## BRITISH CHEMICAL ABSTRACTS

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

FEBRUARY, 1937.

Production of a hydrogen continuum of high intensity by means of a hot-cathode tube. G. JACOBI (Physikal. Z., 1936, 37, 808-810).-The construction of a H<sub>2</sub> discharge tube with a heated cathode for the production of a continuous spectrum in the ultra-violet is described. The advantages of the tube are the low potential required (100 volts) and the fact that H<sub>2</sub>O-cooling is not necessary. A. J. M.

Line intensity variations in the hydrogen highfrequency glow discharge. G. W. Fox and C. H. BACHMAN (Physical Rev., 1936, [ii], 50, 939-942).-Lines of the Balmer series excited in a high-frequency glow discharge in  $H_2$  for  $\lambda\lambda$  range 5.1-32.5 m. and pressure range 5-300 microns, and studied spectroscopically in conjunction with a logarithmic sector disc, show variations in intensity ratios with excitation frequency, a region of which produces min. excitation of cach term with respect to H<sub>a</sub>, and depends on the pressure and term under consideration. Ionisation efficiency and intensities of the higher series terms vary approx. directly with each other if cumulative ionisation is negligible. Intensities of higher terms increase with decreasing pressure down to about 10 microns, below which  $H_{\beta}$  and  $H_{\gamma}$  continue to increase in intensity while higher terms decrease. Satisfactory curves can be calc. N. M. B.

598-620) .- The Lyman bands obtained by Beutler and Mie have been analysed and a theory is developed for the explanation of the anomalous intensities A. E. M. observed.

Comparative measurements of the normal cathodic discharge constants in light and heavy hydrogen. A. GUNTHER-SCHULZE and H. SCHNITGER (Z. Physik, 1936, 103, 491-494).-Discharges in  ${}_{2}^{1}H_{2}$  and  ${}_{2}^{2}H_{2}$  were compared over a pressure range of 1-3 mm. Hg. In  ${}_{2}H_{2}$  the min. discharge voltage was  $9\cdot3\% >$ , the normal current density  $36\cdot7\% <$ , the luminosity  $22\cdot1\% >$ , and the distance from the anode at which the anodic glow disappears  $12 \cdot 1\% > 10^{10}$  H. C. G. 12.1% >, in  ${}_{2}^{1}H_{2}$ .

Field-strength in the column of the glow discharge in light and heavy hydrogen. M. STEEN-BECK (Physikal. Z., 1936, 37, 823-824).—The potential of the positive column in  $D_2$  is < in  $H_2$ . Determination of the field-strength in the column and the electron temp. in discharges in H<sub>2</sub> and D<sub>2</sub> under identical conditions gives results in agreement with

Wave-length standards in the extreme ultraviolet. K. R. MORE and C. A. RIEKE (Physical Rev., 1936, [ii], 50, 1054-1056; cf. Shenstone, A., 1936, 537).-To obviate errors in the method of overlapping orders, the  $\lambda\lambda$  of several lines of C. N. and O were determined by comparison of the first-order lines with certain first-order lines of Cu II. Results are in good agreement with independent data, and weighted mean vals. are suggested as standards from 1658 to 833 A. N. M. B.

Rotation analysis of  $O_2^+$ ,  ${}^{2}\Pi \rightarrow {}^{2}\Pi$  bands. L. von Boźoky (Z. Physik, 1937, 104, 275—290).—New bands in the region  $\lambda\lambda$  4363 to 2343 A. obtained by high-frequency excitation of O2 have been examined at a dispersion of 1.2 A. per mm. The moment of inertia and the internuclear distances for the two states are respectively 26.0902 and  $16.5650 \times 10^{-40}$ cm.<sup>2</sup> g., and 1.406 and 1.121  $\times$  10<sup>-8</sup> cm. L. G. G.

"Clean-up" of inert gases in the electric discharge. I. H. ALTERTHUM, A. LOMPE, and R. SEELIGER (Physikal. Z., 1936, 37, 833-838).-Quant. investigation of the "clean-up" of inert gases, particularly Ne, in the glow discharge leads to results incompatible with the theory that the gas is adsorbed by particles sputtered from the cathode. The best assumption is that the gas is shot into the cathode metal in the form of ions. All observations agree with this theory except the fact that the velocity of removal of the inert gas decreases as the pressure increases. A. J. M.

