# BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

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

JUNE, 1940.

Band spectra of sulphur and selenium excited in ignition tubes containing mixtures of hydrogen and oxygen with traces of sulphuric acid and selenium. M. MIYANISI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1940, **37**, 79—84).—Band spectra of S and Se appear in  $2H_2 + O_2$  flames containing small amounts of  $H_2SO_4$  or Se. In presence of  $H_2O$ vapour in discharge tubes the S and Se bands are enhanced in the neighbourhood of the OH bands 2'-1'', 1'-0'', 1'-2'', and 0'-1''. The effect is ascribed to excited OH. L. J. J.

First spectrum of tin. W. F. MEGGERS (J. Res. Nat. Bur. Stand., 1940, 24, 153—173).—Data are recorded for  $\lambda$  and relative intensity of 341 lines in the Sn I spectrum between 1697.59 and 12536.5 A. photographically, and 37 up to 2473.2 A. radiometrically. Assignment of energy levels for four  $5p^2$ —5pns series gives an abs. val. 59,155 cm.<sup>-1</sup> for the ground level, and a val. 7.297 v. for the principal ionisation potential. L. J. J.

Luminescence spectra of the night sky in the ultra-violet region. P. P. DOBRONRAVIN and I. A. CHVOSTIKOV (Compt. rend. Acad. Sci. U.R.S.S., 1939, 23, 233—237).—Solar short-wave spectra have been photographed for day, night, and twilight using a spectrograph fitted with a slit-reducing attachment. Three series of photographs have been obtained which show that the intensity of the ultra-violet light in the night-sky spectra is > those of day and twilight. This may be due to conditions favourable to the dispersion of short-wave solar radiation in the outer atm. layers. W. R. A.

Excitation of atoms in a gas discharge. V. FABRIKANT (Compt. rend. Acad. Sci. U.R.S.S., 1939, 23, 224—228).—Mathematical. W. R. A.

Interaction of atomic energy levels. II. T.S. SUBBARAYA, K. SESHADRI, and N. A. N. RAO (Current Sci., 1940, 9, 14-18; cf. A., 1940, I, 88).-The spectra of Hg, Cd, and Hg-Cd mixture have been studied. The variations in intensity of the lines of the elements in admixture are noted, and explanations suggested, and the appearance of lines not apparent in the spectra of Cd and Hg separately has been observed in Hg-Cd. The Hg resonance line 2537 A. shows complete self-reversal in Hg but no reversal in Hg-Cd. The 2540 A. line is present in Hg and Hg-Cd. but not in Hg-Zn. Similarly the ZnH bands in Zn appear in Hg-Zn, whilst the CdH bands, although present in Cd, are absent in Cd-Hg. No interaction has been found between some levels of Hg and Cd which are close to each other, e.g.,  $6^1P_1$  of Hg and  $6^1S_0$  of Cd. W. R. A.

Effects of chemical combination on the  $K\beta$ lines of chlorine. H. TAZAKI and M. HUZITA (J. Sci. Hirosima Univ., 1940, A, 10, 73-75).—The position and strength of the weak non-diagram lines observed by Tazaki (A., 1936, 1311) in the  $K\beta$  spectrum of Cl have been investigated for MgCl<sub>2</sub>, AlCl<sub>3</sub>, and KClO<sub>3</sub> on an Al anticathode, CaCl<sub>2</sub> and CuCl on Al and Cu anticathodes, and BaCl<sub>2</sub>, KClO<sub>4</sub>, and NaClO<sub>3</sub> on a Cu anticathode, O. D. S.

Thermal ionisation of barium. B. N. SRIVA-STAVA (Proc. Roy. Soc., 1940, A, 175, 26-36).—A method for the study of thermal ionisation of gases is described and is applied to Ba vapour. The results are in agreement with theory and also support the explanation usually given for the fact that Ba is completely ionised in the sun although Na with lower ionisation potential is not. G. D. P.

Rôle of ionisation by positive ions in spark breakdown. R. N. VARNEY, L. B. LOEB, W. R. HASELTINE (Phil. Mag., 1940, [vii], **29**, 379—390; cf. Townsend, A., 1939, I, 395).—Theoretical. Townsend's theory (*loc. cit.*) of ionisation by positive ions is erroneous. The probability of such ionisation under sparking conditions is negligible. O. D. S.

Groups of protons emitted during the bomhardment of hydrogenated substances by polonium  $\alpha$ -rays. II. T. SAN-TSIANG (J. Phys. Radium, 1940, 1, 103—111).—In the diffusion of  $\alpha$ -particles by the H nucleus, the relation between the effective experimental cross-section and that calc. from the Rutherford formula varies periodically as a function of the energy of the  $\alpha$ -particles. The angular variations of the effective section show that the orbital moments, l = 0 and l = 1, are equally important in diffusion experiments. <sup>5</sup><sub>2</sub>He is stable, the upper limit of its mass being 5·0124, and <sup>5</sup><sub>3</sub>Li is unstable. The results on anomalous diffusion are discussed from the viewpoint of the theories of Mott, Beck, and Bethe. W. R. A.

β-Ray spectrum of radium-E. G. J. NEARY (Proc. Roy. Soc., 1940, A, 175, 71-87).—The spectrum was studied by means of a magnetic spectrograph of special design to facilitate observation at low energies. The energy curve has a max. at 150 ke.v. and an end point at 1.17 Me.v. with a mean energy of 340 ke.v. in agreement with calorimetric observations. G. D. P.

Weak radioactive substance. R. DE (Indian J. Physics, 1939, 13, 407–409).—Monazite contains two constituents possessing similar chemical properties. One of these constituents is weakly radioactive and appears to emit  $\alpha$ -rays; it gives some of the tests of Po. Its average life is  $\geq 10^{20}$  years. W. R. A.

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Volcanism and nuclear chemistry. I. M. NOETZLIN (J. Phys. Radium, 1940, [viii], 1, 90—98). —Mathematical. Nuclear chain reactions on a macroscopic scale, produced by neutron bombardment, are studied and the conditions and the stability of a mixed material containing a neutron source are formulated. The application of the theory to the explanation of volcanic phenomena is outlined.

W. R. A.

Neutron sources consisting of a radium salt mixed with beryllium. Z. OLLANO (Nuovo Cim., 1939, 16, 456—458; cf. A., 1939, I, 293).—The lower yield of a neutron source consisting of a Ra salt mixed with Be compared with that of a Rn + Be source is due to poor distribution of the Ra salt in the Be. O. J. W.

β-Radioactivities of rhenium. F. YAMASAKI and K. SINMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1940, **37**, 10—16).—When metallic Re powder was bombarded with neutrons from Be + D, retarded by paraffin, two strongly active substances were produced with half-life  $16\pm1$  and  $90\pm2$  hr., respectively. These were identified by chemical separation as <sup>188</sup>Re and <sup>186</sup>Re. The upper limits of energy are 1·2 Me.v. for <sup>186</sup>Re and 2·5 Me.v. for <sup>188</sup>Re. Both emit β- and γ-radiations. A. J. M.

Theory of cosmic-ray showers. I. Furry model and fluctuation problem. A. NORDSIECK, W. E. LAMB, jun., and G. E. UHLENBECK (Physica, 1940, 7, 344—360).—A general method, based on Furry's treatment (A., 1937, I, 591), is developed for calculating the fluctuation in the no. of particles after penetration of any thickness of matter. L. J. J.

Penetrating cosmic-ray showers. L. JÁNOSSY and P. INGLEBY (Nature, 1940, 145, 511-512).--Counter experiments affording evidence of the occurrence at sea-level of a small no. of penetrating showers different from cascades or knock-on showers are described. Some of the observed showers may be due to the creation of mesons in the Pb absorber.

L. S. T.

Secondary radiation of cosmic rays. G. COC-CONI and V. TONGIORGI (Nuovo Cim., 1939, 16, 447— 455).—Measurements of the angular distribution of very soft, soft, and hard showers show that small angles do not prevail in the last-named. The secondary radiations produced by the hard component in various substances are the more numerous the lower is the at. no. of the substance which produces them.

0. J. W.

Twelve-hour period of mesotron intensity and height of origin of mesotrons. A. EHMERT (Naturwiss., 1940, 28, 28—29).—A crit. review of results obtained for the amplitude of oscillation of the isobar responsible for the 12-hr. period of mesotron intensity. A. J. M.

Photon component of cosmic radiation and its absorption coefficient. L. JÁNOSSY and B. ROSSI (Proc. Roy. Soc., 1940, A, 175, 88—100).—The method described for the study of cosmic-ray photons consists in the detection of the electrons generated by photons in a metal plate. The transition effect of showers in Pb was measured and good agreement with theory was obtained. Absorption coeffs. of cosmic-ray photons in Pb, Fe, and Al were measured. G. D. P.

**Evaluation of** e, h, m. C. G. DARWIN (Proc. Physical Soc., 1940, 52, 202–209).—A simplified treatment of Du Mond's discussion of small discrepancies (cf. A., 1939, I, 507), based on consideration of the logarithms of the quantities concerned. N. M. B.

Velocity of propagation of light in vacuo in a transverse magnetic field. C. J. BANWELL and C. C. FARR (Proc. Roy. Soc., 1940, A, 175, 1–25).— The investigation was carried out by means of an interferometer of the Michelson type using a field of 20,000 oersted. The effect is <1 part in  $5 \times 10^8$ . G. D. P.

Temperature of electrons in [an] electric field and calculation of Townsend's a. A. A. ZAITZEV (Compt. rend. Acad. Sci. U.R.S.S., 1939, 23, 229— 232).—Mathematical. The temp. of electrons moving in a homogeneous electric field has been calc. from at. consts. W. R. A.

Theory of the deuteron. J. SOLOMON (Compt. rend., 1940, 210, 477-478).—The extent to which the <sup>3</sup>D state occurs in the fundamental level of the deuteron ( ${}^{3}S + {}^{3}D$ ) is >40%. The photo-electric effect for the deuteron should deviate considerably from Bethe and Peierls' theory, and the magnetic moments should not be additive. A. J. E. W.

Theory of the electric charge and the quantum theory, I. H. T. FLINT (Phil. Mag., 1940, [vii], 29, 330-343).—Mathematical. O. D. S.

Origin of colour in paramagnetic salts and solutions. D. M. BOSE (Indian J. Physics, 1939, 13, Part VI, Suppl., 18 pp.).—An address.

W. R. A.

Absorption spectra of organic substances in phosphoric and sulphuric acids at various concentrations. F. BANDOW (Z. physikal. Chem., 1939, 45, B, 156—164).—The absorption spectra of several org. substances (BzOH, PhCHO, furfuraldehyde, anisaldehyde) in  $H_2SO_4$  from 2200 to 5600 A. are displaced to longer  $\lambda\lambda$  with respect to the corresponding spectra of these compounds in non-charring solvents ( $H_2O$ , EtOH). The displacement, however, appears for a narrow concn. range only (~70—80 wt.-%  $H_2SO_4$ ). The data are compared with the various spectra in  $H_3PO_4$ , and differences are explained on the basis of the  $H_2O$ -attracting power of  $H_2SO_4$ . W. R. A.

Absorption of light by ionic crystals in the ultra-violet. L. M. SCHAMOVSKI (J. Phys. Chem. Russ., 1939, 13, 835—839).—Vals. for the long- $\lambda$  limit of absorption of heteropolar crystals cale. by means of the equations previously derived (A., 1937, I, 11) agree with existing directly determined vals. The absorption spectra of mixed crystals exhibit absorption bands of both salts. R. C.

Absorption spectra of complex compounds. I. A. V. BABAEVA (Ann. Sect. Platine, 1939, No. 16, 87—107).—The ultra-violet absorption spectra of 21 Pt complexes were studied. All gave a max. at 285 mµ., and all complexes with acidic substituents (Cl, NO<sub>2</sub>) in the inner sphere exhibited a second max.

242

at 335 mµ. Complexes not containing basic radicals (NH<sub>3</sub>, NH<sub>2</sub>OH) gave a third max. at 400-410 mµ. The ultra-violet spectrum is not affected by cis-trans-R. T. isomerism. With a nation of the work

Vibrational analysis of the absorption spectrum of furan in the Schumann region. (MISS) L. W. PICKETT (J. Chem. Physics, 1940, 8, 293-297).—Furan vapour has three band systems between 2200 and 1550 A. One region consists of bands with sharply-defined max. with a 0-0 band at 52,230 cm.<sup>-1</sup> and 21 other bands, including three prominent max. which correspond with three totally symmetrical  $\nu\nu$  of the excited mol. of 1395, 848, and 1068 cm.<sup>-1</sup> These bands are assigned to combination- and overtones of four fundamental vv. A second region has three broad bands with separations of 1215 and 1095 cm.-1, whilst the third region begins so near the point at which the H<sub>2</sub> spectrum is discontinuous that the bands cannot easily be measured. This third region may represent the predicted four  $N \rightarrow V$ transitions with max. ~58,500 cm.-1 (found, 59,580 cm.<sup>-1</sup>) and total f val. 0.3. W. R. A.

Absorption spectra. III. Spectra of anthracene, octahydroanthracene, and perhydro-anthracene in the ultra-violet. P. M. HEERTJES and H. I. WATERMAN (Bull. Soc. chim., 1940, [v], 7, 187-191; cf. A., 1939, I, 385).-The absorption spectra of anthracene (I), octahydroanthracene (II), and of a mixture of hydroanthracenes have been measured over the  $\lambda$  range 2200—4000 A. The strong absorption band of (I) around 2520 A. and the bands between 3100 and 3800 A. disappear on hydrogen-The absorption spectrum of (II) resembles that ation. of an alkylbenzene, but with the bands displaced towards higher  $\lambda\lambda$ . Comparison with the spectra of PhBu<sup>a</sup>, tetrahydronaphthalene, and m-xylene supports Schroeter's view (A., 1925, i, 128) that (II) is s-bistetramethylenebenzene. J. W. S.

Spectral and physico-chemical properties of colchicine. H. SCHUHLER (Compt. rend., 1940, 210, 490-493).-Vals. of pK of 1.8, 7.2, and 10.3 are obtained by electrometric titration of  $2 \times 10^{-5}$ % colchicine (cf. Kolthoff, A., 1926, 125). Beer's law applies to  $2 \times 10^{-4}$  to  $2 \times 10^{-5}$ N. solutions for  $\lambda 2600 - 3200$  A. at const.  $p_{\rm H}$ . Between  $p_{\rm H} 3$  and 7 there is little change in the spectrum, but about  $p_{\rm H}$  1 the absorption bands are displaced and altered in intensity. J. L. D.

Absorption spectra of liquid hydrogen fluoride and of its aqueous solution in the region 8000-11,000 A. A. L. WAHRHAFTIG (J. Chem. Physics, 1940, 8, 349-350).—The absorption spectra of liquid HF and of 25% and 50% aq. HF have been investigated between 8000 and 11,000 A. Anhyd. liquid HF has an absorption band (max.  $9940 \pm 75$  A. at 19°, 10,380 A. at  $-75^{\circ}$ ) very similar to the H<sub>2</sub>O band at 9722 A. The third harmonic band of unassociated HF gas is at 8790 A. (A., 1936, 406) indicating a frequency decrease of  $\sim 1320$  cm.<sup>-1</sup> in passing from the gaseous to the liquid phase. This diminution in frequency, attributed to the formation of H bonds of the type  $F - H \cdots F$ , is  $\gg$  the corresponding decrease due to 0-H...O H bonds. For the aq. solutions no apparent difference exists between their spectra and those of H<sub>2</sub>O. W. R. A.

Effect of temperature on the Raman spectrum of quartz. T. M. K. NEDUNGADI (Proc. Indian Acad. Sci., 1940, 11, A, 86-95).-Fifteen fundamental internal vibration frequencies of quartz are recorded and all show a broadening and shift to lower vv as temp. is raised from liquid air temp. to 530°. One frequency (207 cm.-1) broadens very markedly but unsymmetrically at high temp. and disappears as the temp. approaches 575° (temp. of  $\alpha \rightarrow \beta$  transformation). The behaviour of this line is paralleled by the behaviour of other physical properties, e.g., thermal expansion, piezo-electric activity, and elastic moduli, and it is concluded that this vibration is chiefly responsible for these changes and for the transition. With unpolarised incident light three lines (263, 794, and 805 cm.-1) are not found in the light scattered longitudinally along the optic axis. W. R. A.

Raman effect in arsenates and heat of dissociation of As-O. S. M. MITRA (Indian J. Physics, 1939, 13, 391–395).—The Raman spectra of aq.  $Na_3AsO_4$  and  $K_3AsO_4$  have been examined. The AsO4" ion is characterised by four w (349, 463, 837, and 878 cm.<sup>-1</sup>) and from the close resemblance to the  $ClO_4'$  and  $SO_4''$  ions it is concluded that the  $AsO_4'''$ ion has a tetrahedral structure. From the Raman vv the binding energy of the As-O link has been calc. and a val. for the heat of dissociation of this link has been deduced (71 kg.-cal.; cf. val. from thermal data, 110.1 kg.-cal.). W. R. A.

Raman spectra of aqueous solutions of gaseous hydrogen chloride. (MLLE.) L. OCHS, J. GUÉRON, and M. MAGAT (J. Phys. Radium, 1940, [viii], 1, 85-89).-Aq. solutions of HCl up to 19N. have been investigated at room temp. In the more conc. solutions (>9N.) a band due to non-ionised HCl is found. The influence of HCl on the Raman spectrum of H<sub>2</sub>O is discussed, particularly a band due to association of HCl and H<sub>o</sub>O in a quasi-cryst. structure. The theory of the hydrated proton  $[H_3O]^+$  is discussed in the light of these results. W. R. A.

Raman effect. CVIII. Spectral transformations  $XY_4 \rightarrow XZ_4$ : correction. K. W. F. Kohl-RAUSCH and J. WAGNER. CIX. Pentaerythritol and related molecules. O. Ballaus and J. WAGNER (Z. physikal. Chem., 1939, 45, B, 93-100, 165-174).-CVIII. A reconsideration of previous results (A., 1935, 681; A., 1938, I, 386) from a new viewpoint with particular reference to the transformations  $CH_4 \rightarrow CCl_4$ ,  $CH_4 \rightarrow CBr_4$ ,  $CHCl_3 \rightarrow CXCl_3 \rightarrow$  $CCl_3$  (X = D, F, Cl, Br), and  $CCl_4 \rightarrow CBr_4$ .

CIX. Raman spectra of crystal powders of  $C(CH_2X)_4$  (X = OH, Cl, Br, I), of molten  $C(CH_2Cl)_4$ , and of liquid C(CH, OMe), are recorded and discussed. W. R. A.

Raman spectra of coumarins and chromones. (MISS) A. MOOKERJEE and J. GUPTA (Indian J. Physics, 1939, 13, 439-444).-Raman spectra of coumarin (solid, in CHCl<sub>3</sub>, in MeOH), chromone (molten, in CHCl<sub>3</sub>, in MeOH), and of CHCl<sub>3</sub> solutions of 7-hydroxy-3: 4-dimethylcoumarin, 7-hydroxy-2:3dimethylchromone, and β-methylumbelliferone Me ether are recorded and discussed with reference to shifts in the C:O frequency. W. R. A.

Raman spectrum of substituted ketimines; isomerism of these bases. R. CANTAREL (Compt. rend., 1940, 210, 480-483).-The C:N v in Ph, ketimine is 1649 cm.<sup>-1</sup>; the more intense C:O v in COPh, is 1658 cm.-1 Attachment of Ph groups to C:N in benzhydrylidene-benzylamine and -benzhydrylamine (I) reduces its v to 1622 and 1618 cm.-1, respectively, and also reduces the intensity. In benzylidenebenzhydrylamine (II), the isomerisation product of (I), the C.N  $\nu$  is raised to 1636 cm.<sup>-1</sup> The CPh<sub>2</sub>: grouping gives lines at ~1274 and 1490 cm.<sup>-1</sup>; the latter is also given at much lower intensity by CHPh: in (II). Numerous other unassigned Raman vv are given for the compounds named and CHPh<sub>2</sub>·NH<sub>2</sub>

A. J. E. W.

Raman spectra of cholesterol and cholic acid. C. SANNIÉ (Compt. rend., 1940, 210, 400-402).-Data for the v range 500-3000 cm.-1 are given, and comparison is made with carvomenthone (I) and carvomenthene (II). Cholesterol (20 g. in 100 c.c. of CCl<sub>4</sub>; 27 bands) gives numerous weak bands at 800-1300 cm.<sup>-1</sup>, which are ascribed to large saturated rings; a band at 1135 cm.<sup>-1</sup> ( $C_5-C_{10}$  chain?) is somewhat stronger. At 1300—1500 cm.<sup>-1</sup> the spectrum resembles that of (I) with the bands displaced 20-25 cm.-1 towards higher vv. A band at 1670 cm.-1 indicates a double linking attached at one end to a quaternary C [as in (II)]. The spectrum of 30% aq. Na cholate (17 bands) shows little resemblance to those of cholesterol, (I), or (II), and the bands are broad and diffuse. A. J. E. W.

Influence of foreign substances on the absorption of dyes in solution. S. MITRA (Indian J. Physics, 1940, 13, 397-405).-An attempt has been made to determine whether the phenomena of quenching of the fluorescence of dyes in solution is due to deactivating collisions between active dye mols. and the foreign substance or to a gradual "complex formation" between the dye mols. and the quencher. Quenching of fluorescence of fluorescein, rhodamine B, and eosin by KI has been examined. W. R. A.

Properties of oxide-coated cathodes. I. J. P. BLEWETT (J. Appl. Physics, 1939, 10, 668-679).-A review of oxide cathode technique and the thermal and electrical properties of alkaline-earth oxides.

0. D. S.

Photoconductivity of semi-conducting layers composed of some heavy-metal sulphide or selenide. I. Relation between spectral sensitivity and light absorption in the photoconducting layer composed of cadmium selenide and the microscopic examinations of its structure in relation to its photoconductivity. II. Microscopic examinations of the semi-conducting layer composed mainly of thallous sulphide in relation to its photoconductivity. C. ASAI (Bull. Inst. Phys. Chem. Res. Japan, 1940, 19, 1-3, 4-5).-I. The max. of the spectral sensitivity of a Cd-Se photoconducting layer is displaced towards longer  $\lambda\lambda$  compared with the corresponding absorption band. Microscopical examination reveals a close connexion

between the growth of crystal grains in the layer and its photoconductivity.

II. The larger are the crystal grains in a Tl-S semiconducting layer, the greater is its sensitivity, and the less its dark resistance. A. J. M.

Conductivity of metals. K. ARIYAMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1940, 37, 1-9).-Theoretical. A. J. M.

Corpuscular theory of electrical conductivity of metals. T. V. IONESCU (Compt. rend., 1940, 210, 502-504).—Previous theory (A., 1940, I, 139) is extended; the mobility of electrons in a cubic ionic lattice is considered, and vals. are deduced for the thermal conductivities of Cu, Al, Au, and Na, at 20—373° к. A. J. E. W.

Dielectric constant of ionised air. III. F. RAHMAN and S. R. KHASTGIR (Phil. Mag., 1940, [vii], **29**, 344—352; cf. A., 1938, I, 387).—Measurements of the electron density and temp., by the Langmuir probe method, and of the dielectric const.,  $\epsilon$ , of air in a discharge tube have been carried out simultaneously at a series of pressures and currents. Results are consistent with the theory that the anomalous increase in  $\epsilon$  to vals. >1 with increasing current is due to the formation of a positive ion sheath on the walls of the tube. O. D. S.

Dielectric constant of diamond. L. G. GROVES and A. E. MARTIN (Trans. Faraday Soc., 1940, 36, 575-581).-The dielectric const. of diamond has been determined by two methods. Apparatus and procedure are described. The vals. obtained by the two methods are 5.26 and 5.35, the latter being preferred.  $\epsilon$  is the same for the two types of diamond (cf. A., 1934, 583). F. L. U.

Dielectric constant and electrical conductivity of gases and vapours ionised by X-rays at ultrahigh radio frequency. S. R. KHASTGIR and F. RAHMAN (Phil. Mag., 1940, [vii], 29, 353-366).-A change in the capacity at ultra-high radio frequency,  $\lambda 460$  and 480 cm., of a condenser filled with air, SO2, A, or a mixture of the vapours of MeI and EtI, on ionisation of the gas by X-rays is ascribed to a decrease in the dielectric const. of the gas. This decrease may be explained by supposing that ejected photo-electrons remain free for an appreciable time after ionisation. The high-frequency conductivity of A and SO<sub>2</sub> ionised by X-rays is  $\sim 10^4$  or  $10^5$  e.s.u. and decreases with increase in pressure. O. D. S.

Ionic character and dipole moments. F. T. WALL (J. Amer. Chem. Soc., 1940, 62, 800-803).-Mathematical. A theory of dipole moments of diat. mols. is developed and shows that the sum of the dipole moments of two states produced by resonance is the same as the sum of the dipole moments of the original states. W. R. A.

Dipole moment, induction, and resonance in tetra-, penta-, and hexa-substituted benzenes. C. P. SMYTH and G. L. LEWIS (J. Amer. Chem. Soc., 1940, 62, 721–727).—Vals. of  $\mu$  for C<sub>6</sub>H<sub>6</sub> solutions at 25° are given for C6Me5Cl, C6MeCl5, C6EtCl5,  $C_6HCl_5$ , 1:2:3:4- $C_6H_2Cl_4$ , trichloromesitylene, dichlorodurene, 1:2:4:6-C6H2MeCl3, trichloro-4-cumene, tetrachloro-, 4:5-dichloro-, and 3:4:5-trichloro-o-xylene, dichloro- and dinitro-prehnitene. Observed and calc. vals. are in agreement when allowance for inductive effects is made. The effects of resonance of Me and Cl groups on the ring have not been definitely established. W. R. A.

Optical activity and chemical structure in tartaric acid. Influence of substituent and solvent effect.—See A., 1940,  $\Pi$ , 203.

Optical anisotropy of molecular crystals. I. NITTA (Sci. Papers. Inst. Phys. Chim. Res. Tokyo, 1940, **37**, 114—130).—The double refraction of a mol. crystal with a body-centred tetragonal lattice can be resolved into terms dependent on the anisotropy of the mol. and the cryst. parameters. Mol. polarisabilities calc. from X-ray and optical data on this basis are in agreement with the accepted mol. structure for C(CH<sub>6</sub>·OH)<sub>4</sub>, C(CH<sub>6</sub>·O·NO<sub>6</sub>)<sub>4</sub>, and

ture for  $C(CH_2 \cdot OH)_4$ ,  $C(CH_2 \cdot O \cdot NO_2)_4$ , and  $C(CH_2 \cdot OAc)_4$ . The temp. coeff. calc. for the double refraction of  $C(CH_2 \cdot OH)_4$  is in agreement with the observed val. L. J. J.

Constitution of sulphon-amides and -anilides. —See A., 1940, II, 214.

Polymerisation of anthracene to dianthracene from the magnetic standpoint. (A) J. FARQU-HARSON and M. V. C. SASTRI. (B) S. S. BHATNAGAR, P. L. KAPUR, and (MISS) G. KAUR (Current Sci., 1940, 9, 135—136, 136).—(A) The correction factor ( $\lambda$ ) for the ring formed in the polymerisation of anthracene as determined by Bhatnagar *et al.* (A., 1940, I, 153) differs from that established by Farquharson and Sastri (A., 1938, I, 20) for a four-membered ring. The bridging group in dianthracene is shown to be an eightmembered puckered ring.

membered puckered ring. (B) The authors' "bridged four-membered ring" is identical with the "eight-membered puckered ring" of the preceding abstract. F. R. G.

Modern quantum mechanics and the benzene problem. VI. G. ELSEN (Chem. Weekblad, 1940, 37, 199—209; cf. A., 1940, I, 60, 99).—The review is concluded with a discussion of resonance between double and single C-C linkings. D. R. D.

Continuous passive spectra. V. K. ARKADIEV and O. I. VELETSKAJA (Bull. Acad. Sci. U.R.S.S., Cl. Sci. Tech., 1938, 2, 55—70).—Equations and curves of dispersion and absorption are given for media of large and small inner friction, based on the assumption that the time consts. of the electric and magnetic centres in the media are spread over a certain range in the logarithmic frequency scale. As examples the spectral properties of soft Fe (transformer shrouding) and glycerol are given. L. G. G.

Bond strength and potential energy relationships in acetylene. H. HENKIN and M. BURTON (J. Chem. Physics, 1940, 8, 297–300).—Four divergent vals. for the C:C bond strength are reviewed. From the spectroscopic val. for the heat of formation of free C-H and the val. of 125·1 kg.-cal. for the heat of sublimation of graphite, the bond strength of C:C is ~137·9 kg.-cal. This is used in studying the potential energy levels of  $C_2H_2$  and gives vals. in agreement with experimental data on the spectrum of  $C_2H_2$ .

W. R. A.

Surface tension of liquid deuterium. A. VAN ITTERBEEK (Physica, 1940, 7, 325—328).—The ratio of the surface tension of  $D_2$  to that of  $H_2$ , measured by the capillary-rise method, is 1.74, 1.70, and 1.67 at 20.4°, 19.4°, and 18.7° K., respectively. The ratio of the densities is const. at ~2.40. Extrapolation of surface tension vals. gives ~46° K. for the crit. temp. of  $D_2$ . L. J. J.

Epimeric alcohols of the cyclohexane series. Parachor as a criterion for cis-trans-isomerism. —See A., 1940, II, 169.

X-Ray diffraction by finite and imperfect crystal lattices. P. P. EWALD (Proc. Physical Soc., 1940, 52, 167—174; cf. Patterson, A., 1940, I, 61).— Mathematical. A discussion of the Fourier transform of a crystal and its relation to diffraction properties. N. M. B.

Tables of extinction for the 230 crystallographic spatial groups. J. D. H. DONNAY and D. HARKER (Natural. Canad.; 1940, 67, 33-69; cf. A., 1937, I, 171).—Tables correlate the morphological aspects of the crystal with the spatial groups. O. D. S.

Consistent notation for point positions in space-group. L. W. MCKEEHAN (J. Chem. Physics, 1940, 8, 346).—A new notation with six characters per point is advocated. W. R. A.

