Tôhoku, 1938, 26, 641—676; cf. A., 1935, 1087).—The action of Mg on photographic plates increased linearly with exposure time; it decreases slowly after the specimens have been polished. Glass exerts a greater screening



effect than quartz; the effect of other surfaces was:  $\text{Cu}_2\text{O} > \text{Cu} > \text{CuO}$ ;  $\text{Fe} > \text{Fe}_2\text{O}_3$ ;  $\text{NiO} > \text{Ni}$ . Tests at various distances in air,  $\text{N}_2$ , and  $\text{H}_2$  show that deactivation  $\propto$  (pressure)<sup>1</sup>. The rate of diffusion of activated particles on photographic plates approx.  $\propto$  (time)<sup>1</sup>; the rate of diffusion rises with temp. Diat. gases and  $\text{H}_2\text{O}$  vapour are strongly activated whereas monat. gases are not. C. M. A.

**Fluorescence of sodium salicylate in photographic photometry.** R. MONTAGNE and L. HERMAN (Sci. Ind. phot., 1936, [ii], 7, 225—232; Chem. Zentr., 1936, ii, 2277).—The  $\gamma$  of plates sensitised with Na salicylate (I) (cf. Tien Kiu, B., 1938, 188) is nearly const. for  $\lambda \leq 700$  Å. Duclaux-Jeantet gelatin-free plates are more sensitive only for low intensities. Reliable data for the energy yield of fluorescent (I), for use in accurate measurements, are not available. A. J. E. W.

**Action of ultra-violet rays on mercury fulminate.** A. BOROCCHI (Compt. rend., 1938, 207, 166—168).—The change of colour of Hg fulminate (I) on exposure to ultra-violet radiation depends on the duration of exposure and on the intensity of the radiation. Measurements of  $\rho$  and X-ray spectrum and microscopical examination show that the structure of (I) has not been affected. Exposure of (I) in vac., however, indicates partial decomp. to Hg,  $\text{CO}_2$ , and  $\text{N}_2$ . The total effect of exposure to ultra-violet radiation is thus analogous to that produced by heating. W. R. A.

**Statistical interpretation of reactions between solids at high temperatures.** T. PECZALSKI (Compt. rend., 1938, 207, 45—46).—A theory is given to explain previous experimental results (A., 1938, I, 450). W. R. A.

**Geometrical factors in reactions involving solids.** J. D. BERNAL (Trans. Faraday Soc., 1938, 34, 834—839).—Consideration of X-ray analysis data on a variety of reactions involving solids shows that in all such reactions there is a marked tendency to preserve crystal orientations and at. positions as unchanged as possible. W. R. A.

**Rôle of supersaturation and the limiting stage in topochemical reactions.** S. Z. ROGINSKY (Trans. Faraday Soc., 1938, 34, 959—969).—In reactions involving solids sometimes the chemical and sometimes the crystallisation processes determine the course of the reaction; the influence of supersaturation of the reaction (distance from equilibrium) on which of these processes will predominate is discussed. W. R. A.

**Preparation of anhydrous acetates.**—See A., 1938, II, 390.

**Potassium nitrilosulphonate.** H. SISLER and L. F. AUDRIETH (J. Amer. Chem. Soc., 1938, 60, 1947—1948).—Max. yields are obtained when the ratio  $\text{KHSO}_3 : \text{KNO}_2$  is  $\leq 4 : 1$ , and when hot solutions are used. Hydrolysis has been studied at 25—100°; the consecutive reactions (1)  $\text{N}(\text{SO}_3)_3''' + \text{H}_2\text{O} \rightarrow \text{NH}(\text{SO}_3)_2'' + \text{H}^+ + \text{SO}_4''$ , (2)  $\text{NH}(\text{SO}_3)_2'' + \text{H}_2\text{O} \rightarrow \text{NH}_2\text{SO}_3' + \text{H}^+ + \text{SO}_4''$  occur. E. S. H.

**Chemical changes of fused alkali nitrates at temperatures of 460—600°.** K. LESCHEWSKI and W. DEGENHARD (Z. anorg. Chem., 1938, 239, 17—26).—The decomp. of  $\text{NaNO}_3$ ,  $\text{KNO}_3$ , and mixtures of these in presence of Fe, Al, duralumin, and laural at 460—600° has been studied. As a rule the % of nitrite or of alkali oxide formed is greatest with  $\text{NaNO}_3$  and least with  $\text{KNO}_3$  and is increased by the presence of the metals. F. J. G.

**Complex salts of the alkali and alkaline-earth metals.** P. PFEIFFER and W. CRISTELEIT (Z. anorg. Chem., 1938, 239, 133—144).—o-Phenanthroline perchlorate,  $\text{C}_{12}\text{H}_8\text{N}_2\text{HClO}_4 \cdot 2\text{H}_2\text{O}$ , m.p. 193—194.5° and mercurichloride,  $\text{C}_{12}\text{H}_8\text{N}_2\text{HgCl}_3$ , bis-dipyridyl Pb perchlorate,  $[\text{Pb}(\text{C}_{10}\text{H}_8\text{N}_2)_2](\text{ClO}_4)_2$ , and the following complex salts containing o-phenanthroline are described:  $[\text{Li}(\text{C}_{12}\text{H}_8\text{N}_2)]\text{ClO}_4$ ;  $[\text{Na}(\text{C}_{12}\text{H}_8\text{N}_2)]\text{ClO}_4 \cdot 3\text{H}_2\text{O}$ ;  $[\text{Ag}(\text{C}_{12}\text{H}_8\text{N}_2)]\text{NO}_3 \cdot \text{H}_2\text{O}$ ;  $[\text{Ti}(\text{C}_{12}\text{H}_8\text{N}_2)_2]\text{NO}_3 \cdot 2.5\text{H}_2\text{O}$ ;  $[\text{Ca}(\text{C}_{12}\text{H}_8\text{N}_2)_4](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ ;  $[\text{Ca}(\text{ClO}_4)_2 \cdot 6\text{C}_{12}\text{H}_8\text{N}_2 \cdot 4\text{H}_2\text{O}]$ ;  $[\text{Sr}(\text{C}_{12}\text{H}_8\text{N}_2)_4](\text{ClO}_4)_2 \cdot 8\text{H}_2\text{O}$ ;  $[\text{Ba}(\text{C}_{12}\text{H}_8\text{N}_2)_4](\text{ClO}_4)_2 \cdot 8\text{H}_2\text{O}$ ;  $[\text{Pb}(\text{C}_{12}\text{H}_8\text{N}_2)_4](\text{ClO}_4)_2$ ;  $[\text{Hg}(\text{C}_{12}\text{H}_8\text{N}_2)_3](\text{ClO}_4)_2$ ; and  $[\text{Bi}(\text{C}_{12}\text{H}_8\text{N}_2)_3](\text{ClO}_4)_3$ . The co-ordination nos. 8 for Ca, Sr, Ba, and 6 for Hg, are noteworthy. F. J. G.

**Dehydration of salt hydrates.** J. COLVIN and J. HUME (Trans. Faraday Soc., 1938, 34, 969—976).—In dehydration of salt hydrates two factors are involved: (1) retardation of the reaction rate by  $\text{H}_2\text{O}$  vapour is greater when the new solid phase is amorphous than when it is cryst., and (2) formation of a cryst. new phase is catalysed by  $\text{H}_2\text{O}$  vapour. The conditions under which  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  is formed in the dehydration of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  are discussed. The results of Topley and Smith (A., 1935, 588) and of Volmer and Seydell (A., 1937, I, 468) on the dehydration of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  are discussed. W. R. A.

**Active substances. XXXI. Heat content and lattice condition of different active varieties of CuO and heat of formation of  $\text{Cu}(\text{OH})_2$ .** R. FRICKE, E. GWINNER, and C. FEICHTNER (Ber., 1938, 71, [B], 1744—1754).—The prep. of various forms of CuO is described. Measurements of the heat of dissolution of CuO pptd. at 35° and then heated at various temp. show a max. difference in heat content of 1.45 kg.-cal. (difference between specimens preheated at 80° and 600°, respectively). Small particle size and admixture with amorphous material are the cause of the increase in heat content of material preheated at only a low temp. Particle sizes are calc. for monoclinic CuO by the method of von Laue and Brill. The % of admixed amorphous material is directly deduced from measurements of the interference intensities since larger, irregular lattice disturbances of the cryst. portion, judged by the course of the intensities with increasing angle of reflexion, are not present. Lattice extensions cannot be detected in varieties of CuO rich in energy. Hahn's emanation method gives particle sizes for preps. poorer in energy which agree in order of magnitude with those estimated röntgenographically; these indicate a loose, secondary structure for the oxides



poorer in energy. From the heats of dissolution of cryst.  $\text{Cu}(\text{OH})_2$ , determined under the conditions used for  $\text{CuO}$ , it is shown by the approximations of Nernst and Ulich that cryst.  $\text{Cu}(\text{OH})_2$  at room temp. is in equilibrium only with those varieties of  $\text{CuO}$  which are richest in energy. H. W.

**Copper salts of imidosulphonic acid.** (MLLE.) L. CHAUMETON (Compt. rend., 1938, 207, 162—163).—In distinction to the action of  $\text{NH}_2\cdot\text{SO}_3\text{H}$  on Ag and Hg to give derivatives with the metal attached to the N atom (A., 1936, 944)  $\text{NH}(\text{SO}_3\text{H})_2$  produces with Cu simple salts and mixed salts. Starting with the Ba salt,  $\text{NH}(\text{SO}_3)_2\text{Ba}\cdot 2\text{H}_2\text{O}$ , and a saturated solution of  $\text{CuSO}_4$ , pale blue crystals of  $\text{NH}(\text{SO}_3)_2\text{Cu}\cdot 5\text{H}_2\text{O}$  (I) were obtained. They are readily hydrolysed and on drying lose 2  $\text{H}_2\text{O}$ . Addition of  $\text{EtOH}$  to the aq.  $\text{NH}_3$  solution of (I) yields the violet salt,  $\text{NH}(\text{SO}_3)_2[\text{Cu}(\text{NH}_3)_4]\cdot \text{H}_2\text{O}$ . When  $\text{CuSO}_4$  or  $\text{Cu}(\text{NO}_3)_2$  is added to tribarium imidosulphonate,  $\text{Ba}[\text{N}(\text{SO}_3)_2\text{Ba}]_2\cdot 5\text{H}_2\text{O}$ , long, deep blue needles of  $\text{N}_2(\text{SO}_3)_4\text{Ba}_2\text{Cu}\cdot x\text{H}_2\text{O}$  (II) are obtained. (II) is insol. in  $\text{H}_2\text{O}$ , org. solvents, and aq.  $\text{NH}_3$ , and has birefringent crystals. The magnetic susceptibilities of (I), (II),  $(\text{NH}_2\cdot\text{SO}_3)_2\text{Cu}\cdot 2\text{H}_2\text{O}$ ,  $\text{NH}(\text{SO}_3)_2\text{Cu}\cdot 5$  (and 2)  $\text{H}_2\text{O}$ , and  $(\text{NH}_2\cdot\text{SO}_3)_2[\text{Cu}(\text{NH}_3)_4]\cdot 5\text{H}_2\text{O}$  have been measured at  $20^\circ$  by a Curie-Cheneveau balance. The susceptibility of Cu has been deduced and is approx. 1500 for all compounds except (II), for which it is 1712. This indicates that in (II) the Cu atoms are not attached to the  $\text{SO}_3$  groups. The structure  $\text{Cu}[\text{N}(\text{SO}_3)_2\text{Ba}]_2\cdot 6\text{H}_2\text{O}$  is assigned to (II).

W. R. A.

**Pharmaceutically important arsenic compounds.** V. Silver and thallium arsenites. K. BRAND and E. ROSENKRANZ (Pharm. Zentr., 1938, 79, 537—542).—The reaction between  $\text{Ag}_3\text{AsO}_3$  and  $\text{EtI}$  affords only  $\text{As}(\text{OEt})_3$  and no  $\text{O}:\text{AsEt}(\text{OEt})_2$ . *Tl meta-arsenite*,  $\text{TlAsO}_2$ , is described. F. J. G.