Zeeman effect of alkali metals according to the Dirac equation. R. SCHLATTERER (Ann. Physik. 1936, [v], 27, 643-663).-Mathematical. The Voigt-Sommerfeld formula for the Zeeman splitting of doublet systems is deduced from the Dirac equation. O. D. S.

Mg I-like spectra of the elements Ti to Co, Ti XI, V XII, Cr XIII, Mn XIV, Fe XV, and Co XVI B. EDLÉN (Z. Physik, 1936, 103, 536-541).-In the vac. spark spectra of Ti, V, Cr, Mn, Fe, and Co in the region 126-47. A. 10-15 lines for each element are identified as combinations in a Mg I-like spectrum; term systems are calc. The same elements also exhibit doublet combinations in an Al 1-like spectrum.

H. C. G.

S I-like spectra of the elements titanium to iron, Ti VII, V VIII, Cr IX, Mn X, and Fe XI. B. EDLÉN (Z. Physik, 1937, 104, 188-193).

L. G. G. Quadrupole moment and magnetic moment of <sup>31</sup><sub>31</sub>Ga and <sup>71</sup><sub>31</sub>Ga. H. SCHÜLER and H. KORSCHING (Z. Physik, 1936, 103, 434–442).—From the triplet

the diffusion theory of the positive column.

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4s5s,  ${}^{3}S_{1}$ -4s5p,  ${}^{3}P_{0, 1, 2}$  of the Ga II spectrum the quadrupole moment of  ${}^{69}$ Ga was found to be  $q = +1 \times 10^{-24}$ ; for  ${}^{71}$ Ga  $q = 0 \pm 0.5 \times 10^{-24}$ . Magnetic moments obtained from Ga I and Ga II were in good agreement;  $\mu_{69} = +2.0$  and  $\mu_{71} = +2.5$  nuclear magnetons.

A. E. M.

Continuous absorption band of rubidium in the presence of foreign gases. N. T. ZE and C. S. YI (Nature, 1936, 138, 1055). The position of the new band observed in presence of Ne, He,  $H_2$ , or  $N_2$ depends on the nature of the foreign gas. The absorption may be produced by a Rb atom at the moment of a collision with a foreign gas atom.

L. S. T.

Hyperfine structure of Rb resonance lines. H. KOPFERMANN and H. KRÜGER (Z. Physik, 1936, 103, 485—490).—The hyperfine structure of the two resonance lines  $\lambda = 7947$  A.  $(5^{4}S_{4} - 5^{2}P_{4})$  and  $\lambda =$ 7800 A.  $(5^{2}S_{4} - 5^{2}P_{3/2})$  has been examined. The separation of the ground states  $5^{2}S_{4}$  was  $\Delta v = 0.228$ cm.<sup>-1</sup> for Rb 87 and  $\Delta v = 0.101$  cm.<sup>-1</sup> for Rb 85. The ratio of the nuclear magnetic moments  $\mu_{87}$ :  $\mu_{85}$  is 2.03;  $\mu_{87} = 2.8$  and  $\mu_{85}$  is 1.4 nuclear magnetons. H. C. G.

Absorption and fluorescence spectra of indium vapour. R. WAJNKRANC (Z. Physik, 1936, 104, 122-131).—These spectra have been studied over the temp. range  $600-1000^\circ$ . The fluorescence spectrum consists exclusively of at. lines, whereas the absorption contains in addition a band system. The existence in the vapour of In<sub>2</sub> mols. is established.

L. G. G.

Absorption of light in cæsium vapour in the presence of foreign gases. R. W. DITCHBURN and J. HARDING (Proc. Roy. Soc., 1936, A, 157, 66— 79; cf. A., 1935, 907).—The absorption of Cs vapour in the presence of Ne, A, Kr, Xe, N<sub>2</sub>, H<sub>2</sub>, D<sub>2</sub>, and  $C_6H_6$  has been measured. All gases cause a reduction in the amount of absorption. The shape of the absorption curve undergoes a change near the serieslimit, the max. absorption being shifted to shorter  $\lambda\lambda$ and the slope of the curve becoming less. L. L. B.