Structure of a cold-worked metal. W. L. BRAGG (Proc. Physical Soc., 1940, 52, 105—109).—It is suggested that a cold-worked metal is in dynamical rather than statical equilibrium. The existence between crystallites produced by cold-working and distortion of boundaries similar to the films separating bubbles in a foam is proposed by analogy with the state of affairs in superlattices. N. M. B.

Crystalline structure and deformation of metals. W. A. WOOD (Proc. Physical Soc., 1940, 52, 110-116; cf. B., 1939, 497).-A survey, based on mechanical, metallographic, and X-ray tests, of changes in cryst. structure of polycryst. metals and large single crystals subjected to deformation by coldwork and by static and cyclic stressing. It is shown that the grains may be dispersed into crystallites characterised by a lower limiting size depending on the metal, and that internal lattice strains, considered to be related to the process of strain-hardening, can be observed. The response of the cryst. structure depends on the manner and speed of application of stress, and it is thus possible to inhibit the dispersed crystallite formation and suppress the primitive yield point of a metal, so varying the hardness independently of the external deformation. N. M. B.

Lattice distortion in cold-worked metals. G. W. BRINDLEY (Proc. Physical Soc., 1940, 52, 117— 126; cf. A., 1939, I, 305).—Available data on intensities of X-ray reflexions from cold-worked metals indicate that in this respect the lattice distortion resembles a frozen heat motion. For filed powders of Cu, Ni, and Rh, the intensity effect decreases in this order. Measurements of the widths of reflexions from Cu, Ni, and Rh are discussed in relation to various theories of broadening (which is shown to increase in that order) of X-ray reflexions. The most satisfactory theory is that the mean lattice parameter varies from one crystallite to another. The decrease in broadening of the reflexions with an increase in the intensity effect, and the relation of these phenomena to the cohesional properties of the metals, are briefly considered. N. M. B.

Crystal boundaries in tin. B. CHALMERS (Proc. Roy. Soc., 1940, A, 175, 100—110).—A method for preparing specimens of Sn consisting of two crystals of specified orientation is described. The temp. at which the crystals in such a specimen separate under tension is < the m.p. of Sn, the difference being independent of the orientation of the crystals and of impurities, provided these are >0.02%. The effect is ascribed to a boundary layer in which there is some departure from exact geometrical regularity of arrangement of the atoms. G. D. P.

Oriented overgrowths of somatoids. J. WIL-LEMS (Kolloid-Z., 1940, 90, 298—301).—The oriented overgrowths of  $(C_6H_4\cdot OH-p)_2$  obtained by evaporating solutions in various org. solvents on freshly cleaved surfaces of calcite (cf. A., 1939, I, 308) are explained by the analogous two-dimensional structures of the respective lattices. Photomicrographs are reproduced. F. L. U.

Molecular structure factors and their application to the solution of the structures of complex organic crystals. G. KNOTT (Proc. Physical Soc., 1940, 52, 229—238).—The mol. structure factors or Fourier transforms of  $C_6H_6$ ,  $Ph_2$ , and PhMe are derived and their application to the solution of crystal structures is illustrated by reference to  $C_{10}H_8$ . The transform of a complex mol. can be built up from those of its component parts. N. M. B.

Constitution of sulphur nitride. (A) M. A. G. RAU. (B) N. L. PHALINKAR and B. V. BHIDE (Current Sci., 1940, 9, 28).—A criticism and a reply (cf. A., 1940, I, 58). W. R. A.

Crystal structure of sodium peroxide octahydrate. I. Determination of density, unit cell, and possible space-groups. B. P. Korov (J. Phys. Chem. Russ., 1939, 13, 829—834).—The crystals belong to the monoclinic system. The bodycentred unit cell contains 4 mols. of Na<sub>2</sub>O<sub>2</sub>,8H<sub>2</sub>O, and the periods of identity are a 13.49, b 6.45, c 11.49 A., with  $\beta$  110° 31'. The space-group is probably either  $C_2^{\text{GA}}$  or  $C_4^{\text{GA}}$  R. C.

Single crystals of metaboric acid. Structure of orthorhombic metaboric acid,  $\text{HBO}_2(\alpha)$ . Changes of density of metaboric acid under heating. H. TAZAKI (J. Sci. Hirosima Univ., 1940, **A**, **10**, 37—54, 55—61, 63—71).—I. Crystals of  $\text{HBO}_2(\alpha)$  (I), orthorhombic, and  $\text{HBO}_2(\beta)$  (II), monoclinic, can be obtained by heating  $\text{H}_3\text{BO}_3$  in moist air at ~150°. Refractive indices are given. The dimensions of the unit cells (X-ray diffraction) are (I):  $a 8.01_5$ ,  $b 9.67_9$ ,  $c 6.24_4$  A., (II):  $a_0 6.76$ ,  $b_0 8.80$ ,  $c_0 7.15$  A.,  $\beta 92^\circ 40'$ . In each case the cell contains 12 mols. The v.p. of the systems  $\text{H}_3\text{BO}_3$ -(I)- $\text{H}_2\text{O}$ and  $\text{H}_3\text{BO}_3$ -(II)- $\text{H}_2\text{O}$  have been measured between 71° and 120° and 100° and 120°, respectively. The v.p. of (II) is > that of (I) in this range.

II. The detailed structure of the (I) crystal has

been investigated by Fourier analysis of X-ray diffraction patterns.

III. X-Ray diffraction patterns of (I) and (II) after heating at temp. up to 250° show only lines of (I) and (II) and B<sub>2</sub>O<sub>3</sub>. No intermediate compound was observed. The density of H<sub>3</sub>BO<sub>3</sub> at various temp. up to 200° has been measured and correlated with the loss of wt. of the specimen. Up to 100°, densities (p) are equal to those calc. for mixtures of H3BO3 and (I). Above  $100^{\circ} \rho$  correspond with mixtures of  $H_3BO_3$  and  $H_3BO_3$ , (I), and (II). At  $140^{\circ} \rho$  is that of (II). Above  $140^{\circ} \rho$  is that of mixtures of (II) and  $B_2O_3$ . The changes of p on heating at temp. up to 145° of (I) correspond with a continuous conversion without intermediary into  $B_2O_3$ . The  $\rho$  of  $B_2O_3$  produced by heating (I) and (II) differ significantly. Measurements of the v.p. of (I) and (II) between 85° and 145° and 117° and 145°, respectively, have been made and are shown thermodynamically to confirm the hypothesis that B<sub>2</sub>O<sub>3</sub> is produced in different forms by the decomp. of (I) and (II). O. D. S.

Dynamical theory of electron diffraction by crystal lattice. C. H. MACGILLAVRY (Physica, 1940, 7, 329—343).—The dependence of intensity on direction of the diffracted electron bundle in Kossel and Möllenstedt's results (A., 1940, I, 101) is used to test the applicability of Bethe's theory of electron diffraction by crystals. An abs. measure of the structure factor of the reflexions can be obtained by simple geometrical measurements. L. J. J.

Molecular structure of isobutane. J. Y. BEACH and J. WALTER (J. Chem. Physics, 1940, 8, 303-305).—Recalculation of the electron-diffraction theoretical scattering curve for iso-C<sub>4</sub>H<sub>10</sub> (A., 1938, I, 181) yields C—C distance  $1.54\pm0.02$  A. and C–C–C angle 111° 30′±2° in agreement with the data of Pauling and Brockway (A., 1937, I, 448).

W. R. A.

X-Ray studies of crystallite orientation in cellulose fibres. III. Fibre structures from coagulated cellulose. W. A. SISSON (J. Physical Chem., 1940, 44, 513-529; cf. A., 1936, 670).-The hydrate cellulose crystallite present in fibres produced from coagulated cellulose possesses a major orientation tendency with reference to the b axis (axis of cellulose chains) and a minor or selective one with reference to the 101 plane. An increase in dimension of the sample in one direction causes a tendency for the b axes of the unit cell to orient parallel to that direction, whilst a relative decrease in dimension in one direction causes the 101 plane to orient perpendicular to that direction. In each case the degree of orientation  $\propto$  the relative change in dimension. These phenomena are illustrated by the orientation of the 101 planes in Cellophane during shrinkage normal to the plane of the film and in rayon fibre spun without stretching. In either case simultaneous stretching produces an orientation of the b axis. J. W. S.

Internal strains and magnetism. R. BEOKER (Proc. Physical Soc., 1940, 52, 138—151).—Mathematical. The magnetic properties from which a numerical val. can be obtained for the internal stress are developed and co-ordinated, with detailed consideration for the 180° walls. The theoretical and experimental determination of their energy is examined. N. M. B.

Glide and hardening in metal single crystals. E. N. DA C. ANDRADE (Proc. Physical Soc., 1940, 52, 1-7).—A survey of recent experimental work on slip in metal single crystals. Temp. has a great influence on the plastic properties, and the behaviour of different metals with the same crystal structure depends mainly on the ratio of the experimental temp. to the m.p. of the metal. Results are discussed in terms of the dislocation theory of slip. N. M. B.

Problems of plastic gliding. E. OROWAN (Proc. Physical Soc., 1940, 52, 8—22).—A discussion of the rate of flow in metal single crystals. Flow is believed to be due to the presence of dislocations; the rate of production and movement of dislocations is examined mathematically. N. M. B.

Geometrical considerations on structural irregularities to be assumed in a crystal. J. M. BURGERS (Proc. Physical Soc., 1940, 52, 23—33).— A description of investigations of the geometrical and mechanical properties of some types of dislocation the motion of which through the lattice has been assumed to propagate slip. It is shown that plane systems of simple dislocations can break up a crystal into Braggtype mosaic pattern crystallites. N. M. B.

Size of a dislocation [in a crystal]. R. PEIERLS (Proc. Physical Soc., 1940, 52, 34—37).—Calculations of the size of a dislocation and of the crit. shear stress for its motion are made. N. M. B.

Problems of the solid state. J. E. LENNARD-JONES (Proc. Physical Soc., 1940, 52, 38—53).—A discussion of unsolved theoretical problems. One of these is the occurrence of small crystallites even in the most perfect crystals, and reasons are given for attributing such imperfections to the conditions of growth from the melt. Treatment of slip and of the melting problem is examined. Local melting may be due to slip and be a factor in producing strain-hardening. A method of evaluating the stress-strain relation outside the usual elastic limits and at temp. approaching the m.p. is given. N. M. B.

Internal friction in solids. C. ZENER (Proc. Physical Soc., 1940, 52, 152—166).—A discussion of available data on the causes of internal friction shows that it depends in general on thermal currents arising from the inhomogeneous strains set up by the vibrations in the solid and from variations in the elastic consts. from point to point in polycryst. materials. The influence of ferromagnetism is considered.

N. M. B.

Physics of stressed solids. R. W. GORANSON (J. Chem. Physics, 1940, 8, 323—334).—By dividing the internal energy of a system into potential and kinetic functions, and examining these functions for variations of temp., hydrostatic pressure, stress, etc., a theory is evolved explaining the phenomena of deformation, plastic flow, cold-working, elastic afterworking, rupture, shear, and "anomalous" effects. The effect of hydrostatic pressure on deformation and compressive strength is caused by a mechanism which consists of an elastic deformation and a deformation by a two-phase transfer, the former being a function of the potential energy, and the latter a function of the thermodynamic potential relations of the system. Expressions are given for plastic flow of polycryst. substances, and for the "brittle" potential type of rupture by combined thrust and hydrostatic pressure. W. R. A.

Supersonic velocity in gases and vapours. IX. Specific heats and dispersion of supersonic velocity in organic vapours. S. K. K. JATKAR (Indian J. Physics, 1939, 13, 445-449).-Sp. heats of org. vapours have been calc. (i) from velocity data obtained by Railston (J. Acoust. Soc. Amer., 1939, 11, 107) and (ii) from spectroscopic data ob-tained at higher temp. The two methods give results in agreement for the supersonic velocities of  $C_6H_6$ , EtOH, and Et<sub>2</sub>O. For MeOH and CCl<sub>4</sub> the vals. of  $C_p$  from (i) are < those from (ii), indicating the loss of vibrational sp. heats below 100 kc. per sec. The observed val. of  $C_p$  agrees with the val. calc., assuming the disappearance of deformation vibrational terms, for C<sub>6</sub>H<sub>6</sub> and the disappearance of both deformational and longitudinal vibrational terms for  $CS_2$ . The  $C_p$ of  $COMe_2$ ,  $CHCl_3$ ,  $CH_2Cl_2$ , and EtOH from (i) are > those calc. from (ii) owing to uncertain corrections for saturation. W. R. A.

Calculation of b.p. of aliphatic hydrocarbons. C. R. KINNEY (Ind. Eng. Chem., 1940, **32**, 559—562; cf. A., 1939, I, 134). F. J. G.

Physical constants of pentanol-3. F. C. WHIT-MORE and J. D. SURMATIS (J. Amer. Chem. Soc., 1940, 62, 995).—Pentan- $\gamma$ -ol, prepared by dehydrogenation of EtCHO with Cu catalyst, has b.p. 114.4/740 mm.,  $n_D^{\circ0}$  1.4104,  $\rho_4^{\circ0}$  0.8218. W. R. A.

Measurement of the heat capacity of a small volume of liquid by the piezo-thermometric method. I. Apparatus for measuring  $(\partial T/\partial P)_s$ , and results for benzene and toluene. II. Coefficient of thermal expansion of benzene and of toluene measured with a new type of weight dilatometer. III. Heat capacities of benzene and toluene from 8° to b.p. J. S. BURLEW (J. Amer. Chem. Soc., 1940, 62, 681-689, 690-695, 696-700).-I. Constructional and operational details are given of an apparatus for measuring  $(\partial T/\partial P)_s$ and vals. for C<sub>6</sub>H<sub>6</sub> (from 7.80° to 79.82°) and PhMe (from 7.79° to 109.83°) are recorded at 3° intervals.

II. A wt. dilatometer for measuring accurately the coeff. of thermal expansion of 5-c.c. samples is described and manipulative details are given. Vals. for  $C_6H_6$  and PhMe at 3° intervals are given from 8° to b.p. and compared with recorded data. For PhMe  $\rho^0 = 0.8854$ ,  $\rho^{25} = 0.8622$  g. per c.c.

III. From the above data  $C_p$  for  $C_6H_6$  and PhMe have been evaluated; the vals. agree well with existing data. There is no evidence that  $C_6H_6$  is allotropic. W. R. A.

Specific heat of tantalum at low temperatures and the effect of small amounts of dissolved hydrogen. K. K. KELLEY (J. Chem. Physics, 1940, 8, 316—322).—Vals. of  $C_p$  from 53° to 298° K. and of  $e_1^{25}$  are given for Ta and for five samples containing from 2.84 to 9.58 at.-% H, one of which (I) was prepared by pumping H<sub>2</sub> from a "hydrogenated" sample at 720°. Pure Ta and (I) give the same  $C_p$  vals. The  $C_p$ -T curves for "hydrogenated" samples show max. of approx. 40.7 g.-cal. per degree per g.-atom of dissolved H, for which temp. and height both increase with increase in H<sub>2</sub> content. The curves coincide at temp. < temp. of max. At <100° K. the higher is the amount of H<sub>2</sub>, the lower is  $C_p$ . The entropy of Ta at 298.1° K. is 9.9 ±0.1 g.-cal. per degree per mol. Differences in S are attributed to differences in the no. of positions in the Ta lattice available to H at various temp. W. R. A.

Specific heats at low temperatures of tantalum oxide and tantalum carbide. K. K. KELLEY (J. Amer. Chem. Soc., 1940, 62, 818—819).—Vals. of sp. heat have been measured for Ta<sub>2</sub>O<sub>5</sub> (from 53.4° to 294.2° K.) and TaC (from 54.6° to 294.5° K.). For Ta<sub>2</sub>O<sub>5</sub>  $S_{298:1} = 34.2 \pm 0.4$ ,  $\Delta G^{\circ}_{298:1} = -453,700$  and for TaC  $S_{298:1} = 10.1 \pm 0.1$ . W. R. A.

Heat capacity and entropy, heats of fusion and vaporisation, and vapour pressure of methyl chloride. G. H. MESSERLY and J. G. ASTON (J. Amer. Chem. Soc., 1940, 62, 886—890).—The heat capacity of MeCl has been measured from  $11.95^{\circ}$  K. to the b.p. The v.p. is  $\log_{10} P \text{ (mm.)} = -1822\cdot60/T - 9\cdot287119 \log_{10} T + 0\cdot00555556T + 31\cdot07167$ ; m.p.,  $175\cdot44\pm0\cdot05^{\circ}$  K.; b.p.  $248\cdot943^{\circ}$  K.; heats of fusion and vaporisation,  $1537\pm1$  and  $5147\pm10$  g.cal. per mol.;  $S_{298\cdot94^{\circ}}$  and  $S_{298\cdot16^{\circ}}$ ,  $54\cdot27$  and  $54\cdot31$ , and  $55\cdot94$  and  $55\cdot98$  g.-cal. per degree per mol. from thermal and spectroscopic data, respectively.

W. R. A. Resonance method for measuring the ratio of the specific heats of a gas,  $C_p/C_v$ . II. A. L. CLARK and L. KATZ (Canad. J. Res., 1940, 18, A, 39-63).—Using the method already described (A., 1940, I, 271) the following vals. for  $\gamma$  at ~24° have been obtained: N<sub>2</sub>, 1.402 at 1 atm., 1.400 at zero pressure; CO<sub>2</sub>, 1.300 at 1 atm., 1.294 at zero pressure; H<sub>2</sub>, 1.403 at 1 atm. and at zero pressure; A, 1.669 at 1 atm., 1.666 at zero pressure; He, 1.665 at 1 atm. and at zero pressure. In appendices, further details of theory and of apparatus are given. F. J. G.

Thermodynamical properties of real gases. M. P. VUKALOVITSCH and I. I. NOVIKOV (Bull. Acad. Sci. U.R.S.S., Cl. Sci. Tech., 1939, No. 5, 33-48).— The equations obtained (A., 1940, I, 18) are similar to those of Born and Fuchs (A., 1938, I, 445). J. J. B.

Heat capacity of real gases. M. P. VUKA-LOVITSCH and I. I. NOVIKOV (Bull. Acad. Sci. U.R.S.S., Cl. Sci. Tech., 1939, No. 6, 111—128).—The theory of the preceding abstract is applied to calculation of the heat capacity of associated gases. J. J. B.

Volatility of small particles of salt crystals with and without polymorphic change. N. KOLAROV (Kolloid-Z., 1940, 90, 294—298; cf. A., 1937, I, 453). —V.p.-particle size curves for RbCl and RbBr, which undergo no polymorphic change within the experimental temp. range, pass through a min., whilst those for  $Bb_2SO_4$  and  $Cs_2SO_4$ , which undergo transitions at 649° and 660°, respectively, do not. F. L. U.

Thermodynamic properties of fluorochloromethanes and -ethanes: vapour pressure of three fluorochloromethanes and trifluorotrichloroethane. A. F. BENNING and R. C. MC-HARNESS (Ind. Eng. Chem., 1940, **32**, 497—499).— V.p. data at 0·1—50 atm. have been determined by a static method for CHCIF<sub>2</sub> (I), CHCl<sub>2</sub>F (II), CCl<sub>3</sub>F (III), and CCl<sub>2</sub>F·CCIF<sub>2</sub> (IV). They are represented by  $\log_{10} p = A - B/T - C \log_{10} T + DT$ , where the coeffs. A, B, C, and D, have the following respective vals.: for (I), 25·1144, 1638·82, 8·1418, 0·0051838; for (II), 38·2974, 2367·41, 13·0295, 0·0071731; for (III), 34·8838, 2803·95, 11·7406, 0·0064249; for (IV), 29·5335, 2406·10, 9·2635, 0·0036970. The b.p. are (I), -40·80°; (II), 8·92°; (III), 23·77°; (IV), 47·57°. F. J. G.

Vapour pressures of certain unsaturated hydrocarbons. A. B. LAMB and E. E. ROPER (J. Amer. Chem. Soc., 1940, **62**, 806—814).—Using the static method, the v.p. over the range 10—1000 mm. have been measured for  $C_2H_4$ , propylene,  $CMe_2:CH_2$ ,  $\Delta^{\alpha}$ butene, *cis*- and *trans*- $\Delta^{\beta}$ -butene,  $\Delta^{\alpha\delta}$ -pentadiene, and  $\beta$ -methyl- $\Delta^{\beta}$ -butene. All the data fit a general equation log p = A/T + BT + C and most of these substances obey the Ramsay-Young and Dühring rules. Vals. of b.p., slopes of v.p. curves, and heats of vaporisation are deduced. V.p. measurements for liquid and cryst. propadiene (triple point = 136.94 $\pm$ 0.02° K. at 0.1448 mm.) are given. W. R. A.

Empirical equation for thermodynamic properties of light hydrocarbons and their mixtures. I. Methane, ethane, propane, and *n*butane. M. BENEDICT, G. B. WEBB, and L. C. RUBIN (J. Chem. Physics, 1940, 8, 334—345).—An equation for the isothermal variation with  $\rho$  of the work content of pure hydrocarbons in the gaseous and liquid states is given and from it may be computed the P-V-T properties of the gas or liquid phase, crit. properties, effect of pressure on H, the fugacity, v.p., and latent heats of vaporisation. Numerical vals. for parameters of the equation are given for  $CH_4$ ,  $C_2H_6$ ,  $C_3H_8$ , and  $n-C_4H_{10}$  and compared with observed vals. W. R. A.

Determination of thermodynamic parameters of real gases, and investigation of water vapour, air, and diatomic gases. M. P. VUKALOVITSCH and I. I. NOVIKOV (Bull. Acad. Sci. U.R.S.S., Cl. Sci. Tech., 1939, No. 8, 101—129).—Equations for various thermodynamic magnitudes have been deduced from the equation of state previously derived (A., 1940, I, 18). The results agree well with the existing data for the thermodynamic properties of air and  $H_2O$  vapour. The methods previously employed have been successfully applied to the investigation of the thermodynamic properties of diat. gases. R. C.

Viscosity of gases for low pressures at room temperature and at low temperatures. A. VAN ITTERBEEK and O. VAN PAEMEL (Physica, 1940, 7, 273-283).—Measurements by the oscillating-disc method, at  $10^{-3}$ —10 mm. Hg and room temp. and liquid O<sub>2</sub> and H<sub>2</sub> temp., show that for H<sub>2</sub>, D<sub>2</sub>, Ne, and He  $\eta$  varies with pressure in the manner previously found with He at low pressures (A., 1938, I, 304). L. J. J.

Temperature variation of viscosity of nonpolar and dipolar inorganic liquids. S. T. BOWDEN and A. R. MORGAN (Phil. Mag., 1940, [vii], 29, 367—378).—The variation with temp. of the viscosities of SiCl<sub>4</sub>, 0—35°, PCl<sub>3</sub>, 0—50°, AsCl<sub>3</sub>,  $S_2$ Cl<sub>2</sub>, and POCl<sub>3</sub>, 0—80°, SOCl<sub>2</sub>, 0—65°, and SO<sub>2</sub>Cl<sub>2</sub>, 0—50° have been measured for the temp. ranges stated. Results and previous vals. for BiCl<sub>3</sub> and SnCl<sub>4</sub> conform fairly closely to the Andrade relation, the largest deviations being shown by PCl<sub>3</sub> and SnCl<sub>4</sub>. O. D. S.

Activation energy and heat of melting of fatty acids and triglycerides calculated from temperature relations of viscosity. M. P. VOLARO-VITSOH and G. B. RAVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1939, 23, 252-255).—An attempt has been made to apply the equation  $\eta = A e^{B/RT}$  (where A, B, and R are consts.) to the data obtained previously (A., 1936, 156) for the higher fatty acids and triglycerides (I) of varying degrees of saturation. Fatty acids in the liquid state show no changes in coordination no. of mols. within the temp. range 20-110°. For (I), an increase in co-ordination no. of mols. occurs on raising the temp., owing to the smaller influence of directed forces, and both acids and (I) are regarded as mol. liquids with a OH or H bond. In contrast to Ward's results (A., 1937, I, 125), the heats of melting L for fatty acids are found to be >B, the activation energy. Comparison of L and  $\dot{B}$  for (I) cannot be made because of the lack of reliable vals. of L. W. R. A.

Calculation of vapour pressures of binary liquid mixtures. V. DE LANDSBERG (Bull. Soc. chim. Belg., 1940, 49, 21-58).—The first part of a review of methods of verifying and calculating v.p.concn. isotherms. F. L. U.

Viscosity of hydrocarbon solutions : methaneethane-crystal oil system. B. H. SAGE and W. N. LACEY (Ind. Eng. Chem., 1940, **32**, 587–589).—Data on  $\eta$  for CH<sub>4</sub>-C<sub>2</sub>H<sub>6</sub>-crystal oil mixtures at 100° F. and at >2500 lb. per sq. in. are given. F. J. G.

Freezing points of the system ethylene glycolmethanol-water. F. H. CONRAD, E. F. HILL, and E. A. BALLMAN (Ind. Eng. Chem., 1940, **32**, 542— 543).—F.p. data for the system are recorded.

F. J. G.

Freezing points in mixtures of strong electrolytes. M. RANDALL and B. LONGTIN (J. Physical Chem., 1940, 44, 427—435).—Theoretical. For solutions containing mixed electrolytes the f.p. function j(cf. A., 1928, 365) is defined as  $1 - (\theta/\lambda \Sigma_i m_i)$  ( $\theta = f.p.$ lowering,  $\lambda = \text{mol.}$  lowering, and  $\Sigma_i m_i / 2\mu^{1.5}$  against  $\mu^{1.5}$  ( $\mu = \text{total}$  ionic strength) curves are obtained which are in approx. superposition for all electrolytes and which approach the same point at  $\mu = 0$ . For single electrolytes  $\Sigma_i m_i / 2\mu^{1.5} = 1 / w m^{0.5}$ , where w is a valency factor. This form of plotting has the advantage of permitting the curve to be drawn by analogy if one f.p. measurement is made. J. W. S.

 $0^{**}$  (A., I.)

Chlorofluoroethanes as solvents for cryoscopic determination of mol. wt. J. BERNSTEIN and W. T. MILLER (J. Amer. Chem. Soc., 1940, **62**, 948—949).—  $C_2Cl_5F$ , (CCl\_2F)<sub>2</sub>, and CCl\_3·CClF<sub>2</sub> are suitable for cryoscopic determination of mol. wts., the cryoscopic consts. being 42.0, 37.7, and 38.6, respectively.

R. S. C.

Cryoscopy in hydrazine hydrochloride. A. CHRÉTIEN and A. NESSIUS (Bull. Soc. chim., 1940, [v], 7, 258-275).-The cryoscopic const. of anhyd.  $N_2H_4$ ,HCl (I), as determined with CO(NH<sub>2</sub>)<sub>2</sub>, is 50.2.  $NH_4Cl, (N_2H_4)_2, H_2SO_4, N_2H_4, 2HCl, and N_2H_4, HNO_3 as$ solutes also yield a similar val. This may be due to non-dissociation of these salts or to the circumstance that the N<sub>2</sub>H<sub>5</sub> or Cl' ions formed by dissociation do not affect the m.p. of (I).  $N_2H_4, H_2SO_4$  (II),  $HgCl_2$ , and PbCl, yield a val. of ~100 for the cryoscopic const. of (I). This behaviour, in spite of the fact that dissociation would be expected to yield N<sub>2</sub>H<sub>5</sub> or Cl' ions, is attributed to the formation of complex ions with (I), or in the case of (II) to the formation of  $H^{\bullet}$  and  $SO_4^{\prime\prime}$ ions. J. W. S.

Effect of irradiated electrical energy on crystallisation. K. HOFER (Atti X Congr. Internaz. Chim., 1938, IV, 449—460).—When glass vessels in which substances (e.g.,  $CaCO_3$ , NaCl) are crystallising from aq. solution are fitted with Sn plates and inserted as condensers in the circuit of a radio receiving or transmitting set, the crystals formed are smaller than, and of different shape from, those separating under normal conditions. F. O. H.

Absorption and dispersion of sound in a solution of a weak electrolyte. I. G. SCHAPO-SCHNIKOV and M. A. LEONTOVITSCH (J. Phys. Chem. Russ., 1939, 13, 781—785).—The theory of absorption and dispersion is developed on similar lines to Einstein's theory for gases. R. C.

Anisotropy of light absorption of dissolved molecules in an electrical field. W. KUHN, H. DÜHRKOP, and H. MARTIN (Z. physikal. Chem., 1939, 45, B, 121-155).-If a solution of a coloured dipolar substance is placed in an electrical field partial orientation of the mols. results. The absorption of light by these mols. is determined by the magnitude of the orientation with respect to the incident beam. The magnitude of the electrodichroism is theoretically dependent on the dipole moment of the mols., the direction of vibration for a given  $\lambda$ , and the strength of the applied electrical field. The electrodichroism for solutions of p-NO·C<sub>6</sub>H<sub>4</sub>·NMe<sub>2</sub> (I) in C<sub>6</sub>H<sub>14</sub> has been measured for 4359, 4047-4078, and 3655 A. There is complete dichroism for 4359 A., the mols. absorbing only light of which the electrical vector vibrates perpendicular to the dipole axis of the mols. For 4047-4078 A. and 3655 A. the dichroism is weaker; the absorption of light of which the electrical vector vibrates parallel to the dipole axis of the mols. is approx. double that of which the electrical vector vibrates parallel to this axis. Since all these belong to the same absorption band of the mols. the absorption band must be a superposition of at least two bands which possess different modes of vibration. The measurements establish the presence of anisotropy of the modes of vibration of absorption bands of org.

mols. From the anisotropy of optical absorption of dissolved mols. on the one hand and of crystals on the other, the possibility of determining the orientation of mols. in crystals is discussed. Data on the anisotropy of light absorption of crystals of (I) are given. W. B. A.

Viscosity and solvation. II. S. BEZZI (Gazzetta, 1940, 70, 110—118).—Measurements of  $\eta$  of dil. solutions of polydimethyl glycols in various solvents have been made. Some of the solutions behave normally,  $\eta_{sp}$ , being  $\propto$  mol. wt. Abnormal variations of  $\eta$  with concn. are attributed to solvation. O. J. W.