**Mercuri-iodides.** F. GALLAIS (Ann. Chim., 1938, [xi], 10, 117—193).—The formation of complex salts from  $\text{HgI}_2$  in solution and in the solid state, and their magnetic properties, have been studied. At room temp. the curves for conductometric titration of  $\text{HgCl}_2$  with alkali iodides, and the magnetic rotations of mixtures of  $\text{HgCl}_2$  with  $\text{BaI}_2$  and with  $\text{HI}$ , indicate that only one complex ion, viz.,  $\text{HgI}_4^{2-}$ , exists and that it is somewhat dissociated in  $\text{H}_2\text{O}$  but not in 20%  $\text{EtOH}$ . The vals. of  $\Lambda$  for solutions of  $\text{HgI}_2 + 2\text{KI}$  and  $\text{HgI}_2 + 2\text{HI}$  agree respectively with those for tri-ionic salts and for dibasic acids. Attempts to prepare an ester of  $\text{H}_2\text{HgI}_4$  were unsuccessful. From measurements of magnetic rotation for conc. solutions of  $\text{Hg}(\text{NO}_3)_2 + \text{KI}$  the const.  $[\text{HgI}_2][\text{I}^-]^2/[\text{HgI}_4^{2-}]$  is  $\sim 2.5 \times 10^{-5}$  at  $20^\circ$ , whereas at  $99^\circ$  the complex ion is  $\text{HgI}_3^-$  and the const.  $[\text{HgI}_2][\text{I}^-]/[\text{HgI}_3^-]$  is  $\sim 5.6 \times 10^{-2}$ . Solutions of the salt  $\text{KI}\cdot\text{HgI}_2\cdot\text{H}_2\text{O}$  give a different Raman spectrum from those of  $\text{K}_2\text{HgI}_4$ ; their conductivity agrees with that for a di-ionic salt, and the  $\text{H}_2\text{O}$  is relatively firmly bound, so that this salt is to be regarded as  $\text{K}[\text{HgI}_3(\text{H}_2\text{O})]$ .  $\text{Ag}_2\text{HgI}_4$  and  $\text{Cu}_2\text{HgI}_4$  have  $\chi \times 10^6 = -0.19$  and  $-0.26$ , respectively. Attempts to prepare  $\text{AgHgI}_3$  and  $\text{CuHgI}_3$  were unsuccessful. The action of boiling aq.  $\text{NH}_3$  on  $\text{Cu}_2\text{HgI}_4$  yields Hg and  $[\text{Cu}(\text{NH}_3)_4][\text{HgI}_4]$

whilst double decomp. between  $\text{K}_2\text{HgI}_4$  and  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$  affords the *hydrate*  $[\text{Cu}(\text{NH}_3)_4][\text{HgI}_4]\cdot 15\text{H}_2\text{O}$ . Attempts to prepare the salt  $2\text{HgI}_2\cdot\text{CuI}_2\cdot 4\text{NH}_3$  (Jørgensen, J. pr. Chem., 1870, [ii], 2, 347) were unsuccessful. *Tl mercuri-tetraiodide*,  $\text{Tl}_2\text{HgI}_4$ , has been obtained as a yellow ppt.,  $\chi \times 10^6 = -0.24$ , and its individuality established by means of X-rays. Conductometric titration of  $\text{K}_2\text{HgI}_4$  with  $\text{Tl}_2\text{SO}_4$  indicates that it is the only  $\text{Tl}^{\text{I}}$  mercuri-iodide. Dil. solutions of  $\text{Na}_2\text{HgI}_4$ ,  $\text{K}_2\text{HgI}_4$ , and  $\text{K}[\text{HgI}_3(\text{H}_2\text{O})]$  are diamagnetic. F. J. G.

**Mercury-sensitivity of aluminium.** H. LICHTENBERG (Z. anorg. Chem., 1938, 239, 189—196).—The gain in wt. on exposure to air of Al activated by  $\text{Hg} \propto t^{\frac{1}{2}}$ . Impurities decrease the rate of oxidation, and it is completely inhibited by 0.2% Cu, 1% Fe, or 5% Si. Both  $\text{O}_2$  and  $\text{H}_2\text{O}$  are necessary for the reaction, and the product is  $\gamma\text{-Al}_2\text{O}_3$ , with adsorbed  $\text{H}_2\text{O}$ . F. J. G.

**$\text{NH}_4\text{AlF}_4$ .** E. THILO (Naturwiss., 1938, 26, 529).—The thermal decomp. of  $(\text{NH}_4)_3\text{AlF}_6$  takes place in stages. If the compound is heated in dry  $\text{N}_2$  at  $350^\circ$  the reaction  $(\text{NH}_4)_3\text{AlF}_6 \rightarrow \text{NH}_4\text{AlF}_4 + 2\text{NH}_3\text{F}$  occurs. Above  $350^\circ$  pure  $\text{AlF}_3$  is obtained in complete absence of  $\text{H}_2\text{O}$ .  $\text{NH}_4\text{AlF}_4$  is isomorphous with  $\text{TlAlF}_4$ , the unit cell having  $a\ 3.59$ ,  $c\ 6.34 \pm 0.01$  Å. A. J. M.

**Preparation and crystal structure of europium sulphide, EuS, and fluoride,  $\text{EuF}_2$ .** G. BECK and W. NOWACKI (Naturwiss., 1938, 26, 495—496).— $\text{EuF}_2$ ,  $d\ 6.495$ , was prepared from  $\text{EuF}_3$  by reduction in  $\text{H}_2$  at a red heat. Impure EuS was obtained by heating  $\text{Eu}_2\text{O}_3$  in a current of  $\text{H}_2\text{S}$ . The violet product contained some oxysulphide. By heating  $\text{Eu}_2(\text{SO}_4)_3$  in a current of  $\text{H}_2\text{S}$ , a brownish-violet sulphide was obtained. It is pyrophoric, insol. in  $\text{H}_2\text{O}$ , but readily sol. in very dil. acids. Attempts to make EuO were unsuccessful. EuS has the NaCl type of crystal structure with  $a\ 5.957 \pm 0.002$  Å. The ionic radius of  $\text{Eu}^{++}$  is 1.24 Å. A powder photograph of  $\text{EuF}_2$  with NaCl as standard gave a cubic structure for  $\text{EuF}_2$  with  $a\ 5.796 \pm 0.006$  Å. There are 4 mols. in the unit cell. The probable space-groups are  $T_h^2$ — $Fm3$ ,  $O^2$ — $F43$ , and  $O^2$ — $Fm3m$ .  $\text{EuF}_2$  has the fluorite structure, a result confirmed by determination of the relative intensities of the X-ray spots. Comparison with the lattice consts. of  $\text{BaF}_2$  and  $\text{SrF}_2$  shows that the dimensions of the  $\text{EuF}_2$  crystal are nearer those of  $\text{SrF}_2$  than  $\text{BaF}_2$ . A. J. M.

**Thermal decomposition of some gallium salts and structure of the resulting oxide.** G. CENTOLA (Congr. int. Quim. pura apl., 1934, 9, III, 230—238; Chem. Zentr., 1936, ii, 2322).—The following are formed successively on heating  $\text{Ga}_2(\text{C}_2\text{O}_4)_3\cdot 4\text{H}_2\text{O}$ :  $\text{Ga}_2(\text{C}_2\text{O}_4)_3\cdot 2\text{H}_2\text{O}$  ( $140$ — $150^\circ$ ),  $\text{Ga}_2(\text{C}_2\text{O}_4)_3$  ( $166$ — $180^\circ$ ), and  $\text{Ga}_2\text{O}_3$  ( $195$ — $200^\circ$ ).  $\text{Ga}(\text{OH})(\text{OAc})_2$  gives  $\text{GaO}(\text{OAc})$  ( $140$ — $150^\circ$ ) and  $\text{Ga}_2\text{O}_3$ . In each case the  $\text{Ga}_2\text{O}_3$  formed gives an amorphous X-ray diagram,  $\beta\text{-Ga}_2\text{O}_3$  being formed on heating to  $>480$ — $600^\circ$ . Decomp. of  $\text{Ga}(\text{OH})_3$  or  $\text{Ga}(\text{NO}_3)_3$  gives  $\alpha\text{-Ga}_2\text{O}_3$ .

A. J. E. W.

**[Pentacarbon dioxide.]** A. KLEMENC (Ber., 1938, 71, [B], 1625—1626; cf. A., 1937, I, 575).—A reply to Diels (A., 1938, I, 410). H. W.



**Reactions of dicarbon gas.** A. KLEMENC and G. WAGNER (Z. anorg. Chem., 1938, 239, 1—13).—The reactions of  $C_2$ , formed in the decomp. of  $C_3O_2$  (cf. A., 1934, 1314), with  $O_2$  and  $H_2$  at  $200^\circ$  have been studied. Reasons are given for the belief that they are reactions of  $C_2$  and not of  $C_3O_2$ . With  $O_2$ , CO and  $CO_2$  and at the same time two solid C oxides,  $C_3O_4$  and  $C_3O_6$ , are formed. These are colourless or faintly yellow and stable to alkali. At  $300^\circ$  they decompose to CO and  $CO_2$ . It is suggested that  $C_3O_4$  and  $C_3O_6$  result from addition of  $O_2$  to  $C_3O_2$ , whilst  $C_2$  affords at first  $C_2O_2$  which may then decompose to  $2CO$  or to  $C + CO_2$ , followed by  $C + O_2 = CO_2$ . With  $H_2$  the products are  $C_2H_2$  and higher hydrocarbons. Some observations on the thermal decomp. of  $C_3O_2$  and on the photochemical polymerisation of  $C_2$  to red solid C are recorded. F. J. G.

**Influence of keto- and keten groups, adsorbed molecules and ions on the mechanism of carbon oxidation.** V. SIHVONEN (Trans. Faraday Soc., 1938, 34, 1062—1074).—Theories concerning the mechanism of the breakdown of the C lattice are based on extensive experimental evidence on the influence of keto- and keten groups, and of adsorbed mols. The mechanism of C oxidation, the reduction of  $CO_2$ , the adsorption of  $O_2$ , the effect of  $H_2O$ , and the anodic oxidation of C both in the electrolytes and in the gas phase are considered. W. R. A.

**Surface reaction of graphite with oxygen, carbon dioxide, and water vapour at low pressures.** L. MEYER (Trans. Faraday Soc., 1938, 34, 1056—1061).—An apparatus for the investigation of the surface reactions of graphite with oxidising gases is described and the requirements necessary for the investigation of the true primary surface reaction are indicated. The reaction with  $O_2$  shows two different types, viz., a low-temp. (up to  $1500^\circ K.$ ) reaction of the first order, characterised by dissolution of  $O_2$  in the graphite according to Henry's law, and a high-temp. ( $>1800^\circ K.$ ) reaction of zero order. The surface reaction with  $CO_2$  is also of zero order. A description of the experiment with  $H_2O$  vapour is given; the reaction is of zero order as found by Sihvonon, no  $CO_2$  being formed as primary product. The large difference in the abs. rate of formation of CO is attributed to differences in the structure or purity of the graphite. W. R. A.

**Formation of salts from graphite by strong acids.** U. HOFMANN and W. RÜDOFF (Trans. Faraday Soc., 1938, 34, 1017—1021).—Graphite salts of  $HClO_4$ ,  $H_2SeO_4$ ,  $HNO_3$ ,  $H_3PO_4$ ,  $H_4P_2O_7$ , and  $H_3AsO_4$ , analogous to the compound formed between graphite and  $H_2SO_4$ , have been prepared. They are stable only in the presence of their parent acid (conc.) and are decomposed by  $H_2O$  (even by atm.  $H_2O$ ). X-Ray examination of these salts shows that the hexagon structure of graphite persists. The acid is absorbed into the graphite lattice, one acid mol. for 8 C. The compounds, which are formed only in the presence of an oxidising agent, can be reduced by a reducing agent sol. in the appropriate conc. acid. Data on oxidation and reduction indicate that, with  $H_2SO_4$ , a graphite H sulphate,  $C_2H_2SO_4$ , is formed; and similarly with other acids. Undissociated acid

L. L. (A., I.)

mols., as well as anions, become absorbed between lattice layer planes; it is suggested that for 24 C two mols. and one anion of acid are taken up. Both formation and reduction of salts take place in stages of definite structure. The stabilities of the salts are: perchlorate and H sulphate  $>$  selenate  $>$  nitrate  $>$  phosphate and pyrophosphate  $>$  arsenate. The electrochemical behaviour of the salts, their reversible formation, their interconvertibility by anionic exchange, and the X-ray data favour the view that they are salts, not esters, of graphite. W. R. A.

**Cold combustion of carbon monoxide by transformation into ammonium carbonate using ammoniacal solutions of copper salts.** K. LESCHEWSKI, H. MÖLLER, and B. STEINMANN (Z. anorg. Chem., 1938, 239, 180—188; cf. A., 1935, 1332; 1938, I, 262).—CO is not oxidised by  $Cu^{II}$  in absence of  $NH_3$ , whilst accumulation of  $(NH_4)_2CO_3$  retards the absorption of CO. After a time the absorption of CO mixed with  $O_2$  ceases when all the  $Cu^I$  is used, but treatment with CO alone regenerates  $Cu^I$  and restores the absorptive power of the solution. The process can be made continuous, with separation of solid  $(NH_4)_2CO_3$ , by using alternately CO mixed with  $O_2$  and CO alone. F. J. G.