Excitation of light by collision between cæsium ions and helium atoms. W. MAURER (Z. Physik, 1936, 104, 113—121).—A method previously given (A., 1936, 1167) is used to study the influence of current and pressure on the intensity of Cs and He lines obtained as a result of Cs<sup>+</sup>  $\rightarrow$  He collisions. L. G. G.

Structure of the band spectrum of mercury vapour. II. S. MROZOWSKI (Z. Physik, 1937, 104, 228-247).—A consideration and extension of previous work (A., 1934, 232). L. G. G.

Spectra of high-frequency discharges in mercury vapour. II. Comparison of electrodeless with external electrode excitation. III. Modification due to wave-length. J. K. ROBERTson and R. H. HAY (Canad. J. Res., 1936, 14, A, 201-208).—Comparison has been made of the spectra of Hg vapour excited by electrodeless discharge and by external electrode discharge at  $100-250^{\circ}$  and at  $\lambda\lambda$  5, 35, 75, and 200 m. Excepting for the highest frequency, external electrode excitation was more efficient for the emission of arc and spark lines. At a low v.p., a very brilliant discharge free from spark

lines is obtained at 5 m. The results are discussed theoretically. J. W. S.

Excitation of mercury by collision with slow positive mercury ions. H. MOSER (Ann. Physik, 1937,  $[\nabla]$ , 28, 97—103).—The variation in intensity of the 2537 and 3125 Hg lines with the velocity of the exciting Hg<sup>+</sup> was determined up to 5000 volts. The excitation function is different from that for excitation by electrons. The resonance line  $\lambda$  2537 is particularly strong in the ionically excited spectrum. Investigation of the intensity distribution of singlet and triplet lines shows that the latter are more strongly excited than the former by exciting ions of low velocity, but that this is reversed for higher velocities.

A. J. M.

Sparking potential of mercury vapour. F. L. JONES and W. R. GALLOWAY (Nature, 1936, 138, 973). —Over a wide range of v.d., the sparking potential is a linear function of pressure  $\times$  distance between the electrodes from approx. 500 to 5000 volts. Min. sparking potentials for cathode surfaces of Ni, "staybrite" steel, and Ni or steel coated with Hg are recorded and the process of formation of ions is discussed. L. S. T.

Spectral energy distribution and light efficiency of the discharge in mercury vapour at high pressures. H. KREFFT, K. LARCHE, and F. Rössler (Physikal. Z., 1936, 37, 800-803).-The energy distribution and light efficiency of the discharge in Hg vapour were determined at pressures up to 30 atm. The light efficiency of lines  $\lambda$  5770 and 5790 increases more slowly with pressure than the 5461 line. For the first term of the triplet subsidiary series, the efficiency increases with increasing pressure steadily up to 30 atm., but for higher terms a decrease occurs before this pressure is reached, the decrease commencing at a lower pressure the higher is the term. The lines are considerably broadened on the side of longer  $\lambda$  at higher pressures, and a continuous background is produced extending from the Schumann region into the visible. Self-absorption has a great A. J. M. effect on the spectral energy distribution.

Zeeman phenomenon. É. SEVIN (Compt. rend., 1936, 203, 1147—1149).—Two solutions of the Schrödinger equation, allowing for at. spin, correspond with normal and abnormal Zeeman effects.

A. J. E. W. **Paschen-Back effect:** <sup>2</sup>S<sup>2</sup>P multiplets in strong fields. J. B. GREEN and R. A. LORING (Physical Rev., 1936, [ii], 50, 975; cf. A., 1936, 653).— Jacquinot's letter (cf. *ibid.*, 1310) reports 44,000 gauss as against 4400 gauss in his original paper.

N. M. B.

Potential gradient in negative dark space of normal glow discharge. W. H. ERNST (Helv. phys. Acta, 1935, 8, 381—404; Chem. Zentr., 1936, i, 1377).—Probe measurements in the Faraday dark space, negative glow, and Crookes dark space of H and A glow discharges show no cathodic space charge sheath to exist. The potential fall follows the theory of Compton and Morse (Physical Rev., 1927, [ii], 30, 305). J. S. A.