Diffusion in solids. R. M. BARRER (Proc. Physical Soc., 1940, 52, 58—70).—A summary and discussion of data on diffusion consts. in ionic and metallic systems in terms of the Fick-Matano diffusion equation  $D = D_0 e^{-E/RT}$ , where E = energy of activation for diffusion. Data for 18 ions in salts and 56 metal systems are tabulated. Theories of diffusion are outlined, and expressions for D and its relation to other physical quantities are considered. Similarities between diffusion and chemical reaction are brought out by considering the entropy of activation and periodicity curves for  $D_0$ . N. M. B.

Isomorphous relationships of organic compounds of analogous constitution.—See A., 1940, II, 196.

Generalisation of the Heisenberg-Bloch theory [applied to] binary ferromagnetic alloys. S. V. VONSOVSKI (Compt. rend. Acad. Sci. U.R.S.S., 1940, 26, 570-572).—Mathematical. W. R. A.

Formation of nuclei [in alloys] during precipitation. R. BECKER (Proc. Physical Soc., 1940, 52, 71—76).—Mathematical. An application of the treatment of condensation in vapours shows that when an alloy in which pptn. is to take place is cooled, the process begins with observable velocity only when the temp. has fallen by a definite amount below that at which the single-phase alloy is in equilibrium. This fact is explained by a theory of nuclear formation. Calculation of the rate of formation of nuclei is examined. N. M. B.

Influence of elastic strain on the shape of particles segregating in an alloy. F. R. N. NABARRO (Proc. Physical Soc., 1940, 52, 90—93).— Mathematical. An estimate of the dependence of strain energy associated with a particle of ppt. on the shape of the particle shows that the energy can be reduced only if the ppt. forms in flat plates, and then only in the case of particles which have broken away from the lattice of the matrix. N. M. B.

Estimate of degree of precipitation-hardening [in alloys]. N. F. MOTT and F. R. N. NABARRO (Proc. Physical Soc., 1940, 52, 86—89).—Mathematical. Assuming diffusion to result in an interchange of atoms, the internal strains produced by pptn. are calc. on the basis of a simple model. By the dislocation theory these strains are responsible for the hardness of the material and so the degree of hardening can be predicted. N. M. B.

Modulus of elasticity of alloys.—See B., 1940, 366.

Variation of principal elastic moduli of  $Cu_3Au$ with temperature. S. SIEGEL (Physical Rev., 1940, [ii], 57, 537—545).—Single crystals of Cu–Au alloy, containing 24·92 at.-% Au, prepared in a vac. furnace were brought to the ordered state at room temp. by annealing. The elastic moduli, measured by the composite piezoelectric oscillator method, are tabulated as a function of temp. for the range 20— 450°. At the crit. temp.  $387 \cdot 5°$  there is a discontinuity in each modulus-temp. curve. Results indicate that the elastic consts. are closely related to the degree of local order. N. M. B.

Optical constants of the copper-aluminium  $\alpha$ -alloys. L. McPHERSON (Proc. Physical Soc., 1940, 52, 210—216).—Experimental vals. of n, extinction coeff., absorption coeff., and reflecting power in the range 5000—9500 A. are given. Curves show the variation of the consts. with  $\lambda$ , and interpretation is briefly discussed. N. M. B.

Age-hardening of copper-aluminium alloys. G. D. PRESTON (Proc. Physical Soc., 1940, 52, 77— 79).—The ageing of Al alloys containing 4% of Cu is discussed. At room temp. the Cu atoms segregate on the (100) planes of the crystals, but no new phase is formed. At 200° a pseudomorphic form of CuAl<sub>2</sub> is pptd. N. M. B.

Alloys of germanium with bismuth, antimony, iron, and nickel [and of silicon with nickel]. K. RUTTEWIT and G. MASING (Z. Metallk., 1940, 32, 52-61).—All the systems were examined by thermal and micrographic methods using alloys melted in a N2 atm. Bi and Ge are insol. in one another in the solid state; they form no eutectic and no compound. Sb and Ge are also insol. in one another in the solid state but form a eutectic at 588°, Ge 19 at.-%. Fe dissolves 13 at.-% of Ge at 700° and 19 at.-% at  $1100^{\circ}$ ; two compounds are formed at max. on the liquidus curve corresponding with Fe,Ge, 1180°, and FeGe, 866°; FeGe, forms, however, only on slow cooling, a eutectic crystallising at 835° if molten FeGe<sub>2</sub> is cooled rapidly. Fe,Ge forms a eutectic with Fe at 1125°, Ge 29 at.-%. In the Ni-Ge system there is only one compound, Ni<sub>2</sub>Ge ( $\varepsilon$ ), m.p. 1200°, which forms a eutectic with Ge at 775°, Ge 60·3 at.-%; Ni dissolves 12 at.-% of Ge at all temp. <1160° but Ge does not appear to dissolve Ni below 900°. The system is very complex between 23 and 33 at.-% of Ge, four intermediate phases being formed, two of which,  $\gamma$  and  $\gamma'$ , have remarkably small composition and temp. ranges; at 1161°  $\beta$  (Ge 22.8 at.-%) is formed from liquid +  $\alpha$ , at 1155°  $\gamma$  (Ge 26.4 at.-%) from liquid +  $\beta$ , at 1135°  $\delta$ (Ge 29.6 at.-%) from liquid +  $\varepsilon$ , and at 1015°  $\gamma'$ (Ge 26.3 at.-%) from  $\beta + \delta$ . At 850°  $\varepsilon$  reacts with liquid to form  $\eta$  with Ge 50 at.-%, and below 970° the  $\gamma$  and  $\delta$  phases decompose into  $\beta + \delta$ . There appears to be a second eutectic at 1130°, Ge 28.9 at.-%, but owing to the close proximity of this point to the  $\delta$ peritectic a true eutectic structure is difficult to obtain. A re-examination of the Ni-Si system up to 35 at.-% of Si has confirmed in general the diagram of Iwasé and Okamoto (cf. B., 1940, 452) except that the various horizontals are placed at slightly higher temp. owing to the greater purity of the Si used; the heat effects previously observed at 1040° (Si 10-28

at.-%) and at 1214° (Si 28—34 at.-%) do not occur in A. R. P. A. R. P.

Order-disorder transformation in the alloy  $Ni_3Mn$ . N. THOMPSON (Proc. Physical Soc., 1940, 52, 217—228).—Curves for the temp. variation of magnetisation, electrical resistance, and sp. heat during and after various heat-treatments are given. Results indicate an order-disorder transformation at 510°, the ordered structure being ferromagnetic with a Curie point at 460°. The sharp decrease of resistance on slow cooling takes place at the Curie point. The effect of the degree of order and size of the ordered regions on resistance and magnetisation is discussed. N. M. B.

Recrystallisation of iron-nickel alloy.—See B., 1940, 362.

X-Ray evidence of intermediate stages during precipitation from solid solution. A. J. BRADLEY (Proc. Physical Soc., 1940, 52, 80-85).—On heating for shorter times than are necessary for attainment of equilibrium, intermediate metastable structures resulting from the partial decomp. of solid solutions were found in the Cu-Ni-Al, Fe-Ni-Al, and Fe-Cu-Ni systems. In each case a single-phase structure, stable at high temp., breaks up into two phases on cooling. The first stage in the decomp. is the formation of islands in which atoms segregate prior to pptn.:  $CuNi_2Al$  from a Cu-rich solid solution, and FeNiAl from an Fe-rich solid solution. During the decomp. of FeCu<sub>4</sub>Ni<sub>3</sub> into two phases, a laminated structure is produced in which Cu-rich and Fe-Ni-rich laminæ alternate. Each has a tetragonal structure with the same a axes as in the solid solution; in the Cu-rich laminæ c > a; in the other c < a. N. M. B.

X-Ray study of structure of ternary solid solutions of aluminium with magnesium and silicon and their ageing. V. G. KUZNETZOV and E. S. MAKAROV (Compt. rend. Acad. Sci. U.R.S.S., 1939, 23, 245-249).—An X-ray study has been made of homogeneous alloys tempered at 550°, 500°, 400°, and 200° the compositions of which are represented by points along six radial sections, up to a Mg + Si content of 2.2%, in the Al corner of the phase diagram of the system Al-Mg-Si. The solubility data agree with those given by Urazov and Schuschpanova (cf. B., 1937, 1357) for all temp. except 200°. Experimental curves representing the changes in the parameters of the solid solution differ from the calc. linear curves for one radial section passing along the line of simultaneous saturation with Si and Mg<sub>2</sub>Si. This indicates that Mg<sub>2</sub>Si is molecularly dispersed in the Al solid solution, but in too small a concn. for its lattice to be detected by X-ray methods. The ageing of the tempered alloys at room temp. does not cause parameter changes, but with artificial ageing the lattice consts. approach the Al parameter. After both natural and artificial ageing a heterogeneity in composition is indicated. W. R. A.

Solubility of carbon dioxide in water at various temperatures from 12° to 40° and at pressures to 500 atmospheres. Critical phenomena. R. WIEBE and V. L. GADDY (J. Amer. Chem. Soc., 1940, 62, 815-817; cf. A., 1939, I, 194).—Determinations of the solubility of  $CO_2$  in  $H_2O$  at  $12^\circ$ ,  $18^\circ$ ,  $25^\circ$ ,  $31.04^\circ$ , and  $40^\circ$  at pressures up to 500 atm. indicate complete miscibility, particularly for the lower temp. An approx. crit. curve has been obtained with a pressure max. at 75°. Solid  $CO_2, 6H_2O$  separates at pressures >50 atm. at  $10^\circ$  and over the pressure range 300-500 atm. at  $12^\circ$ . W. R. A.

Binary and ternary systems separating into two liquid layers. Inversion of densities. P. MONDAIN-MONVAL and J. QUIQUEREZ (Bull. Soc. chim., 1940, [v], 7, 240—253).—The d of the two layers in the systems  $H_2O-NH_2Ph$  and  $H_2O-o-C_6H_4Me\cdotNH_2$  have been measured, and the temp. at which the d of the layers become equal have been determined. The compositions and d of the conjugated solutions in the systems  $H_2O$ -EtOH-PhMe and  $H_2O$ -EtOH-m-xylene have been measured at 25°. In each case inversion of d occurs near the crit. solution point. The conditions under which inversion of densities occurs in such systems are discussed.

J. W. S. **Partial miscibility in liquid alloys. System lead-zinc-tin.** P. MONDAIN-MONVAL and G. GABRIEL (Bull. Soc. chim., 1940, [v], 7, 113—121).— Pb-Sn-Zn alloys of [Sn] <29% separate into two phases at 520°. The crit. miscibility point occurs with Pb 30.5, Sn 29, and Zn 40.5%. The [Sn] in the Pb layer is < in the Zn layer, and evidence is obtained of the existence of Pb<sub>3</sub>Sn, partly dissociated, in the Pb phase. J. W. S.

Solubility and molecular rotation of tetra-, penta-, and hexa-substituted benzenes. C. P. SMYTH and G. L. LEWIS (J. Amer. Chem. Soc., 1940, **62**, 949—952).—The solubilities in  $C_6H_6$  at various temp., temp. below which rotation ceases, heats and entropies of fusion, and dipole moments are given and discussed for  $C_6Cl_6$ ,  $C_6Me_6$ , 1:3:5:2:4:6- and  $1:2:5:3:4:6-C_6Me_3Cl_3$ ,  $1:2:3:4:5:6-C_6Me_4Cl_2$ ,  $C_6Me_5Cl, C_6HCl_5, C_6MeCl_5$ ,  $1:2:3:4:5:6-C_6Me_2Cl_4$ ,  $1:2:3:4:5-C_6HMe_2Cl_3$ ,  $1:2:4:5-C_6H_2Me_2Cl_2$ , and  $C_6MeCl_5$ . W. R. A.

Solubility in the systems NaBr-NaBrO3-H2O-NaHCO3 and -Na2CO3. G. S. KLEBANOV and E. P. BASOVA (J. Appl. Chem. Russ., 1939, 12, 1601-1609).-Phase diagrams are given for the systems NaBr-NaBrO<sub>3</sub>-NaHCO<sub>3</sub>-H<sub>2</sub>O at 25° and 35°, and NaBr-NaBrO<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub>-H<sub>2</sub>O at 80°. NaBr greatly depresses the solubility of all the other salts, whilst NaBrO<sub>3</sub> depresses only that of NaHCO<sub>3</sub>. When solutions containing NaBr and NaBrO<sub>3</sub> are evaporated until crystallisation commences, and the temp. is lowered to  $>10^\circ$ , NaBrO<sub>3</sub> separates in 80% yield. Recovery of further NaBrO<sub>2</sub> from the motherliquors is not possible; pure NaBr is obtained by reducing NaBrO<sub>3</sub> to NaBr. NaHCO<sub>3</sub> separates out together with NaBr or NaBrO<sub>3</sub>; this may be prevented by converting it into more sol.  $Na_2CO_3$ , by heating the solutions, and then returning the liquor for bromination, or by adding bromides the cation of which combines with  $CO_3''$  to form insol. carbonates.

R. T.

Distribution of bromine between crystals and solution of potassium chloride and bromide. S. K. TSCHIRKOV (J. Appl. Chem. Russ., 1939, 12, 1747—1752).—Polemical against Schlesinger *et al.* (A., 1939, I, 253). R. T.

Determination of constants of water absorption by dry organic substances. C. A. SHULL and S. P. SHULL (Plant Physiol., 1939, 14, 351—357).— Mathematical. A. G. P.

Gibbs' relation and adsorption formulæ. A. BOUTARIC (J. Phys. Radium, 1940, [viii], 1, 99— 102).—Theoretical. The basis and utility of the Gibbs relation are discussed and an equation is deduced of the form  $p = \mathbf{R}Tu/m$ , where p is the diminution in  $\gamma$ due to surface-adsorbed mols. and u is the concn. per unit area of surface. When the adsorption is represented by the Langmuir-Perrin equation m = 1. The relation between u and the concn. of the solution is also given. W. R. A.

Elasticity of organo-gels in relation to hysteresis in sorption. K. S. RAO (Current Sci., 1940, 9, 19-21).—Ča arabate (I), activated at 60° in a vac. for 30 min., was degassed for 5 hr. in a vac. and a series of sorptions and desorptions was conducted at 30° using the quartz fibre spring balance. 14 days were required to complete each cycle. Hysteresis exhibited in the first cycle falls away in subsequent cycles and completely disappears in the fourth. This behaviour, similar to that of rice grain (B., 1939, 985), can be similarly explained on the cavity concept of hysteresis. The hysteresis loop in the first cycle extends to a R.H. of 0.78, corresponding with a max. cavity radius of 40.5 A. The loop extends to zero pressure, indicating that the necks of the cavities have mol. dimensions. The behaviour of dhal grain (Cajanus indicus) is similar. A series of sorptions and desorptions of CHCl<sub>3</sub> vapour on the activated grain shows the existence of a permanent hysteresis loop reproducible at the ninth cycle, whereas the loop of H<sub>2</sub>O disappears in the third cycle. W. R. A.

Permanence of the hysteresis loop in sorption. K. S. RAO (Current Sci., 1940, 9, 68-70).-In a series of sorptions and desorptions of H<sub>2</sub>O vapour on suitably treated Al<sub>2</sub>O<sub>3</sub> gel (cf. A., 1937, I, 129) at 30° two months elapsed between the beginning of the first sorption and the ending of the tenth desorption, and the hysteresis loop obtained was permanent and reproducible. This is explained on the basis of the cavity concept (see above). Al<sub>2</sub>O<sub>3</sub> retains 2.6% of H<sub>2</sub>O irreversibly at the end of the first desorption, and this remains almost unaltered, owing to the H<sub>2</sub>O being trapped in the gel interstices, or held on the surface as OH attached to Al<sub>2</sub>O<sub>3</sub> (cf. silicic acid, A., 1936, 272). The peak of the loops extends to the saturation point, showing that some of the cavities in the  $Al_2O_3$  gel are microscopic. W. R. A.

Rate of sorption in relation to hysteresis. K. S. RAO (Current Sci., 1940, 9, 70–72).—The idea of a cavity (cf. preceding abstract) having narrow necks has been supported by measuring the rates of sorption of  $H_2O$  vapour on SiO<sub>2</sub> (I), TiO<sub>2</sub> (II), Al<sub>2</sub>O<sub>3</sub> (III), and Fe<sub>2</sub>O<sub>3</sub> (IV) gels. These gels were activated, and degassed in a vac. for 5 hr., and a series of sorptions and desorptions conducted at 30°, hysteresis being exhibited by all. After a definite no. of cycles, 2

for (I), 29 for (II), 9 for (III), and 9 for (IV), the rates of sorption of H<sub>o</sub>O on the gels were measured, by measuring the amount of H<sub>2</sub>O held reversibly by the gels. Except for (I), the sorption isotherms show a clear inflexion marking a transition from a unimol. adsorption to capillary condensation, and the rate of sorption is shown to be mainly the rate of filling of the capillaries. The time intervals for complete sorption vary widely, but the amounts of sorbed H2O at equilibrium, per g. of gel, are almost identical. The rate differences are ascribed to the difference in size and no. of the cavities, and the rate of sorption is the rate of creeping of condensed liquid in the neck into the interior of the cavity, dependent on the difference in v.p. outside and inside the cavity. This explains the quick filling up of gels having small cavities, such W. R. A. as (I).

Characteristics of adsorptive and catalytic properties of iron catalysts.—See B., 1940, 356.

Adsorption of hydrochloric and sulphuric acids by commercial active charcoals. A. A. Kor (J. Appl. Chem. Russ., 1939, **12**, 1653—1663).— HCl and  $H_2SO_4$  are removed from aq. solutions by active C, which is regenerated by treatment with aq. NaOH, Na<sub>2</sub>CO<sub>3</sub>, or NaHCO<sub>3</sub>. R. T.

Adsorption of proteins by montmorillonitic clays.—See B., 1940, 385.

Ion adsorption by pectin. G. H. JOSEPH (J. Physical Chem., 1940, 44, 409—411).—The conclusions of Spencer (A., 1930, 418) are incorrect owing to mathematical inaccuracies, and the original view of Tarr (Univ. Delaware Expt. Sta. Bull. 134, 1923) that pectin possesses a buffer action in acid solutions owing to the adsorption of H<sup>-</sup> ions is substantiated.

J. W. S. Surface tension of ethyl alcohol-water mixtures. W. S. BONNELL, L. BYMAN, and D. B. KEYES (Ind. Eng. Chem., 1940, **32**, 532—534).— Vals. of  $\gamma$  for EtOH-H<sub>2</sub>O mixtures (EtOH 2·33— 92·72%) between room temp. and the b.p. are given.  $\gamma$  decreases linearly with rising temp., and at const. temp. decreases at first rapidly and then more slowly with increasing [EtOH]. F. J. G.

Type III surface tension curves with minimum in dilute solution in pure hydrocarbons. M. E. L. MCBAIN and L. H. PERRY (J. Amer. Chem. Soc., 1940, 62, 989—991).—Type III  $\gamma$  curves are given by nonelectrolytic detergents, and show a lowering of  $\gamma$  in solutions, which remains const. on further concn. (A., 1940, I, 209). Using hydrocarbons as solvents, type III curves with min. occur in non-ionising media. Dodecanesulphonic acid (I) in Nujol (II), mineral oil (III), and hydrogenated tetra*iso*butylene (IV) shows this min., but in *iso*-C<sub>8</sub>H<sub>18</sub> (type I curve), xylene, C<sub>6</sub>H<sub>6</sub>, and C<sub>7</sub>H<sub>16</sub>,  $\gamma$  is scarcely lowered. Nonylglucoside does not lower the  $\gamma$  of (II) or (IV) although it is polar, and a non-electrolytic detergent in (II) showed no appreciable lowering. Pr<sup>c</sup>Co<sub>2</sub>H in 20% solution gives a lowering of only 2 dynes, which is given by lauric acid in 3% solution. Ca and Zn stearates have no effect. The production of a type III curve in these hydrocarbons requires such high polarity that the solute forms a colloidal electrolyte or strong electrolyte in  $H_2O$ . The only explanation suggested for the min. in type III curves is that advanced by McBain (A., 1937, I, 130). W. R. A.

Surface equilibrium of complex solutions. P. L. DU NOUX (Compt. rend., 1940, **210**, 334—335).— The du Nouy effect has been observed in non-colloidal media (glycerol, sugars, electrolytes; cf. also A., 1940, III, 283). Addition of a trace of Na oleate to 10% aq. glucose reduces the surface tension ( $\gamma$ ) from 72 to 47 dynes per cm.; the  $\gamma$ -t curve then rises logarithmically for 28 min., and becomes linear. At 3 hr. the curve bends over, and the initial  $\gamma$  val. is reached or slightly exceeded at 5 hr. With 10% aq. glycerol  $\gamma$ rises logarithmically for 2 hr. after addition of Na oleate. The mechanism of the effect is probably identical with that of neutralisation by colloids.

A. J. E. W.

Interfacial tension between a benzene solution of palmitic acid and an aqueous solution of ammonia. Tensiometric study of neutralisation of ammonia by hydrochloric acid. L. GAY and L. RAYMOND (J. Chim. phys., 1940, 37, 19—29; cf. A., 1937, I, 130, 612).—The curves obtained by plotting interfacial tension ( $\gamma$ ) against log [NH<sub>3</sub>] (for const. palmitic acid concn. > 1%) consist of 4 straight lines, alternately horizontal and downward-sloping, the latter indicating const. excess concn. of NH<sub>3</sub> in the interface. Possible interpretations are discussed. Tensiometric titration of aq. HCl with aq. NH<sub>3</sub> is inexact when the solutions are dil., since no sharp change in  $\gamma$  occurs at the point of chemical equivalence. F. L. U.

Interfacial tension between a benzene solution of palmitic acid and an aqueous solution of mono-, di-, or tri-sodium orthophosphate. L. GAY, P. MÉJEAN, and A. BRUNEL (J. Chim. phys., 1940, **37**, 30–39).—The  $\gamma$ -concn. curves consist of a nearly horizontal portion followed by a steeply descending one, the latter becoming linear when plotted logarithmically. The curves for Na<sub>2</sub>HPO<sub>4</sub> have a third less steeply inclined part in addition to the two mentioned, whilst those for NaH<sub>2</sub>PO<sub>4</sub> have two additional portions. Tensiometric titration of H<sub>3</sub>PO<sub>4</sub> with NaOH, as in the case of NH<sub>3</sub> and HCl (cf. preceding abstract), is impracticable when the solutions are dil. F. L. U.

Surface tension between polarised mercury and an aqueous solution of sulphuric acid. F. Bon (Compt. rend., 1940, 210, 567—569).—The interfacial tension ( $\gamma$ ) between aq. H<sub>2</sub>SO<sub>4</sub> (concn. c) and Hg at different potentials (E, measured with reference to a large mass of Hg in the same solution) has been determined by the drop-wt. method. The  $\gamma$ -log c curves are initially horizontal, but as log c increases a linear fall in  $\gamma$ , which is pronounced if E is  $\gg$  or  $\ll 0.8 \text{ v.}$ , is followed by a further less rapid fall, also linear with log c. The two breaks on each curve lie on parallel straight lines which are slightly inclined to the  $\gamma$  axis. A. J. E. W.

Preparative studies with unimolecular films. I. Continuous preparation of unimolecular layers. F. Kögl and E. HAVINGA (Rec. trav. chim., 1940, 59, 249-258).—An apparatus for the investigation of reactions in unimol. films is described. It incorporates a horizontally rotating cylinder half immersed in the liquid on which the films are spread, and by suitable rotation of the cylinder the films can be continuously removed and replaced by new films. C. R. H.

Effect of surface-active substances on rate of evaporation of water from solutions. II. N. I. GLAZOV (J. Phys. Chem. Russ., 1939, 13, 840—845; cf. A., 1938, I, 571).—Adsorbed films of n-C<sub>8</sub>H<sub>17</sub>·OH, n-C<sub>7</sub>H<sub>15</sub>·OH, and n-C<sub>6</sub>H<sub>13</sub>·OH on the surface of H<sub>2</sub>O retard evaporation. The relative retardation increases with decrease in the rate of evaporation from the uncontaminated surface. With increase in the amount of alcohol the rate of evaporation, v, falls, passes through a min. when the surface film is still unsaturated, and, in absence of special precautions, rises again. If, however, the system is freed from suspended droplets by cooling and filtering, v remains const. after reaching the min. val. (cf. A., 1939, I, 467). It is inferred that the retardation of the evaporation of H<sub>2</sub>O by adsorbed films is connected with their stabilising action and mechanical properties.

R. C. Residual active layer [of aluminium oxide]. A. MIYATA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1940, **37**, 30—57).—The dielectric properties of an anodic film of  $Al_2O_3$  produced in  $H_2C_2O_4$  solutions have been investigated. The wetted film acts as if it had a large capacity; the effect is greater in the ordinary film than in one which has been heated in steam, the difference being due to alteration in porosity. The dielectric const. of the dry film is ~8. That of an anodic  $Al_2O_3$  film produced by a.c. is decreased by heating. The effect of a large no. of compounds on the destruction of the film has been investigated. A. J. M.

Structure and physico-chemical properties of surface layers of substances of high mol. wt. III. Molecular structure and surface properties of hair and wool keratin. V. A. PTSCHELIN (J. Appl. Chem. Russ., 1939, 12, 1495—1500).—The surface layer of defatted hair (human, horse) is shown by measurement of the angles of contact with  $H_2O$  and  $C_6H_6$  to be hydrophobic; mechanical removal of this layer exposes a hydrophilic surface. The polar groups of the keratin mol. are therefore oriented towards the interior of the hair. R. T.

Mechanism of boundary lubrication suggested by the static friction of esters. A. Fogg (Proc. Physical Soc., 1940, 52, 239—245).—The relation between the coeff. of friction and the mol. wt. of a series of Me and Et esters lubricating steel surfaces was investigated. The coeff. showed a max. val. at a mol. wt. of  $\sim$ 120. Results are explained on the assumption that the mols. in the boundary layer are attached to the surface by means of the double-bond O atom in the ester, that each mol. has two divergent arms projecting from the surface, and that the orientation of these parts of the mol. relative to the surface varies with mol. wt. and depends on the relative wts. of the arms. N. M. B.

Mechanical effects of intercrystalline boundaries. B. CHALMERS (Proc. Physical Soc., 1940, 52, 127—131).—The effect of a single-crystal boundary on the crit. shear strength of a metal is discussed. N. M. B.

Water-in-oil emulsifying agents.—See B., 1940, 402.

Properties of superconducting colloids and emulsions. D. SHOENBERG (Proc. Roy. Soc., 1940, A, 175, 49—70; cf. A., 1939, I, 257).—The variation of magnetic susceptibility with particle size was investigated, the material used being colloids and emulsions of Hg. The results are in agreement with those obtained by other workers using thin films of Hg, but suggest that the London law of penetration is not quantitatively valid. The crit. field at which magnetisation disappears is greater for colloids and emulsions than for Hg in bulk. Observed differences between the shape of the magnetisation curves and hysteresis features are discussed.

London-van der Waals forces between two disc-like particles. G. P. DUBE and H. K. DAS GUPTA (Indian J. Physics, 1939, 13, 411-417).--A detailed account of work already noted (A., 1939, I, 520). W. R. A.

Brownian movement and the Einstein formula. J. DUCLAUX (J. Phys. Radium, 1940, [viii], 1, 81— 84).—Theoretical. The application of the Einstein formula to the Brownian movement of a particle in a viscous liquid is reviewed and its inadequacy indicated. W. R. A.

Optical and magnetic properties of a magnetite suspension. C. W. HEAPS (Physical Rev., 1940, [ii], 57, 528-531).—A suspension of magnetite powder in oil acts in a limited way as a light shutter. Transmission is greater when a magnetic field is parallel than when it is transverse to the light direction. Magnetic examination shows that the particles form elongated groups, each particle being probably a single magnetic domain magnetised to saturation and hence attracting neighbouring particles. An equation (not well verified by experiment) for the amount of transmitted light in terms of magnetic field strength is deduced. The experimental magnetisation curve of a dense suspension fits the Langevin curve fairly well. The group of particles forming the magnetic element has an intensity of magnetisation  $\ll$  the saturation val., although the individual particles are probably single saturated domains.

N. M. B.

Sediment volumes and rate of sedimentation of multidisperse kaolin, quartz, and soil powders in electrolyte solutions. I. G. G. KAN-DILAROV (Kolloid-Z., 1940, 90, 320—340).—The vol. (V) of sediment from a kaolin suspension increases slightly with increasing concn. of NaCl to a max., and then decreases steeply to a min. at ~0.2N. The curve for Na<sub>2</sub>SO<sub>4</sub> is similar, but displaced towards lower concns. With CaCl<sub>2</sub> V shows little change with concn., whilst with AlCl<sub>3</sub> it rises to a high max. at ~5 mmol. per l. and thereafter falls rapidly. Quartz powder suspensions give V vals. which are much less affected by salts than are those for kaolin, and mixtures of quartz and kaolin behave in an additive manner. Two washed soil samples behaved similarly to quartz. The rate of sedimentation of quartz powder in aq. AcOH runs parallel with the mutual adhesion of the particles. F. L. U.

Silicic acid as a protective colloid for manganese dioxide sols. F. HAZEL (J. Physical Chem., 1940, 44, 422—427).—Addition of SiO<sub>2</sub> sol increases the stability of MnO<sub>2</sub> sols towards flocculation by KCl, BaCl<sub>2</sub>, and Th(NO<sub>3</sub>)<sub>4</sub>. The mobilities of MnO<sub>2</sub> sols, SiO<sub>2</sub> sols, and of MnO<sub>2</sub> sols protected by SiO<sub>2</sub> have been measured in the presence of various concess. of KCl, BaCl<sub>2</sub>, or Th(NO<sub>3</sub>)<sub>4</sub> and at various  $p_{\rm H}$  vals. The fact that the migration velocity of the particles is frequently uniform suggests that the SiO<sub>2</sub> and MnO<sub>2</sub> are mutually adsorbed. SiO<sub>2</sub> sols are flocculated by very low [Th<sup>••</sup>], but are recharged in  $10^{-5}$ — $10^{-6}$ M-Th(NO<sub>3</sub>)<sub>4</sub>. J. W. S.