**Silicon nitride.** A. G. NASINI and A. CAVALLINI (Congr. int. Quim. pura apl., 1934, 9, III, 280—293; Chem. Zentr., 1936, ii, 2320).— $SiO_2$  is converted into  $Si_3N_4$  without formation of intermediate products by treatment with  $N_2$  at  $1300$ — $1380^\circ$ . The reactions (at  $900$ — $1300^\circ$ ) of  $Si_3N_4$  with a no. of metallic oxides have been studied; they are regarded as involving  $O_2$ :  $Si_3N_4 + 5O_2 = 3SiO_2 + 4NO + 349.4 \text{ kg.-cal.}$

A. J. E. W.

**Affinity. LXXXIV. Zirconium phosphides.** E. F. STROTZER and W. BILTZ [with K. MEISEL] (Z. anorg. Chem., 1938, 239, 216—224).—The existence of  $ZrP_2$  (cf. A., 1908, ii, 597) has been confirmed. It is the highest Zr phosphide, and is stable to air, Br, and most acids, but is completely dissolved by hot conc.  $H_2SO_4$ . A monophosphide,  $ZrP$ , is indicated by tensimeter curves and X-ray photographs, and the latter also indicate the existence of a subphosphide. Data for  $\rho$  and mol. vol. of Zr-P preps. are recorded.

F. J. G.

**Preparation of pure metals of the titanium group by thermal decomposition of their iodides.** IV. Appearance of lower zirconium iodides in the preparation of ductile zirconium. J. D. FAST (Z. anorg. Chem., 1938, 239, 145—154).—When  $ZrI_4$  is heated with Zr lower iodides, which decompose  $H_2O$  with evolution of  $H_2$ , are formed. The effects of this reaction on the course of the prep. of Zr by decomp. of  $ZrI_4$  vapour at a glowing filament under various conditions have been investigated, and from the results it is concluded that  $ZrI_4$  and Zr afford  $ZrI_3$  at  $400^\circ$  and  $ZrI_2$  at  $560^\circ$ , that  $ZrI_3$  partly decomposes to  $ZrI_2$  and  $ZrI_4$  above  $310^\circ$ , and that  $ZrI_2$  partly decomposes to Zr and  $ZrI_4$  above  $430^\circ$ .

F. J. G.

**Basic zirconium sulphate obtained by hydrolysis of the normal sulphates.** (MLLE.) M. FALINSKI (Compt. rend., 1938, 206, 1479—1480).—A study of the system  $ZrO_2$ — $SO_3$ — $H_2O$  by the residue



method shows that the salt described by Hauser (A., 1910, ii, 872) is  $7\text{ZrO}_2 \cdot 5\text{SO}_3 \cdot n\text{H}_2\text{O}$ . Analysis of the solid phases gives  $n = 29.5 \pm 0.5$ . A. J. E. W.

**Lead oxides.** A. BARONI (Gazzetta, 1938, 68, 387—393).—X-Ray and magnetic investigations show that the supposed  $\text{Pb}_2\text{O}$  of various investigators is a mixture of Pb and of tetragonal  $\text{PbO}$ . X-Ray examination of the products of the thermal decomp. of  $\text{PbO}_2$ , both at atm. pressure and in vac., indicates the existence of only  $\text{Pb}_2\text{O}_3$  and  $\text{Pb}_3\text{O}_4$ . No evidence for the existence of black  $\text{Pb}_3\text{O}_4$  or of  $\text{Pb}_7\text{O}_{11}$  was obtained, and these are probably additive products of  $\text{Pb}_2\text{O}_3$  with O. In the action of  $\text{O}_2$  on  $\text{PbO}$  pressure (5—200 atm.) has no influence on the products formed, which are identical with those obtained by the decomp. of  $\text{PbO}_2$ . Magnetic measurements for the system  $\text{PbO}$ —O confirm this. O. J. W.

**Nitrosyl fluoborate, its preparation, properties, and use for fluorination.** S. A. VOZNESENSKI and P. P. KURSKI (J. Gen. Chem. Russ., 1938, 8, 524—528).— $\text{NO}$ , and conc. aq.  $\text{HBF}_4$  yield  $\text{NOBF}_4$ .  $\text{NH}_2\text{Ph} \cdot \text{HCl}$  in  $\text{EtOH}$  and  $\text{NOBF}_4$  give  $\text{PhN}_2 \cdot \text{BF}_4$  in 90% yield. R. T.

**$\alpha$ - and  $\beta$ -Monohydrates of molybdic anhydride.** V. AUGER (Compt. rend., 1938, 207, 164—166).—The prep. and properties of the  $\alpha$ - and  $\beta$ -monohydrates of  $\text{MoO}_3$  are discussed and the results of Rosenheim and Davidson (A., 1904, ii, 128) are criticised. The  $\beta$ -monohydrate is actually  $\text{MoO}_3$  containing adsorbed  $\text{H}_2\text{O}$ . W. R. A.

**Preparation and analysis of aqueous hydrobromous acid.** E. A. SCHILOV and N. P. KANJAEV (J. Gen. Chem. Russ., 1938, 8, 445—447).—0.01—0.05M-Br is shaken with excess of  $\text{Ag}_3\text{PO}_4$ ; the solution, when distilled in vac. at 25—30° in absence of light, yields pure aq.  $\text{HOBr}$ . Sensitive methods of detecting  $\text{Br}'$  and  $\text{BrO}_3'$  in presence of  $\text{HOBr}$  are described. R. T.

**Reduction of potassium permanganate by oxalic acid in aqueous solution.** J. A. MULLER and (Mlle.) E. PEYTRAL (Bull. Soc. chim., 1938, [v], 5, 1168—1171).—If 2 mols. of  $\text{KMnO}_4$  and 3 mols. of  $\text{H}_2\text{C}_2\text{O}_4$  are allowed to interact,  $(\text{MnO}_2)_9 \cdot 2\text{K}_2\text{O} \cdot n\text{H}_2\text{O}$  is formed. After treatment with conc.  $\text{HNO}_3$  and heating to 110°  $\text{Mn}_2\text{O}_3 \cdot 4—5\text{H}_2\text{O}$  is formed, which, when heated to 350—400°, loses  $\text{H}_2\text{O}$  to form  $\text{Mn}_2\text{O}_3$ . C. R. H.

**Preparation of a stable hydrate of manganese dioxide in dry air at room temperature.** J. A. MULLER (Bull. Soc. chim., 1938, [v], 5, 1166—1168).—If  $\text{KMnO}_4$  is reduced, in presence of conc.  $\text{HNO}_3$ , by  $\text{H}_2\text{C}_2\text{O}_4$  in an amount insufficient for complete reduction, the ppt., after drying at room temp., corresponds with  $(\text{MnO}_2)_2 \cdot \text{H}_2\text{O}$ . C. R. H.

**Active substances. XXX. Chemical specificity of different forms, richer in energy, of one on the same type of crystal. I. Different forms, rich in energy, of  $\alpha\text{-Fe}_2\text{O}_3$ .** R. FRICKE, F. BLASCHKE, and C. SCHMITT (Ber., 1938, 71, [B], 1738—1743).—Different, active preps. of  $\alpha\text{-Fe}_2\text{O}_3$  are immersed in solutions of  $\text{K}_3\text{PO}_4$  until adsorptive equilibrium is attained and the adsorbed  $\text{KOH}$  and  $\text{H}_3\text{PO}_4$  are measured. The transition from  $\alpha\text{-FeO}_2\text{H}$

to the very irregularly distorted lattice of  $\alpha\text{-Fe}_2\text{O}_3$  causes an immediate increase in the ratio of adsorbed  $\text{KOH}$  to adsorbed  $\text{H}_3\text{PO}_4$ , which diminishes greatly with lessened distortion of the oxide (with increasing temp. of preheating). It thus appears that  $\alpha\text{-Fe}_2\text{O}_3$  with very irregular lattice distortion has much stronger acidic in relationship to its basic properties than an  $\alpha\text{-Fe}_2\text{O}_3$  with mainly ordered crystal lattice. According to conditions with respect to energy content, a chemical compound can exhibit different chemical properties. H. W.

**Hydroxides and oxide hydrates. LI. Dependence of the chemical properties of polymorphous compounds on the type of crystal.**

**II. Ferric hydroxides.** R. FRICKE, F. BLASCHKE, and C. SCHMITT (Ber., 1938, 71, [B], 1731—1737).—From equally conc. solutions of  $\text{K}_3\text{PO}_4$ , equal amounts of different, finely-divided preps. of  $\alpha\text{-FeO}_2\text{H}$  and  $\gamma\text{-FeO}_2\text{H}$  adsorb  $\text{KOH}$  and  $\text{H}_3\text{PO}_4$  in such a manner that the quotient of the adsorbed amounts of the two types of ion is nearly identical for both types of crystal. The basic and acidic properties of the two crystal types are therefore closely similar. According to these results and to measurements of  $p_H$   $\gamma\text{-FeO}_2\text{H}$  is rather more strongly acidic than  $\alpha\text{-FeO}_2\text{H}$ . In their amphoteric behaviour the two cryst. modifications of  $\text{FeO}_2\text{H}$  differ less from one another than do the two cryst. types of  $\alpha\text{-AlO}_2\text{H}$  (Fricke *et al.*, A., 1937, I, 19). H. W.

**Magnetic contribution of the constituents of ferric hydroxide formed in alkaline media.** R. CHEVALLIER and (Mlle.) S. MATHIEU (Compt. rend., 1938, 207, 58—61).— $\text{Fe}(\text{OH})_3$  formed in alkaline media contains goethite,  $\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  (I), which can be isolated by  $\text{HNO}_3$ , and a  $\text{HNO}_3$ -sol.  $\text{Fe}(\text{OH})_3$  (II). The individual contributions of (I) and (II) are considered. The susceptibility of (I) is small, whilst that of (II) is high and increases with time. The high val. for (II) may arise from the presence of some ferromagnetic  $\text{Fe}_3\text{O}_4$  formed during the reaction; this theory has not yet been proved but evidence of the heterogeneity of (II) is cited in its favour. W. R. A.

**Higher oxygen compounds of nickel.** B. A. PETROV and B. ORMONT (J. Gen. Chem. Russ., 1938, 8, 563—571).—Repetition of Goralevitch's work (A., 1930, 1141; 1931, 324; 1932, 585) does not lead to production of  $\text{Ni}^{\text{VI}}$  or  $\text{Ni}^{\text{VIII}}$  oxides, but only to  $\text{NiO}$ ,  $\text{Ni}_2\text{O}_3$ , and  $\text{NiO}_2$ .  $\text{NiO}_2$  was also prepared by anodic oxidation of Ni. R. T.

**Artificial radioactivity as a test for minute traces of elements.** G. T. SEABORG and J. J. LIVINGOOD (J. Amer. Chem. Soc., 1938, 60, 1784—1786).—Small amounts of impurities can be detected by means of their characteristic half-lives after the substance containing the impurities has been rendered artificially radioactive. With the aid of chemical separation, 6 p.p.m. of Ga were detected in Fe. E. S. H.

**Review of the application of microscopical study to metallurgical problems.** G. M. SCHWARTZ (Econ. Geol., 1938, 33, 440—453).—The



val. of methods of microscopical analysis, particularly the study of polished surfaces of ores, is illustrated.

L. S. T.

**Qualitative analysis by the semi-micro-method.** G. W. SMITH (J. Chem. Educ., 1938, 15, 324—329).—Apparatus and methods are briefly described. A comparison of results obtained by macro- and semi-micro-methods shows the latter to be satisfactory.

L. S. T.

**Quantitative mineralogical analysis of dusts.** J. H. HELLMERS and H. UDLUFT (Zeiss-Nachr., 1936, 2, 1—10; Chem. Zentr., 1936, ii, 2178).—A method of analysing dusts, employing an immersion method of determining  $n$  for the particles in conjunction with a polarising microscope, is described.

A. J. E. W.

**Report of [A.O.C.S.] Committee on Indicators.** J. L. MAYFIELD (Oil & Soap, 1938, 15, 206—207).—Thymolphthalein and Me-blue are considered undesirable; thymol-blue is better, but the colour change is not adequate in all cases. All three indicators show an unsatisfactory lack of uniformity between different batches of the dyes. An aniline-blue (G. Grubler) gives a sharp, distinct red-blue change and the results obtained with it up to almost 30% free fatty acids were identical with those obtained with phenolphthalein.

E. L.

**6:7-Dimethoxyisoquinoline-1-carboxylic acid as a fluorescence indicator.** L. SZEPELLÉDY and J. JÓNÁS (Z. anal. Chem., 1938, 113, 326—334).—The oxidation ( $\text{KMnO}_4$ ) product of papaverine having the properties of a fluorescent indicator is shown to be 6:7-dimethylisoquinoline-1-carboxylic acid. The data tabulated for the limits of visibility of the fluorescence of the indicator show that the presence of the commoner ions and cations has little or no effect. The colour change interval of the fluorescence ranges from  $p_H$  9.5 (yellow) to  $p_H$  11.0 (blue). The indicator is suitable for the titration of strong and weak acids and strong bases in coloured solutions. Data for the titration of 0.1N- and N-NaOH with AcOH alone (compared with phenolphthalein) and in presence of Columbia-brown R, tartrazine XX, and methylene-blue are recorded. Anhyd. glycerol is the most suitable solvent for the prep. of a solution (0.1%) of the indicator. For colourless solutions 0.2 c.c. of this solution, after dilution with an equal vol. of EtOH, is recommended for each 100 c.c. to be titrated; for coloured solutions, 1 c.c. is preferable.