Investigation of electrical discharges in gases with the cloud chamber. E. FLEGLER and R. RAETHER (Z. Physik, 1937, **104**, 219–220).—A reply to criticism (cf. A., 1936, 770). L. G. G.

Spark discharge with alternating voltage. Spark discharge with pulsating illumination. W. FUCKS (Z. Physik, 1936, 103, 709—727).—The Townsend equation has been extended to cover the case of alternating-voltage spark discharge. If the frequency is not too great, it is shown that the striking voltage is increased (e.g., 10% at 5280 cycles per sec.). The striking voltage with intermittent illumination of the cathode is independent of the frequency of the pulsations. A. E. M.

"Tube "discharges. G. ZIMMERMANN (Z. Physik, 1937, 104, 309-334).—A study of the "tube" discharge in HCl gas from which are derived expressions for the distribution of the charge carriers, and their relation to the diameter of the tubes.

L. G. G.

Increase of spark potential by irradiation. R. SCHADE (Naturwiss., 1936, 24, 813).—The increase of spark potential on irradiation in a homogeneous field at low pressures observed by Seitz *et al.* (A., 1936, 770) could not be confirmed. A decrease was observed with Ne and A, the lowering being the greater the more intense was the radiation. The discrepancy between the results is probably due to avoidance of impurities (particularly grease) on the electrodes in the present work. A. J. M.

Red and sunlit auroras and the state of the upper atmosphere. L. VEGARD (Nature, 1936, 138, 930—931). L. S. T.

Stellar atmospheres. A. UNSÖLD (Physikal. Z., 1936, 37, 792—797).—The physical foundations of a quant. theory of the Fraunhofer lines, including the thermal Doppler effect, radiation damping, collision damping, pressure effect, and rotation of the star, are considered. Examination of the intensity of Fraunhofer lines in the light of the theory enables conclusions to be reached concerning the constitution of stellar atm. A. J. M.

Spectrum of Nova Lacertae. H. CAMICHEL (Compt. rend., 1936, 203, 1130—1132).—Absorption and emission lines in the range 4850—6600 A. are given for the two phases of the Nova.

A. J. E. W.

Accuracy of calibration of X-ray doses. H. BEHNKEN (Physikal Z., 1936, 37, 878—881).—Abs. determination of X-ray doses can be made in international Röntgen units with an accuracy of 0.1%. A. J. M.

Polarisation of hard X-rays. E. RODGERS (Physical Rev., 1936, [ii], 50, 875-878).—X-Rays scattered at 90° from the primary beam were again scattered at 90° and relative intensities of the tertiary rays parallel and perpendicular to the primary rays were determined with a Geiger-Müller counter. At 80 kv. polarisation was almost complete, but decreased to 69.6% at 800 kv. Results are in general agreement with Nishina's theory. N. M. B.

Scattering of X-rays by a spinning electron. A. H. COMPTON (Physical Rev., 1936, [ii], 50, 878— 881).—Mathematical. A theory based on classical electrodynamics is presented. N. M. B. Characteristics of the Compton modified band. P. KIRKPATRICK, P. A. Ross, and H. O. RITLAND (Physical Rev., 1936, [ii], 50, 928—935; cf. A., 1934, 1282).—The shapes of Compton modified bands, calc. for all scattering elements from H to A, vary periodically with at. no. Breadths of observed modified bands exceed calc. breadths by 75% for C scatterers and 140% for Be. The intensity of modified to unmodified radiation from graphite scatterers agrees. within 10% with predictions based on the Wentzel-Waller theory of scattering angles 27—139°. A still smaller shift of the max. in the modified band than that given by the Compton equation is indicated.

N. M. B.

Coincidence in time in Compton scattering. B. HOFFMANN, A. G. SHENSTONE, and L. A. TURNER (Physical Rev., 1936, [ii], 50, 1092).—In the use of a photon counter, the possibility of a time-lag between the arrival of a photon and the ejection of a scattered electron is discussed. N. M. B.