Variation in composition of intermicellar liquid during ultrafiltration of a colloidal solution. A. BOUTARIC (Ann. Soc. Sci. Bruxelles, 1940, 60, 31–36).—Ultrafiltration of a colloid of the type Na<sup>+</sup>R<sup>-</sup> in presence of, *e.g.*, NaCl does not result in a significant difference between the compositions of ultrafiltrate and intermicellar liquid if the Donnan membrane equilibrium is established on both sides of the filter. L. J. J.

Sodium palmitate curd as studied in the centrifuge. J. W. MCBAIN and T. F. FORD (J. Amer. Chem. Soc., 1940, **62**, 866—869).—Soap curd, a felt of hydrated cryst. fibres enclosing slightly alkaline  $H_2O$ , has been examined in the centrifuge. Its structure is firm enough for Na palmitate curd of conen. >0.2M. not to sediment or crush in a centrifugal field of 250,000g. From the rate of collapse of the structure, the pore diameter was calc. as 400 A., which is due to the bundling of parallel fibres, in themselves <100 A. in diameter. Glycerol softens the curd, and NaCl gives it a form which is too rigid to collapse but yields  $H_2O$  readily on cutting; the cut curd then collapses. The effect is one of structure or of reduced hydration rather than of a retardation of "capillary" flow. W. R. A.

Colloid chemistry of system soaps-cresolwater. V. Viscosity of stearate solutions in presence of electrolytes and cresol. E. AN-GELESCU and S. Szász (Kolloid-Z., 1940, 90, 302— 315; cf. A., 1940, I, 71).—Data are recorded for  $\eta$  of 0.2N-K and -Na stearate solutions in presence of varying conens. of KCl and of NaCl respectively and of cresols. The  $\eta$  changes due to cresol become more marked in presence of the salt, but the form of the curves remains unchanged. The effectiveness of the cresols increases in the order o < m - < p. The data are interpreted in terms of the theory previously put forward. F. L. U.

Viscosity of dilute solutions of long-chain molecules. III. Staudinger viscosity law. M. L. HUGGINS (J. Appl. Physics, 1939, 10, 700-704).—Sources of error in the derivation (cf. A., 1939, I, 318) of Staudinger's viscosity law for dil. solutions of long-chain mols. are discussed. O. D. S.

Polybutylenes.—See B., 1940, 342.

G. D. P.

Stability relations in organosols of macromolecular compounds. H. ERBRING (Kolloid-Z., 1940, 90, 257-268).-Work previously reported (A., 1939, I, 75) has been extended to organosols of polyvinyl chloride (I), polyisobutylene (II), Me polymethacrylate (III), and benzylcellulose (IV) in various solvents. The pptg. power of aliphatic *n*-alcohols decreases with increasing mol. wt.  $(C_1 - C_9)$  for (I) and (II), whilst the reverse order holds for (III). (IV) exhibits max. stability towards C<sub>6</sub>H<sub>13</sub>·OH. There is a linear relation between 1/c and  $1/\epsilon$  (c = pptg. concn. of alcohol). F. L. U.

Gelatinisation of cellulose nitrates. (MLLE.) T. PETITPAS (J. Chim., phys., 1940, 37, 6-18).-Previous work (e.g., Mathieu, A., 1934, 956; B., 1939, 443) on the absorption of ketones by cellulose nitrates is summarised, and attention is drawn to the stabilisation of the internal structure which occurs when the mol. fraction of the gelatinising liquid is 0.5 (counting glucose unit as 1 mol.), independently of the N content. With MeNO<sub>3</sub> as the gelatinising liquid the di- and trinitrates show differences in behaviour when the mol. fraction is >0.5. F. L. U.

Cellulose esters of dibasic organic acids.-See B., 1940, 350.

Viscosities of arabogalactan solutions.-See A., 1940, II, 207.

Physical chemistry of secalin. Electrophoresis and diffusion constant studies of the prolamine of rye. A. C. ANDREWS (J. Amer. Chem. Soc., 1940, 62, 942-948) .- The diffusion const. of secalin in 70% aq. EtOH, at 25°, calc. to  $H_2O$  basis, is  $4.78 \times 10^{-7}$  sq. cm. per sec., giving a mol. wt. of ~40,000. The isoelectric point is at  $p_{\rm H}$  6.67. The dielectric dispersion curve has been determined over a frequency range of 24.2 kc. to 24.2 Mc.; solutions containing 0.695 and 0.526 g. of secalin per 100 c.c. had  $[\alpha] - 66.2^{\circ}$  and  $-69.3^{\circ}$ , respectively. The extraction and purification of secalin are described.

W. R. A.

Coacervation. A. DOBRY (Bull. Soc. Chim. biol., 1940, 22, 75-86).-A review of work published previously (cf. A., 1938, I, 246; 1939, I, 198, 418). A. L.

Mutual coagulation of colloidal solutions. Interaction of copper ferrocyanide with ferric hydroxide. P. M. BARVE, V. C. VORA, and B. N. DESAI (J. Indian Chem. Soc., 1939, 16, 645-651).-The zone of mutual coagulation of Fe(OH)<sub>3</sub>, of  $Th(OH)_4$ , and of  $Ce(OH)_4$  with  $Cu_2Fe(CN)_6$  depends on the charge on the particles as in the case of Prussianblue (A., 1940, I, 162). Reaction of the peptising electrolytes and impurities has no important influence. F. R. G.

ζ-potential at the solid-water interface in relation to the inner micellar or crystalline structure of the former. II. Change of ζpotential of hydrous cellulose on change of the degree of micellar parallelism. K. KANAMARU and T. TAKADA (Z. physikal. Chem., 1940, 186, 1-9; cf. A., 1940, I, 113).—The initial and equilibrium vals. of  $\zeta$  for viscose fibres in H<sub>2</sub>O are respectively greater and smaller, the lower are the degree of parallelism of the crystallites, in accordance with the theory of Kanamaru (A., 1937, I, 80). F. J. G.

Surface conductivity. I. Surface conductivity of cellulose and its derivatives in relation to their lyophily. K. KANAMARU and T. TAKADA (Z. physikal. Chem., 1940, 186, 10-18).—The surface conductivity  $(\chi)$  of cellulose nitrate (I) in H<sub>2</sub>O, MeOH, and EtOH at 20° increases with decreasing N content, *i.e.*, increasing lyophilic character of the solid phase.  $\chi$  for cellulose and cellulose hydrate increases with time to a limiting val., with both stationary and streaming fluid.  $\chi$  for glass in H<sub>2</sub>O and for (I) in EtOH decreases as the degree of drying of the solid before use increases. Results are discussed in terms of solvation and are compared with  $\zeta$ -potentials.

R. S. B.

Electrokinetic potential of cellulose and its derivatives. K. KANAMARU and T. TAKADA (Kolloid-Z., 1940, 90, 315-319).-Vals. of the ζ-potential of various kinds of cellulose and of cellulose acetates and nitrates, determined by an improved method, are recorded. These vals. supersede those published previously (cf. A., 1931, 1232). F. L. U.

Comparison of the cataphoretic and electroosmotic methods of measuring electrokinetic potential. D. N. GHOSH and P. C. ROY (J. Indian Chem. Soc., 1939, 16, 634-638).-The velocities of cataphoresis and electro-osmotic flow, measured for spherical particles (kaolin and SiO<sub>2</sub>, uncoated and coated with protein, and As<sub>2</sub>S<sub>3</sub>) having the same electrokinetic potential, give identical vals. for the coeff. in the expression for the respective velocities. The coeff. for the cataphoresis of spherical particles is therefore  $1/4\pi$  in agreement with Smoluchowski and contrary to Hückel. F. R. G.

Electrophoretic technique. I. Electrophoresis of hæmocyanins. A. TISELIUS and F. L. HORSFALL, jun. (Arkiv Kemi, Min., Geol., 1939, 13, A, No. 18, 20 pp.).—Using the hæmocyanins of Helix pomatia and H. nemoralis, electrophoretic diagrams obtained by the multiple scale method have been employed to study the accuracy with which mobility determinations can be repeated, changes of mobility as a result of dissociation and reassociation, the accuracy with which the concn. of various components can be estimated, the asymmetry of the migrating boundaries, and reversible spreading of the boundaries. The two hæmocyanins probably exist in a no. of forms having the same mol. wt. but slightly different electrophoretic properties. T. H. G.

Action of ionising radiations on electrophoretic mobility of colloid particles. J. A. CROWTHER, H. LIEBMANN, and R. JONES (Phil. Mag., 1940, [vii], **29**, 391–399; cf. A., 1939, I, 470).—The effect of  $\gamma$ -rays and of Mo K and Se K X-rays on the electrophoretic mobility, u, of colloidal particles of Au of definite size has been investigated.  $D_n$ , the radiation dose required to bring the solution to the *n*th turning point, max. or min., in the curve of u against dose,  $= k^n$ , where k is a const. of mean val. 1.82, independent of particle size. This rule is obeyed by graphite sols illuminated with Mo K-radiation (k = 1.77). The ratio of the energies absorbed in producing a given

change in u, measured for Au sols illuminated with Mo K- and Se K-radiation, is 1.58, or approx. the ratio of the  $\lambda\lambda$  of the radiations. O. D. S.

Interpretation of simple electrophoretic patterns. L. G. LONGSWORTH and D. A. MACINNES (J. Amer. Chem. Soc., 1940, 62, 705—711).—Electrophoretic experiments, using the moving boundary method, have been made on ovalbumin at 0°. Changes in concn. during electrophoresis are computed from "electrophoretic patterns" obtained by recording refractive index gradients (A., 1937, I, 305), using the scanning method (A., 1939, I, 222). The nature of the  $\delta$  and  $\epsilon$  boundaries and the distribution of protein concn. in the rising and descending boundaries have been examined. Only the falling boundary gives the correct mobility vals. The mobilities are almost unchanged by varying protein concn., and gradients of buffer concn. exist in all boundaries. W. R. A.

Physical-chemical analysis. N. S. KURNAKOV and M. A. KLOTSCHKO (Compt. rend. Acad. Sci. U.R.S.S., 1939, 25, 383—386).—The problem of the dependence of properties of chemical systems on their equilibrium conditions has been investigated. The general principles applying to curves expressing this dependence are considered. It is possible to recognise certain common features in the curves. A. J. M.

Raman study of alcohol association. L. BRÜLL, J. ERRERA, and H. SACK (Rec. trav. chim., 1940, 59, 284—288).—The Raman effect in  $C_6H_{14}$ solutions of EtOH has been investigated. As the concn. of EtOH is increased a band at 3370 cm.<sup>-1</sup> (multimol.) becomes more pronounced, whilst the intensity of a band at 3640 cm.<sup>-1</sup> (unimol.) remains const. at all EtOH concns. Both bands are absent in pure  $C_6H_{14}$ . The data, together with similar data obtained in the near infra-red, indicate that association of EtOH increases with increase in concn. The ratio of associated to non-associated mols. in 5% EtOH is probably  $\leq 7$ . C. R. H.

Spectrographic researches on molecular compounds between organic molecules in solution. I.  $\beta$ -Carotene and deoxycholic acid in a mixed solvent containing ethyl alcohol and carbon tetrachloride in the ratio 2:1. G. MILAZZO and G. GIACOMELLO (Gazetta, 1940, 70, 73-86).— Measurements of the absorption spectra in the region 2500—5500 A. of mixtures of  $\beta$ -carotene (I) and deoxycholic acid (II) in a 2:1 mixture of EtOH and CCl<sub>4</sub> show that a 1:1 compound between (I) and (II) is formed. The dissociation const. is  $\sim 1 \times 10^{-3}$ .

O. J. W. Ionisation constants of weak acids at 25° from conductance measurements. Method of extrapolating data. B. SAXTON and L. S. DARKEN (J. Amer. Chem. Soc., 1940, 62, 846—852).— Thermodynamic ionisation consts. measured at 25° by the conductance method are  $CN \cdot CH_2 \cdot CO_2 H$   $3 \cdot 360 \times 10^{-3}$ ,  $HCO_2 H$   $1 \cdot 825 \times 10^{-4}$ , and  $Pr^{\circ}CO_2 H$  $1 \cdot 518 \times 10^{-5}$ . W. R. A.

Dissociation of acetic, glycollic, and malonic acids in glycerol-water mixtures. B. ADELL (Z. physikal. Chem., 1940, 186, 27–53; cf. A., 1940, I, 116).—The concn. dissociation consts. ( $K_g$  or  $K'_g$ 

and  $K''_g$  for AcOH, OH·CH<sub>2</sub>·CO<sub>2</sub>H (I), and CH<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub> (II), in a series of glycerol (III)-H<sub>2</sub>O mixtures at ionic strengths ( $\mu$ )  $\Rightarrow$ 3·01, and by extrapolation the corresponding vals. ( $K_0$  etc.) for  $\mu = 0$ , have been determined. By comparison with the thermodynamic dissociation consts. ( $K_a$  etc.) the activity functions  $\phi_g = K_a/K_g$  are evaluated, and log  $\phi_g/\phi$  (where  $\phi$  is the activity function for H<sub>2</sub>O solution at the same  $\mu$ ) is used as a measure of the medium effect due to (III). At const.  $\mu$ , log  $\phi_g/\phi$  is  $\propto$  [(III)], except for AcOH, for which log  $\phi_g/\phi = k_1$  [(III)] +  $k_2$ [(III)]<sup>2</sup>. At const. [(III)], log  $\phi_g/\phi$  for AcOH has a min. at  $\mu \sim 0.15$ , and log  $\phi'_g/\phi'$  and log  $\phi''_g/\phi''$  for (II) have min. at  $\mu \sim 0.35$  and  $\mu \sim 2.0$  respectively. pK is a linear function of 1/D, where D is the dielectric const. The results are discussed in terms of current theories. F. J. G.

Ionisation constants and hydrolytic degradations of cyameluric and hydromelonic acids.— See A., 1940, II, 110.

Temperature-dependence of the dissociation constant of deuteroacetic acid. F. BRESCIA, V. K. LAMER, and F. C. NACHOD (J. Amer. Chem. Soc., 1940, 62, 614—617).—From the equiv. conductivities of NaCl, NaOAc, HCl, and AcOH, measured at 14.36°, 25°, 35°, and 44.86° in a solvent of D-fraction 0.925, the dissociation const.  $K_D$  of AcOD has been calc. at the corresponding temp.  $K_D$  follows a Harned -Embree type of equation (A., 1934, 732), viz., -log  $K_{D,\theta} = 4.5 \times 10^{-5} (\theta - 31.06) + 5.2550$ , and passes through a max. at 31.06° (22° for AcOH). The ratio  $K_{H}/K_{D}$  decreases with increasing temp. The differences in the heat contents, free energies, and entropies of ionisation of AcOD and AcOH have been calc.  $\Delta C_p$  for the exchange process AcOH (H<sub>2</sub>O)  $+ D' (D_2O) + OAc' (D_2O) = AcOD (D_2O) + H'$  $(H_2O) + OAc'$   $(H_2O)$  is practically zero;  $\Delta S$  is approx. const. at -1.3 g.-cal. per degree per mol. W. R. A.

Effect of variation in ionic strength and temperature on the apparent dissociation constants of thirty substituted barbituric acids. M. E. KRAHL (J. Physical Chem., 1940, 44, 449-463).—The effect of NaCl concn. on the dissociation consts. (K') of 30 substituted barbituric acids has been determined at 25° by  $p_{\rm ff}$  measurements using a glass electrode. For [NaCl] < 2M. K' varies approx. in accord with the modified Debye-Hückel equation  $-\log \gamma_{A} = A \sqrt{\mu}/(1 + Ba \sqrt{\mu})$ , where a is an empirical const. dependent on the nature of the anion. The thermodynamic dissociation consts. (K) at  $25^{\circ}$  have been calc. by this equation. The effects of temp. on K' and K for 5-ethyl-5-isoamylbarbituric acid have been determined at  $15-40^{\circ}$  and the vals. of  $\Delta G^{\circ}$  calc. For this temp. range  $\Delta S^{\circ}$  is -3.1 g.-cal. per degree. An equation is derived whereby the vals. of K' for the 30 compounds can be calc. for any ionic strength and at any temp. within the physiological range.

J. W. S. Vapour-liquid equilibrium. V. Carbon tetrachloride-benzene mixtures. G. SCATCHARD, S. E. WOOD, and J. M. MOCHEL (J. Amer. Chem. Soc., 1940, 62, 712—716).—The system  $CCl_4-C_6H_6$  has been investigated over the entire range at 40° and 70° and for equimol. mixtures at 30°, 50°, and  $60^{\circ}$ .  $\rho$  at 25° has also been measured. The equations derived for the thermodynamic functions are slightly asymmetric. W. R. A.

Vapour pressure of ammonia over fused zinc chloride ammoniate. A. Z. KRASNOV (J. Appl. Chem. Russ., 1939, **12**, 1595—1597).—The v.p. of NH<sub>3</sub> over fused ZnCl<sub>2</sub>,NH<sub>3</sub> at 400—483° is given by  $\log P = \log x + (\alpha_0 + \alpha_1 x + \alpha_2 x^2) \log e$ , where x is the concn. of NH<sub>3</sub> in the liquid phase, and  $\alpha_0$ ,  $\alpha_1$ , and  $\alpha_2$  are complicated functions of temp. R. T.

Convergence of tie lines in ternary liquid systems. I. BACHMAN (J. Physical Chem., 1940, 44, 446—449; cf. A., 1939, I, 313).—It is shown that, when less conc. solutions are concerned, the lines connecting the compositions of conjugated solutions on ternary liquid diagrams have no common focal point. J. W. S.

Azeotropic system ethyl alcohol-water-benzene. W. D. BONNER and M. B. WILLIAMS (J. Physical Chem., 1940, 44, 404—408).—The compositions of the two liquid layers formed in the product from the distillation of  $EtOH-H_2O-C_6H_6$  mixtures at 160—960 mm. have been investigated by refractive index measurements. The proportion of  $H_2O$  in the heavier phase increases rapidly with increasing pressure <600 mm., but the effect is small at >1 atm., and therefore the advantage of increased pressure in this process of dehydrating EtOH becomes slight.

J. W. S.

System mercuric iodide-rubidium iodidewater. (MLLE.) M. PERNOT (Compt. rend., 1940, 210, 603—605; cf. A., 1938, I, 252; Grossmann, A., 1904, ii, 406).—The system has been studied by the Schreinemakers method at 34°. The stable solid phases are HgI<sub>2</sub>, RbI, and the *double salts* RbI,HgI<sub>2</sub>,H<sub>2</sub>O and 5RbI,3HgI<sub>2</sub>. A. J. E. W.

Ternary systems. XXIV. Solid solutions of alums at 25°. A. E. HILL, N. O. SMITH, and J. E. RICCI (J. Amer. Chem. Soc., 1940, 62, 858—866).— The isotherm at 25° for the system  $\text{Tl}_2\text{SO}_4$ -Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>-H<sub>2</sub>O consists of the three solubility curves of  $\text{Tl}_2\text{SO}_4$ ,  $\text{TlAl}(\text{SO}_4)_2$ ,12H<sub>2</sub>O, and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>,nH<sub>2</sub>O. The solubility of  $\text{Tl}_2\text{SO}_4$  = 5·213% and that of

TIAl(SO<sub>4</sub>)<sub>2</sub>,12H<sub>2</sub>O, and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>,nH<sub>2</sub>O. The solubility of Tl<sub>2</sub>SO<sub>4</sub> = 5·213% and that of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>,nH<sub>2</sub>O = 27·86%. A complete series of solid solutions is found in the ternary systems, TIAl(SO<sub>4</sub>)<sub>2</sub>-NH<sub>4</sub>Al(SO<sub>4</sub>)<sub>2</sub>-H<sub>2</sub>O, TIAl(SO<sub>4</sub>)<sub>2</sub>-KAl(SO<sub>4</sub>)<sub>2</sub>-H<sub>2</sub>O, NH<sub>4</sub>Cr(SO<sub>4</sub>)<sub>2</sub>-KCr(SO<sub>4</sub>)<sub>2</sub>-H<sub>2</sub>O. At 25° the solubility of TIAl(SO<sub>4</sub>)<sub>2</sub> is 6·989%, of NH<sub>4</sub>Al(SO<sub>4</sub>)<sub>2</sub>  $6\cdot15\%$ , and of KAl(SO<sub>4</sub>)<sub>2</sub> · 6·58%. For the system NH<sub>4</sub>Fe(SO<sub>4</sub>)<sub>2</sub>-KAl(SO<sub>4</sub>)<sub>2</sub>-H<sub>2</sub>O investigations have been made in the region where the compositions are representable in terms of NH<sub>4</sub>Fe(SO<sub>4</sub>)<sub>2</sub>, KAl(SO<sub>4</sub>)<sub>2</sub>, and H<sub>2</sub>O. It behaves as a system of > four components when the concn. of KAl(SO<sub>4</sub>)<sub>2</sub> is large relatively to the concn. of NH<sub>4</sub>Fe(SO<sub>4</sub>)<sub>2</sub>, but all the quaternary solids are solid solutions of alums. W. R. A.

Systems  $MnO-TiO_2$  and  $MnO-FeO-TiO_2$ . J. GRIEVE and J. WHITE (J. Roy. Tech. Coll., 1940, 4, 660-670; cf. A., 1939, I, 322).—Thermal equilibrium diagrams have been determined. The binary system has  $MnO,TiO_2$  (incongruent m.p.) and  $2MnO,TiO_2$ . In the ternary system a complete series of mixed crystals is given by  $MnO,TiO_2$  and  $FeO,TiO_2$  and by  $2MnO,TiO_2$ and  $2FeO,TiO_2$ , and a limited series by MnO and FeO. Diagrams and photomicrographs are given.

F. L. U.

Equilibrium in the system calcium oxidephosphorus pentoxide-water. K. L. ELMORE and T. D. FARE (Ind. Eng. Chem., 1940, **32**, 580–586).— Equilibrium data, and vals. of  $\rho$  for the saturated solution, of Ca phosphates in 2—98% aq. H<sub>3</sub>PO<sub>4</sub> at 25—100° are given. There is no evidence of solid solution. The solubility product of Ca<sub>2</sub>HPO<sub>4</sub> is  $3\cdot3 \times 10^{-7}$ . F. J. G.

Direction of crystallisation in quaternary systems. T. A. POPOVA (J. Phys. Chem. Russ., 1939, 13, 826—828; cf. A., 1937, I, 138).—The calculation from temp. data for the liquidus surface is described. R. C.

Quaternary system calcium hypochloritecalcium chloride-calcium hydroxide-water. J. OURISSON (Atti X Congr. Internaz. Chim., 1938, IV, 40-50).—Equilibrium diagrams at 10°, 30°, 40°, and, in greater detail, at 20° are given and discussed with special reference to the formation of

 $3Ca(OCl)_2, 2Ca(OH)_2, 2H_2O$  (cf. B., 1937, 1044). F. O. H.

Osmotic pressure, heat of dilution, and entropy of dilution. G. V. SCHULZ (Z. physikal. Chem., 1939, 45, B, 110–115).—A reply to Boissonnas and Meyer (cf. A., 1938, I, 400). W. R. A.

Osmotic pressure and mol. wt. of serumalbumin and -globulin of selachians and cyclostomes.—See A., 1940, III, 530.

Specific heats of aqueous sodium and potassium chloride solutions at several temperatures. I. C. B. HESS and B. E. GRAMKEE. II. C. M. WHITE (J. Physical Chem., 1940, 44, 483—494, 494—512).—I. A modified twin calorimeter has been used to determine the sp. heats of 0.01—0.1M-NaCl and -KCl at 15°, 25°, 35°, and 45°. II. The sp. heats of 0.01—0.2M-NaCl have been

II. The sp. heats of 0.01-0.2M-NaCl have been determined at 35°, 38°, 41°, and 45°. At each temp, the apparent mol. heat capacity is a linear function of  $m^{0.5}$  (m = mol. concn.). Empirical equations are derived to express the apparent mol. heat capacities of both NaCl and KCl solutions. The relative partial mol. heat contents at several temp, are calc. by the Person-Kirchhoff equation. J. W. S.

Conductometric behaviour of potassium chloride solutions. M. M. JACOPETTI (Gazzetta, 1940, 70, 95—109).—Measurements of  $\eta$  and  $\Lambda$  for 1·0— 4·0M-KCl at 18° to 70° have been made. The fraction of free ions in the solutions is calc. from Ghosh's theory. O. J. W.

Maxima on current-voltage curves. B. BRUNS, A. FRUMKIN, S. JOFA, L. VANJUKOVA, and S. ZOLO-TAREVSKAJA (J. Phys. Chem. Russ., 1939, 13, 786— 793; cf. A., 1935, 1079; 1939, I, 148).—The max. are traced to mixing of the Hg by surface movements caused by differences of surface tension between various parts of the surface and by variations of surface tension with time. R. C.

Electrode potential of crystal surfaces of metals. I. Zinc. M. SATÔ and K. MARUYAMA (Sci. Rep. Tôhoku, 1940, **28**, 386—397).—The electrode potentials of polycryst. rods and sublimed crystals of Zn in aq. HCl have been measured and the variations with time followed. From the method of prep. of the electrodes it is deduced that the initial vals. for the rods correspond with the potential of the (1010) and for the sublimed crystals with that of the (0001) crystal surface. The final val. in each case is that for the most stable, (1121), surface. Normal potentials at 25° are ( $E_{\rm H} = 0$ ) (0001) 870, (1010) 851, (1121) 809 mv. and agree with the vals. of Straumanis for single cryst. Zn in aq. H<sub>2</sub>SO<sub>4</sub> (A., 1930, 705).

Mutual polarity of silver and nickel in aqueous potassium iodide. E. TOPORESCU (Compt. rend., 1940, 210, 602—603).—The reversal of the normal relative polarity of Ag and Ni and the increased p.d. between Ag and Pt in aq. KI (cf. A., 1938, I, 402) are due to replacement of K by Ag, with deposition of K on the Ag plate. This replacement is confirmed analytically. A. J. E. W.

Periodic oscillations of the potential of tin in contact with HCl-CrO<sub>3</sub> solutions. II. G. EHRENSVÄRD, M. KARSCHULIN, and I. EHRENSVÄRD (Arkiv Kemi, Min., Geol., 1939, 13, A, No. 20, 11 pp.; cf. A., 1939, I, 83).-The frequencies of the oscillating potentials developed by Sn in  $\mathrm{HCl-CrO}_3$  solutions have been measured with the cathode-ray oscillograph. Three typical regions have been recognised. The first and second of these are characterised by a slow oscillation of the e.m.f. between approx. -100 and -150 mv. on the H scale at fairly low and at higher concns. of CrO<sub>3</sub>, respectively, and the third by a high frequency oscillation between 250 and 350 mv. at high (6-7.6M.) concn. of CrO3. The frequency in the third region varies with the concns. of both HCl and  $CrO_3$  and reaches vals. as high as 250 vibrations per sec. These frequencies are  $\gg$  any recorded previously in similar systems. The properties of the system Sn-HCl-CrO3 resemble the phenomena resulting from nerve stimulation more closely than do those of the system Fe-H2SO4-CrO3 suggested by Lillie. T. H. G.

Mercurous bromide electrode. W. D. LARSON (J. Amer. Chem. Soc., 1940, **62**, 764—765).—The e.m.f. of the cell Ag|AgBr, KBr, Hg<sub>2</sub>Br<sub>2</sub>|Hg has been measured at 20°, 25°, and 30°. The standard potential of the Hg|Hg<sub>2</sub>Br<sub>2</sub> electrode at 25° is 0·1397 v.  $S_0$  for Hg<sub>2</sub>Br<sub>2</sub>, evaluated from the temp. coeff., is 48.7 g.-cal. per degree per mol. W. R. A.

Theory of galvanic cells subject to fields of force. I. Gravitational field. F. O. KOENIG and S. W. GRINNELL (J. Physical Chem., 1940, 44, 463—482).—From the condition for quasi-reversible conduction (A., 1940, I, 165) general equations are derived to express the e.m.f. of a cell subject to gradients of gravitational potential (g) and of the mol. fractions as a function of the chemical state at each point and the configuration. When g = 0 these equations become the general equations of cells with liquid-liquid junctions. The p.d. in a cell subject to a gravitational field is calc. as a function of chemical state and configuration and is shown to be thermodynamically indeterminate. J. W. S.

Photo-voltaic cells with silver-silver bromide electrodes. III. Optical sensitising by dyes. S. E. SHEPPARD, W. VANSELOW, and G. P. HAPP (J. Physical Chem., 1940, 44, 411-421; cf. A., 1939, I, 315, 480).—The effect of a cyanine dye on the photopotential changes occurring during the first sec. of illumination in cells with Ag|AgBr electrodes in various electrolytes has been recorded photographically (cf. A., 1929, 1242). The dye causes an optical sensitisation of the primary electronegative (photoelectronic) effect and light absorbed by the dye but not by the AgBr produces relatively large photocurrents. The dye also acts as a Br-acceptor, thereby decreasing the positive effect. These results are in accord with observations of the photo-decomp. of dyed AgBr. They confirm that the photo-electric effect can be analysed into an initial effect produced by photo-electrons released from the AgBr passing to the metal, and a slow reaction of Br with Ag, producing an e.m.f. which opposes the primary effect. The mechanism of the sensitisation is discussed. J. W. S.

Oxidation-reduction potential of vitamin- $K_1$ B. RIEGEL, P. G. SMITH, and C. E. SCHWEITZER (J. Amer. Chem. Soc., 1940, **62**, 992).—The oxidationreduction potential of pure synthetic vitamin- $K_1$ , determined in 3% solution, is 363 mv. at 20°. In conjunction with C-H and absorption spectrum analyses this val. indicates that the vitamin is a 2:3-dialkyl-1:4-naphthaquinone. W. R. A.