L. S. T.

**Orcinolaurin as a fluorescence indicator.** J. JÓNÁS and L. SZEPELLÉDY (Z. anal. Chem., 1938, 113, 422—428).—Orcinolaurin can be used as a fluorescence indicator for titration of strong acids and bases in deeply coloured solutions by ordinary light. Its greenish fluorescence develops at  $p_H$  between 6.5 and 8.0. The usual cations (except  $\text{Fe}^{+++}$ ) and anions have only slight effects on the fluorescence.

J. W. S.

**Anthocyanins as indicators in neutralisation analysis.** V. H. MATULA and C. B. MACEK (Chem. Obzor, 1936, 11, 83—84; Chem. Zentr., 1936, ii, 2758).—The anthocyan prepared from the flowers of *Althaea rosea* (A., 1930, 1143) is rose-red at  $p_H$

1—4, sepia-brown at neutralisation point, and green at  $p_H$  11; it possesses the advantage of changing colour near to the neutralisation point. The colouring matter of red cabbage is also an indicator.

A. H. C.

**Quantitative analysis of mixtures of strong and weak acids, buffer and neutral salts.**—See B., 1938, 1082.

**Determination of hydrogen in steels.**—See B., 1938, 1048.

**Determination of chlorine by Mohr's method in presence of manganese.** I. C. RITSEMA (Pharm. Weekblad, 1935, 75, 1017—1018).—Mn interferes with the end-point in the titrimetric determination of Cl in drinking- $\text{H}_2\text{O}$ , using  $\text{Ag}_2\text{CrO}_4$  as indicator. It may be removed by shaking the sample with MgO and filtering off the ppt. before titration. MnO reacts with  $\text{Ag}_2\text{CrO}_4$  to give  $\text{Ag}$ ,  $\text{CrO}_4^{--}$ ,  $\text{Mn}^{+++}$ , and  $\text{MnO}_2$ .

S. C.

**Micro-analytical determination of bromine.**—See A., 1938, III, 862.

**Determination of iodine and potassium iodide in tincture of iodine.**—See B., 1938, 1097.

**Titration of small quantities of fluorides with thorium nitrate.** I. Effect of changes in amount of indicator and acidity. II. Effects of chlorides and perchlorates. D. DAHLE, R. U. BONNAR, and H. J. WICHMANN (J. Assoc. Off. Agric. Chem., 1938, 21, 459—467, 468—474).—I. Rowley and Churchill's procedure (A., 1938, I, 95) is modified so as to apply to small amounts of F by titrating a blank with NaF to an exact colour match with the experimental sample. The relation between colour developed, [F], and  $p_H$  is worked out in detail; greatest accuracy and sensitivity are obtained at  $p_H$  2.75.

II. In presence of  $\text{Cl}^-$  and  $\text{ClO}_4^-$  the vals. obtained are too high. Neutralisation of the distillate is to be avoided. A procedure for titrating without neutralisation and means of avoiding high acidity in the distillate are presented.

E. C. S.

**Rapid determination of fluorine in apatites.** See B., 1938, 1033.

**Determination of sulphur by means of oxidising alkali melts.** A. L. BERNOULLI and H. STAUFER (Z. anal. Chem., 1938, 113, 340—342).—0.1—0.2 g. of the sample is covered with 2 g. of  $\text{KClO}_3$ , 5 g. of KOH, and 2—5 c.c. of  $\text{H}_2\text{O}$  in a Ni crucible. A smaller Ni crucible is inverted over the mixture, and both crucibles are heated to redness from top and bottom in a regulated manner. After treatment of crucibles and the fused mass with hot  $\text{H}_2\text{O}$ , the solution is weakly acidified with conc. HCl, and filtered. The  $\text{SO}_4^{--}$  is then pptd. as usual. For org. compounds containing S, the error is  $\pm 0.3\%$ , and with care no explosion occurs. Advantages of the method are its simplicity and the avoidance of ions, such as  $\text{NO}_3^-$ , strongly adsorbed by  $\text{BaSO}_4$ .

L. S. T.

**Determination of pyritic sulphur in coal.**—See B., 1938, 1002.

**Rapid potentiometric method for determination of sulphate.** B. E. CHRISTENSEN, H. WYMORE,



and V. H. CHELDELIN (Ind. Eng. Chem. [Anal.], 1938, 10, 413—414).— $\text{SO}_4^{2-}$  (0.05—0.25N) can be determined in 25—60% aq. MeOH, containing  $\geq 1$  mg. of  $\text{K}_2\text{S}_2\text{O}_8$  in 25 c.c., by electrometric titration with  $\text{BaCl}_2$ . E. S. H.

Errors in the use of standard sodium thiosulphate solutions containing borax as preservative. C. W. JORDAN (Amer. J. Pharm., 1938, 110, 316—321).—The use of borax and other substances for preserving standard aq.  $\text{Na}_2\text{S}_2\text{O}_3$  is discussed. Erroneous results are obtained when alkaline preservatives ( $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$ , borax, etc.) are used; the error is up to 50% in Mellhiney's Br method of determining unsaturated linkings (A., 1903, ii, 340). F. O. H.

Semi-micro-determination of nitrogen in coke.—See B., 1938, 1003.

Aspiration method in determining ammonia and other volatile gases. L. A. SARVER (Ind. Eng. Chem. [Anal.], 1938, 10, 415).—Relative advantages of aspiration and distillation are discussed. E. S. H.

Colorimetric determination of ammonia with phenol and hypochlorite. Application in Fuchs' carcinoma reaction. K. HINSBERG and K. MÜCKE (Biochem. Z., 1938, 297, 332—335).—For the photometric determination of  $\text{NH}_3$  (e.g., after heating with  $\text{H}_2\text{SO}_4$  as in the Kjeldahl method) the procedure depending on the colour produced with phenol and  $\text{NaOCl}$  (cf. Van Slyke and Hiller, A., 1934, 94) is superior to the Nessler method, which, however, is to be preferred in applying Fuchs' test (Z. ges. exp. Med., 1936, 98, 70). W. McC.

Micro-determination of ammonium. Micro-alkalimetric studies. III. J. MIKA (Mitt. berg.-hüttenmänn. Abt. Palatin-Joseph-Univ., 1935, 7, 92—110; Chem. Zentr., 1936, ii, 2180).—The sample is distilled to dryness with aq.  $\text{NaOH}$  in a current of air, the  $\text{NH}_3$  being absorbed in  $\text{H}_3\text{BO}_3$  and titrated. The apparatus and technique are described. An average negative error of  $\geq 0.6\%$  is claimed. A. J. E. W.

Microchemical examination of explosives and ammunition.—See B., 1938, 1105.

Field test for phosphates. M. C. OAKES (Econ. Geol., 1938, 33, 454—457).—Utilisation of the  $\text{NH}_4$  phosphomolybdate test is described. The test is sensitive to  $< 0.5\%$   $\text{P}_2\text{O}_5$  in nodules, limestone, shale, and chert. L. S. T.

Sensitisation of paper strips with filtered mercuric bromide solution in Gutzeit method of arsenic analysis. R. S. ROSENFELS (J. Assoc. Off. Agric. Chem., 1938, 21, 493—496).—The  $\text{HgBr}_2$  solution can be used for 3—4 months provided it is filtered before strips are prepared from it. Strips kept  $\geq 21$  days were satisfactory. E. C. S.

Determination of traces of arsenic by electrolytic hydrogenation. Experimental study of the mechanism of the technique. Comparison with chemical hydrogenation. H. GRIFFON and J. THURET (Bull. Soc. chim., 1938, [v], 5, 1129—1142).—The electrolytic method is applicable in presence of all concns. of neutral salts, gives a const. evolution

of  $\text{H}_2$ , and yields very reproducible results. The chief disadvantage is the necessity for comparatively complex and expensive apparatus. The accuracy of both methods is about the same. C. R. H.

Determination of small quantities of carbon in steel.—See B., 1938, 1048.

Determination of traces of carbon monoxide in the air of mines.—See B., 1938, 1005.

Laboratory measurements by means of physical methods. T. KRASSÓ (Tech. Kurir, 1938, 9, 63—65).—For determining minute amounts of  $\text{CO}_2$  the change in conductivity of a  $\text{Ba}(\text{OH})_2$  solution when  $\text{CO}_2$  is introduced is measured. In measurement of short periods by means of a micro-coulometer with reactions which can be followed electrometrically, the quantity of the gas evolved in the coulometer  $\propto$  the time of the reaction; a detailed description of the apparatus is given. E. P.

Determination of ferrocyanide. R. HÜNERBEIN (Angew. Chem., 1938, 51, 539—540).—The reaction  $\text{K}_4\text{Fe}(\text{CN})_6 + 3\text{Hg}(\text{OH})_2 \rightleftharpoons \text{Fe}(\text{OH})_2 + 3\text{Hg}(\text{CN})_2 + 4\text{KOH}$ , can be caused to proceed to completion by use of  $\text{Hg}(\text{OAc})_2$  in slightly alkaline solution. Conversion of  $\text{Hg}(\text{CN})_2$  into  $\text{HCN}$  is best effected by distillation with  $\text{HCl}$  or, preferably,  $\text{HBr}$ . A suitable apparatus is described. Salts  $\text{Hg}_2\text{Fe}(\text{CN})_6 \cdot 2\text{H}_2\text{O}$ ,  $\text{Hg}_3[\text{Fe}(\text{CN})_6]_2 \cdot 3\text{H}_2\text{O}$ , and  $\text{Hg}_3[\text{Co}(\text{CN})_6]_2 \cdot 2.5\text{H}_2\text{O}$  have been isolated. The last is considerably more stable than the corresponding Fe compounds; when heated at  $300^\circ$  it gives  $\text{Hg}(\text{CN})_2$ ,  $\text{Co}_3[\text{Co}(\text{CN})_6]_2$ , and  $\text{C}_2\text{N}_2$ . H. W.

Electrolytic determination of non-metallic inclusions in steel.—See B., 1938, 1048.

Microscopical determination of potassium with naphthol-yellow S. H. A. FREDIANI (Ind. Eng. Chem. [Anal.], 1938, 10, 447—449).— $\text{K}^+$  can be determined in presence of excess of  $\text{NH}_4^+$  (200:1) at a limiting concn. of 7.5 mg. per ml. by microscopical observation of the cryst. ppt. formed with aq. naphthol-yellow S saturated at  $20^\circ$ . Rb forms similar crystals, but  $\text{Mg}^{++}$ ,  $\text{Na}^+$ ,  $\text{Li}^+$ , and  $\text{Cs}^+$  do not interfere. Acid samples should first be neutralised by K-free  $\text{NaOH}$ . E. S. H.

Spectrocolorimetric determination of potassium. H. LUNDEGÅRDH and K. BORATYNSKI (Svensk Kem. Tidskr., 1938, 50, 135—144).—Determination of elements by direct photometry of spectral line intensity is the most accurate method available, but the apparatus is costly and very sensitive to external disturbances. A simpler method is to determine the amount of light passing a filter of appropriate range. K is determined by its lines at 7665 and 7699 Å., using a filter transparent between 7000 and 10,000 Å. When determining K in soils or plant ash interference is caused by Ba, Cs, Rb  $>$  Mn, Sr, Fe  $>$  Na, Li, Ca. Mg and Cu do not interfere. When Ca is present in excess it may be compensated for by its determination by the band in the red in the same way, but owing to imperfections of the filter Na interferes.  $\text{NH}_4\text{Cl}$  causes errors by lowering the flame temp. The method is accurate to about 5%. M. H. M. A.



**Inorganic micro-methods. I. Cations. II.** CLAUDATUS and G. GHIMICESCU (Ann. Sci. Univ. Jassy, 1938, 24, I, 357—369).—Methods are described for the following: *Na*. Pptn. with Zn uranyl acetate and colorimetry with  $K_4Fe(CN)_6$ . *K*. Pptn. as the cobaltinitrite, treatment with 5%  $Na_3PO_4$ , and colorimetric determination of  $NO_2^-$  by means of an AcOH solution of salipyryne. *NH\_4^+*. Adsorption of  $NH_4^+$  on zeolite, liberation of  $NH_3$  by NaOH, and nesslerisation. *Fe*.  $Fe(CNS)_3$  extracted with EtOAc and determined colorimetrically. *Mn*. Conversion into  $MnO_4^-$  ( $S_2O_8^{2-}$  and  $Ag^+$ ) and colorimetric determination. *Pb*. Pptn. as  $PbCrO_4$  in dil. AcOH, and colorimetric determination with diphenylcarbazide. L. S. T.