Interference from lattice sources on excitation by X-rays. G. BORRMANN (Ann. Physik, 1936, [v], 27, 669—693; cf. A., 1935, 1193).—Interference patterns have been observed due to multiple reflexions of the secondary radiation excited by X-rays in single crystals of Cu, magnetite, Fe pyrites, stroutianite, Zn blende, and KBr. The intensity of the interference patterns decreases in this order. Results are in agreement with the theory of Laue (*ibid.*, 1306) and differ from those obtained by excitation with electrons on account of the deeper penetration of X-rays into the crystal. All lines appear bright for angle of emergence <17° to the crystal surface. At larger angles lines may be bright, or dark, or show a bright-dark structure. Qual. explanations of these appearances are given.

0. D. S.

Fine structure of the emission of a copper single-crystal anticathode. H. VOGES (Ann. Physik, 1936, [v], 27, 694—720; cf. A., 1935, 1306).— All the interference lines calc. from the theory of Laue have been observed. The measured breadth of dark lines is > that calc. without allowance for the breadth of the focal spot, but follows a similar curve with increasing Bragg angle. At an angle of emergence  $<6^{\circ}$  to the crystal surface all lines appear bright. At greater angles all lines show an intermediate region of bright–dark structure. Theoretical explanations of the structure of the lines are given. It is deduced that X-rays are coherent over an angle of 144°. O. D. S.

Effects of chemical combination with oxygen and fluorine on the  $K\alpha_{1,2}$  doublet of some of the lighter elements [Ne to C1]. N. G. JOHNSON (Nature, 1936, 138, 1056—1057; cf. A., 1936, 1311).— The displacement in the  $K\alpha_{1,2}$  doublet which occurs appears to increase as the square of the max. valency of the combining element. L. S. T.

 $K_{\alpha}$  Satellite lines for elements Zn (30) to Pd (46). C. H. SHAW and L. G. PARRATT (Physical Rev., 1936, [ii], 50, 1006—1012).—Investigations previously reported (cf. A., 1936, 1041) are extended to Zn (30)—Pb (46). In the  $K_{\alpha_{1,4}}$  group, components

55

1 (a)

 $\alpha', \alpha_3, \alpha_4$ , and  $\alpha_3'$  are found for Zn and As,  $\alpha_3, \alpha_4$ , and  $\alpha_3'$  for Se, Br, Sr, and Zr, and  $\alpha_4$  and  $\alpha_3'$  for Nb, Mo, and Pd. Data for  $\lambda\lambda$ , relative intensity, and line width at half-max. intensity for each component are given. N. M. B.

**X-Ray spark lines.** F. WISSHAK (Ann. Physik, 1937, [v], 28, 71-86).—The intensity of X-ray spark lines, or satellites, has been investigated with the  $K\alpha_{3,4}$  lines of Cu, the variation of relative intensity with potential being determined. The relative intensity is practically const. for potentials between 19 and 48 kv. The excitation potential of the lines is  $11\pm1.5$  kv. A. J. M.

Influence of chemical combination on the form of the  $L\alpha$  line of copper and nickel. E. SAUR (Z. Physik, 1936, 103, 421-433).—With a high-vac. crystal spectrograph and microphotometer the  $L\alpha$  line of Cu and Ni and of some of their alloys and compounds was examined. The half-width val. of the Cu  $L\alpha$  line showed variations with mode of combination up to 14%, but the line components showed no changes of position. Variations were negligible in the case of Ni. A. E. M.

X-Ray levels and atomic constants. II. H. R. ROBINSON (Phil. Mag., 1936, [vii], 22, 1129—1136; cf. A., 1935, 139).—Results obtained for h/e by various methods are compared. The magnetic spectrometer gives  $e/m_0 \times e/h \times \rho = 1.277_4 \times 10^{24}$  in the usual mixed units ( $\rho = \text{ratio}$  of true to conventional Moseley–Siegbahn  $\lambda$  of X-radiation). Using the most trustworthy vals. for  $e/m_0$  and  $\rho$ , this gives  $1.379 \times 10^{-17}$  for h/e, agreeing well with the val. obtained from the Rydberg const., but less well with those obtained from the inverse photo-electric effect (Kirkpatrick *et al.*, A., 1934, 586). A. J. M.