Behaviour of cathode-polarised iron in nitric acid. M. KARSCHULIN (Atti X Congr. Internaz. Chim., 1938, IV, 371—380).—Measurements of c.d.– p.d. were made on Fe in 14.5, 11.6, and 9.2N-HNO<sub>3</sub>. Strongly positive p.d. in absence of current corresponded with the passive state of the Fe. The course of the c.d.–p.d. curve for cathode-polarised Fe was const. up to vals. of 0.3 ma. per sq. cm. and then showed periodic variations in p.d. and c.d., the amplitude and frequency of which were dependent on c.d. and [HNO<sub>3</sub>]. C.d. of 250—750 ma. per sq. cm. corresponded with a negative p.d. Variations in p.d. with decreased cathode polarisation are described. The reduction of HNO<sub>3</sub> to HNO<sub>2</sub> or, alternatively, formation of H<sub>2</sub> from H is analogous to the reaction at a Pt cathode (Ellingham, A., 1932, 705).

F. O. H.

Polarographic study of reduction of chromate ion at the dropping mercury electrode. J. J. LINGANE and I. M. KOLTHOFF (J. Amer. Chem. Soc., 1940, **62**, 852—858).—The reduction of  $\text{CrO}_4^{\prime\prime}$  at the dropping Hg electrode has been investigated polarographically (A., 1939, I, 325) in buffered and unbuffered solutions, and in strongly alkaline media. In unbuffered solutions of K<sub>2</sub>CrO<sub>4</sub>, with KCl as supporting electrolyte, the current–voltage curve of K<sub>2</sub>CrO<sub>4</sub> consists of three waves. Addition of 0·2N-NaOH eliminates the first and third, but leaves the second, at -1.0 v. Curves are also given for K<sub>2</sub>CrO<sub>4</sub> in N-NaOH, and only one wave is obtained, with a const. half-wave potential independent of [K<sub>2</sub>CrO<sub>4</sub>]; the diffusion current is  $\propto$  [CrO<sub>4</sub><sup>''</sup>], and shows that in alkaline media CrO<sub>4</sub><sup>''</sup> is reduced to Cr<sup>III</sup>. In un-

0. D. S.

buffered KCl solutions the current-voltage curve has four waves, the last three corresponding respectively with  $\operatorname{CrO}_4'' \rightarrow \operatorname{Cr}^{II}$ ,  $\operatorname{CrO}_4'' \rightarrow \operatorname{Cr}^{II}$ , and  $\operatorname{CrO}_4'' \rightarrow \operatorname{Cr}$ . Study of the first wave, at -0.3 v., shows it to be due to the formation of a film (stable at  $p_{\rm H}$  10.5 to 13.5) of  $\operatorname{Cr}(OH)_3$  or basic chromic chromate at the electrode surface, this film preventing further reduction. The behaviour in buffered solutions of various  $p_{\rm H}$  range has been investigated and the film of basic salt is stable only within the range  $p_{\rm H}$  10.5–13.5. N-NaOH is the most suitable supporting electrolyte for the polarographic determination of chromate.

W. R. A. Lead electrode. II. Capacity of double layer and measurement of true surface. B. KABANOV and R. JUDKEVITSCH (J. Phys. Chem. Russ., 1939, 13, 813—817; cf. A., 1940, I, 28).—A method of finding the true surface area of Pb electrodes by measuring the capacity, C, of the double layer with a const. current is described. Surface-active org. substances depress C considerably. R. C.

Brownian motion in a field of force and the diffusion model of chemical reactions. H. A. KRAMERS (Physica, 1940, 7, 284—304).—The applicability of the transition state method in calculating the rate of chemical reactions is examined by considering the escape of a particle from a potential hole over a potential barrier through the effect of Brownian motion. L. J. J.

Temperature distribution in reaction vessel, and stationary theory of thermal explosion. D. A. FRANK-KAMENETZKI (J. Phys. Chem. Russ., 1939, 13, 738—755).—By mathematical analysis of the mechanism of heat loss in a gas mixture it has been possible to devise a method of calculating the inflammation limit from the kinetics and heat effect of the reaction, the thermal conductivity of the gas mixture, and the dimensions of the vessel. The results agree generally with existing experimental data. R. C.

Elimination and metathetical reactions and the electronic theory of rearrangements.—See A., 1940, II, 201.

Thermal explosion of diethyl peroxide. E. J. HARRIS (Proc. Roy. Soc., 1940, A, 175, 254—261).— The crit. explosion pressure has been measured in vessels of different dimensions, the conditions determining the explosion being found to be in agreement with those predicted by the thermal theory. The effect of the addition of  $H_2$  and He was investigated. The behaviour of  $Et_2O_2$  is shown to be similar to that of  $Me_2N_2$  and  $EtN_3$ . G. D. P.

Thermal decomposition of diacetyl. W. D. WALTERS (J. Amer. Chem. Soc., 1940, 62, 880— 886).—The kinetics of the decomp. of Ac<sub>2</sub> at various temp. between 383° and 436° have been investigated. Undecomposed Ac<sub>2</sub> was determined by conversion into dimethylglyoxime and pptn. with a Ni salt. Pressure increases, corresponding with different amounts of decomp., have been measured. Although the reaction is of first order ( $k = 8.7 \times 10^{15} e^{-63,200/RT}$ per sec.) with variation of the initial pressure, the first-order coeff. falls during a run. Keten increases as the % decomp. decreases.  $C_3H_8$  retards the decomp. A chain mechanism is postulated.

W. R. A. Thermal decomposition of gaseous benzaldehyde. R. E. SMITH and C. N. HINSHELWOOD (Proc. Roy. Soc., 1940, A, 175, 131–142).—The predominant reaction is PhCHO  $\rightarrow C_6H_6 + CO$ ; it is homogeneous of the first order above 100 mm. pressure and subject to partial inhibition by NO. The activation energy increases as the pressure decreases. The results are explained by the superposition of a chain reaction and a mol. reaction in which the decomp. of the radical CHO is an essential step. G. D. P.

Primary reaction in the thermal polymerisation of styrene. (A) J. W. BREITENBRACH. (B) G. V. SCHULZ, A. DINGLINGER, and E. HUSE-MANN (Z. physikal. Chem., 1939, 45, B, 101—104, 105—109).—Polemical (cf. Schulz *et al.* A., 1939, I, 526). W. R. A.

Oxidation of tetrahydronaphthalene in condensed phase. S. MEDVEDEV and A. PODJAPOL-SKAJA (J. Phys. Chem. Russ., 1939, 13, 719-737; cf. A., 1939, I, 149).—Oxidation by O<sub>2</sub> at 65—95° yields chiefly tetralin H peroxide (I) and tetralone (II); no acids or aldehydes are formed. (I) accelerates the reaction, whilst (II), which is formed by the decomp. of (I), retards, by an amount which rises and then becomes const. as the concn. of (II) increases. The oxidation can be resolved into two independent stationary chain reactions. One arises from the thermal activation of tetralin, is retarded by (II), and proceeds by a mechanism similar to that of the oxidation of MeCHO (A., 1931, 572), and the second depends on the decomp. of a compound formed on the wall by collision of a (I) mol. with an adsorbed (II) mol., and is accelerated by (II). Both reactions lead to the accumulation in the system of (I), which gives the oxidation an autocatalytic character. R. C.

Alkaline hydrolysis of the sulphur chlorides  $(S_2Cl_2 \text{ and } SCl_2)$  in alcoholic solution. G. HOLST (Bull. Soc. chim., 1940, [v], 7, 276–278).— The hydrolysis of  $S_2Cl_2$  and  $SCl_2$  (x mols.) by KOH in 95% EtOH is accompanied by the immediate neutralisation of 2x mols. of KOH, followed by the slow neutralisation of a further 2x mols. of KOH. In 99% EtOH the hydrolysis stops almost completely when 2x mols. of KOH are neutralised. The rapid reaction is attributed to the formation of  $S_2(OH)_2$ and  $S(OH)_2$ , respectively, and the slow reaction to the further hydrolysis of these compounds.

J. W. S. Chain polymerisation of styrene in solution. Polymerisation of styrene in heavy alcohol. T. TITANI and T. YOSIDA (Proc. Imp. Acad. Tokyo, 1940, 16, 33—35).—The H<sub>2</sub>O resulting from combustion of polystyrene (I) produced by polymerisation in EtOD has a D content < would correspond with exchange of one H per mol. of (I). That this D content is not due to exchange, but to inclusion of solvent by (I), is further shown by the fact that a similar result is obtained after polymerisation in C<sub>2</sub>H<sub>4</sub>D-OH. Accordingly no stage of the polymerisation, including the chain-breaking step, involves a loosening or migration of H such as would lead to an exchange reaction. F. J. G.

Kinetics of addition of hypochlorous acid to double linkings. V. Formation of  $\alpha\beta$ -dichloroethane from ethylene and hypochlorous acid at low hydrochloric acid concentrations. E. A. SCHILOV, S. N. SOLODUSCHENKOV, and A. N. KURAKIN (J. Phys. Chem. Russ., 1939, 13, 759—766; cf. A., 1938, I, 36).—In aq. HCl C<sub>2</sub>H<sub>4</sub> and Cl<sub>2</sub> react to form (CH<sub>2</sub>Cl)<sub>2</sub> (I) and Cl·[CH<sub>2</sub>]<sub>2</sub>·OH (II). If [HCl] is  $\geq 0.006$ M. the amount of (I) formed is 3.4 mol.-% of that of (II), independent of [HCl]. A similar relation is true for the formation of the chloro-alcohol and dichloride in the reaction of Cl<sub>2</sub> with allyl alcohol. It is inferred that there is a mode of formation of (I) from C<sub>2</sub>H<sub>4</sub> and Cl<sub>2</sub> which does not involve the participation of Cl' ions or the direct, non-catalysed union of Cl<sub>2</sub> to the double linking: R. C.

Relative velocity of chloralkoxylation of olefines. II. V. A. SKLJAROV (J. Appl. Chem. Russ., 1939, 12, 1835—1839; cf. A., 1940, II, 150).—The velocity of the reaction olefine + EtOCl  $\rightarrow$  chloroether rises in the order C<sub>2</sub>H<sub>4</sub> < CH<sub>2</sub>:CHMe < (CHMe:)<sub>2</sub> < CH<sub>2</sub>:CMe<sub>2</sub> < CHMe:CHEt. That of the reaction chloroamine + EtOH  $\rightarrow$  EtOCl rises in the order NHAcCl < CO(NHCl)<sub>2</sub> < PhSO<sub>2</sub>·NCl<sub>2</sub>. R. T.

Reaction of alkyl halides with hydrogen halides and decomposition of methyl bromide.— See A., 1940, II, 147.

Kinetics of decomposition of carbamide in aqueous solution. A. I. KRASILSCHTSCHIKOV (J. Phys. Chem. Russ., 1939, 13, 767—770).—The reaction at 50—100° is unimol., the velocity coeff. rising slightly with the initial dilution. The energy of activation is 28,400 g.-cal. R. C.

Exchange reaction of the hydrogen atoms of the nucleus of aniline hydrochloride in aqueous solutions. III. Activation energy. M. KOIZUMI (Bull. Chem. Soc. Japan, 1940, 15, 37—46; cf. A., 1940, I, 30).—The rate of the stoicheiometric reaction  $NH_3PhCl + HDO = C_6H_4D\cdot NH_3Cl + H_2O$  is given by  $\log k = 11.6 - 29,500/4\cdot574T$  l. mol.<sup>-1</sup> sec.<sup>-1</sup> For the true reaction,  $NH_2Ph + H_2DO^* = C_6H_4D\cdot NH_2 + H_3O^*$ ,  $\log k = 9.7 - 20,800/4\cdot574T$  l. mol.<sup>-1</sup> sec.<sup>-1</sup> Consideration of analogous reactions would lead to the expectation of a greater activation energy, and possible causes of the discrepancy are discussed. In reactions of this type the steric factor is determined mainly by the structure of the deuterating agent and the energy of activation by that of the mol. to be deuterated. F. J. G.

Kinetics of bromination of  $\alpha$ -phenylsulphonylpropionic acid in aqueous solution. L. RAMBERG and I. HEDLUND (Arkiv Kemi, Min., Geol., 1939, 13, A, No. 17, 34 pp.).—The bromination proceeds as a reversible unimol. conversion of the PhSO<sub>2</sub>·CHMe·CO<sub>2</sub>H (I) into an active modification (II) which then reacts with the Br in an irreversible bimol. change giving PhSO<sub>2</sub>·CBrMe·CO<sub>2</sub>H (III). The velocity coeff. of the activation process is identical with the racemisation coeff. and depends on the properties of the medium, and, in solutions containing concns. of mineral acid  $\geq 0.1$ N., depends on the nature and concn. of the inorg. anions. This reaction is a combination of four simultaneous changes, among which one involving undissociated mols. of (I) as reactant and H<sub>2</sub>O as a basic catalyst predominates. The concn. of (II) is <0.0002 of that of (I). Both Br<sub>2</sub> and Br<sub>3</sub>' are concerned in the change (II)  $\rightarrow$  (III), the Br<sub>2</sub> reacting five times as rapidly with (II) as the Br<sub>3</sub>'. In this process (II) reacts exclusively or at least predominantly as neutral mols. Under high [Br] the complete reaction (I)  $\rightarrow$  (III) is entirely unimol., but at very much lower [Br] it is bimol. Racemisation is always more rapid than bromination but they become more nearly equal as [Br] increases.

T. H. G.

Kinetics of decarboxylation in solution. P. JOHNSON and E. A. MOELWYN-HUGHES (Proc. Roy. Soc., 1940, A, 175, 118—131).—The decomp. of  $CCl_3 \cdot CO_2H$ ,  $CBr_3 \cdot CO_2H$  and  $C_6H_2(NO_2)_3 \cdot CO_2H$  in aq. solution was investigated over a wide range of temp. To represent the results the Arrhenius equation must be modified by the addition of a term of the form  $b \log T$ . The consts. in the equation are deduced, and the kinetics of reactions in solution are discussed. G. D. P.

Hydrolysis of fats and fatty acid esters. VII. T. ONO (J. Agric. Chem. Soc. Japan, 1940, 16, 197-205).-The rate of hydrolysis of tri-, di-, and monoglycerides of stearic, palmitic, and oleic acids increases in the order tri-, di-, and mono-glycerides in homogeneous and heterogeneous systems. The ratio reaction velocity coeff. of mono-: tri-stearin is > that of mono-: tri-olein. Mixed triglycerides such as  $\alpha$ -oleo- and  $\beta$ -morocto-distearin (I) are hydrolysed more rapidly than are simple triglycerides. The fatty acid radicals in the  $\alpha$ - and  $\beta$ -positions in (I) are hydrolysed at the same rate in homogeneous system but in heterogeneous system moroctic acid in the  $\beta$ - is hydrolysed more rapidly than is that in the  $\alpha$ -position. In homogeneous system there is no difference in the rates of hydrolysis of  $\alpha$ - and  $\beta$ oleostearin. J. N. A.

Hydrolysis of fats and fatty acid esters. VI. See A., 1940, III, 533.

Decomposition of fructose with acid. Determination of reaction constant at high temperature.—See A., 1940, II, 206.

Diffusion theory of heterogeneous reactions. D. A. FRANK-KAMENETZKI (J. Phys. Chem. Russ., 1939, 13, 756—758).—The kinetics of heterogeneous reactions are worked out for the case where the rate of reaction at the interface and the rate of diffusion of reactants to the interface are comparable in magnitude. R. C.

Action of carbon monoxide on ammoniacal solutions of cupric salts. III. Absorption of carbon monoxide in different cupriammine solutions having the same concentration of copper. IV. Absorption of carbon monoxide in solutions of cupriammine salts at different concentrations of copper and in solutions of cupriammine salts with oxidising anions. H. MÖLLER and K. LESCHEWSKI (Z. anorg. Chem., 1940, 243, 330–345, 346–354).—III. The effect of the anion on the rate of absorption of CO by ammoniacal solutions of  $Cu^{II}$  salts at a fixed conen. of Cu has been studied. In general the initial rate is least for salts of strong acids, greater for those of weak acids, and greater still for the hydroxide, suggesting that in all cases the effective agent is undissociated  $[Cu(NH_3)_x](OH)_2$  resulting from hydrolysis. Detailed results are discussed and compared with thermochemical data and ionic radii and deformabilities.

IV. The initial rate of absorption of CO by ammoniacal solutions of  $Cu^{II}$  salts increases at first with increasing [Cu], but decreases again at high [Cu]. The latter effect is attributed to decreased degree of dissociation and consequently decreased hydrolysis (see above), and also to increased viscosity. In IO<sub>3</sub>' solutions the anion is only slightly, and in ClO<sub>3</sub>' and ClO<sub>4</sub>' solutions not at all, reduced by CO or metallic Cu. F. J. G.

Unification of data on the kinetics of cracking of hydrocarbons. M. D. THITSCHEEV (J. Appl. Chem. Russ., 1939, 12, 1808—1815).—The static method is preferred to the dynamic one. R. T.

Kinetics of polymerisation of butadiene in presence of metallic sodium. A. ABKIN and S. MEDVEDEV (J. Phys. Chem. Russ., 1939, 13, 705— 718).—An earlier paper (A., 1936, 296) is amplified. Polymerisation is not confined to the surface of the polymeride but proceeds throughout it. The sorption of butadiene by the polymeride has been examined at  $30-60^{\circ}$ ; the order of the polymerisation reaction varies with temp. between 1 and 2, corresponding with variations in the index of the sorption isotherm. The relation between the rate of polymerisation and the rate of diffusion of the monomeride in the polymeride has been established, and vals. of the diffusion coeff. and energy of activation have been calc.

R. C. Kinetics of carbide dissolution in hypoeutectoid plain carbon and low alloy steels.—See B., 1940, 363.

Sensitisation of the hydrogen-oxygen reaction by nitrous oxide. C. J. DANBY and C. N. HINSHELwood (J.C.S., 1940, 464-468).-When N<sub>2</sub>O is added to a  $H_2-O_2$  mixture at 550°, it behaves as an inert gas; its effect on the explosion limit is similar to that of  $CO_2$ . On the other hand addition of  $O_2$ to a H<sub>2</sub>-N<sub>2</sub>O mixture at 550° results in either immediate explosion or an autocatalytic reaction leading to explosion. The explosion is hastened by increasing  $[H_2]$  or  $[N_2O]$ , or the time during which they have been in contact, and also by decreasing  $[O_2]$ . The H<sub>2</sub> and N<sub>2</sub>O react to form a sensitiser which is present in the bulk of the gas, not on the walls, and must be NO. It is removed by FeSO<sub>4</sub>, and the amount is too small for detection by NHPh2. The mechanism is  $N_2O + H_2 = N_2 + OH + H$ ; H + N<sub>2</sub>O = N<sub>2</sub> + OH; OH + H<sub>2</sub> = H<sub>2</sub>O + H; N<sub>2</sub>O + H = NO + NH (slow). The sensitisation by NH<sub>3</sub> also involves NO. F. J. G.

Thermal decomposition of acetone catalysed by iodine. G. M. GANTZ and W. D. WALTERS (J. Amer. Chem. Soc., 1940, **62**, 996–997).—I or, less well, EtI catalyses the decomp. of COMe<sub>2</sub> at 493° or 506° (cf. Bairstow *et al.*, A., 1933, 1125).

R. S. C. Chlorine-induced decomposition of diethyl ether [and of acetaldehyde].—See A., 1940, II, 150.

Heterogeneous catalytic decomposition of hydrogen peroxide in heavy water. P. A. GIGUÈRE and O. MAASS (Canad. J. Res., 1940, 18, B, 84-89).—The rates of decomp. at 30° of  $H_2O_2$  on glass in an alkaline medium and on Au in  $D_2O$  have been compared with those in  $H_2O$ .  $D_2O_2$  is much more stable than  $H_2O_2$ . On Au the two reactions appear to follow different courses, that in  $H_2O$  being of zero order and that in  $D_2O$  being autocatalytic. F. J. G.

Correlation of adsorption and catalytic activity II. Carbon monoxide and hydrogen adsorption on zinc-chromium catalysts. F. RUMFORD (J. Roy. Tech. Coll., 1940, 4, 643—649).—Measurements of the adsorption of  $H_2$  (cf. A., 1939, I, 329) and of CO on Zn-Cr catalysts at 300°, 360°, and 400° show that the adsorption of CO decreases rapidly with increasing Zn content and becomes negligibly small at ~80 at.-%. The catalytic activity for the decomp. or synthesis of MeOH is a max. at the composition at which  $H_2$  and CO are adsorbed equally, viz., at ~67 at.-% of Zn. F. L. U.

Magnetism and catalysis. I. Catalytic decomposition of potassium chlorate by manganese dioxide and ferric oxide. II. Catalysis of persulphate and iodide reaction by ferrous ions. S. S. BHATNAGAR, B. PRAKASH, and J. SINGH (J. Indian Chem. Soc., 1940, **17**, 125—132, 133—137).—I. The chemical and magnetic changes in the reactants during the decomp. of KClO<sub>3</sub> catalysed by MnO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> indicate the formation of an intermediate compound between KClO<sub>3</sub> and catalyst. In the case of MnO<sub>2</sub> the intermediate compound is either diamagnetic or at least less strongly paramagnetic than the original MnO<sub>2</sub>. The magnetic properties of the compound with Fe<sub>2</sub>O<sub>3</sub> may be similar, but the agreement between observed and calc. vals. suggests that the compound is very unstable. Possible reaction mechanisms are discussed.

II. In the reaction between  $S_2O_8''$  and I', catalysed by Fe<sup>\*\*</sup>, magnetic data indicate the formation of a relatively stable diamagnetic or feebly paramagnetic compound. The formation of  $Fe_2(SO_4)_3$  cannot, of itself, account for the increase in reaction velocity. A suggestion is made that the compound is a sixfold complex co-ordination compound of Fe<sup>\*\*</sup> having zero magnetic moment. C. R. H.

Catalytic exchange of hydrogen atoms between molecular deuterium and propane and butane. A. FARKAS (Trans. Faraday Soc., 1940, 36, 522—527).—C<sub>3</sub>H<sub>8</sub> and n-C<sub>4</sub>H<sub>10</sub> exchange all their H reversibly when in contact with D<sub>2</sub> and a Pt catalyst; with an active catalyst the exchange occurs readily at room temp. The exchange of C<sub>3</sub>H<sub>8</sub> is 4—5 times slower than that of C<sub>4</sub>H<sub>10</sub>, but 36 times faster than that of C<sub>2</sub>H<sub>6</sub> (cf. A., 1938, I, 149). The activation energy for C<sub>4</sub>H<sub>10</sub> varies from 26 kg. cal. at 26—41° to 11 at 77—95°, and that for  $C_3H_8$  from 12 kg.-cal. at 26—53° to 9 at 97—126°. The mechanism is probably dissociative. F. L. U.

Catalytic exchange of gaseous oxygen. VI. Exchange reaction of the oxygen atoms between oxygen and water vapour at the surfaces of the oxides of the second, fourth, and sixth groups of the periodic system. I. Experimental. N. MORITA (Bull. Chem. Soc. Japan, 1940, 15, 47—55; cf. A., 1940, I, 225).—Results on the catalysis of the exchange of heavy O between H<sub>2</sub>O and O<sub>2</sub> by Mg, Sr, Ba, Zn, Cd, Ti, Zr, Th, Sn, Cr, Mo, and W oxides are recorded in tables. F. J. G.

Catalytic formation of methane from carbon monoxide and hydrogen. VI. Poisoning by carbon deposition. K. M. CHAKRAVARTY (J. Indian Chem. Soc., 1939, 16, 663—670).—An analysis of the data of Litkenhous and Mann (A., 1937, I, 521) and others shows that the reaction 2CO = C + $CO_2$  is catalysed by both Ni and Ni<sub>3</sub>C; the reaction  $CO + 3H_2 = CH_4 + H_2O$  is accelerated by Ni. Poisoning is due mainly to C adsorbed on the surface, which in the latter reaction is also due to  $CO + H_2 =$  $C + H_2O$ . F. R. G.

Catalytic toxicity and chemical structure. VI. Poisoning of platinum catalysts by metals. E. B. MAXTED and A. MARSDEN (J.C.S., 1940, 469-474).-The toxic effects of a no. of metallic ions (present as acetates) in the catalytic hydrogenation of crotonic acid by Pt-black have been studied. Cu, Ag, Zn, Cd, Hg, Tl, Sn, Pb, Bi, Mn, Fe, Co, and Ni are toxic, Au, In, and Ti slightly so, and Mg, Be, Al, Zr, Th, Cr, and the alkali and alkaline-earth and rare-earth metals non-toxic. Vals. of true relative toxicity (referred to amount adsorbed) are as follows : Cu, Ag, Sn ~1; Hg 1.7; Tl 2.8; Pb, Fe, Co, Ni, Mn, Zn, Cd, ~4. This suggests a grouping into univalent metals and bivalent metals with toxicities  $\sim$ 1 and  $\sim$ 4. The larger vals. for Hg and Tl may be connected with the larger at. radii, but the val. for F. J. G. Sn is anomalous.

Vapour-phase esterification of benzoic acid with ethyl alcohol : effect of oxides on catalytic activity of silica gel. A. A. VERNON and B. M. BROWN (Ind. Eng. Chem., 1940, 32, 534—536).—In the esterification of BZOH with EtOH at 370—450°, SiO<sub>2</sub> gel alone has considerable catalytic activity, which is enhanced by ZrO<sub>2</sub>, BaO, MnO, and TiO<sub>2</sub>, little affected by MgO and  $Cr_2O_3$ , and impaired by Al<sub>2</sub>O<sub>3</sub>, SrO, and BeO. The max. esterification of BZOH was 87%, in presence of TiO<sub>2</sub>. F. J. G.

Catalytic dehydrogenation of mono- to diolefines.—See B., 1940, 342.

Catalytic alkylation of *iso*butane with gaseous olefines.—See B., 1940, 341.

Rate of reaction in the system mineral oiloxygen and mechanism of the influence of copper and tin on this system.—See B., 1940, 338.

Catalytic hydrogenation of phenolic oil in low-temperature tar.—See B., 1940, 337. Lower stages of oxidation of ruthenium in hydrochloric acid solution. G. GRUBE and H. NANN (Z. Elektrochem., 1939, 45, 874—880).—The lower valencies of Ru have been studied by electrolytic reduction of RuCl<sub>3</sub> in aq. HCl, followed by potentiometric titration of the reduced solutions with H<sub>2</sub>O<sub>2</sub>. In 2N-HCl, Ru<sup>•••</sup> is reduced simultaneously to Ru<sup>••</sup>, Ru<sup>•</sup>, and metallic Ru; the formation of Ru<sup>••</sup> or Ru<sup>••</sup> is favoured by higher or lower [HCl], respectively. Ru<sup>••</sup> is moderately stable in 2N-HCl, but decomposes (3Ru<sup>••</sup>  $\rightarrow$  Ru + 2Ru<sup>•••</sup>) if [HCl] is reduced. Ru<sup>•</sup> is very unstable; in 0.01M. solution in 0.1N-HCl the reaction 2Ru<sup>•</sup>  $\rightarrow$  Ru + Ru<sup>••</sup> is complete after 24 hr. The oxidation-reduction potential for Ru<sup>•</sup>  $\rightarrow$  Ru<sup>••</sup> in 0.1N-HCl is  $\epsilon_{\rm H} = + 0.03 - 0.05$  v., showing that the reducing action of Ru<sup>•</sup> is not sufficiently strong to decompose H<sub>2</sub>O.

A. J. E. W.

Periodic electrolytic depositions of the alloy Zn-Cd from sulphate baths.—See B., 1940, 368.

Electrolysis of higher aliphatic organomagnesium halides in diethyl ether.—See A., 1940, II, 158.

Electrochemical oxidation of *n*-hexanol.—See A., 1940, II, 202.

Cracking of methane in the electric arc at low pressures. II. N. P. BOSHKO (J. Appl. Chem. Russ., 1939, 12, 1816—1825).—CH<sub>4</sub> decomposes in an electric arc at 30—80 mm. pressure, with production of  $C_2H_2$  and  $H_2$ . The yield of  $C_2H_2$  per unit of current at 50—80 mm. is > at 30 mm., but the final  $[C_2H_2]$  of the reaction product is smaller.

Formation of ozone and oxides of nitrogen during certain electrical discharge, and their reaction. II. G. A. GORODETZKI (J. Appl. Chem. Russ., 1939, 12, 1637—1643).—Silent discharges give rise chiefly to  $O_3$ , with  $\sim 2\%$  of  $N_2O_5$ . Spark discharges give approx. 1:2 NO-NO<sub>2</sub> mixtures, with  $\geq$  traces of  $O_3$ ; in pure  $O_2$ ,  $O_3$  is formed in very small amount.  $O_3$  does not react with  $N_2$ , but it rapidly oxidises NO and NO<sub>2</sub> to  $N_2O_5$ . If NO and NO<sub>2</sub> are produced during an electrical discharge it must be assumed that  $O_3$  is not a product of the given reaction. R. T.

Photo-expansion of chlorine : recombination of chlorine atoms. M. RITCHIE and R. L. SMITH (J.C.S., 1940, 394—401).—On illumination of dil.  $Cl_2$  the pressure increases to a max. which is > the steady val., and when the light is cut off the pressure falls to a min. which is < the final "dark" val. The effect is most marked for moderate pressures of diluent, and is attributed to the formation, on illumination, of some species which becomes adsorbed on the walls. A detailed study of the photo-expansion under varying conditions, taking account of diffusion and thermal conductivity, gives results according with the mechanism  $Cl + Cl_2 + M = Cl_3 +$ M;  $2Cl_3 = 3Cl_2$ . F. J. G.

(A) Reaction of atomic hydrogen with hydrazine. (B) Photolysis of ammonia. E. A. B. BIRSE and H. W. MELVILLE (Proc. Roy. Soc., 1940, A, 175, 164-186, 187-207).-(A) The efficiency of

R. T.

the reaction has been measured in the temp. range  $20-200^{\circ}$ . The results show that  $N_2H_4$  is not responsible for the low H atom concn. in the photolysis of  $NH_3$ . Although the H atoms react very efficiently with  $N_2H_4$  the quantum efficiency of this reaction is unexpectedly low; an explanation of this result is suggested. It is shown that photodecomp.  $N_2H_4$  converts p-H<sub>2</sub> and it is concluded that the primary decomp. is  $N_2H_4 + h\nu = N_2H_3 + H$ .