**Determination of the soda-potash content of combined alkali in soaps etc.**—See B., 1938, 1070.

**Separation and detection of the elements of the silver and thallium group.** I. WADA and R. ISHII (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1938, 34, 787—818).—A procedure for the separation of Ag, Tl and Au, Ga, and In from each other and from the elements with which they are likely to be associated has been developed. Ag is pptd. with HBr, and Tl with most of the Au is extracted from the filtrate (N in acid) with  $Et_2O$ . The acid solution is converted into a 5.5N-HCl solution, and  $Et_2O$ -extracted, whereby all the Ga and  $Fe^{III}$  are removed, and some of the Mo, Re, Ir, and the remaining Au. These latter are pptd. with  $H_2S$ , when the  $Et_2O$  extract has been converted into a HCl solution. The filtrate is diluted to be 0.1N and the  $Fe^{III}$  reduced to  $Fe^{II}$  with  $H_2S$ , the solution being again extracted with  $Et_2O$ ; the extract now contains all the Ga but very little Fe. The small amount of Fe with the Ga may be removed by adding NaOH to the  $Et_2O$  extract, when it has been made into an aq. solution. Ga can now be detected by adding  $K_4Fe(CN)_6$ , with which it gives a white ppt. The original 5.5N-HCl solution from which the Ga was extracted may contain In, together with  $Fe^{III}$  and traces of Mo, Ir, Te, and Re; it is converted into a 4.5N-HBr solution, which is  $Et_2O$ -extracted, the extract is converted into a HCl solution, from which Mo, Te, Re, and Ir are pptd. with  $H_2S$ . The filtrate is boiled, and  $NH_4Cl$  and aq.  $NH_3$  are added, whereby In and Fe are pptd. The ppt. is dissolved in 6N-HCl, and the Fe extracted with  $Et_2O$ , In being practically inextractable from so acid a solution. R. C. M.

**Quantitative analysis based on spectral energy.** M. SLAVIN (Ind. Eng. Chem. [Anal.], 1938, 10, 407—411).—Limitations of the internal-standard method are discussed, and measurement of energy of spectral emission is recommended in place of intensity. The spectral energy in a C are  $\propto$  the wt. of element causing the emission. Results for Ca in various minerals show an average error of 8.3% and a max. error of 18.5%. The presence of other elements does not interfere. E. S. H.

**Microchemical test for magnesite.** H. L. PIOTROWSKI (Spraw. Tow. Nauk. Lwow, 1934, 14, 233—234).—On treating magnesite with a solution of 1 part of KOH and 0.1 part of Ti-yellow in 100 parts of  $H_2O$ , the mineral turns fire-red. Dolomite

and calcite are unaffected. Clay minerals turn citron-yellow. CH. ABS. (e)

**Rapid determination of magnesium in aluminium alloys.**—See B., 1938, 1057.

**Electrochemical separation [differentiation] of alloys.**—See B., 1938, 1057.

**Determination of lead.** O. BRUNCK (Z. anal. Chem., 1938, 113, 385—389).—Methods of determining Pb as  $PbSO_4$ ,  $PbCrO_4$ ,  $Pb_3(PO_4)_2$ , and PbS are discussed. The recommended method of determination as PbS is to dissolve the sample in about 10 c.c. of  $HNO_3$  ( $d$  1.18), heat until all the  $HNO_3$  is expelled, dilute to 150—200 c.c., and then pass a slow stream of  $H_2S$ . Pptn. is complete in  $\frac{1}{2}$  hr. The ppt. is collected in a weighed sintered glass crucible, washed with cold  $H_2O$ , and dried at 110—120°. Amounts of Zn  $>0.2$  g. per 100 c.c. are not pptd. under these conditions, and other ions are not adsorbed on the cryst. PbS so deposited. Separation of Cd and Zn by an analogous procedure is impossible, even with a higher  $[HNO_3]$ , since the CdS pptd. is partly amorphous. J. W. S.

**Detection of lead ions in the lead compounds of the homeopathic pharmacopoeia.**—See B., 1938, 1097.

**Spectroscopic analysis of the products of lead, cadmium, and zinc plants.**—See B., 1938, 1051.

**Comparison of gravimetric and electrolytic methods of determining copper in copper sulphate.** F. I. BOGOJAVLENSKI (Utschen. Zap. Univ. Kazan, 1938, 97, No. 8, 95—113).—Six pptn. and seven electrolytic methods have been tested. Pptn. by KSCN after reduction by  $SO_2$  or  $NH_4HSO_3$ , and electrodeposition in presence of  $HNO_3$  (Luckow's method) are recommended. J. J. B.

**Determination of copper and cadmium in zinc.**—See B., 1938, 1050.

**Reactions of rare earth and allied elements with polyhydric phenols and alkaloids. VI. Colorimetric determination of cerium, with brucine.** F. M. SCHEMJAKIN, V. A. VOLKOVA, and A. S. BOSHKO (J. Gen. Chem. Russ., 1938, 8, 452—455).—A mixture of Ce-containing mineral, conc.  $H_2SO_4$ ,  $(NH_4)_2S_2O_8$ , and aq.  $AgNO_3$  is heated for 1 hr., the product is dissolved in  $H_2O$ , an aliquot part containing 0.014—1 mg. Ce is made neutral with aq.  $NH_3$ , 0.5 ml. of 0.1M- $H_2SO_4$  and 2 ml. of 0.01M-brucine acetate are added, and the coloration is compared after 16 hr. with those given by a series of standards. R. T.

**Volumetric determination of cerous in presence of ceric salts.** L. WEISS and H. SIEGER (Z. anal. Chem., 1938, 113, 305—325).—Numerous methods have been critically examined. (1) *Ce<sup>IV</sup> by reduction*. The  $H_2AsO_3$  method using ICl (HCl solutions) or  $OsO_4$  ( $H_2SO_4$  solutions) as catalysts is satisfactory, but titration of  $Ce^{IV}$  with  $H_2O_2$ , especially in presence of  $HNO_3$ , is inaccurate.  $FeSO_4$  or  $K_4Fe(CN)_6$  gives exact results with o-phenanthroline- $Fe^{II}$  indicator in presence of HCl or  $H_2SO_4$ , but  $HNO_3$  must be absent. (2) *Ce<sup>III</sup> by oxidation*.



Job's  $\text{PbO}_2$  method (A., 1899, ii, 334) is inaccurate. Knorre's  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  method (A., 1898, ii, 311) in its original form gives low results, but has been modified satisfactorily. Oxidation in alkaline medium with  $\text{K}_2\text{S}_2\text{O}_8$  and iodometric titration of the  $\text{Ce}^{+++}$  according to Šterba-Böhm and Matula (A., 1925, ii, 716) gives high (10–20%) results. Similar oxidation in presence of  $\text{Ni}^{++}$  and titration with  $\text{H}_3\text{AsO}_3$  by Lang and Zwerina's method (A., 1933, 137) gives low (0.2–3.4%) results. The  $\text{Bi}_2\text{O}_4$  method (Waegner and Müller, A., 1903, ii, 242) also gives low (10%) results. Lang's  $\text{CrO}_3$  method (A., 1934, 982) is accurate in  $\text{HNO}_3$ , but less so in  $\text{HCl}$  and especially in  $\text{H}_2\text{SO}_4$  solutions. Oxidation in alkaline solution with  $\text{K}_3\text{Fe}(\text{CN})_6$  and titration of the  $\text{K}_4\text{Fe}(\text{CN})_6$  formed with  $\text{KMnO}_4$  (A., 1908, ii, 736) is considered to be the best and the simplest method for the determination of  $\text{Ce}^{+++}$  in presence of  $\text{Ce}^{+++}$ . Tomiček's potentiometric method (A., 1925, ii, 716) is very accurate. L. S. T.

**Quantitative spectrographic analyses of alloys. Influence of a third metal on the Al : Mg intensity ratio in light metal analysis.**—See B., 1938, 1057.

**Determination of manganese and of the active oxygen in its higher oxides.** J. A. MÜLLER (Bull. Soc. chim., 1938, [v], 5, 1162–1165).—Mn is determined as  $\text{MnSO}_4$  and the latter can be converted into  $\text{Mn}_3\text{O}_4$ . Active O is determined by the liberation of I from KI by means of  $\text{HCl}$  in an atm. of  $\text{CO}_2$ . C. R. H.

**Rapid determination of minute amounts of iron in must, wine, and cider.**—See B., 1938, 1090.

**Application of citric acid to determination of nickel in presence of salts of iron and of phosphoric acid.** V. P. GOLENDEEV (Rept. U.S.S.R. Fat and Marg. Inst., 1935, No. 2, 22–26).—10 c.c. of 10% aq. Na citrate are added to 20 c.c. of the solution, the mixture is heated at  $100^\circ$  for 15–20 min., cooled, 10 c.c. of 10% aq.  $\text{NH}_3$  are added, and the solution is made up to 250 c.c. with  $\text{H}_2\text{O}$ . 10 c.c. of 0.04N-KCN are added to 20 c.c. of this solution and the excess of KCN is titrated with 0.02N- $\text{AgNO}_3$ . CH. ABS. (e)

**Determination of small amounts of nickel in presence of large amounts of iron.** E. REICHEL and L. STUZIN (Z. anal. Chem., 1938, 113, 389–419).—A method has been developed for determination of  $3 \times 10^{-5}$  to  $10^{-4}$  g. of Ni in presence of 1000–15,000 times its wt. of Fe.  $\text{Zn}^{++}$  corresponding with about 100 times the wt. of the Ni present is added to the  $\text{HCl}$  solution of the sample,  $\text{NH}_4\text{F}$  solution run in until the solution is decolorised, and the Zn and Ni are then pptd. together with  $\text{K}_3\text{Fe}(\text{CN})_6$ . The ppt. is ashed, dissolved in conc.  $\text{HCl}$ , and after making the solution slightly alkaline with  $\text{NH}_3$  the Ni is pptd. by addition of an excess of solid dimethylglyoxime. This ppt. is washed, ignited, and redissolved in  $\text{HCl}$ , the solution being evaporated to dryness on a water-bath. The  $\text{NiCl}_2$  is dissolved in  $\text{H}_2\text{O}$  and Ni determined colorimetrically as  $\text{NiS}$ . J. W. S.

**Determination of molybdenum in steels with the Pulfrich photometer.**—See B., 1938, 1048.

**Hydroxyanthraquinones as analytical reagents. Colorimetric determination of zirconium or hafnium.** H. A. LIEBHAFSKY and E. H. WINSLOW (J. Amer. Chem. Soc., 1938, 60, 1776–1784).—Procedure for the colorimetric determination of small amounts of Zr or Hf by means of 1:2-di-, 1:2:4-tri-, and 1:2:5:8-tetra-hydroxyanthraquinone, using a photo-electric recording spectrophotometer, is described. The method involves lake formation at great dilution in 95% EtOH. The influence of acid concn. on the formation of the lakes has been studied. Zr and Hf are qualitatively indistinguishable in the test. Other cations interfere only when they are present in considerable excess. E. S. H.

**Determination of antimony.** (A) P. E. WINKLER (Bull. Soc. chim. Belg., 1938, 47, 403). (B) J. PENS (*ibid.*, 404).—(A) The principle of Pens' method (A., 1938, I, 274) has been suggested previously by various authors. Winkler's iodometric method (A., 1927, 1160) has also proved satisfactory. (B) A reply. J. W. S.

**M.p. and b.p. on a micro- and macro-scale under various pressures.** C. ROSENBLUM (Ind. Eng. Chem. [Anal.], 1938, 10, 449).—Apparatus is described. E. S. H.

**Low-temperature evaporator.** D. S. STEVENS (J. Lab. clin. Med., 1938, 23, 978–979).

**Constant-temperature water-bath for solubility measurements.** W. J. KNOX, jun. (J. Chem. Educ., 1938, 15, 343–344).—Details of construction are given. L. S. T.

**Photo-electric thermoregulator.** A. GROSS and M. BASSIÈRE (Bull. Soc. chim., 1938, [v], 5, 1228–1231).—A regulator is described in which a relay is operated by a light source which is interrupted by means of a piece of Al foil attached to the end of a needle of a galvanometer, the latter acting as the temp. indicator. A drop in temp. is followed by a deflexion of the needle with the result that light passes to the photo-electric cell connected with the relay. The regulator will maintain temp. of  $200 \pm 120^\circ$  within  $\pm 0.5^\circ$ . C. R. H.

**Liquefaction of helium.** I. L. ZELMANOV (Compt. rend. Acad. Sci. U.R.S.S., 1938, 19, 469–470).—In the process based on the Joule-Thomson effect, the discrepancy between the yield of liquid He and that expected from Keesom's  $T$ - $S$  diagram is attributable to miscalculation of the liquefaction coeff.; for certain isenthalpies heat exchange may be impossible. Practical modifications to avoid this are outlined. I. McA.

**Light filter for the isolation of the green mercury line.** O. STOLL (Ber., 1938, 71, [B], 1576–1577).—A half-saturated solution of  $\text{NdCl}_3$  to which 20 wt.-% of  $\text{CuCl}_2$  (calc. on  $\text{H}_2\text{O}$  used) has been added has 80% transparency for the green lines and >0.1% transparency for the yellow and blue lines and is opaque to the red, violet, and ultraviolet lines of the Hg spectrum. A saturated solution of  $\text{Nd}(\text{NO}_3)_3$  containing  $\text{CuCl}_2$  removes all light from the Hg spectrum or white light except a small spectral



region around 5460 Å. The solution is stable to light and can be preserved unchanged. H. W.