Cooling of a surface by photo-electric emission. H. M. ZENOR (Physical Rev., 1936, [ii], 50, 1050— 1053).—The cooling of a thin Cs surface deposited on Pt, when photo-electrons flowed from the surface, was measured by a Fe-Ni thermocouple. The energy loss agreed approx. with theory. N. M. B.

Relationship between corpuscular and thermal oscillations in electron tubes. W. SCHOTTKY (Z. Physik, 1937, 104, 248—274).—A description of work in this field and theoretical discussion. L. G. G.

Emission of negative electricity by glowing platinum in chlorine. S. KALANDYK (Z. Physik, 1936, 103, 583—597).—At a pressure of 0.01 mm. Hg, below 1200°,  $Cl_2$  greatly increases the negative emission from Pt, but not the energy of emission. An active layer is formed which evaporates above 1200°. For 1.5 mm. Hg, below 900°, the energy of emergence of electrons is about 1 volt, but above 1000° is comparable with Pt in vac. (6 volts).

## A. E. M.

Experiments on the theory of electron emission under the influence of strong fields. (A) E. W. MÜLLER. (B) W. SCHOTTKY (Physikal. Z., 1936, 37, 838-841, 841-842).-(A) It has been shown experimentally, in agreement with theory, that no cooling of the cathode occurs when electrons are emitted from it under the action of a powerful field. The energy distribution of the field electrons was determined; it indicates that electrons leave the cathode without the necessity of exceeding a potential threshold. The effect of the emission work ( $\phi$ ) on the field current is > that required by the wavemechanical theory of penetration of a potential barrier. For Ba and Mg layers a  $\phi^3$  instead of a  $\phi^{3/2}$ law is followed.

(B) A discussion of the above results from the viewpoint of wave-mechanics. A. J. M.

Anomalous charging phenomena for very slow positive rays. F. WOLF (Physikal. Z., 1936, 37, 854-855).—Investigation of numerous collision processes between H<sub>2</sub>, N<sub>2</sub>, He, Ne, and A and their ions indicates that for slow rays the charging cross-section with respect to ions shows a type of Ramsauer effect. A. J. M.

Absolute values of the electron drift velocity in nitrogen, helium, neon, and argon. R. A. NIELSEN (Physical Rev., 1936, [ii], 50, 950—954).— The vals. obtained experimentally by the electrical shutter method (cf. A., 1936, 540) show a discrepancy from calc. vals., and in every case the deviation is explained on the view that the distribution of electron velocities is such that occasional inelastic collisions occur. Assuming these, a val. for the probability of excitation of electronic levels in He, Ne, and A is calc. N. M. B.

Mass-spectrographic examination of negative ions in gas discharges at higher pressures. O. TUXEN (Z. Physik, 1936, 103, 463-484).—The negative charge carriers in gas discharges are examined mass-spectrographically at pressures between 0.5 and 10 mm. Hg, by acceleration through a perforated anode. In air, besides electrons, O<sup>-</sup>, and O<sub>2</sub><sup>-</sup>, are found NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>, in H<sub>2</sub> only H<sup>-</sup>, and in the inert gases no negative ions. L. G. G.

Measurement of velocity and energy distributions. R. KOLLATH (Ann. Physik, 1936, [v], 27, 721—741).—Methods used in the deduction from experimental data of the velocity and energy distributions in beams of charged particles are criticised and found to be in error in many cases. The methods of measurement by retarding electric field, transverse magnetic field, and transverse electric field are treated in detail. Important alterations in published data result from the corrections applied. O. D. S.

Determination of at. wts. by means of the micro-balance, and the values obtained for carbon, nitrogen, and fluorine. W. CAWOOD and H. S. PATTERSON (Phil. Trans., 1936, A, 236, 77-102; cf. A., 1935, 425) .-- The theory of the quartz microbalance is discussed and a description is given of an improved accurate instrument in which the beam is suspended on quartz fibres. Adsorption was compensated by adjusting the instrument to give the accepted val. for the mol. wt. of SO<sub>2</sub>, and errors due to inadequate temp. control, refraction in manometer wall, change in centre of gravity of closed bulb with pressure, etc. were also removed. It was shown that pv is a linear function of p at pressures of 1-3 m. The prep. of pure gases is described. The mol. and at. wts. (0 = 16.0000) are: N<sub>2</sub>O 44.0135, N = 14.007; CO<sub>2</sub>  $44.0101 \pm 0.0020$ ,  $C = 12.010_1 \pm 0.0020$ ;  $C_2H_428.0556 \pm 0.0020$  $0.00087, C = 12.0122 \pm 0.0004; CF_4 87.989_4, F = 18.995$ 