(B) The anomalously low stationary H atom concn. in the photodecomp. of  $NH_3$  is due to inefficiency of the primary process. The efficiency of the primary process is 0.58 for  $NH_3$  and 0.28 for  $ND_3$ . A revised scheme for the  $NH_3$  photolysis is given. G. D. P.

Action of ultra-short waves on complex compounds. D. I. ERISTAVI and O. E. ZVJAGINTZEV (Ann. Sect. Platine, 1939, No. 16, 81–86).—The conductivity and temp. of aq. solutions of *cis*- $[Pt(NH_3)_2]Cl_2$ , *trans*- $[Pt(NH_3)_2]Br_2$ ,  $[Pt(NH_3)_4]Cl_2$ , and  $[Co(NH_3)_3(NO_2)_3]$  are raised by exposure to ultrashort waves ( $\lambda = 2$ —10 m.). Disruption of the mols. is supposed to occur. R. T.

Cadmium-photosensitised reactions of ethylene. E. W. R. STEACIE and R. POTVIN (Canad. J. Res., 1940, **18**, **B**, 47—54; cf. A., 1939, I, 330).—In absence of H<sub>2</sub>, the Cd-photosensitised decomp. of  $C_2H_4$  at 278° has a very low quantum yield, ~0.01. In presence of H<sub>2</sub> the quantum yield is 0.5—0.7, the products being CH<sub>4</sub>,  $C_2H_6$ ,  $C_3H_8$ ,  $C_4H_{10}$ ,  $C_3H_6$ , and higher hydrocarbons. The suggested mechanism is Cd  $(3P_1) + H_2 = CdH + H$ ;  $H + C_2H_4 = C_2H_5$ ;  $H + C_2H_5 = C_2H_6$ ;  $H + C_2H_5 = 2CH_3$ ; etc. F. J. G.

Quantum yield of the hydrolysis of monochloroacetic acid. L. KÜCHLER and H. PICK (Z. physikal. Chem., 1939, 45, B, 116–120).—Reexamination of the hydrolysis of aq.  $CH_2Cl\cdot CO_2H$  by ultra-violet light gives a quantum yield of  $0.62\pm0.04$ for 254 mµ. instead of the recorded val. of 1.0.

#### W. R. A.

Mechanism of polymerisation of vinyl acetate and methyl vinyl ketone. H. W. MELVILLE, T. T. JONES, and R. F. TUCKETT (Chem. and Ind., 1940, 267-272).-The rate of polymerisation of CH<sub>2</sub>:CH·OAc vapour by light of  $\sim 2500$  A.  $\propto (p - p_0)I^{\frac{1}{2}}$ ,  $p_0$  being a limiting pressure below which polymerisation does not occur. The temp. coeff. is negative, corresponding with  $E \sim -4700$  g.-cal. The existence of the limiting pressure  $(p_0)$  cannot be explained. With rising temp.  $p_0$  decreases to become  $\overline{\sim}0$  at ~90°. The temp. coeff. of  $p_0$  indicates some process having  $E \sim 3000$  g.-cal. A radical-sensitised polymerisation, brought about by Me radicals or H atoms, is easily studied at pressures  $< p_0$ . Its kinetics accord with a simple radical mechanism, and are quite different from those of the direct reaction, suggesting that this does not involve free radicals. The alternative is a mechanism whereby a H atom migrates when the monomeride reacts with the active polymeride. The photopolymerisation of  $CH_2$ :CH-COMe is kinetically very abnormal. Both the rate and the order of the reaction increase with increasing pressure, orders as high as 5 or 6 being found. The temp. coeff. is negative, and the plot of log (rate) against 1/T exhibits a curvature which increases with increasing pressure. The product neither swells nor dissolves in solvents, which suggests extensive cross-linking. The general character of the kinetics is in accordance with a radical mechanism whereby in a suitable collision a polymeride radical having two free valencies, which can propagate independently, is produced. F. J. G.

When is a substance oxidised or reduced to another substance? H. G. Bos (Chem. Weekblad, 1940, **37**, 56—57).—A list of rules for defining when a substance is oxidised is given. S. C.

Enrichment of krypton isotopes by the separation tube process. W. GROTH and P. HARTECK (Naturwiss., 1940, 28, 47).—The method of Clusius and Dickel has been used to separate Kr into light and heavy fractions. After 5—8 days' separation the lighter fraction had at. wt. 1.51 <normal.

A. J. M.

[Biological] water decomposition and oxidation as coupled reactions. K. YAMAFUGI, M. NISHIOEDA, and R. RYUSHI (Biochem. Z., 1939, 303, 260—265; cf. A., 1939, I, 530).—In the mechanism expressed by the equations previously given, the decomp. of water is coupled with the oxidations which occur at the same time, part of the energy required for the decomp. being provided by the heat liberated in the oxidations. W. McC.

Reactions between dry inorganic salts. V. Reactions below fusion point. H. L. LINK [with L. J. WOOD] (J. Amer. Chem. Soc., 1940, **62**, 766— 769; cf. A., 1938, I, 633).—42 double decomp. reactions, involving Li, Na, K, Rb, Cs, F, Cl, Br, and I, have been investigated at various temp. below the fusion point. Reaction takes place to a considerable extent at  $\geq 100^{\circ}$  below the melting range but at  $\geq 200^{\circ}$  below the melting range very little reaction occurs. The nature and stability of the products are discussed. W. R. A.

Isolation of alkali argentiperiodates, complexes of tervalent silver. L. MALAPRADE (Compt. rend., 1940, 210, 504—505).—Oxidation of AgOH by a boiling conc. solution of KOH and KIO<sub>4</sub> gives a brown solution from which a cryst. *complex*, in which K: Ag: I = 6:1:2, can be isolated by evaporation in the cold; the product can be recrystallised from aq. KOH. A *salt* in which Na: K: Ag: I =  $4 \cdot 5 : 1 \cdot 5 : 1:2$  is pptd. on addition of NaOH to the brown solution. Determinations of available O show that these substances are derived from Ag<sub>2</sub>O<sub>3</sub>; they are stable in alkaline solution and in the solid state, give ozonised O<sub>2</sub> with dil. acids, and generally resemble the cupriperiodates (cf. A., 1937, I, 319). A. J. E. W.

Action of cuprous oxide on various compounds. E. MONTIGNIE (Bull Soc. chim., 1940, [v], 7, 229–231).—Cu<sub>2</sub>O reduces cold aq. SnCl<sub>2</sub> and SnCl<sub>4</sub>, yielding Cu<sub>2</sub>Cl<sub>2</sub> and Sn(OH)<sub>2</sub> and Sn(OH)<sub>4</sub>, respectively. With CuCl<sub>2</sub> it gives Cu<sub>2</sub>Cl<sub>2</sub> and CuCl<sub>2</sub>,3Cu(OH)<sub>2</sub>. This reaction is reversible and is the more complete the higher is the temp. The action of CuSO<sub>4</sub> on KI in presence of Cu<sub>2</sub>O yields a mixture of  $Cu_2I_2$  and basic iodide.  $Cu_2O$  reduces cold aq.  $HgCl_2$  to  $Hg_2Cl_2$  and then to Hg and reduces  $Hg_3N_2$  to Hg. With  $N_2H_4$ , HCl  $Cu_2O$  yields  $Cu_2Cl_2$ , Cu, and  $N_2$ , whilst with  $NH_2$ ·CO·NH·NH<sub>2</sub>, HCl NH<sub>3</sub> is also formed.  $Cu_2O$  liberates  $NH_3$  from  $NH_4$  salts; with aq. solutions of these salts deep blue solutions of complex salts are formed.  $HgCl\cdot NH_2$ , which is not decomposed by KOH, yields  $NH_3$  with  $Cu_2O$ . On boiling with an aq. suspension of S  $Cu_2O$  gives  $Cu_2S$ . With aq. AsI<sub>3</sub>  $Cu_2O$  yields  $As_2O_3$  and  $Cu_2I_2$ . It also reacts with alkali and alkaline-earth halides, especially on boiling, yielding the  $Cu_2^{II}$  salt. J. W. S.

Copper sulphate-sodium silicate reaction. H. V. ANDERSON and F. P. HOCHGESANG (J. Physical Chem., 1940, 44, 439—446).—Admixture of 0·1M. aq. CuSO<sub>4</sub> and Na<sub>2</sub>SiO<sub>3</sub> at the b.p. yields ppts. varying in colour from light bluish-green to deep blue and from cryst. to colloidal in character as the relative mol. concns. of CuSO<sub>4</sub> and Na<sub>2</sub>SiO<sub>3</sub> are changed from 2:1 to 1:2. X-Ray and chemical analysis indicates that the ppts. comprise 4CuO,SO<sub>3</sub>,3H<sub>2</sub>O or a mixture of this compound with 3CuO,SO<sub>3</sub>,2H<sub>2</sub>O and varying amounts of amorphous SiO<sub>2</sub>. J. W. S.

Complex compounds of diguanide with bivalent metals. I. Copper diguanidines.—See A., 1940, II, 208.

Derivatives of diethylenetriamine [di- $\beta$ -aminoethylamine].—See A., 1940, II, 207.

Reaction of solutions of gold salts with natural sulphides. O. E. ZvJAGINTZEV and A. PAULSEN (Ann. Sect. Platine, 1939, No. 16, 109–137).—The following reactions are shown to take place between aq. AuCl<sub>3</sub> or NaAuO<sub>2</sub> and certain natural sulphides:  $3PbS + 2AuCl_3 \rightarrow 3PbCl_2 + 2Au + 3S$ ;  $3PbS + 8NaAuO_2 + 4NaOH \rightarrow 8Au + 3Na_2SO_4 + 3Na_2PbO_2 + 2H_2O$ ;  $9FeS_2 + 40AuCl_3 + 6FeCl_3 + 7H_2O \rightarrow 8FeSO_4 + 7FeCl_2 + 10H_2SO_4 + 40Au + 124HCl; <math>2FeS_2 + 10NaAuO_2 + 4H_2O \rightarrow 2Fe(OH)_3 + 4Na_2SO_4 + 10Au + 2NaOH$ ;  $6FeCuS_2 + 14AuCl_3 + 2H_2O \rightarrow 14Au + 6FeCl_2 + 6CuCl_2 + 3H_2SO_4 + 9S + 18HCl; 14(4ZnS,FeS) + 40AuCl_3 + 20HCl + 52H_2O \rightarrow 49H_2S + 40Au + 8S + 56ZnCl_2 + 14FeCl_2 + 13H_2SO_4; 10FeAsS + 40AuCl_3 + 5Fe_2O_3 + 65H_2O \rightarrow 8FeSO_4 + 12FeCl_2 + 40Au + 10H_3AsO_4 + 2H_2SO_4 + 96HCl; 3(4ZnS,FeS) + 34NaAuO_2 + 10H_2O \rightarrow 34Au + 12Zn(OH)_2 + 3Fe(OH)_2 + 12Na_2SO_4 + 3S + 10NaOH. NaAuO_2 is very unstable in aq. alkaline solution, and probably could not exist under natural conditions. Deposition of Au in the cementation zone of natural sulphide deposits from AuCl<sub>3</sub> formed in the oxidation zone is quite possible. R. T.$ 

Magnesium phosphonitrilamide; existence of compounds analogous to cyanamides in the phosphorus series. H. MOUREU and G. WETROFF (Compt. rend., 1940, 210, 436-438).—The reaction between  $P_3N_5$  and compact Mg during progressive heating from 500° to 810° is  $4P_3N_5 + 21Mg =$  $6Mg_2PN_3 + N_2 + 3Mg_3P_2$ . The compound Mg\_PN\_3 (Mg phosphonitrilamide) is a yellow powder, stable in air and in a vac. at 900°; its hydrolysis affords an unidentified cryst. solid, but no gaseous products. Mg\_PN\_3 and Cl<sub>2</sub> at 700° give PN chlorides, chiefly  $(PNCl_2)_3$ , MgCl<sub>2</sub>, and N<sub>2</sub>. The corresponding Ca compound has been obtained in admixture with  $Ca_3P_2$  by a similar but more violent reaction at ~200°. A. J. E. W.

XI CALITIX

Preparation of fluorescent calcite. G. R. FONDA (J. Physical Chem., 1940, 44, 435-439).-Natural fluorescent calcite loses its fluorescence after ignition, but fluorescent material can be produced by heating CaO or CaCO<sub>3</sub> containing <0.1% (preferably 0.005%) of MnO in CO<sub>2</sub> at 1000° for 30-60 min. This product contains 1.5-10 mol.-% of CaCO<sub>3</sub>, and is distinct from CaO and CaCO3 phosphors since the fluorescence disappears when all the  $CaCO_3$  is decomposed or when the  $CaCO_3$  content is unduly increased. Fluorescent calcite can be prepared by pptn. from a mixture of dil. aq. CaCl<sub>2</sub> (30 mols.) and MnCl<sub>2</sub> (1 mol.) with excess of aq.  $(NH_4)_2CO_3$  at ~70°. The product should be boiled for 10 min. or kept for several weeks before filtering, when it has 30% of the fluorescence of the natural product. The addition of Mn is shown to cause a contraction of the lattice parameters. No fluorescence was observed in calcite pptd. in presence of Pb, Cu, Bi, or Sm. Attempts to prepare fluorescent aragonite by pptn. at 100° in presence of Mn, Pb, Cu, or Sm have been unsuccessful. In the presence of 16.6 mol.-% of Mn", calcite is J. W. S. pptd. even at 100°.

**Preparation of phosphors.** E. STRECK (Z. physikal. Chem., 1940, **186**, 19–26).—Ignition of the materials in a sealed quartz tube avoids losses by volatilisation, and the high pressure and even heating are also advantageous. The optical behaviour of ZnS-Cu phosphors obtained in this way is quite independent of the duration of ignition, and the max. luminescence occurs at [Cu] < with phosphors prepared in the usual way. F. J. G.

Preparation and properties of diborane diphosphine. E. L. GAMBLE and P. GILMONT (J. Amer. Chem. Soc., 1940, 62, 717-721).-2 vols. of PH<sub>3</sub> react with 1 vol. of B<sub>2</sub>H<sub>6</sub> slowly in (a) the gas phase at  $> -30^{\circ}$ , fairly rapidly in (b) the liquid phase at  $> -110^{\circ}$ , yielding diborane diphosphine (I), B<sub>2</sub>H<sub>6</sub>,2PH<sub>3</sub> or BH<sub>3</sub>,PH<sub>3</sub>, white cryst. needles (a), microcryst. mass (b). (I) dissociates at  $> -30^{\circ}$  to give B<sub>2</sub>H<sub>6</sub> and PH<sub>3</sub>, the dissociation pressure at 0° being  $\sim 200$  mm. It is spontaneously inflammable, is decomposed by H<sub>2</sub>O to H<sub>2</sub>, PH<sub>3</sub>, and H<sub>3</sub>BO<sub>3</sub>, and when heated rapidly to 200° affords H<sub>2</sub> and a nonvolatile product (unidentified). It dissolves very slowly in liquid NH<sub>3</sub> at  $-78^{\circ}$  with no apparent reaction, but at higher temp. PH<sub>3</sub> is evolved, but never to  $> \sim 55^{\circ}$ % of the total PH<sub>3</sub>. After keeping, and removal of the liquid NH<sub>3</sub>, a white pasty solid, diborane diphosphine ammine, B<sub>2</sub>H<sub>6</sub>,PH<sub>3</sub>,NH<sub>3</sub> (II), remains. Depending on the time and temp. of the reaction, gaseous NH<sub>3</sub> reacts with (I) and displaces part of the PH<sub>3</sub>. (II) is more stable than (I) and is probably the NH<sub>4</sub> salt, NH<sub>4</sub>(BH<sub>3</sub>PH<sub>2</sub>BH<sub>3</sub>). (I) with HCl, under certain conditions, yields a chlorinated clear, viscous, non-volatile liquid of empirical composition B<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>,2PH<sub>3</sub> which reacts with more HCl to give white, cryst. B<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>,2PH<sub>3</sub> [m.p. 68° (decomp.)]; this when heated at 100° for 1 hr. yields BCl<sub>3</sub>,PH<sub>3</sub>. HBr gives compounds of (I) similar

to those of HCl. Four structures of (I) are considered,  $(PH_4)_2B_2H_4$ ,  $BH_3,PH_3$ ,  $PH_4(BH_3PH_2BH_3)$ , and  $B_2H_6,2PH_3$ , but none is completely satisfactory. No trace of  $B_3P_3H_6$ , the cyclic analogue of  $B_3N_3H_6$ , could be obtained. W. R. A.

**Translucent films of aluminium oxide.** R. E. VOLLRATH (J. Physical Chem., 1940, 44, 401—404).— Anodic oxidation of Al foil 0.002 cm. thick in 3% aq.  $H_2C_2O_4$  yields translucent films of  $Al_2O_3$  containing small specks of Al. The formation of these specks can be avoided by allowing the level of the  $H_2C_2O_4$  to rise slowly up the surface of the foil, so that the oxidation proceeds systematically upwards. J. W. S.

Hydrogen cyanide. XI. Constitution of the double compound of hydrogen cyanide and aluminium chloride. L. E. HINKEL and T. I. WATKINS (J.C.S., 1940, 407–409).—Br reacts with HCN in  $C_6H_6$  affording HBr, CNBr, PhBr, PhCN, PhCHO, CHPh<sub>2</sub>·NH<sub>2</sub>, and cyaphenin. With AlCl<sub>3</sub>,2HCN (I) suspended in  $C_6H_6$ , Br affords no CNBr. The product is CHPh<sub>3</sub> (II), or in presence of additional AlCl<sub>3</sub>, COPh<sub>2</sub> (III). The formation of (III), but not of (II), is easily accounted for in terms of the structure AlCl<sub>3</sub>,NH:CH·NC for (I). F. J. G.

Cyanates of silicon, phosphorus, and boron. Instability of certain ternary boron compounds. G. S. FORBES and H. H. ANDERSON (J. Amer. Chem. Soc., 1940, 62, 761-763).-By treating AgNCO with SiCl<sub>4</sub> in boiling C<sub>6</sub>H<sub>6</sub> a product was obtained separable into high- and low-boiling fractions which gave identical analyses. Structures have been assigned to these fractions (i) by analogy with EtNCO and EtOCN, (ii) by investigating the products of their hydrolysis: Si isocyanate, Si(NCO)<sub>4</sub>, b.p. 185.6±  $0.3^{\circ}$ , m.p.  $26.0\pm0.5^{\circ}$ ,  $\log_{10} p$  (mm.) = 9.0198 - 2816/T,  $\rho$  1.409, 1.413 $\pm0.005$  g, per c.c., n 1.4610 $\pm$ 0.0003, and Si cyanate, Si(OCN)<sub>4</sub>, b.p. 247.2 $\pm0.5^{\circ}$ , m.p.  $34.5\pm0.5^{\circ}$ ,  $\log_{10} p$  (mm.) = 9.8211-3611/T,  $\rho = 1.414\pm0.005$  g, per c.c., and n 1.4646 $\pm0.0003$  $\rho = 1.414 \pm 0.005$  g. per c.c., and  $n \ 1.4646 \pm 0.0003$ . PCl<sub>3</sub> treated similarly with AgCNO gave P iso-cyanate, P(NCO)<sub>3</sub>, m.p.  $-2.0^{\circ}$ , b.p. 169.3°,  $\log_{10}$ p (mm.) = 8.7455 - 2595/T, p 1.439 g. per c.c., n 1.5352. This after cooling to  $-20^{\circ}$  and keeping yielded a white polymeride insol. in org. solvents, but reconverted into sol. liquid when heated. B cyanate, B(OCN)<sub>3</sub>, prepared from BBr<sub>3</sub> and AgNCO, decomposed without melting and could not be sublimed. Attempts to prepare B chlorobromides, fluorobromides, oxychloride, and oxybromide have proved unsuccessful. W. R. A.

Enrichment of <sup>15</sup>N by the Clusius-Dickel separation tube process. R. FLEISCHMANN (Physikal. Z., 1940, 41, 14—18).—A fraction containing 9.2% of <sup>14</sup>N<sup>15</sup>N, and from this, one containing 18% of <sup>14</sup>N<sup>15</sup>N, have been obtained from ordinary N<sub>2</sub>. A. J. M.

Nitrogen bromide. M. SCHMEISSER (Naturwiss., 1940, 28, 63).—The compound  $NBr_{3}$ ,  $6NH_{3}$  has been obtained by the action of Br on  $NH_{3}$  under 1—2 mm. pressure at -95°. It is a purple-red solid, decomp. violently above -70° according to the equation  $NBr_{3}$ ,  $6NH_{3} = N_{2} + 3NH_{4}Br + 2NH_{3}$ . A. J. M. Niobium oxides. G. BRAUER (Naturwiss., 1940, 28, 30).—Chemical and X-ray investigations of the Nb-O<sub>2</sub> system indicate the existence of Nb<sub>2</sub>O<sub>5</sub>, NbO<sub>2</sub>, and NbO. Nb<sub>2</sub>O<sub>5</sub> occurs in at least two different forms, one of which is obtained when niobic acid, pptd. from aq. solution, is dehydrated at 600—800°. When this form is heated to temp. >800° a form giving a different X-ray pattern is produced. The m.p. of Nb<sub>2</sub>O<sub>5</sub> in O<sub>2</sub> is 1460°. NbO<sub>2</sub> was obtained by reduction of Nb<sub>2</sub>O<sub>5</sub> by H<sub>2</sub> or Nb. H<sub>2</sub>, even at 1600°, does not reduce Nb<sub>2</sub>O<sub>5</sub> beyond the NbO<sub>2</sub> stage. Contrary statements in the literature are due to the use of impure H<sub>2</sub>. By heating mixtures of Nb<sub>2</sub>O<sub>5</sub> and NbO<sub>2</sub> at 1400°, phases of the type NbO<sub>x</sub> (x = 2.0-2.5) were produced. The structure of NbO<sub>2</sub> approximates to the rutile type, but is not identical with it. When NbO<sub>2</sub> is heated with Nb to 1750° in an atm. of A, NbO is obtained. It is a metallicgrey powder, cubic, a = 4.20 A. A. J. M.

Reduction of niobium pentoxide by hydrogen. G. GRUBE, O. KUBASCHEWSKI, and K. ZWIAUER (Z. Elektrochem., 1939, 45, 885—888).—The reduction of Nb<sub>2</sub>O<sub>5</sub> by a mixture of H<sub>2</sub> and H<sub>2</sub>O vapour (partial pressure  $p_{\rm H,0}$ ), at atm. pressure, is studied. NbO<sub>2</sub> is formed from Nb<sub>2</sub>O<sub>5</sub> in A at 1150—1300°; NbO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> are in equilibrium with H<sub>2</sub>-H<sub>2</sub>O at 860  $\pm$  10° or 1070  $\pm$  12°, with  $p_{\rm H,0} = 11\cdot3$  or 31·7 mm., respectively. With  $p_{\rm H,0} = 1\cdot44$  mm. at 1300— 1350° the reduction product is nearly pure Nb<sub>2</sub>O; a similar product is obtained more rapidly with pure H<sub>2</sub>. "Nb<sub>2</sub>O<sub>3</sub>" and NbO are obtained by appropriate interruption of the reduction process. The individuality of Nb<sub>2</sub>O, NbO, NbO<sub>2</sub>, and Nb<sub>2</sub>O<sub>5</sub> is proved by Debye–Scherrer data, but "Nb<sub>2</sub>O<sub>3</sub>" is a mixture of NbO and NbO<sub>2</sub>. A. J. E. W.

Preparation of alkali bismuth saccharates. See A., 1940, II, 204.

Chromium chromate. P. C. R. CHAUDHURY (J. Indian Chem. Soc., 1939, **16**, 652–656).—AgCrO<sub>4</sub> with conc. aq. CrCl<sub>3</sub> gives Cr[Cr(CrO<sub>3</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>], which is shown by cryoscopic measurement to dissociate into two ions, whereas  $Cr_2(CrO_4)_3$  would give five ions. Also the  $p_{\rm H}$  of the solution is  $\gg$  that of H<sub>2</sub>CrO<sub>4</sub>, and the adsorption spectrum shows by comparison with CrCl<sub>3</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, and H<sub>2</sub>CrO<sub>4</sub> the presence of an ion other than Cr<sup>III</sup>, CrO<sub>4</sub>", or Cr<sub>2</sub>O<sub>7</sub>". The magnetic susceptibility is 1942.72  $\times$  10<sup>6</sup> and the magnetic moment 10.79 per g.-atom of Cr and is independent of the state of ionisation. F. R. G.

Reaction of uranium dioxide with compounds of the noble metals. R. LYDÉN (Finska Kem. Medd., 1939, 48, 115—123).—UO<sub>2</sub> displaces Ag, Au, Pt, and Pd from solutions of their salts, giving, e.g.,  $3UO_2 + 2KAuCl_4 \rightarrow 3UO_2Cl_2 + 2KCl + 2Au$ . With Pt<sup>IV</sup> salts the reaction takes place in two stages :  $UO_2 + Pt^{\cdots} \rightarrow [UO_2]^{\circ} + Pt^{\circ}$ , followed by:  $UO_2 + Pt^{\cdots} \rightarrow [UO_2]^{\circ} + Pt$ . M. H. M. A.

Reaction of  $U_3O_8$  with alkali hydrogen carbonate solutions. R. LYDÉN (Finska Kem. Medd., 1939, 48, 124—128).— $U_2O_5$  is formed from  $U_3O_8$  by the reaction:  $U_3O_8 + 4KHCO_3$ , aq.  $\rightarrow K_4[UO_2(CO_3)_3]$ , aq.  $+ U_2O_5 + CO_2 + H_2O$ , after >24 hr. on the H<sub>2</sub>O- bath; it is not decomposed when heated in a sealed tube with excess of aq. KHCO<sub>2</sub>. M. H. M. A.

Affinity. XCIII. Uranium sulphides. E. F. STROTZER, O. SCHNEIDER, and W. BILTZ (Z. anorg. Chem., 1940, 243, 307—320).—The system U–S has been studied preparatively, and by means of X-rays and (in part) of tensimeter curves. In addition to US<sub>2</sub> and U<sub>2</sub>S<sub>3</sub>, a *trisulphide* US<sub>3</sub>, and a *subsulphide*, apparently U<sub>4</sub>S<sub>3</sub>, exist. US<sub>3</sub> is obtained by heating US<sub>2</sub> with S at 600—800°, the excess of S being removed by means of CS<sub>2</sub> or at 300° in a vac. It has  $\rho_2^{45} 5 \cdot 81$ , mol. vol. 57·5, and (from the tensimeter curves) heat of formation from US<sub>2</sub> +  $\frac{1}{2}$ S<sub>2</sub> 40 kg.-cal. per g.-mol. at ~650°. US<sub>2</sub> has  $\rho_4^{25} 7 \cdot 96$ , mol. vol. 38·0. Data on  $\rho$  and mol. vol. for preps. having S: U < 1·5:1 are given. The mol. vol. in this region is not a linear function of composition. F. J. G.

Reduction of solutions of inorganic oxidising compounds by active carbon. A. RAMAT (Bull. Soc. chim., 1940, [v], 7, 227—229).—On agitation with activated C aq. KMnO<sub>4</sub> changes in colour to green. When kept it returns to reddish-brown, but the green colour is restored by further agitation. Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and K<sub>3</sub>Fe(CN)<sub>6</sub> show similar reduction, and it is suggested that adsorption by activated C is frequently preceded by reduction. J. W. S.

Precipitation of manganous carbonate.—See B., 1940, 357.

**Preparation of high-purity iron on a large laboratory scale.** F. ADCOCK (J.S.C.I., 1940, **59**, 28—31).—The prep. of high-purity Fe at the rate of 500 g. per working day is described. Commercial electrolytic Fe was converted into FeCl<sub>2</sub>, which was then treated with superheated steam to obtain Fe oxide. The finished Fe was produced by H<sub>2</sub> reduction of the oxide and subsequent vac. fusion of the metal. Difficulties in the provision of suitable refractory crucibles were overcome by the use of sintered Al<sub>2</sub>O<sub>3</sub>.

Preparation of iron, copper, and nickel in powder form by reduction of oxides with hydrogen. I. P. KISLJAKOV (J. Appl. Chem. Russ., 1939, 12, 1668—1677).—Direction 3 for reduction of  $Fe_2O_3$ , CuO, and Ni<sub>2</sub>O<sub>3</sub> to the metals are given. R. T.

#### Ferritartrates.—See A., 1940, II, 153.

Stereochemistry of complex inorganic compounds. VII. Mechanism of the Walden inversion in some reactions leading to the formation of the carbonatodiethylenediaminecobaltic ion. J. C. BAILAR, jun., and D. F. PEPPARD (J. Amer. Chem. Soc., 1940, 62, 820-823).-Evidence is advanced confirming the suggested explanation of the conversion of l-[Co en<sub>2</sub>Cl<sub>2</sub>]Cl (I) into d-[Co en<sub>2</sub>CO<sub>3</sub>]<sub>2</sub>CO<sub>3</sub> as arising from intermediate formation of l- $[Co en(H_2O)Cl]Cl_2$  (II) (A., 1940, I, 80) whilst conversion of (I) into l-[Co en2CO3]2CO3 takes place directly. The conversions of l-[Co en<sub>2</sub>ClBr]Cl and of l-[Co en<sub>2</sub>Br<sub>2</sub>]Br agree with those of (I) but none of the three with oxalates gives a product of inverted configuration. (II) is converted into (I) by sus-W. R. A. pending it in SOCl<sub>2</sub>.

Complex salts of cobalt<sup>III</sup> with dimethylglyoxime [and aromatic amines].—See A., 1940, II, 162.

Cobaltic bisdiguanidines and trisphenyldiguanidines.—See A., 1940, II, 208.

Electron diffraction study of surface reaction between nickel oxide and corundum. H. R. THIRSK and E. J. WHITMORE (Trans. Faraday Soc., 1940, 36, 565-574).-Ni vapour condensed on the surface of corundum consists of unoriented crystals, as does also the NiO formed by heating the condensed Ni film in air. If, however, NiO vapour is condensed on the corundum the crystals assume special orientations depending on the crystallographic direction of the surface. NiO reacts slowly with corundum at 900° to form Ni spinel, which takes up orientations similar to those of the NiO. The most perfect orientation occurs on the prism face  $\{11\overline{2}, 0\}$ . Some of the observations suggest that diffusion of metal ions can occur only in the spinel lattice. F. L. U.