**Inexpensive microscope lamp for critical illumination.** J. G. CARLSON (Stain. Tech., 1938, 13, 97—100).—A microscope lamp with light of adjustable intensity is described. Light filters can be made by mounting layers of coloured Cellophane in balsam between glass slips. E. E. H.

**Photo-electric colorimeter.** K. HARE and R. E. PHIPPS (Science, 1938, 88, 153—154).—The instrument described utilises a balanced circuit achieved by the use of a variable resistance in the circuit of one of the photo-electric cells. L. S. T.

**Simplified colorimetric technique.** R. SEIFERT (Süddeuts. Apoth.-Ztg., 1936, 76, 376—377; Chem. Zentr., 1936, ii, 823).—Measurements carried out with very simple apparatus are described. H. J. E.

**Objective measurement of colour.** J. W. PERRY (J. Sci. Instr., 1938, 15, 270—277).—The general principles of direct colour measurement based on the use of filter-screened photocells and the exact determination of the coeffs. in a trichromatic specification, and the application of these principles to "blancometers," are examined. Categories embracing spectrophotometrically similar colours and colorimetry over the whole colour field are distinguished. The instruments and their application to the measurement of colour differences are described. N. M. B.

**New fluorometer.** O. MAERCKS (Z. Physik, 1938, 109, 685—699).—A method for measuring fluorescence resonance periods with an accuracy of  $2 \times 10^{-10}$  sec. is described. The exciting radiation is interrupted by a train of supersonic waves of known frequency and the fluorescent light is passed through the same or another train of supersonic waves. The resulting displacement is a measure of the fluorescence resonance period. H. C. G.

**Application of the neon lamp and copper oxide photo-electric cell to volumetric analysis (photometric titration).** T. SOMIYA (Congr. int. Quim. pura apl., 1934, 9, VI, 63—69; Chem. Zentr., 1936, ii, 3152; cf. B., 1935, 854).—The titration solution is placed between a source of light and a Cu oxide photo-electric cell or a Ne lamp (which is silvered except for a small window) and, using a liquid light filter if necessary, titration is followed by galvanometer deflexions. Increased accuracy and sensitivity are claimed. A. H. C.

**Instructions for crystal measurement with new model of the two-circle goniometer.** P. TERPSTRA (Rec. trav. chim., 1938, 57, 893—904).

F. L. U.

**Graphic method of determining the optic sign and the true axial angle from the refractive indices of biaxial minerals.** J. H. LANE, jun., and H. T. U. SMITH (Amer. Min., 1938, 23, 457—460).

L. S. T.

**Ultra-violet rays in the laboratory.** H. PIRAUX (Tech. Ind. Chim., 1938, No. 277 bis, 190).—The application of ultra-violet (Wood's) light to fluorescence analysis etc. is reviewed. I. C. R.

**Quantitative X-ray analysis of crystalline powders.** K. SCHÄFER (Z. Krist., 1938, 99, 142—152; cf. Glocker, A., 1934, 979; Brindley, A., 1938, I, 124).—Detailed procedure is given for the optimum application of standard (Laue) theory of abs. X-ray intensities to the analysis of fine-grained mixtures by photometry of selected reflexions from cylindrical specimens. Results for 50–50% binary mixtures or alloys (NaCl–KBr, CuAl<sub>2</sub>–Al) are accurate to 3%. For components in low concn. or complicated lattices, calibration is preferable. I. MCA.

**Extension of the double-crystal X-ray spectrometer.** M. RENNINGER (Z. Krist., 1938, 99, 181—187).—A three-crystal arrangement aiming at the high resolution necessary for the analysis of real crystal reflexions is compared in substance and scope with DuMond's instrument (A., 1938, I, 15). The advantage of its highly monochromatic narrow beam is shown in consideration of calcite reflexions of Mo K $\alpha$  rays monochromatised by two "ideal" diamonds. I. MCA.

**Determination of indices of stereographically projected crystal surfaces.** H. TERTSCH (Z. Krist., 1938, 99, 61—66).—A discussion of (known) graphical methods. I. MCA.

**Apparatus for electrometric titrations of high precision.** E. STENHAGEN (Ind. Eng. Chem. [Anal.], 1938, 10, 432—433).—Apparatus for general purposes and for titrations in org. solvents is described. A special stirring device renders the apparatus suitable for titrations in an inert atm. E. S. H.

**Glass electrode for differential titrations.** M. PAÍÓ (Compt. rend., 1938, 207, 151—153).—A glass electrode for differential titrations consists essentially of a glass U-tube slightly constricted at the middle and separated into two compartments by a glass (Corning 015) membrane. Each compartment contains the same amount of liquid for titration. Various amounts of titrating liquid are added and the difference between the amounts added to the two compartments is maintained at a const. small quantity. With each addition the difference in potential between the two sides of the membrane is measured and a differential titration curve is thus obtained. By using a standardised glass electrode the differential and abs. titration curves are obtained simultaneously. The dissociation consts. of weak acids and bases and the  $p_H$  at the point of neutralisation can be determined with greater accuracy than from an abs. curve either alone or combined with a calc. differential curve. W. R. A.

**Electrical measurement of  $p_H$ .** J. VASSILLIÈRE-ARLHAC (Tech. Ind. Chim., 1938, No. 277 bis, 185—187).—A review of the principles of the method, methods of measurement, and the electrodes available. I. C. R.

**Purification of organic solvents intended for conductometric measurements.** L. DE BROUCKÈRE and A. PRIGOGINE (Bull. Soc. chim. Belg., 1938, 47, 399—402).—Commercial PrOH was purified by heating for  $\leq 15$  hr. in presence of CaO, distilling, and then fractionating. The fraction of b.p. 97—97.3° and  $\kappa 3-6 \times 10^{-8}$  ohm was redistilled at 40°/40—50 mm. in a slow stream of H<sub>2</sub>. The



conductivity of the distillate was a min. for the middle fraction, the lowest val. of  $\kappa$  observed being  $0.44 \times 10^{-8}$  ohm. The same method can be applied to other solvents. J. W. S.

**Measuring e.m.f. and very small direct currents with the help of electrometer tubes.** F. MÜLLER (Korros. u. Metallschutz, 1938, 14, 193—198).—The principles and technique of the method are described, and the conditions to be observed in its use are discussed. C. E. H.

**Measurement of large electrolytic resistances.** L. DE BROUCKÈRE and A. PRIGOGINE (Bull. Soc. chim. Belg., 1938, 47, 382—398).—A d.c. potential is applied to a conductivity cell containing the liquid of high sp. resistance ( $\rho$ ), and the current passing is compared with that observed when the cell is replaced by known resistances. Measurements of  $\rho$  for  $H_2O$ ,  $MeOH$ , and  $PrOH$  are complicated by polarisation, but if the resistance of the cell is high and the c.d. low this may be corr. by extrapolation of the current-time curve. Ohm's law holds for  $PrOH$  providing that a low p.d. is used and electrolysis is not prolonged. J. W. S.

**Electrodialysis.** H. DE BRUYN and S. A. TROELSTRA (Kolloid-Z., 1938, 84, 192—195).—Improved apparatus, the chief features of which are simplicity of construction and economy of wash- $H_2O$ , is described. F. L. U.

**Electrostatic generator operating under high air pressure.** R. G. HERB, D. B. PARKINSON, and D. W. KERST (Physical Rev., 1937, [ii], 51, 58).—A belt type electrostatic generator operating under an air pressure of 100 lb. per sq. in. gives a max. potential of approx. 2500 kv., and has been successfully used in experiments on at. disintegration. L. S. T.

**Electrostatic generator for the production of positrons.** G. B. COLLINS, R. SCHAGER, and A. L. VITTE (Physical Rev., 1937, [ii], 51, 58). L. S. T.

**Million-volt cyclotron.** P. G. KRUGER and G. K. GREEN (Physical Rev., 1937, [ii], 51, 57).—A cyclotron producing 2.5  $\mu$ amp. of deuterons at  $10^6$  e.v. energy and permitting the study of nuclear disintegrations without the intense fields of the cyclotron affecting the detecting apparatus has been constructed. L. S. T.

**Direct current of stabilised voltage for the Tag-Heppenstall moisture meter and other laboratory instruments.** E. B. WORKING (Cereal Chem., 1938, 15, 500—508).—The Tag-Heppenstall moisture meter requires d.c. of widely variable magnitude, at very const. voltage. Two rectifier circuits, and a third incorporating an electronic voltage regulator, which fulfil these requirements are shown. E. A. F.

**Electron microscope.** G. SELÉNYI (Tech. Kurir, 1938, 9, 57—58).—A review. E. P.

**Particle counter.** D. DE SOUZA SANTOS and G. WATAGHIN (Nuovo Cim., 1938, 15, 104—107).—A modified Geiger-Müller counter, with plane and parallel grating electrodes, is described. O. J. W.

**Electron scanning microscope.** M. VON ARDENNE (Z. Physik, 1938, 109, 553—572).—A very fine beam of electrons is produced by means of a two-

stage electron optical reducing system. The beam is made to scan the object by the application of suitably synchronised electric or magnetic fields. Electron indicators are arranged to measure either the transmitted portion of the beam or the intensity of the electrons scattered or reflected through any selected angle by the object. The result is recorded in conjunction with the synchronised deflecting field to produce an image of the object. The various factors limiting the definition are considered and the limit of resolution is assessed at  $\approx 10^{-5}$  mm. H. C. G.

**Apparatus for determining the transmission of slow electrons through thin collodion films.** M. FERENC and R. J. STEPHENSON (Rev. Sci. Instr., 1938, 9, 246—248).—A description and operational details are given of an apparatus for determining the transmission of slow electrons (800—34,000 e.v.) through thin collodion films ( $10^{-3}$ — $7 \times 10^{-6}$  cm.). W. R. A.

**Electronic voltage regulator with supplementary circuit to supply low voltages.** E. B. WORKING (Ind. Eng. Chem. [Anal.], 1938, 10, 434—435).—Apparatus is described. E. S. H.

**Method of determining the direction and for the separation of  $\alpha$ - and H-rays in an ionisation chamber.** J. SCHINTLMESTER (Physikal. Z., 1938, 39, 612—615).—An ionisation chamber which is divided into two compartments by a gauze electrode is described. By double registration of each ray it is possible to determine the range and direction of the rays in the chamber and to decide whether the ray is an  $\alpha$ - or an H-ray. A. J. M.

**Measurement of high-energy  $\gamma$ -rays.** E. R. GAERTNER and H. R. CRANE (Physical Rev., 1937, [ii], 51, 58—59).—The target in a small thimble is constructed inside a cloud chamber, which is bombarded by an ion beam for an instant at the time of expansion. Tracks appearing in the chamber originate in the thin wall of the thimble. With Li bombarded by protons, using 0.7 mm. brass wall, many electron pairs and single negative electrons having the entire available energy, 17 Me.v., were observed. L. S. T.

**Semi-micro-fractionating column.** S. D. LESENE and H. L. LOCHTE (Ind. Eng. Chem. [Anal.], 1938, 10, 450).—The apparatus is for use at atm. pressure on 1—10 c.c. of liquid. The packing is replaced by a metal band rotating at 1000 r.p.m. E. S. H.

**Powder measurer.** R. P. WODEHOUSE (Ind. Eng. Chem. [Anal.], 1938, 10, 423—424).—Apparatus is described. E. S. H.

**Anti-foaming device for use in concentration of non-inflammable liquors.** E. A. GASTROCK and J. D. REID (Ind. Eng. Chem. [Anal.], 1938, 10, 440).—An electrically heated coil in the vapour disrupts the foam bubbles without contact. E. S. H.

**Ring method for measurement of surface tensions.** D. G. DERVICHIAN and C. CLARK (Compt. rend., 1938, 207, 277—279).— $\gamma$  may be calc. from the pull  $P$  necessary to drag a ring from the surface of the liquid, using the experimentally deduced relation



$\gamma/\rho = aP/\rho + b$ ,  $a$  and  $b$  being consts. for a given ring. The independence of the menisci inside and outside the ring (cf. Freud, A., 1930, 853) has been confirmed. The ring may cause rupture of adsorption layers, which is indicated by a progressive increase in the vals. of  $\gamma$  given by successive measurements.

A. J. E. W.

**Maintenance of clean surfaces in glass tubes containing mercury.** W. H. J. VERNON and E. G. STROUD (Chem. and Ind., 1938, 796).—Introduction of sufficient syrupy  $H_3PO_4$  ( $d$  1.16–1.75) to cover the Hg surface prevents fouling of the walls of manometer tubes through oxidation of the exposed Hg surface, and for many purposes has no countervailing disadvantage.