if C = 12.011; MeF 34.0318, F = 18.997 if C = 12.011. Compressibilities deduced from micro-balance results are in agreement with vals. obtained with Andrew's apparatus. If an at. wt. 1.0081 (from mass spectrograph) be used for H instead of 1.0078, the at. wt. of C obtained from  $C_2H_4 = 12.0116$ , in better agreement with the val. from CO<sub>2</sub>, and F from MeF = 18.996. The results are compared with those of other workers. R. S. B.

Difference in at. wt. of oxygen from air and water. E. R. SMITH and H. MATHESON (J. Res. Nat. Bur. Stand., 1936, 17, 625–628).—The density of  $H_2O$  formed by combustion of electrolytic  $H_2$  in air, brought to the same H-isotopic composition as ordinary  $H_2O$ , is 8.6 p.p.m. > that of ordinary  $H_2O$ . The difference is also obtained between  $H_2O$  formed by recombining electrolytic  $H_2$  and  $O_2$  and  $H_2O$  formed by burning electrolytic  $H_2$  in air, and corresponds with a difference of 0.0001 at. wt. unit between the at. wts. of atm. and aq.  $O_2$ . J. W. S.

Relative at. wts. of oxygen in water and air. II. Relative at. wt. of oxygen in fresh water, salt water, and atmospheric water vapour. M. DOLE (J. Chem. Physics, 1936, 4, 778-780).— Purified Lake Michigan  $H_2O$  appears to be nearly exactly intermediate in density between purified Atlantic Ocean  $H_2O$  and  $H_2O$  condensed from the atm., the difference being due to differences in the ratios of the O isotopes. The bearing of these results on theories explaining the relatively large concn. of <sup>18</sup>O in the atm. is discussed. W. R. A.

Molar ratios  $CO_2: O_2$  and  $N_2O: O_2$ . Revision of the at. wt. of carbon and nitrogen. E. MOLES and (SENORITA) T. TORAL (Monatsh., 1936, 69, 342— 362).—The method of limiting densities furnishes the most exact vals. for the mol. and at. wt. of gases. At. wts. calc. from the molar ratios  $CO_2: O_2$  and  $N_2O: O_2$ are  $12.007 \pm 0.0005$  and  $14.008(3) \pm 0.0005$  for C and N, respectively. The slightly higher vals. obtained with the micro-balance are attributed to adsorption.

R. S.

Revision of the at. wt. of arsenic. II. Synthesis and analysis of arsenic tribromide. J. H. KÉEPELKA and M. KOČNAR (Coll. Czech. Chem. Comm., 1936, 8, 485–495).—The synthesis of AsBr<sub>3</sub> from pure As and Br is described. From determinations of the ratios AsBr<sub>3</sub>: 3Ag and AsBr<sub>3</sub>: 3AgBr, the at. wt. of As is 74.923 (Ag 107.880, Br 79.916) in better agreement with Aston's val. than is the International val. J. G. A. G.

At. wt. of iodine. E. MOLES (Coll. Czech. Chem. Comm., 1936, 8, 479–484).—Discrepancies between the accepted at. wt. of I and the vals. derived from the ratios  $I_2O_5$ : 2Ag (A., 1909, ii, 225) and  $I_2$ :  $I_2O_5$  (A., 1931, 543) are removed by using, in the *d* correction, the recently determined  $d_4^{15}$  5.278 of  $I_2O_5$  in place of the lower val. previously accepted. The at. wt. of I is  $126.917 \pm 0.001$ . J. G. A. G.

Double-focussing mass spectrograph and the masses of <sup>15</sup>N and <sup>18</sup>O. J. MATTAUCH (Physical Rev., 1936, [ii], **50**, 1089 ; cf. A., 1936, 1440).—A correction. N. M. B.