Hydrate isomerism and hydrolysis of ruthenium trichloride. G. GRUBE and H. NANN (Z. Elektrochem., 1939, 45, 871—874).—RuCl<sub>3</sub>,H<sub>2</sub>O, prepared by evaporation of aq. RuCl<sub>3</sub> in a vac. over H<sub>2</sub>SO<sub>4</sub>, dissolves in ice-H<sub>2</sub>O to give a brown or greenish-brown solution which contains no ionic Cl. When kept the solution becomes green, and after 80 min. at 2°  $\frac{1}{3}$  of the total Cl is pptd. on addition of AgNO<sub>3</sub>, probably owing to the change [RuCl<sub>3</sub>H<sub>2</sub>O] + H<sub>2</sub>O  $\rightarrow$  [RuCl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]Cl. When heated the solution again becomes brown, and conductivity measurements indicate hydrolysis, possibly [RuCl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]Cl + H<sub>2</sub>O  $\rightarrow$  [RuOHCl(H<sub>2</sub>O)<sub>2</sub>]Cl + HCl, etc.; after 47 hr. at 50°, 2.91 atoms of Cl per Ru are titratable by AgNO<sub>3</sub>, and are largely present as HCl, although no insol. products are formed. A. J. E. W.

Preparation of ternary rhodium salts. N. K. PSCHENITZIN and S. K. SCHABARIN (Ann. Sect. Platine, 1939, No. 16, 45—52).—When  $[Pt(NH_3)_4]Cl_2$ (I) is added to a solution of  $(NH_4)_3RhCl_6$  (II) in aq.  $NH_4NO_3$ , a ppt. of  $NH_4[RhCl_6][Pt(NH_3)_4]$  is obtained. In absence of  $NH_4NO_3$  (II) is converted into  $(NH_4)_2[RhCl_5,H_2O]$ , which combines with (I) to yield  $[RhCl_5,H_2O][Pt(NH_3)_4]H_2O$ . With RbNO<sub>3</sub> or CsNO<sub>3</sub> conc. solutions of (I) give  $[RhCl_5,H_2O]M_2$ (M = Rb, Cs). R. T.

**Rhodium sulphito-ammines.** V. V. LEBEDIN-SKI and N. N. MIASOJEDOV (Ann. Sect. Platine, 1939, No. 16, 65—76).—Aq.  $(NH_4)_3RhCl_6$  and aq. NaHSO<sub>3</sub> (1 hr. at 100°) yield a ppt., which when treated with aq. NH<sub>3</sub> (1—1·5 hr. at 100°) gives  $Na_2[Rh(NH_3)_3,(SO_2)_2,SO_3Na], 6H_2O$ . The salts  $Zn[Rh(NH_3)_3,(SO_2)_2,SO_3Na], 6H_2O$ ,  $[C(NH)(NH_2)_2H]_2[Rh(NH_3)_3,(SO_3)_2,SO_3Na]$ , and  $Ag_3Rh(NH_3)_3(SO_3)_3,1\cdot5H_2O$  are prepared therefrom. R. T. Compounds of iridium [salts] with aceto-

nitrile. V. V. LEBEDINSKI and P. V. SIMANOVSKI (Ann. Sect. Platine, 1939, No. 16, 53–56).—MeCN and a boiling solution of  $(NH_4)_3IrCl_6$  in aq.  $NH_4Cl$ yield' $(NH_4)_2[IrCl_5, MeCN], H_2O$  (corresponding  $K_2$  salt, +2H\_2O; diguanidino-salt;  $[Pt(NH_3)_4]$  salt). R. T.

Oxalates of ammonium-pyridine platinum compounds. V. I. GOREMIKIN and K. A. GLADI-SCHEVSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1939, 23, 242-244).-Prep. of the following salts is described  $[Pt(C_5H_5N)_4]C_2O_4, H_2O; [Pt(NH_3)(C_5H_5N)_3]C_2O_4; cis \begin{array}{l} [Pt(NH_3)_3(C_5H_5N)_1]C_2O_4, P_2O_5, P_1O_1(P_1A_3)(O_5H_5N)_3]C_2O_4, O_2O_4\\ Pt(NH_3)_3(C_5H_5N)_2]C_2O_4; \ \ cis-[Pt(C_5H_5N)_2(C_2O_4)] \ \ and \ \ [Pt(NH_3)_3(C_5H_5N)(HC_2O_4)_2], H_2O. \end{array} \right.$ 

Hydroxylamine-thiocarbamide platinum compounds. V. I. GOREMIKIN (Compt. rend. Acad. Sci. U.R.S.S., 1939, 23, 238-241).-Prep., properties, and  $\mu^{25}$  of the compounds [Pt(NH<sub>2</sub>OH)<sub>2</sub>{CS(NH<sub>2</sub>)<sub>2</sub>}<sub>2</sub>]Cl<sub>2</sub>,  $[Pt NH_2OH NH_3 (CS(NH_2)_2)_2]Cl_2, \\ [Pt NH_2OH C_5H_5N (CS(NH_2)_2)_2]Cl_2, and$  $[Pt NH_3 C_5 H_5 N \{ CS(NH_2)_2 \}_2 ] Cl_2 are given. W. R. A.$ 

Tetra-amminodisulphitoplatinum. S. A. BORI-SOV-POTOTZKI (Ann. Sect. Platine, 1939, No. 16, 41-44).-SO<sub>2</sub> passed into a solution of Pt(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub> in aq. KNO<sub>2</sub> yields  $[Pt(NH_3)_4(SO_3)_2], 2H_2O$ , converted by heating into  $Pt(NH_3)_4SO_4$ . R. T.

(A) Quadrivalent platinum triammines. (B) Quadrivalent platinum tetrammine. I. TSCHERNIAEV (Ann. Sect. Platine, 1939, No. 16, TSCHERNIAEV (Ann. Sect. Platine, 1939, No. 16, 5—11, 13—19).—(A) Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and aq. NH<sub>3</sub> at 95—98° yield  $[Pt(NH_3)_3Cl_3]Cl$  (I), converted by aq. KOH into  $[Pt_i(NH_3)_2,NH_2,Cl]$ , which with HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub> gives  $[Pt(NH_3)_3Cl_3]NO_3,H_2O$  or  $[Pt(NH_3)_3Cl_3]_2SO_4,3H_2O$ , respectively. (I) and AgNO<sub>2</sub> afford  $[Pt_i(NH_2)_3,Cl,NO_2,Cl]Cl$ , which with KOH yields  $[Pt_i(NH_3)_2,NH_2,Cl,NO_2,Cl]$ .  $[Pt(NH_3)_3Cl]Cl$  and aq. AgNO<sub>3</sub> give  $[Pt_i(NH_3)_3,H_2O,(NO_3)_2]$ , which with Br in aq. KBr affords  $[Pt(NH_3)_3Br_3]Br_1H_2O$ . (B) 20% aq. NH<sub>2</sub> when added to (I) affords

(B) 20% aq.  $NH_3$  when added to (I) affords  $[Pt,(NH_3)_3,Cl,NH_3,Cl]Cl_2$  (II), which with aq. KOH gives  $[Pt,(NH_3Cl)_2,NH_2,NH_3]OH,H_2O.$  (II) is reduced by  $N_2H_4$  to  $[Pt(NH_3)_3Cl]Cl$ . R. T.

Ethylene compounds of platinum nitrochlorides. (MISS) A. GELMAN and I. B. LITVAK (Ann. Sect. Platine, 1939, No. 16, 29-33).-Aq. NaNO<sub>2</sub> added to conc. aq. K[PtCl<sub>3</sub>,C<sub>2</sub>H<sub>4</sub>] gives  $K[Pt,C_2H_4,Cl,(NO_3)_2]$ , which with  $Pt(NH_3)_4Cl_2$ affords  $[Pt(NH_3)_4][Pt,C_2H_4,Cl,(NO_3)_2]_2$ . Attempts to prepare analogous Co and Ni complexes were unsuccessful. R. T.

Compounds of platinum [salts] with acetonitrile. V. V. LEBEDINSKI and V. A. GOLOVNIA (Ann. Sect. Platine, 1939, No. 16, 57–64).—Aq.  $[Pt(NH_3)_2Cl_2]$  is shaken with MeCN (1–1.5 hr. at  $100^{\circ}$ ), the solution is filtered, and Na picrate is added to the filtrate, giving a ppt. of

 $[Pt, Cl, (NH_3)_2, MeCN] \cdot O \cdot C_6 H_2(NO_2)_3;$ the corresponding *platinochloride* is obtained analogously. Very sol.  $[Pt(NH_3)_4, MeCN]Cl$  (I) is obtained by boiling the filtrate with aq. NH<sub>3</sub>, or similarly from [PtCl<sub>2</sub>,NH<sub>3</sub>,MeCN] or [PtCl<sub>3</sub>,MeCN]; the platinochloride and picrate of (I) are described. One of the  $NH_3$  groups of (I) is probably combined with MeCN.

R. T. Compounds of platinum [salts] with ethylenic hydrocarbons. A. GELMAN (Ann. Sect. Platine, 1939, No. 16, 21–28).—Ag. K<sub>2</sub>PtCl<sub>4</sub> and CHR:CH<sub>2</sub> give complexes of the type K[PtCl3,CHR·CH2], converted by aq. NH<sub>3</sub> or C<sub>5</sub>H<sub>5</sub>N into

 $[PtCl_2, NH_3, CH_2; CHR]$  or  $[PtCl_2, C_5H_5N, CHR; CH_2]$  $(R = Me, Et, Ph); (PtCl_2, CHPh: CH_2)_2$  is a by-product in the case of CHPh:CH<sub>2</sub>. NH<sub>4</sub>[PtBr<sub>3</sub>,NH<sub>3</sub>] and C<sub>2</sub>H<sub>4</sub> affords cis- and trans- PtBr, NH3, C2H4]; cis- and trans- $[PtBr, C_5H_5N, C_2H_4]$  are prepared analogously. **R. T**.

Fluorescence analysis. I. Fluoremetry of fluorescein and eosin. II. Fluorescence indicators. H. Gotô (Sci. Rep. Tôhoku, 1940, 28, 458-464, 465-479).-I. Apparatus using filtered ultra-violet light is described. Changes in intensity of fluorescence between  $p_{\rm H} 2.71$  and 12.84 are recorded for fluorescein (I) and eosin (II). Fluorescence of (I) between  $p_{\rm H}$  5.6 and 13.0 is strong enough to be used, but accurate determinations should be carried out at  $p_{\rm H} > 9.6$ . The intensity of fluorescence of (II) is unchanged over a wide range of  $p_{\rm H}$ , and (II) can be determined at  $p_{\pi} > 4.5$ ; most of the fluorescence disappears between  $p_{\rm H}$  3 and 4.

II. The intensities of fluorescence of various indicators over different ranges of  $p_{\rm H}$  are recorded. The  $p_{\rm H}$  ranges at which fluorescence disappears or changes in colour are: salicylic acid 2.5-4.0, erythrosin 4.0-4.5, phloxin 2.5-4.0, umbelliferone 6.5-8.0, quinine 3.0-5.0, acridine 5.2-6.6,  $\beta$ - $C_{10}H_7 OH 8.5 - 9.5, \beta - OH C_{10}H_6 SO_3H 8.0 - 9.0,$ coumarin 9.5-10.5, naphthionic acid 2.5-3.5 and 11.6. The characteristics and suitability of these indicators are discussed. L. S. T.

Rôle of the temperature factor in determining  $p_{\rm H}$  by means of the glass electrode. V. A. PTSCHELIN (J. Appl. Chem. Russ., 1939, 12, 1548-1554).—The magnitude of the val.  $\Delta E / \Delta p_{\rm ff}$  obtained when e.m.f. is measured by the ballistic method depends chiefly on the degree of saturation of the condenser, i.e., on the duration of charging. With fully charged condensers the vals. of  $\Delta E / \Delta p_{\rm H}$  found for a no. of buffer solutions were identical, using a glass or a  $H_2$  electrode at 30-50°. At 10° the time required for full saturation of the condenser becomes very great. The increase in the temp. factor at low temp. is ascribed chiefly to increase in resistance of the glass electrode, which approaches that of the potentiometer circuit; in that case temp. differences between the electrode and the potentiometer may cause considerable errors. Where errors of  $\pm 0.1 p_{\rm H}$  are admissible temp. variations of 1-2° may be neglected; in other cases calibration curves should be applied. Morton's conclusions as to the applicability of the glass electrode R. T. are not upheld (A., 1934, 492).

Determination of  $p_{\rm ff}$  value of clay by the glass electrode.—See B., 1940, 358.

Electrochemical method of determining iodine. M. TOVBIN and M. FELDMAN (J. Phys. Chem. Russ., 1939, **13**, 818–825).—The method described for the determination of small amounts of free I in solution depends on its depolarising action. The decomp. of KI in aq. solution in ultra-violet light is autocatalysed by I. The rate of reaction of I with starch has been R. C. measured.

Direct determination of oxygen in zinc oxide.---See B., 940, 356.

Oxidation of thiophen-sulphur by calcium hypochlorite solutions. E. G. R. ARDAGH, W. H. BOWMAN, and A. S. WEATHERBURN (J.S.C.I., 1940, 59, 27-28).—Factors influencing the proportion of thiophen-S converted into  $SO_4$ '' as a result of oxidative action of Ca(OCl)<sub>2</sub> solutions (I) are discussed. The  $p_{\rm II}$  vals. most effective for the oxidation of thiophen by this method are ~7-8; such vals. for (I) will result from the use of an initial  $p_{\rm II}$  8 or, for long periods of treatment,  $p_{\rm II}$  9. The use of other acidifying agents for the adjustment of the initial  $p_{\rm II}$  gave essentially the same results as AcOH.

Volumetric determination of sulphuric acid in potassium permanganate solutions.—See B., 1940, 356.

Detection and determination of ortho-, pyro-, and meta-phosphoric acid in the presence of one another. B. WURZSCHMITT and W. SCHUH-KNECHT (Angew. Chem., 1940, 52, 711-715).-PO4"" (I) gives a yellow ppt. in 30 sec. with twice its vol. of Lorenz's molybdate solution, whereas  $PO_3'$  (II) reacts only after 90 sec., and  $P_4O_7'''$  (III) after a much longer time. To detect (III) the solution is saturated with NH<sub>4</sub>I, adjusted just to blue with bromophenol-blue, and boiled with half its vol. of 10% aq.  $ZnI_2$ ; if (III) is present a white flocculent ppt. is formed and the solution becomes yellow. (II) gives a white flocculent ppt. when the solution, just acid with AcOH, is boiled with 10% aq. BaCl<sub>2</sub>; in this test much (III) gives a slight cryst. ppt. whilst (I) gives no ppt.  $(PO_3)_3'''$  (IV) is detected by removing (I), (III), and  $(PO_3)_6^{VI}$  with BaCl<sub>2</sub> in boiling neutral (phenolphthalein) solution and testing the filtrate with molybdate after hydrolysis of (IV). For quant. analysis total  $P_2O_5$  is determined by pptn. with molybdate after boiling with HNO3 and drying the ppt. in vac. for weighing; (III) is determined by treating 100 c.c. of the solution, neutralised to a Me,-yellow-methylene-blue indicator, with 25 c.c. of a solution containing 10% of  $ZnI_2$  and 20% of  $NH_4I$ , and titrating with N-NaOH until a pure green colour is obtained. (I) is determined by treating the solution (100 c.c.) with 15 g. of NaCl, 50 c.c. of 10% aq.  $Na_2MoO_4$ , and 30 c.c. of EtOAc, cooling in ice, and shaking with 50 c.c. of ice-cold N-HCl. The EtOAc layer is separated and evaporated to dryness, the residue oxidised with HNO3 and dissolved in aq. NH<sub>3</sub>, and the solution pptd. with the Lorenz molybdate solution. (II) is determined by difference : total  $P_2O_5$  less that present as (I) and (III). A. R. P.

Cerimetric determination of small amounts of arsenic after reduction with hypophosphite reagent. I. M. KOLTHOFF and E. AMDUR (Ind. Eng. Chem. [Anal.], 1940, **12**, 177—179).—As<sup>III</sup> and As<sup>V</sup> are reduced to As by heating at 80—90° with Ca(H<sub>2</sub>PO<sub>2</sub>)<sub>2</sub> in ~6N-HCl. Reduction is also quant. but slower in 3N-HCl (cf. B., 1929, 1046). The As is dissolved in an excess of 0.005N-Ce(SO<sub>4</sub>)<sub>2</sub>, and the excess back-titrated with 0.005N-As<sub>2</sub>O<sub>3</sub> in presence of OsO<sub>4</sub> as catalyst and with *o*-phenanthroline–Fe<sup>\*\*</sup> complex as indicator. 1 mg. of As can be determined with an accuracy of 0.5% and 0.1 mg. with an accuracy of 1-2%. Sn and Sb do not interfere. 0.05N-Ce(SO<sub>4</sub>)<sub>2</sub> in N-H<sub>2</sub>SO<sub>4</sub> is stable for >8 months, and 0.005N-  $Ce(SO_4)_2$  is stable after keeping for one week to oxidise traces of reducing substances present. Test data, details of procedure, and funnels for filtering small amounts of As are described. L. S. T.

Colorimetric determination of arsenic in alloys.—See B., 1940, 364.

Determination of small amounts of arsenic in copper.—See B., 1940, 365.

Colorimetric determination of carbon monoxide. S. M. TSCHUMANOV and M. B. AXELROD (J. Appl. Chem. Russ., 1939, **12**, 1568—1570).—Fe<sup>III</sup> on SiO<sub>2</sub> gel is reduced by CO, and the Fe<sup>II</sup> produced is indicated by a blue colour given with  $K_3Fe(CN)_6$ ; the reaction is not quant. R. T.

Simplification of Power's method for the determination of carbon dioxide in natural waters and comparison with the titration method. C. A. PETERS, S. WILLIAMS, and P. C. MITCHELL (Ecology, 1940, 21, 107-109).—Temp. corrections and a simplified calculation are given. L. G. G. W.

Rapid determination of hydrogen cyanide in gases.—See B., 1940, 336.

Determination of caustic alkali in soaps.—See B., 1940, 373.

Volumetric determination of small quantities of barium and sulphate with barium rhodizonate as indicator. Determination of sulphur in iron pyrites. C. C. MILLER (J.C.S., 1940, 401-406).—A standard procedure is described, whereby a suspension of the scarlet modification of Ba rhodizonate in EtOH may be used as indicator in the titration of Ba with  $SO_4''$ , and of  $SO_4''$  indirectly. Results are accurate to 1% for 4-20 mg. of  $SO_4''$ , in presence of many cations including Al''' and Fe'', but  $PO_4'''$  causes errors  $\sim +2\%$ . F. J. G.

Spectrographic determination of small concentrations of beryllium in magnesium alloys.— See B., 1940, 367.

Determination of free magnesia in magnesian lime.—See B., 1940, 356.

Empirical mercurimetric method for [determination of] zinc. A. C. TITUS and J. S. OLSEN (Ind. Eng. Chem. [Anal.], 1940, **12**, 133—135).—The routine method described consists of pptg. Zn<sup>••</sup> as ZnHg(CNS)<sub>4</sub> (I), dissolving the washed ppt. in 0·11N-KI, and titrating the apparent excess of KI with 0·1N-Hg(NO<sub>3</sub>)<sub>2</sub> (Fe<sup>III</sup> alum). The relation between the apparent consumption of I' and Zn<sup>••</sup> is represented by a linear equation. With 0·16 g. of Zn the error is ~ 0.6%. Many impurities possibly present in the original sample are removed in the filtrate from (I), and do not interfere. L. S. T.

Separation of cadmium from zinc using granular aluminium. F. E. TOWNSEND and G. N. CADE, jun. (Ind. Eng. Chem. [Anal.], 1940, 12, 163— 164).—Cd and Zn are first separated from other elements of the  $H_2S$  and  $(NH_4)_2S$  groups by standard methods, and Pb is removed by evaporation with  $H_2SO_4$ . The filtrate from the PbSO<sub>4</sub> is eventually boiled twice with granular Al to ppt. Cd, and the Al removed by dissolution in NaOH. The Cd is then determined by titration with standard  $K_4Fe(CN)_6$ , using UO<sub>2</sub> acetate as external indicator, or by electro-deposition from CN' solution. No Cd is left in the filtrate after two pptns. with Al, and no Zn occurs in the washed Al + Cd ppt. From samples containing much Zn or Fe, the Cd and some of the Zn should first be pptd. with H<sub>2</sub>S. Details of procedure and test analyses for Cd in different commercial products are recorded. The use of granular Al reduces the no. of H<sub>2</sub>S separations in determining Cd, and saves time. L. S. T.

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Analysis of cadmium-plating solutions.—See B., 1940, 368.

Micro-detection and micro-determination of silver and mercury. G. BOUILLOUX (Bull. Soc. chim., 1940, [v], 7, 184-187).-Methylene-blue (I) mercuri-iodide reacts with Ag' in solutions acidified with AcOH with liberation of the free dye. This reaction can be utilised for the detection and colorimetric determination of  $1-35 \ \mu g$ . of Ag' in 1 c.c. of solution. Unless the solution is deeply coloured by presence of large amounts of Cu, Ni, Co, Cr, or U, common metals (except  $Fe^{III}$ ) do not interfere with the test, but  $CrO_4''$ ,  $AuCl_4'$ ,  $PtCl_6''$ , and  $Fe(CN)_6'''$ , which ppt. (I), and materials which liberate I from I' must be absent. (I) mercuri-iodide can also be used as an external indicator in the determination of halogens with  $AgNO_3$  and of I' with  $Hg(NO_3)_2$ . The reagent is obtained by pptg. 1% aq. (I) with excess of aq. K2HgI4, prepared by saturating conc. aq. KI with HgI2. The ppt. is washed with 0.01% aq. (I) until the filtrate is slightly coloured, and is then washed with aq. AcOH. It is stored as a suspension in very dil. AcOH. J. W. S.

Polarographic method of determining lead and tin in potassium fluoroxyniobate and niobium. A. S. SCHACHOV (J. Appl. Chem. Russ., 1939, 12, 1555—1559).—Pb may be determined in alkaline or acid citrate solution, but Sn, and Pb in presence of Sn, only in alkaline solution. Trustworthy results are obtained for  $K_2NbOF_5$  and Nb containing Pb 0·2—0·5 and Sn 0·9—1·2%. R. T.

Use of adsorption processes for the detection of "traces." K. L. SUTHERLAND (Nature, 1940, 145, 553).—Air displaces  $H_2O$  from a polished surface of pyrite when 25 mg. per l. of OEt·CS<sub>2</sub>K (I) are added to the  $H_2O$ ; one part of CN' in  $2 \times 10^7$  of  $H_2O$  prevents this. The surface of sphalerite becomes airavid when 0.006 mg. per l. of Pb(NO<sub>3</sub>)<sub>2</sub> is added to  $H_2O$  containing (I). Similarly, 8 parts of Cu" in  $10^8$  of  $H_2O$  can be detected in presence of NEt<sub>2</sub>·CS<sub>2</sub>Na. L. S. T.

Determination of traces of lead and thallium in pharmaceutical chemicals.—See B., 1940, 402.

Iodofluoride method for the determination of copper. Effects of antimony, aluminium, and calcium. W. R. CROWELL and A. T. SPIHER (Ind. Eng. Chem. [Anal.], 1940, 12, 147; cf. A., 1938, I, 271).—Sb in amounts >20 mg. must be absent; Cu<sup>•</sup> is probably adsorbed by antimonic acid during the treatment with mineral acids. 0.3 g. of Al as sulphate, 0.2 g. each of Al and Fe, and 0.2 g. each

of Al, Fe, and As can still be present and the average error in the results be <0.1%. If CaSO<sub>4</sub> is filtered off and washed before the addition of NH<sub>3</sub> and NH<sub>4</sub>F,HF, 0.4 g. of Ca, 0.3 g. each of Ca and Fe, 0.3 g. each of Fe and Ca, and 0.2 g. of As can be present for the same degree of accuracy. Filtration is unnecessary with <0.1 g. of Ca. When Al, Ca, and Fe are present fuming with H<sub>2</sub>SO<sub>4</sub> after the HNO<sub>3</sub> treatment in the opening up of the ore is essential. L. S. T.

Volumetric titrations with potassium bromate. G. TRAVAGLI (Annali Chim. Appl., 1940, 30, 122– 126).— $Cu_2Cl_2$  is titrated by 0.1N-KBrO<sub>3</sub> to Meorange (violet-blue colour change) in presence of HCl and CO<sub>2</sub>. The method is applicable to other Cu salts and to the determination of reducing sugars.

F. O. H.

Quantitative separation of metals by hydrogen sulphide. III. Separation of zinc from iron by hydrogen sulphide, and the induced precipitation of ferrous sulphide by zinc sulphide. IV. Separation of copper from thallium by hydrogen sulphide, and the induced precipitation of thallous sulphide by cupric sulphide. V. Separation of nickel, cobalt, and zinc from manganese. H. KATÔ (Sci. Rep. Tôhoku, 1940, 28, 480-490, 491-499, 500-511; cf. A., 1935, 719). -III. Pptn. of FeS from  $\text{FeSO}_4$  commences at  $p_{\text{H}}$  $3\cdot 3+$  and is complete at  $p_{\rm H}$  4.36. FeS is pptd. on the surface of ZnS under conditions in which [Fe"][S"] is < the solubility product. Evidence that this induced pptn. is due to adsorption is discussed. In practice, the safe  $p_{\rm H}$  range for separating Zn<sup>\*\*</sup> from Fe<sup>\*\*</sup> as sulphide is 2.0—2.9; the most suitable  $p_{\rm H}$  is 2.4. CH<sub>2</sub>Cl·CO<sub>2</sub>' buffer is preferred to formate. The solubility product calc. for FeS is  $3.6 \times 10^{-19}$ . IV. Pptn. of Tl<sub>2</sub>S commences at  $p_{\rm H} \sim 2$ , and is complete at  $p_{\rm H} 4.32$ . The solubility product calc. is

complete at  $p_{\rm H}$  4.32. The solubility product calc. is  $6.7 \times 10^{-23}$ . Induced pptn. of Tl<sub>2</sub>S on CuS occurs, and is due probably to adsorption. For the complete separation of Cu<sup>\*\*</sup> from Tl<sup>\*</sup>, H<sub>2</sub>S should be passed into solutions 2N. with respect to H<sub>2</sub>SO<sub>4</sub> or N. with respect to HCl.

V. Pptn. of Mn commences at  $p_{\rm ff} \sim 5.3$ . The calc. solubility product is  $4.2 \times 10^{-15}$ . The green form of MnS is not pptd. in acid solution, but transformation from pink to green occurs readily at  $p_{\rm H}$  9.5—10. Some induced pptn. of MnS with ZnS, CoS, or NiS can occur. The most suitable  $p_{\rm H}$  ranges for separating Mn from Zn and from Co and Ni are 3—4 and 4.0— 4.8, respectively. In practice, an excess of a buffer solution (AcOH-NaOAc) of  $p_{\rm ff}$  4.4 should be added to the nearly neutral, unbuffered solution containing Ni<sup>\*\*</sup>, Co<sup>\*\*</sup>, and Mn<sup>\*\*</sup>, heated to 70°, and saturated with H<sub>2</sub>S. L. S. T.

Determination of small amounts of copper and manganese in dyes etc.—See B., 1940, 347.

Potentiometric examination of anticorrosive pigments.—See B., 1940, 377.

Detection and micro-determination of rare elements by luminescence. M. SERVIGNE (Bull. Soc. chim., 1940, [v], 7, 121-132; cf. A., 1939, I, 58, 599).—The sample is dissolved in fused CaWO<sub>4</sub>, which is subsequently powdered and distributed in a thin layer on a Pyrex or SiO<sub>2</sub> tube. Its luminescence is excited by placing the specimen around a discharge tube, or, alternatively, by arranging it inside a discharge tube. In either case the temp. of the sample is maintained at 90—150° while the spectrum is photographed. The method permits the detection of 5—100  $\times$  10<sup>-7</sup> g. of rare earth metal in 1 g. of CaWO<sub>4</sub>. Comparison of the intensity of the luminescence obtained with that obtained from standards can be used for the determination of small amounts of these metals. J. W. S.

Application of internal complex compounds in colorimetry (Determination of aluminium with the aid of aurintricarboxylic acid.) A. K. BABKO (J. Appl. Chem. Russ., 1939, 12, 1560— 1567).—The transition point of aurintricarboxylic acid (I) is at  $p_{\rm H}$  13·1. The absorption spectra of (I), its anion, and its Al salt are given. (I) is preferable to alizarin for the colorimetric determination of Al. R. T.

Spectrographic determination of small amounts of aluminium in iron and steel.—See B., 1940, 364.

Determination of manganese as pyrophosphate. B. MORSAN (Arh. Kemiju, 1939, 12, 109—124).— I c.c. of conc.  $H_2SO_4$  and 15 c.c. of saturated aq. Na<sub>2</sub>HPO<sub>4</sub> are added to 20 c.c. of solution, followed by aq. NH<sub>3</sub> to a faint pink colour (phenolphthalein). 200 c.c. of  $H_2O$  are added, and the suspension is heated for 3 hr. at 100°, the ppt. of MnNH<sub>4</sub>PO<sub>4</sub> is collected, washed, ignited (850°), and weighed as Mn<sub>2</sub>P<sub>2</sub>O<sub>7</sub>. R. T.

Ammonium persulphate reaction for manganese. P. G. POPOV (J. Appl. Chem. Russ., 1939, 12, 1738—1739).—Under certain conditions  $S_2O_8''$ oxidises  $Mn^{II}$  to  $Mn^{VII}$  in absence of Ag<sup>•</sup>; this reaction cannot therefore serve as a test for Ag<sup>•</sup> except when a blank test is negative. R. T.