J. W. S.

**Method of diminishing the sticking of mercury in capillaries.** P. ROSENBERG (Rev. Sci. Instr., 1938, 9, 258–259).—The sticking of Hg in a capillary can be greatly reduced by using a capillary the internal surface of which has a ground finish. A method for giving a ground surface to capillary bores with wire and abrasive is described.

W. R. A.

**Speed indicator and control for the ultracentrifuge.** H. KÄHLER (Rev. Sci. Instr., 1938, 9, 257).—A photo-cell method for the determination of the speed of the centrifuge in the range 10–5000 cycles per sec., with an accuracy of 1%, is described. Two alternative methods of speed control are outlined.

W. R. A.

**Engine for smoothening small tungsten wires.** R. P. JOHNSON, A. B. WHITE, and R. B. NELSON (Rev. Sci. Instr., 1938, 9, 253–255).—An engine for removing die marks from the surface of small W. wires (2 to 10 mils diameter) by mechanical abrasion is described.

W. R. A.

**Micro-constant extraction apparatus for liquids.** F. C. MESSER (J. Lab. clin. Med., 1938, 53, 618–620).—An apparatus which permits the const. extraction of 1–10 c.c. of fluid with a lighter, non-miscible solvent is described.

T. H. H.

**Automatic evaporation controller and signal.** H. B. WYLIE (J. Lab. clin. Med., 1938, 53, 642–645).

T. H. H.

**Apparatus for agitating small volumes of liquid at constant temperature.** R. G. WILLCOCKS (J.S.C.I., 1938, 57, 249–250).—A machine in which small tubes or flasks can be shaken vigorously in a thermostatic bath is described. The tubes are fixed vertically in sprung clips and struck by flexible vanes revolving on a vertical shaft, rotated by an electric gramophone motor. The machine is self-contained, silent in operation, admits ease of sampling, and can be used in bacteriological, biochemical, and chemical experiments. A no. of applications are suggested.

**Universal laboratory shaker.** J. M. FEDER (J. Lab. clin. Med., 1938, 23, 974–977).

C. J. C. B.

**Simplified shaking apparatus.** J. H. HOLT (J. Lab. clin. Med., 1938, 23, 533).

C. J. C. B.

**Stirring device for use in micro-titrations.** P. LEVANTINSKY (J. Lab. clin. Med., 1938, 23, 532–533).

C. J. C. B.

**Differential method for the measurement of small amounts of adsorbed gas.** W. HUNSMANN (Z. Elektrochem., 1938, 44, 540–542).—The apparatus incorporates two heated-wire manometers, one of which is connected with the adsorption vessel and the other with a Hg burette. The galvanometer needle, the deflexion of which  $\propto$  the vol. of adsorbed gas, is brought back to the null point by equalising the pressures by running from the burette a vol. of Hg equiv. to the vol. of adsorbed gas.

C. R. H.

**Modern equipment for the chemical laboratory.** J. MARTERET (Tech. Ind. Chim., 1938, No. 277 bis, 175–184).

I. C. R.

**Vacuum relay.** C. W. MILLER (J. Sci. Instr., 1938, 15, 263–265).—In the arrangement described a Pirani gauge is used in an a.c. control circuit to open or close an external circuit when the pressure in a vac. system exceeds any given val.

N. M. B.

**Distillation flasks with condenser for small quantities of substances.** J. ERDÖS (Mikrochem., 1938, 24, 278–279).—A small flask is provided with a ground-in vertical condenser, which delivers into a funnel and side tube (with tap) sealed into the neck of the flask; this is convenient for removing solvents etc.

E. W. W.

**Vapour-jet vacuum pumps.** H. KLUMB (Z. tech. Physik, 1936, 17, 201–202; Chem. Zentr., 1936, ii, 1388).—A simplified glass pump of high pumping speed, and operating with a fore-vac. of several mm. of Hg, is described.

H. J. E.

**Corrosion of platinum apparatus.**—See B., 1938, 1051.

**Burette holder.** O. J. STEWART (J. Chem. Educ., 1938, 15, 335).

L. S. T.

**Separation of gaseous mixtures by diffusion.** E. H. RIESENFELD and T. L. CHANG (Arkiv Kemi, Min., Geol., 1938, 12, A, No. 19, 1–8).—By experiments on the separation of  $O_2$ – $CO_2$  mixtures by diffusion through porous tubes, it was found that the separation factor falls as the concn. of the heavy constituent rises. The relation between separation factor and  $[CO_2]$  is logarithmic. This can be explained qualitatively if it is assumed that  $CO_2$  mols. absorbed on the pores of the diffusion tube are drawn through by the vac. pump, thereby reducing the separation caused by diffusion.

T. H. G.

**Out-gassing of heated metals in a vacuum.** J. A. M. VAN LIEMPT (Rec. trav. chim., 1938, 57, 871–882).—Formulae are derived for the rate of out-gassing of metals in the form of sheet or wire, and for the times required for the loss of 95 and 98% of the gas. The formulae agree with experimental data for Ni.

F. L. U.

**Sedimentation unit and its use in field sampling.** G. H. OTTO (J. Geol., 1938, 46, 569–582).

L. S. T.

**Separation of gases and isotopes.** K. CLUSIUS and G. DICKEL (Naturwiss., 1938, 26, 546).—The apparatus consists of a vertical hot surface (an electrically heated wire) opposite to a cold one. Thermal diffusion and convection result in the heavier



component of the mixture becoming relatively more conc. at the bottom of the apparatus. A 1 : 3 mixture of Br and He was completely separated by this method, and good results were also obtained with a 2 : 3 mixture of  $\text{CO}_2$  and  $\text{H}_2$ , and with air. Normal Ne (at. wt. 20.18) was partly separated into its isotopes, the gas drawn from the bottom of the apparatus having at. wt. 20.68, corresponding with an alteration in the ratio of  $^{22}\text{Ne} : ^{20}\text{Ne}$  from 1 : 9.28 to 1 : 2.20. Normal HCl (23%  $\text{H}^{37}\text{Cl}$ , 77%  $\text{H}^{35}\text{Cl}$ ) gave a mixture of 40% of  $\text{H}^{37}\text{Cl}$  and 60% of  $\text{H}^{35}\text{Cl}$  at the base of the apparatus. A. J. M.

**Theory of the measurement of viscosity and slip of fluids by the oscillating-disc method. II.** G. E. MACWOOD (*Physica*, 1938, 5, 763–768; cf. A., 1938, I, 352).—Theoretical. H. J. E.

**Ultrafilters of graduated porosity.** J. DUCLAUX and M. AMAT (*Compt. rend.*, 1938, 206, 1475–1477).—The filters are prepared by immersing in  $\text{H}_2\text{O}$  a glass plate previously coated with a solution of cellulose acetate (I) in saturated aq.  $\text{Mg}(\text{ClO}_4)_2$ . Filters 0.06–6 mm. thick may be obtained, the porosity varying with the concn. of (I) (2–20%) in the solution used. Very low porosity is obtained by immersing in dil. aq.  $\text{Mg}(\text{ClO}_4)_2$  and drying before use.

Similar filters may be prepared on filter-paper, cloth, or gauze. A. J. E. W.

**Electronic recording analytical balance.** R. H. MULLER and R. L. GARMAN (*Ind. Eng. Chem. [Anal.]*, 1938, 10, 436–440).—Inertia- and lag-free electronic methods are substituted for mechanical or electrical contactors, relays, etc. The sensitivity is about 0.05 mg. for a 20-g. load. E. S. H.

**Rapid solution-dispensing pipette.** B. J. OTTE, P. J. THOMPSON, and G. A. BARBER (*J. Chem. Educ.*, 1938, 15, 344). L. S. T.

**[Laboratory] experiment illustrating the relation between e.m.f. and the equilibrium constant.** R. LIVINGSTON and J. J. LINGANE (*J. Chem. Educ.*, 1938, 15, 320–323).—The reaction utilised is  $\text{quinol} + 2\text{Ag}^+ = p\text{-benzoquinone} + 2\text{Ag} + 2\text{H}^+$ . The e.m.f. method measures the e.m.f. of the cell  $\text{Pt}|\text{quinhydrone}, \text{HNO}_3 (0.1\text{M})|\text{HNO}_3 (0.1\text{M})|\text{HNO}_3 (0.1\text{M}), \text{AgNO}_3 (0.001\text{M})|\text{Ag}$ . Measurements can be made in presence of air, the temp. coeff. is large and practically linear between 19° and 32°, the cell attains const. e.m.f. very rapidly after a change in temp., and the liquid junction potential is negligible. The analytical method starting with known concns. of reactants or reacting products is also described. L. S. T.

## Geochemistry.

**Vertical distribution of ozone in the atmosphere.** V. H. REGENER (*Z. Physik*, 1938, 109, 642–670).—An extension of earlier work (A., 1938, I, 279) involving the use of a self-registering ultra-violet spectrograph for balloon ascents. L. G. G.

**Ice of the Arctic regions.** V. I. VERNADSKI (*Compt. rend. Acad. Sci. U.R.S.S.*, 1938, 19, 625–628).—The mineralogy of Arctic waters, the biochemistry and distribution of the diatomaceous Si and Al, and the nature of cosmic dust in ice inclusions are discussed. I. McA.

**Concentration of calcium carbonate in the waters of the Polar basin.** N. I. TSCHIGIRIN (*Compt. rend. Acad. Sci. U.R.S.S.*, 1938, 19, 633–635).—The solubility of  $\text{CaCO}_3$  in sea- $\text{H}_2\text{O}$  so depends on  $[\text{CO}_2]$ , temp., and hydrostatic pressure that, of the three chemically-differentiated Polar ocean layers, the warm saline Atlantic layer (depth 110–950 m.) containing 3.37–3.39 g. of  $\text{CaCO}_3$  per kg. of solute is ~2% supersaturated, whilst the abyssal and surface layers containing 3.39–3.49, 3.42–3.60 g., respectively, are >98% saturated with  $\text{CaCO}_3$ . The balance of  $[\text{CaCO}_3]$  in Arctic and Atlantic waters and the high concn. in the Polar upper layer are maintained by the drift and melting of old ice, in which the  $[\text{CaCO}_3]$  may reach 1000 times that in sea- $\text{H}_2\text{O}$ . The bearing on marine geology and biology is indicated. I. McA.

**Respiration and assimilation in open water. Quantitative studies on the variations in organic matter in lakes near Seon.** K. HEINRICH (*Intern. Rev. Hydrobiol.*, 1934, 30, 387).—Comprehensive data are given. CH. ABS. (c)

**Analysis of mineral water of Lesignano Bagni (Parma).** G. ILLARI and M. ZUCCHETTI (*Annali Chim. Appl.*, 1938, 28, 258–275).—Data for the chemical and physico-chemical characteristics of the  $\text{H}_2\text{O}$  and dissolved gases are tabulated. F. O. H.

**Salt waters on the coast of Peru containing sodium carbonate.** F. FUCHS (*Bol. Soc. Quim. Peru*, 1935, 1, No. 3, 29–46; *Chem. Zentr.*, 1936, ii, 771).—The material is partly washed from rocks and partly formed by interaction of  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$  with  $\text{CaCO}_3$ . H. J. E.

**Oxygen-poor waters of Chesapeake Bay.** C. L. NEWCOMBE and W. A. HORNE (*Science*, 1938, 88, 80–81).—A well-defined  $\text{O}_2$  stratification occurs in this bay during summer. The surface stratum, which has a low salt content and high  $\text{O}_2$  content, overlies a bottom layer of much higher salinity and very low  $[\text{O}_2]$ . L. S. T.

**Chemical analysis of several mineral waters from Oradea and from the Bihor district.** G. GHIMICESCU and I. VARÓDI (*Ann. Sci. Univ. Jassy*, 1938, 24, II, 134–140).—Data are summarised. L. S. T.

**Analysis of mineral springs of Covasna (Trei-Scaune District).** C. ȘUMULEANU, M. BOTEZATU, and A. VIERIU (*Ann. Sci. Univ. Jassy*, 1938, 24, II, 15–24).—Physico-chemical data for, and chemical analysis of,  $\text{H}_2\text{O}$  from four mineral springs are recorded. L. S. T.

**Water of the Ilidža thermal spring.** S. MIHO-LIĆ (*Arh. Hemijski*, 1938, 12, 83–92).—Analytical data are recorded. R. T.



**Evolution of emanation to running water from rocks containing radium.** H. MACHE and G. MARKSTEIN (Sitzungsber. Akad. Wiss. Wien, IIa, 1935, 144, 489—492; Chem. Zentr., 1936, ii, 951—952).—Measurements are recorded of the amount of emanation carried away by running  $H_2O$  from pitchblende of various grain sizes. The amount is independent of the rate of flow of  $H_2O$ . Dependence on grain size and temp. was apparent only in the early parts of the experiments. H. J. E.