Rapid volumetric determination of iron and titanium; application to ilmenite analysis. P. R. SUBBARAMAN and K. R. KRISHNASWAMI (Proc. Indian Acad. Sci., 1940, **11**, **A**, 106—115).—A mixture containing Fe and Ti is reduced to Fe<sup>II</sup> and Ti<sup>III</sup>. Ti<sup>III</sup> is determined by titration with Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, and both Fe<sup>II</sup> and Ti<sup>III</sup> by KMnO<sub>4</sub>. These methods have been applied to the analysis of ilmenite.

W. R. A. **Potentiometric titration of iron**. D. I. RJABT-SCHIKOV and V. G. SILNITSCHENKO (J. Appl. Chem. Russ., 1939, **12**, 1907—1911).—Fe<sup>III</sup> is reduced to Fe<sup>II</sup> by means of CuCl, and the solution is titrated with standard KMnO<sub>4</sub> solution. R. T.

Oxidation-reduction indicators in qualitative analysis. Use of ferrous dimethylglyoxime. G. CHARLOT (Bull. Soc. chim., 1940, [v], 7, 144—150). —Fe<sup>II</sup> dimethylglyoxime (I) in aq. NH<sub>3</sub> is decolorised by MnO<sub>4</sub>', OI', IO<sub>4</sub>', Fe(CN)<sub>6</sub>''', and S<sub>2</sub>O<sub>8</sub>'', thereby permitting the detection of these ions in the presence of ClO<sub>3</sub>', VO<sub>3</sub>', IO<sub>3</sub>', BrO<sub>3</sub>', AsO<sub>4</sub>''', and ClO<sub>4</sub>'. (I) in aq. NH<sub>3</sub>, previously decolorised by oxidation, is regenerated by S<sub>2</sub>O<sub>4</sub>'' and S'', and can be used for detecting these ions in the presence of CN', I', PO<sub>3</sub>''', PO<sub>3</sub>'', SO<sub>3</sub>'', S<sub>2</sub>O<sub>3</sub>'', or CH<sub>2</sub>O. The reaction can also be used for the detection of Ce<sup> $\cdots$ </sup>, Sn<sup> $\cdots$ </sup>, and VO<sup> $\cdots$ </sup>. Small quantities of  $Fe(CN)_6'''$  can be titrated with (I). J. W. S.

Test for cohalt. B. NILSSEN and A. PAULSEN (Tids. Kjemi, 1940, 20, 52).—The sensitivity of the (CMe:N·OH)<sub>2</sub>-polysulphide test for Co is increased to at least 1 in  $5 \times 10^6$  by oxidation to Co<sup>···</sup> with  $H_2O_2$  before addition of Na polysulphide. Filtration is preferable if Cu is present, but no common cation interferes. M. H. M. A.

Detection of nickel by a flotational reaction. I. M. KORENMAN and V. V. DUDNIK (J. Appl. Chem. Russ., 1939, 12, 1742—1743).—Excess of (CMe:N·OH)<sub>2</sub> in aq. NH<sub>3</sub> is added to 10 ml. of the solution, which is then shaken with 0.5 ml. of CCl<sub>4</sub>. Ni ( $\leq 5$  µg.) is indicated by a red film forming at the phase interface. Co, Mn<sup>II</sup>, Pb<sup>II</sup>, Fe<sup>III</sup>, Cr<sup>II</sup>, Cr<sup>III</sup>, Cu<sup>II</sup>, Bi, Al, Zn, and Ag interfere. R. T.

Volumetric determination of tungsten. M. L. HoLT and A. G. GRAY (Ind. Eng. Chem. [Anal.], 1940, **12**, 144—146).—W<sup>VI</sup> in conc. HCl is reduced to W<sup>III</sup> at ~60° by liquid Pb-Hg in a reductor of special design. The W<sup>III</sup> is at once reoxidised by aq. Fe<sup>III</sup> NH<sub>4</sub> sulphate, and the Fe<sup>II</sup> produced is titrated with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (Ba diphenylaminesulphonate). The method is applicable to macro- and semi-microquantities. Test data and procedures for determining W in tungstate solutions, Fe–W, and electro-deposited W–Ni alloys are given. A Sn amalgam is unsatisfactory for the reduction. L. S. T.

New applications of the silver reductor. Determination of uranium and copper. N. BIRNBAUM and S. M. EDMONDS (Ind. Eng. Chem. [Anal.], 1940, **12**, 155—157; cf. A., 1938, I, 158).— The reduction of  $UO_2^{II}$  to  $U^{IV}$  in the Ag reductor is quant. in hot 4M-HCl. The  $U^{IV}$  is then titrated with  $0\cdot IM-Ce(SO_4)_2$  at room temp. in presence of  $H_3PO_4$ , using o-phenanthroline—Fe<sup>"</sup> complex (I) as indicator. Titrations in hot solution with this indicator are umsatisfactory (cf. A., 1933, 1025), but in presence of  $H_3PO_4$  the reaction is rapid and the end-point sharp at room temp. AcOH (10 ml. per 50 of 4M-HCl) does not interfere, but HNO<sub>3</sub>, Fe, Mo, V, and Cu must be absent. Cu<sup>"</sup> is reduced quantitatively to Cu<sup>'</sup> in the Ag reductor in 2M-HCl. The Cu<sup>'</sup> is collected under Fe<sup>III</sup> alum, and the Fe<sup>"</sup> titrated with  $Ce(SO_4)_2$  [(I)]. Zn, Sn, As<sup>V</sup>, Bi, Cd, and comparatively large amounts of HNO<sub>3</sub> do not interfere; Fe, Mo, U, and V must be absent. L. S. T.

Determination of titanium in aluminium and in light alloys by absolute colorimetry.—See B., 1940, 368.

Determination of germanium by means of 8-hydroxyquinoline. I. P. ALIMARIN and O. A. ALEXEEVA (J. Appl. Chem. Russ., 1939, 12, 1900— 1906).—2 ml. of 5% aq.  $(NH_4)_2MoO_4$  are added per mg. of GeO<sub>2</sub> present in 50 ml. of neutral solution, followed by 3 ml. of 10% H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O to 100 ml. 9 ml. of conc. HCl are added after 5 min., followed by 20 ml. of 2% 8-hydroxyquinoline in 12% AcOH, and the ppt. of  $(C_9H_7ON)_4$ ; H<sub>4</sub>[Ge(Mo<sub>12</sub>O<sub>40</sub>)] is collected after 3—12 hr., washed with a mixture of 7 ml. of conc. HCl with 25 ml. of 8-hydroxyquinoline solution, and then with  $H_2O$ , dried at 110°, and weighed. The method gives trustworthy results for solutions containing 0.05—10 mg. Ge. R. T.

Detection of bismuth by a flotational reaction. I. M. KORENMAN and N. T. SOROKINA (J. Appl. Chem. Russ., 1939, 12, 1740—1741).—2 ml. of 25% KI, a few crystals of Na<sub>2</sub>SO<sub>3</sub>, and a few drops of  $C_5H_5N$  are added to the solution, which is then shaken with 1 ml. of Et<sub>2</sub>O; Bi ( $<8 \mu$ g.) is indicated by a yellow film forming at the phase interface. Al, Fe<sup>III</sup>, Mn<sup>II</sup>, Zn, Cd, Cu<sup>II</sup>, Pb<sup>II</sup>, Hg<sup>II</sup>, Sn<sup>II</sup>, Sb<sup>III</sup>, and Ag interfere; in their presence Na<sub>2</sub>SO<sub>4</sub> is added together with the Na<sub>2</sub>SO<sub>3</sub>, and the Et<sub>2</sub>O layer with the pellicle is shaken with aq. Na K tartrate, the aq. layer is made acid with HCl, and the reaction is repeated (<0.15 mg. Bi). R. T.

Measurement of very small amounts of heat and very small changes of temperature. S. ZAMENHOF (Rev. Sci. Instr., 1940, 11, 123—125).— The gas or vapour thermometer described detects temp. changes  $\sim 0.0001^{\circ}$  and quantities of heat  $\sim 10^{-4}$  g.-cal. by observation through a microscope of the shift of the top of the meniscus due to changes in the shape of the meniscus while the circumference remains stationary. N. M. B.

[Determination of] thermal conductivity of gases by a relative method with an application to deuterium. W. G. KANNULUIK (Proc. Roy. Soc., 1940, A, 175, 36–48).—The method consists of the use of a short, thick "hot wire" for which an approx. theory is given. The ratio of the conductivity of  $H_2$  to that of  $D_2$  at 0° is 1.365. G. D. P.

Direct calibration of a copper-constantan thermel for measurement of temperature differences at a series of temperatures. J. S. BURLEW and R. P. SMITH (J. Amer. Chem. Soc., 1940, 62, 701-704).—A direct differential method of calibration is described. Vals. obtained by it for a Cuconstantan thermel are in complete agreement with those obtained for the same thermel by the integral method. W. R. A.

Resonance method for measuring the ratio of the specific heats of a gas,  $C_p/C_v$ . I. A. L. CLARK and L. KATZ (Canad. J. Res., 1940, 18, A, 22—38).—The apparatus consists of two similar chambers separated by a steel piston which is caused to oscillate by an external alternating magnetic field, and  $\gamma$  is calc. from the resonance frequency.

F. J. G.

**Rhodium mirrors.** M. AUWÄRTER (J. Appl. Physics, 1939, 10, 705—710).—Rh forms an adherent and hard film not subject to either physical or chemical ageing and with relatively const. reflecting power throughout the visible spectrum. Semi-transparent Rh mirrors can be used to reduce light intensity without change in  $\lambda$ -distribution. O. D. S.

New methods in spectroscopy. G. R. HAR-RISON (Science, 1940, 91, 225–228).—An address. L. S. T.

Iron arc as a standard source for spectrochemical analysis. M. SLAVIN (Ind. Eng. Chem. [Anal.], 1940, 12, 131–133; A., 1938, I, 535).—The form of the arc, an Fe bead placed between graphite electrodes, the method of using it as a standard, and applications of its use are described. L. S. T.

Monochromator for spectrophotometric investigations. E. STROHBUSCH (Z. Instrumkde., 1939, 59, 417—421).—The optical system is described. A. J. M.

Generalisation of the Bragg-de Broglie method of focussing for application to double-crystal X-ray spectrographs. H. T. PLASENOIA (Compt. rend., 1940, 210, 395—398).—Conditions for Bragg focussing with two parallel crystals, reflecting from their principal faces or planes perpendicular to a cleavage plane, are derived. The use of a divergent beam renders a collimating system unnecessary, and high luminosity is obtained without loss of resolving power. A. J. E. W.

Concave spherical crystals of barium copper stearate for use in long wave-length X-ray spectrometers. C. L. ANDREWS (Rev. Sci. Instr., 1940, 11, 111—114).—To diffract and focus a monochromatic beam of X-rays, multiple unimol. layers of Ba Cu stearate were deposited on an accurately ground concave spherical glass surface. With a spherical crystal of radius 218 cm., grating space ~50.5 A., photographs of the Al  $K\alpha,\beta$  region (unresolved) were obtained in 30 min. at 3 kv. and 15 ma. The intensity and resolving power from the grating are probably adequate for measurements of absorption coeffs. at  $\lambda\lambda$ . >8 A. with an ionisation chamber.

N. M. B.

Setting crystals for single-crystal X-ray photographs. M. ARNFELT (Arkiv Kemi, Min., Geol., 1939, 13, B, No. 9, 7 pp.).—The method is based on the principle of the reciprocal lattice; the technique is slightly different from that of Bernal (A., 1927, 9). T. H. G.

Two-crystal Weissenberg X-ray goniometer. W. A. WOOSTER and A. J. P. MARTIN (J. Sci. Instr., 1940, 17, 83—89).—The standard and unknown crystal are both arranged on the axis of the cylindrical camera and reflexions from both obtained on the same film. In this way fluctuations of X-ray output and variations in the sensitivity and development of the film do not affect the determination of relative intensity of reflexion. D. F. R.

Very sensitive thermo-element for the determination of radiation. G. ROSENTHAL (Z. Instrumkde., 1939, 59, 432–439, 457–463).—Details of construction are given. A. J. M.

Evaluation of radiation intensities by a simplified spectrographic method. A. J. MADDOCK (J. Sci. Instr., 1940, 17, 89–92).—The radiation is reflected from a MgO screen on to a quartz spectrograph and the spectrum compared with a series of spectra obtained similarly from a standard source of radiation, the intensity of the latter being varied in steps of 10%. Visual comparison of corresponding  $\lambda\lambda$  may be made with an accuracy of 5–10%, and the summation of the whole intensities with an accuracy of ~3%. D. F. R.

Theory of crossed slit method of observation [of concentration gradients]. H. SVENSSON (Kolloid-Z., 1940, 90, 141-156; cf. A., 1939, I, 370).-- The sensitivity of the method and various sources of error are treated mathematically. The use of the different lenses is discussed and the setting-up and adjustment of the apparatus are described. F. L. U.

Photo-electric micro-photometer. M. VERAIN (Atti X Congr. Internaz. Chim., 1938, IV, 478–481). F. O. H.

Photo-effect and its application in photocells. H. VERLEGER (Z. Instrumkde., 1939, 59, 396-415).—A review. A. J. M.

Null-type photo-electric spectrophotometer. C. J. BARTON and J. H. YOE (Ind. Eng. Chem. [Anal.], 1940, 12, 166—168).—Details of construction and operation of an instrument employing barrier-layer photo-cells, and tests of accuracy, sensitivity, and reproducibility, are given. The apparatus can be used for accurate spectrophotometric measurements, the study of colorimetric methods of analysis, and other types of absorption measurements. L. S. T.

Photo-electric cells sensitive to long-wave length radiation. Bismuth sulphide cell.—See B., 1940, 371.

Photo-electric micro-densitometer. M. SPIE-GEL-ADOLF and R. H. PECKHAM (Ind. Eng. Chem. [Anal.], 1940, 12, 182—184).—The apparatus described consists mainly of a light source, a microscope stand, and a photo-electric cell; it permits graphical descriptions of X-ray diffraction patterns to be given.

L. S. T.

Synchronising the illumination for an ultracentrifuge. Y. BJÖRNSTÅHL (J. Sci. Instr., 1939, 16, 254—256).—An ultracentrifuge suitable for the optical measurement of sedimentation velocities is described. A light source of const. intensity is interrupted by means of a rotating aperture disc, and two methods of synchronising this disc with the centrifuge are described. C. R. H.

New results with luminescent substances and their use. N. RIEHL (Chem.-Ztg., 1940, 64, 8—11; cf. A., 1939, I, 124).—A review of new applications of luminescent substances, including the production of more sensitive ZnS fluorescent screens and of luminescent photographic emulsions, for use in X-ray and related technique; also the development of new forms of white and coloured lighting by means of discharge tubes coated with new luminescent substances, e.g.,  $Zn_2SiO_4$ —CaWO<sub>4</sub>. The night illumination of external chemical plant, in the absence of normal lighting, by means of luminous paint and ultra-violet light, is described. D. F. R.

(A) Development of the electron microscope. L. C. MARTIN, D. H. PARNUM, and G. S. SPEAK. (B) Optics of the electron microscope. L. C. MARTIN (J. Roy. Microscop. Soc., 1939, [iii], 59, 203—216, 217— 231).—(A) Testing, modifications, and adjustments of the apparatus previously described (cf. A., 1937, I, 152) are reported. Possible causes of residual effects and attempted methods for their elimination are summarised under 11 heads.

(B) A detailed consideration of the causes of "streaking" in the images, and a brief reference to the effect of spherical aberration on the resolving limit and to depth of focus. N. M. B. Dropping electrode with a constant head of mercury. E. F. MUELLER (Ind. Eng. Chem. [Anal.], 1940, 12, 171)—A Hg reservoir using the principle of the Mariotte flask is sealed on to the dropping electrode, and maintains a const. head of Hg in polarographic measurements. L. S. T.

Temperature corrections in  $p_{\rm H}$  determinations with the glass electrode. O. NYNÄS (Finska Kem. Medd., 1939, 48, 129—138).—Temp. correction is discussed mathematically. The correction factor,  $\Delta E$ , is most easily obtained graphically from measurements of  $dp_{\rm H}/dt$ , apparent and real, of buffer solutions of widely separated  $p_{\rm H}$ .  $\Delta E \propto p_{\rm H}$  over a wide range. M. H. M. A.

Mercury cathode in metallurgical analysis.— See B., 1940, 367.

Electric moments of molecules. M. E. HOBBS, J. W. JACOKES, and P. M. GROSS (Rev. Sci. Instr., 1940, 11, 126-133).-On the basis of the Debye expression, determinations of mol. polarisation over a small temp. interval with an apparatus giving high precision measurements of  $\epsilon$  and its dependence on temp. is a method of obtaining an accurate val. of the dipole moment of gaseous polar substances. The apparatus described consists of oscillators, a measuring condenser operated by a 1-m. arm carrying at one end a micrometer microscope, a high-capacitance gas condenser and fixed reference capacitance, a vapour thermostat with manostat to control the temp. of the gas condenser, and high-precision pressure-measuring N. M. B. gauges.

Action of the Geiger-Müller counter. C. H. COLLIE and D. ROAF (Proc. Physical Soc., 1940, 52, 186—190).—In view of the uncertainty as to the action mechanism, an investigation of the working of a counter filled with He and EtOH vapour was made. Results, combined with available data, show that ionisation by collision is the dominant process over a large voltage range. N. M. B.

**Ten-litre volumetric flask.** E. J. REITHEL (Ind. Eng. Chem. [Anal.], 1940, **12**, 159).—Vols. of  $\sim 10$  l. can be measured with an accuracy of  $\pm 5$  ml. by using a graduated pipette as a vol. indicator in the manner described. The pipette is adjusted so that it touches the surface of the liquid contained in a 12-l. bottle. L. S. T.

Carbonate-veronal buffer solution covering  $p_{\rm H}$ 7.5 to 10.7. E. J. KING and G. E. DELORY (Enzymologia, 1940, 8, 278—279).—25 c.c. of 0.1M-Na veronal are added to the appropriate amount of 0.1N-HCl in a 100-c.c. flask, followed by 25 c.c. of 0.1M-Na<sub>2</sub>CO<sub>3</sub>. The contents are mixed and diluted to 100 c.c. When stored in well stoppered paraffin-waxed bottles the buffers retain their  $p_{\rm H}$  val. for <10 months.

J. N. A.

Universal buffer mixture. H. T. S. BRITTON (Analyst, 1940, 65, 220).—Johnson and Lindsey's (A., 1939, I, 482) modification of Britton and Robinson's universal buffer mixture (A., 1931, 910). has already been adopted by Britton and Welford (A., 1938, I, 34). E. C. B. S.

Apparatus for the Kjeldahl determination of nitrogen. H. LECOQ (Bull. Soc. Chim. biol., 1940, **22**, 112—113).—The vessel containing the  $NH_3$  is placed inside the steam generator. A. L.

Motorised apparatus for rapid determination of calcium and magnesium in water.—See B., 1940, 413.

Apparatus for determination of hardness of water by the Boutron-Boudet method.—See B., 1940, 331.

Weighing bottle. W. A. TAEBEL (Ind. Eng. Chem. [Anal.], 1940, 12, 141).—The bottle consists of a glass tube into which a funnel is sealed; the stem of the funnel is closed by a ground-glass stopper. Liquids or finely-divided or fluffy solids can be transferred directly to a vessel without loss. L. S. T.

Sealable absorption micro-tube. A. N. PRATER (Ind. Eng. Chem. [Anal.], 1940, 12, 184).—The modified Friedrichs tube described and illustrated weighs <15 g. when full and contains sufficient absorbent for 25 analyses. Larger tubes of the same design are suitable for semi-micro-determinations. L. S. T.

Magnetic shaking device. S. KIYOMIZU (Ind. Eng. Chem. [Anal.], 1940, 12, 174).—A device for shaking samples in a thermostat is described and illustrated. L. S. T.

All-glass ball valve stirrer. S. LIOTTA (Ind. Eng. Chem. [Anal.], 1940, **12**, 173).—The stirrer has a hollow glass ball inside a cylindrical moving piston, and provides a slow-motion type of stirring with a positive flow of solution from bottom to top. Constructional details of the stirrer and a method of seating it in a Dewar container are illustrated. L. S. T.

Flow divider for gases. J. H. BRUUN (Ind. Eng. Chem. [Anal.], 1940, 12, 172).—The apparatus described and illustrated divides the main gas stream into desired proportions by varying the resistance of a capillary tube to gaseous flow by inserting a wire of suitable size in the capillary. L. S. T.

Reduction of specific gravity at  $25^{\circ}/25^{\circ}$  to density at any temperature from  $0^{\circ}$  to  $40^{\circ}$ . R. R. DREISBACH (Ind. Eng. Chem. [Anal.], 1940, 12, 160—161).—A graphical method of interpolation, applicable when the coeff. of cubic expansion of the liquid is known, is described. L. S. T.

Apparatus for Pregl-Beckmann micro-determination of mol. wt. K. BÜRGER (Chem. Fabr., 1940, 13, 54—55).—An apparatus using 1.5 c.c. of solvent and 5—7 mg. of solute and incorporating a Hoeppler ultrathermostat is described and claimed to give results <1% in error. J. A. S.

Determination of maximum pore size of filters. H. KNÖLL (Kolloid-Z., 1940, 90, 189— 194).—The interpretation of results given by the max. bubble pressure method as applied to filters is discussed. Further experiments with bacterial filters and single capillaries show that Bechhold's method gives vals. for the max, pore size of filters about half the real vals. The bubbles first appearing at filters when the pressure is gradually raised are not formed by the coalescence of smaller bubbles from neighbouring pores. F. L. U. Filters with pores of known and equal size down to the size of colloidal particles. J. BERNDEL (Kolloid-Z., 1940, 90, 194—196).—The filters are made by fusing together at a temp. low enough to prevent collapse of the bore glass capillaries in bundles of 7. The composite capillary rods thus formed are then drawn out so as to reduce the pore diameter to  $\frac{1}{4}$  of its initial val., and the processes of bundling and drawing out are repeated as often as required. In this way a rod having 7<sup>6</sup> parallel cylindrical pores of ~0.25  $\mu$ . diameter has been made.

Coldextractionapparatus.J.F. L. U.(Science, 1940, 91, 223-224).L. S. T.

Simple apparatus for extraction of liquids with light and heavy solvents. J. PRITZKER and R. JUNGKUNZ (Pharm. Acta Helv., 1939, 14, 223— 225).—The apparatus, which is similar to a Soxhlet apparatus without the siphon tube, is figured. A glass tube, leading from a tap at the bottom of the extraction tube to about the middle of the vapour tube, conveys heavy solvent. Light solvent condensate drops through a funnel with a long stem which is sealed at the bottom and perforated at the side, to the bottom of the liquid, through which it rises, and returns through the vapour tube. E. H. S.

Closing the compression capillary of a McLeod gauge. W. F. C. FERGUSON (Rev. Sci. Instr., 1940, 11, 134).—Distortion of the bore is avoided by fusing in a slightly tapered solid glass rod plug squarely cut or ground off at the inner end.

N. M. B.

Vacuum leak testing. E. J. LAWTON (Rev. Sci. Instr., 1940, 11, 134; cf. Manley, A., 1940, I, 134).— Painting a leak with  $CCl_4$  caused sharply increased electron emission and directing a stream of  $O_2$  or  $H_2$ at the tube caused decreased emission of a W filament ion gauge. The emission change is a more sensitive and satisfactory method of leak detection than measurement of the ion current. The effect of hydrocarbon vapours from stopcock grease is discussed.

N. M. B.

Sensitive automatic pressure control device. R. A. SMITH (Rev. Sci. Instr., 1940, **11**, 120—122).— Control with a Pirani gauge at pressures down to  $0.01 \mu$ . and sensitive to  $0.01 - 0.02 \mu$ . is obtained by passing a current through the Pirani tube and interpreting the pressure from the resistance measured by a bridge. The bridge balance is connected to an electronic circuit controlling a vac. pump which comes into action if resistance falls. N. M. B.

New method for measuring Young's modulus. A. KING (Rev. Sci. Instr., 1940, **11**, 114—116).—For a rapid simple dynamic method the specimen, in the form of a circular loop of wire of radius r, is fastened at one point to a rigid support and at the diametrically opposite point a magnetic field is applied. The frequency of an a.c. in the loop is adjusted until flexural vibrations occur in the plane of the loop. Then the resonance frequency f, linear density m, and radius of the wire a are related to Young's modulus by  $E = 18\cdot395mf^2(r/a)^4(1-g)$  where (1-g) is a gap correction factor. N. M. B.

XI, XIII

[Laboratory apparatus.] J. A. DE BRUIJN, jun. (Chem. Weekblad, 1940, **37**, 249—252).—(i) An improved gas wash-bottle consists of a cylindrical vessel with a long, bell-shaped inlet and a narrow outlet, both of which are fitted with spherical splash heads. (ii) I is sublimed by heating a mixture of I (10), KI (5), and CaO (3-4 parts) in a slow stream of  $N_2$ , passing the vapours over CaO + KI at 200-250°, and condensing the sublimate in a spherical, water-cooled bulb attached directly (ground joint) to the sublimation tube. (iii) Various forms of Soxhlettype extraction apparatus are discussed; the preferred form has a filter-plate in place of a siphon and is fitted with a two-way tap immediately below the extraction chamber to facilitate the taking of samples of the extract during extraction. (iv) Ground-in condensers are not satisfactory in determinations of the maleic acid val. and better results are obtained with 250-c.c. Erlenmeyer flasks with long necks  $(25 \times 2.0 \text{ cm.})$ , which can be surrounded during the heating period by closely fitting, externally cooled jackets ( $20 \times 2.1$ —2.2 cm.). (v) A modified Water-man-Elsbach apparatus for distillation of small amounts of liquid in a cathode-light vac. is also described. S. C.

Viscosimeter for volatile liquids. A. TOROPOV (J. Appl. Chem. Russ., 1939, 12, 1744). R. T.

Modified Kendall tube for purifying nitrogen. G. M. SAVAGE and Z. J. ORDAL (Science, 1940, 91, 222-223).—The modification (cf. A., 1931, 809) illustrated provides for more intimate contact between

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gases and Cu gauze, and increases greatly the capacity for removal of  $O_2$ . L. S. T.

Still for producing metal-free distilled water. J. S. MCHARGUE and E. B. OFFUTT (Ind. Eng. Chem. [Anal.], 1940, **12**, 157—159).—A still with quartz condenser tubes is described and illustrated. The H<sub>2</sub>O contained <1 part of metal per billion.

L. S. T. All-glass still with automatic float feed. G. F. LIEBIG, jun. (Ind. Eng. Chem. [Anal.], 1940, 12, 174).—An electrically-heated Pyrex still, which produces  $\sim 500$  ml. of redistilled H<sub>2</sub>O per hr. and operates for long periods without attention, is described and illustrated. L. S. T.

Fractional distillation.—See B., 1940, 332.

Separation of isotopes. E. H RIESENFELD (Arkiv Kemi, Min., Geol., 1939, 13, A, No. 16, 11 pp.). —An "open" modification of the Hertz diffusion apparatus for the separation of gaseous isotopes is described. Fresh supplies of the mixture to be separated can be introduced continuously, thus permitting the collection of large quantities of the enriched fractions of both light and heavy isotopes. In the open apparatus the separation process need not be carried out without interruption, a smaller no. of diffusion units is needed, and more rapid and more complete separation is achieved. The use of Boltwood Hg pumps instead of diffusion pumps is discussed.

T. H. G.

Apparatus for catalytic dehydration of alcohol to olefine.—See B., 1940, 332.

## Geochemistry.

Metastable  $\gamma$ -phase of Fe<sub>2</sub>O<sub>3</sub> in some samples of magnetite undergoing change. V. MONTORO (Atti X Congr. Internaz. Chim., 1938, II, 736).— X-Ray measurements show the presence of the metastable  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> together with Fe<sub>3</sub>O<sub>4</sub> in samples of polarised magnetite from the island of Elba.

O. J. W.

Isotopic composition of oxygen in carbonate rocks and iron oxide ores. M. DOLE and R. L. SLOBOD (J. Amer. Chem. Soc., 1940, 62, 471— 479).—Improved apparatus for density measurements (described) has been used in the isotopic analysis of O in carbonate rocks and Fe oxide ores. Carbonates of different geological age (Grenville marble, Niagara dolomite, Pennsylvania limestone and clam shells) give approx. the same isotopic composition of the O. When the O in Grenville marble is liberated as CO<sub>2</sub> with acid and reduced with H<sub>2</sub> it gives H<sub>2</sub>O of d 9·2 p.p.m. > normal, but if the CO<sub>2</sub> is liberated by heat the resulting H<sub>2</sub>O is only 7·9 p.p.m. > normal. This variation is attributed to the isotopic fractionation which occurs when the CO<sub>3</sub>" ion is decomposed by acid. The val. 7·9 p.p.m. can be explained quantitatively on the isotopic exchange equilibrium theory of Urey and Grieff (A., 1935, 446). The O in Fe oxide ores of the Keewatin and Middle Huronian ages does not differ significantly in its isotopic composition from that of O in normal H<sub>2</sub>O. Any deviations are probably due to the presence of carbonates in the ores. W. R. A.

Italian bentonite. F. SAVELLI (Atti X Congr. Internaz. Chim., 1938, II, 785—795).—The chemical and mineralogical composition of Italian bentonite (I) from Ponza I. is compared with that of American bentonite from Wyoming. The swelling, plastic, adsorption, and thixotropic properties of (I) are described. O. J. W.

Distribution of indium in rocks. S. A. BORO-VIK, N. M. PROKOPENKO, and T. L. POKROVSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1939, **25**, 618— 621).—The In content of numerous rocks and clays from various parts of the U.S.S.R. has been determined spectroscopically. In is found in acid, intermediate, and partly alkaline rocks, *e.g.*, granites, monzonites, and nepheline syenites, but is absent from basic rocks, *e.g.*, gabbro and dunite. The average In content is  $\sim 5 \times 10^{-6}$ %. C. R. H.

Coal veins in Malaya. (SIR) L. L. FERMOR (Geol. Mag., 1939, 76, 465—472).—Vitrain veins deposited vertically in alluvium at Bidor are described. They demonstrate that vitrain, a gel, can be deposited from solution by a colloidal process, and is not merely the result of the alteration of carbonaceous matter *in situ*. L. S. T.