**Oxidation-reduction potential and  $p_H$  of sediments of the Barentz and Kara seas.** S. V. BRUEVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1938, 19, 637—640; cf. Cooper, A., 1938, I, 81, 103).—Following a positional survey (Arctic expedition), measurements of redox potential ( $E_h$ ) and  $p_H$  have been made, using Pt and quinhydrone electrodes, respectively, for the near-bottom  $H_2O$  and Mn- and Fe-rich sediments characterising the abyssal depths of the Polar basin. The brown (upper) is the primary deposit, ascribed to ice-borne weathered mineral. With the low org. content of Polar seas, its high state of oxidation is maintained by aq. aëration. The greyish (lower) layers of like silicate composition (Gorshkova) are derived by reduction by org. matter of the sunken brown layers; the liberated  $CO_2$  forms H carbonates which diffuse upwards to be reoxidised. This view accords with (i) the absence of the brown deposits in the open southerly areas with ice-free  $H_2O$  of low [Fe] and containing plankton; (ii) the higher concn. of Mn,  $Fe_2O_3$ , and org. matter in the brown layer; (iii) the higher  $E_h$  of the brown layer (270 mv. as against 105—224 mv.), due solely to higher Mn oxides.

I. MCA.

**Colouring of Polar sea sediments.** M. V. KLENOVA (Compt. rend. Acad. Sci. U.R.S.S., 1938, 19, 629—632).—A descriptive review of the geochemical evidence provided by, and precautions necessary in, the study of colour. Relevant results of the Papanin expedition are briefly analysed.

I. MCA.

**Potassium deposits of the southern basin of the Permian Sea and the salt lakes of Western Kazakhstan.** N. S. KURNAKOV, I. N. LEPESCHKOV, D. I. RJABTSCHIKOV, and N. I. BUJALOV (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 13—32).—The occurrence of deposits of K salts is reported.

E. S. H.

**Recent deposition of salt from Great Salt Lake.** T. C. ADAMS (J. Geol., 1938, 46, 637—646).—During the last four years pptn. of NaCl on the bed of the lake has occurred during the summer owing to the reduced vol. of  $H_2O$  then present. Re-dissolution has occurred in winter, when the well-known deposition of the  $Na_2SO_4$  takes place owing to the fall in temp. A large tabular deposit of almost pure  $Na_2SO_4$  lies buried in the beach sands along one shore of the lake and may be related in its formation to past winter pptn. similar to that now being observed.

L. S. T.

**Carotenoids in lacustrine silts.** S. MURAVEISKI and I. CHERTOK (Compt. rend. Acad. Sci. U.R.S.S., 1938, 19, 521—523; cf. Baudisch, A., 1935, 1180).—

The xanthophyll and carotene contents of the dried silts from 10 lakes have been determined. Normally present only in traces or  $>100 \mu g.$  per g. of dried silt, in one instance amounts of 0.3—3.0 mg. per g. are found. Cryst. carotene, two monoketones akin to mixoxanthene and echinenone, two unidentified xanthophylls, and several other pigments spectroscopically akin to lutein have been extracted.

I. MCA.

**Neutrons of rocks.** G. V. GORSCHKOV, N. M. LJATKOVSKAJA, A. G. GRAMMAKOV, and V. S. SHADIN (Compt. rend. Acad. Sci. U.R.S.S., 1938, 19, 499—502; cf. La Cierva, A., 1937, I, 161).—Counter measurements have been made of the intensity of (fast) neutron emission from rock containing 0.2%  $U_3O_8$  and from a Rn-Be prep. The rock emits  $\sim 1$  neutron per 2000  $\gamma$ -ray quanta.

I. MCA.

**Occurrence, crystal habit, and composition of the uraninite from the Ruggles Mine, near Grafton Centre, New Hampshire.** B. M. SHAUB (Amer. Min., 1938, 23, 334—341; cf. A., 1937, I, 588; 1938, I, 283).—The analysis [F. HECHT] is  $SiO_2$  0.80,  $PbO$  3.63 ( $Pb$  3.37),  $Fe_2O_3$  0.66,  $Al_2O_3$  0.44,  $MnO$  0.09, rare earths 0.21,  $ThO_2$  0.43 ( $Th$  0.38),  $U_3O_8$  90.06 ( $U$  76.38),  $CaO$  0.81,  $MgO$  0.17,  $P_2O_5$  0.16,  $S$  0.04,  $H_2O$ —0.73, loss on ignition (100—1000°) 1.74, insol. 0.54, total 100.51%. L. S. T.

**Crystal structure of the clay minerals, dickite, halloysite, and hydrated halloysite.** S. B. HENDRICKS (Amer. Min., 1938, 23, 295—301; cf. A., 1938, I, 484).—X-Ray diffraction data are discussed. Dickite has an at. arrangement based on space-group  $C_4^1$ —Cc. Independent layers of  $[(OH)_4Si_2Al_2O_5]_n$  are superimposed in some random manner in which a shift of  $(2n+1)b_0/6$  of one layer with respect to another is maintained. Hydrated halloysite,  $Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$ , probably possesses a structure in which neutral  $[(OH)_4Si_2Al_2O_5]_n$  layers similar to those of the other clay minerals are interleaved with  $[2(H_2O)]_n$  layers.

L. S. T.

**Algae as rock builders: algal limestones from Colorado.** J. H. JOHNSON (Univ. Colo. Studies, 1936, 23, 217—222).—A review. CH. ABS. (e)

**Nickel in pumice stone.** F. HEIDE (Naturwiss., 1938, 26, 495).—Spectrographic analysis, confirmed by pptn. with dimethylglyoxime, indicates the presence of about 0.001% Ni in pumice stone from the Oetztal (Tyrol). This does not necessarily support the view that the rock is the remains of a meteoric crater as the mean [Ni] in volcanic rocks is about 0.01%.

A. J. M.

**Atomic arrangement and variability of members of the montmorillonite group.** G. NAGELSCHMIDT (Min. Mag., 1938, 25, 140—155).—X-Ray and optical data are given for three end-members montmorillonite  $Si_4O_{10}Al_2(OH)_2 \cdot Si_2O_5$ , Mg-beidellite  $Si_2O_5 \cdot Mg_3(OH)_2 \cdot Si_2O_5$ , and nontronite  $Si_2O_5 \cdot Fe_2(OH)_2 \cdot Si_2O_5$ . Chemical analyses (from the lit.) of materials from the same localities are correlated with respect to a three-layered lattice. L. J. S.

**Francolite from sedimentary ironstones of the Coal Measures.** T. DEANS [with analysis



by H. C. G. VINCENT] (Min. Mag., 1938, 25, 135—139).—Minute (< 1 mm.) platy crystals of a mineral of the apatite group are found embedded in kaolin in oolitic ironstone at Robin Hood quarry near Leeds and at other places in the Yorkshire coalfield. They are optically biaxial ( $2V$  25–40°), with  $\alpha$  1.620,  $\beta$  1.627,  $\gamma$  1.628,  $d$  3.21. Analysis gave  $P_2O_5$  38.25,  $CO_2$  1.98, F 2.80, CaO 54.64, SrO 0.13, MgO trace,  $H_2O$  + 0.66,  $H_2O$  – 0.06, insol. 2.19, total (less O for F) 99.53. Formula,  $(Ca, Sr)_{10}(P, C)_6(F, OH)_2O_{24}$ , with F:OH = 3:1. The formula of Gruner and McConnell (A., 1938, I, 52) is corr. to  $(Ca, Mg, C)_{10}(P, V, C)_6F_2OH(O, F)_{23}$ . L. J. S.

**Tabular spessartine crystals in muscovite.** E. D. MOUNTAIN and L. E. KENT (Min. Mag., 1938, 25, 125–134). L. J. S.

**Withamite from Glen Coe, Scotland.** C. O. HUTTON (Min. Mag., 1938, 25, 119–124).—Analysis of the pink, strongly pleochroic epidote, forming spherulitic growths in vesicles in an altered andesite, shows  $Mn_2O_3$  0.96%, with  $d$  3.39–3.40,  $\alpha$  1.733,  $\beta$  1.750,  $\gamma$  1.762. A gradation to piemontite is suggested. L. J. S.

**Potash-soda-felspars. II. Applications to petrogenesis.** EDMONDSON SPENCER (Min. Mag., 1938, 25, 87–118; cf. A., 1937, I, 269).—Conditions of crystallisation and perthitic exsolution are discussed. A new equilibrium diagram suggests that a residual granite magma at about 800° in presence of much  $H_2O$  and free  $SiO_2$  splits into soda-rich and potash-rich fractions, giving different types of pegmatites. L. J. S.

**Crystalline rocks of Bistrița, Doma-Broșteni region, Câmpulung and Neamț districts.** M. SAVUL (Ann. Sci. Univ. Jassy, 1938, 24, II, 206–286).—Cryst. schists, limestones, etc. are described. L. S. T.

**Ores: from magmas or deeper?** L. C. GRATON (Econ. Geol., 1938, 33, 251–286).—The views of Holmes (A., 1938, I, 163) are criticised (cf. also *ibid.*, 283). L. S. T.

**Geology and origin of sulphur springs.** K. A. WEITHOFER (Berg- u. Hüttenmänn. Monatsh., 1938, 86, 89–97).—The probable chemical reactions involved in the formation of S springs, and the compositions and therapeutic val. of springs in the Alps and Hungary, are discussed. R. B. C.

**Indian bauxite. I. Chromium and vanadium.** S. C. GANGULI and J. DAS-GUPTA (J. Indian Chem. Soc., 1938, 15, 243–244).—Of 15 samples of Indian bauxite, 14 contain 0.043–0.142%  $V_2O_5$  and 0.030–0.125%  $Cr_2O_3$  determined by Sandell's method (A., 1936, 1353); the remaining sample (from Kashmir) contained only 0.0025%  $V_2O_5$  and 0.013%  $Cr_2O_3$ . F. R. G.

**Alumite. IV, V.** Y. ASADA (Bull. Inst. Phys. Chem. Res. Japan, 1938, 17, 553–565; 566–593).—Sp. heat and  $\rho$  measurements have been made. W. R. A.

**Samarskite found in the placer of Rynjomen.** S. IIMORI and S. HATA (Sci. Papers Inst. Phys.

Chem. Res. Tokyo, 1938, 34, 922–930).—The crystals of the mineral are orthorhombic prisms with pyramidal termination and sometimes tabular with edges and corners generally not sharp. The fracture is conchoidal and of velvet-black lustre; cleavage imperfect, streak dark reddish-brown, and hardness ~5.5–6.0. It is strongly radio-active,  $d$  5.96–6.05. Specimens of lower  $d$  occur and they contain less U. A scheme of quant. analysis is given and from analytical data the formula  $R^{II}_3R^{III}_2R^{IV}_1(Nb, Ta)_6O_{23}$  is assigned. The approx. age of the mineral, deduced from the Pb, Th, and U contents, is  $134 \times 10^6$  years. W. R. A.

**Magnetic anisotropy and pleochroism of biotite mica.** P. NILAKANTAN (Proc. Indian Acad. Sci., 1938, 8, A, 39–60).—The paramagnetic anisotropy and susceptibility, the  $Fe^{++}$  and  $Fe^{+++}$  content, and the pleochroism of three varieties of biotite and one each of muscovite and phlogopite micas have been determined. The biotites are highly anisotropic; their anisotropy and pleochroism increase with increasing [Fe] and both depend only on the presence of  $Fe^{++}$  and not on  $Fe^{+++}$ . The anisotropy results are discussed on the basis of the theories of Van Vleck and of Penney and Schlapp and those on pleochroism on Saha's theory. A relationship between pleochroism and paramagnetic anisotropy is established. W. R. A.

**Fluorescent ion of chromium in ruby.**—See A., 1938, I, 495.

**Fluorite in the Kungurian limestones and dolomites of the Ural-Emba region.** V. P. BATURIN (Compt. rend. Acad. Sci. U.R.S.S., 1938, 19, 503–506).—Though the content of quartz and feldspar is negligible, celestite admixed with ~2% of fluorite is present up to 3–20%. The petrology of these and other sedimentary deposits is discussed with reference to components, distribution, and origin. I. MCA.

**Primordial segregation of metals.** J. S. DE LURY (J. Geol., 1938, 46, 756–763; cf. A., 1937, I, 587).—The associations of certain metals with certain igneous rocks are discussed and their fortuitous nature is emphasised. This fortuity and the general unevenness of the geographical distribution of metals are not satisfactorily explained by the current theory that most ore deposits of magmatic origin were derived by differentiation from the same parental magma that gave rise to contemporaneous and associated igneous rocks. The hypothesis now outlined of primordial differentiation of earth material with a consequent primitive segregation of metals eliminates these objections; it also explains the evidence provided by the at. wt. of Pb. L. S. T.

**Mineralogical study of the metalliferous deposit of Păraul Baia, Ditrău, Ciuc, Transylvania.** V. IANOVICI (Ann. Sci. Univ. Jassy, 1938, 24, II, 439–456).—Metallisation of the nepheline syenite and the phyllitic schists has resulted in the deposition of pyrite, blende, galena, and chalcopryite, which are described. The mineral succession and the origin of the deposit are discussed. L. S. T.