Mass-spectrographic study of the isotopes of argon, potassium, rubidium, zinc, and cadmium. A. O. NIER (Physical Rev., 1936, [ii], 50, 1041-1045).—A detailed account of investigations previously reported (cf. A., 1936, 401), with the addition of results for Cd. Isotopes and % abundances for Cd are: 116 (7.3), 114 (28.0), 113 (12.3), 112 (24.2), 111 (13.0), 110 (12.8), 108 (1.0), 106 (1.4). Calculations indicate that the radioactivity of K and Rb is due to the decay of <sup>40</sup>K and <sup>87</sup>Rb, respectively. N. M. B.

Isotopy of radio-iodine <sup>125</sup>I and ordinary iodine <sup>123</sup>I. M. GUILLOT and B. GOLDSOHMIDT (Bull. Soc. chim., 1936, [v], 3, 2371–2374).—<sup>128</sup>I, obtained from EtI containing free I by the method of Szilard and Chalmers (A., 1934, 1152), is converted, together with the added I, into PbI<sub>2</sub>. When the latter is fractionally crystallised all fractions are found to have the same activity, showing that ordinary I and its irradiation product are isotopic. F. L. U.

Second isotope of lutecium and magnetic moment and quadrupole moment of the  ${}^{15}_{11}Lu$ nucleus. H. GOLLNOW (Z. Physik, 1936, 103, 443– 453).—Hyperfine structure examination of Lu I lines leads to the discovery of a hitherto unknown isotope (173 or 177) with relative abundance 1.5% and with spin I = 7/2 (9/2?). For the  ${}^{17}_{71}Lu$  nucleus the magnetic moment is  $\mu = \sim +2.6$  nuclear magnetons and the quadrupole moment  $q = +5.9 \times 10^{-24}$ . A. E. M.

Natural system of the elements from the viewpoint of nuclear physics. W. DE GROOT (Chem. Weekblad, 1937, 34, 3-7).—A lecture. S. C.

Thermal effect of rays from radioactive bodies. A. S. SANIELEVICI (J. Chim. phys., 1936, 33, 759—800).—A sensitive adiabatic non-isothermal calorimeter is described. The data refer to the disintegration of Po and members of the Ac series. Periods of half val. are confirmed and new vals. of thermal effects are recorded. The thermal method affords trustworthy vals. of the Ac content of actiniferous products. J. G. A. G.

Columnar ionisation. W. R. KANNE and J. A. BEARDEN (Physical Rev., 1936, [ii], 50, 935–938).— The ionisation collected from single  $\alpha$ -particles has been measured as a function of the angle between the path of the particle and the direction of the electric field for field strengths of 8, 100, and 500 volts per cm. and air pressures of 1 and 2 atm. Results agree with curves based on Jaffé's theory. For low field strengths the loss of ions by recombination is appreciable.

N. M. B.

Ionisation measurements on single  $\alpha$  rays. W. JENTSOHKE (Sitzungsber. Akad. Wiss. Wien, 1935, [iia], 144, 151—173; Chem. Zentr., 1936, i, 1566).— From measurements of ionisation simultaneously made at two points on the path, the ionisation curve of single  $\alpha$ -rays from Po and Th-C' is constructed. The total ionisation of rays of equal initial velocity is variable, but is related to the range. J. S. A.

Method of counting α-rays emitted from uranium. R. SCHIEDT (Sitzungsber, Akad. Wiss. Wien, 1935, [iia], 144, 175—190; Chem. Zentr., 1936, i, 1566).—A valve electrometer method is described. J. S. A. Simple apparatus for demonstrating scattering of  $\alpha$ -rays. R. MERCIER and P. SCHERRER (Helv. phys. Acta, 1935, 8, 589—590; Chem. Zentr., 1936, i, 1566).—The no. of  $\alpha$ -particles incident at various scattering angles on a counter is measured.

Absolute velocity of  $\alpha$ -particles from radium-C'. G. H. BRIGGS (Proc. Roy. Soc., 1936, A, 157, 183—194).—Precision measurements of  $H_{\rho}$  for the  $\alpha$ -particles from Ra-C' are described; the max. error is of the order of 1 in 10<sup>4</sup>. Using for E/M for the  $\alpha$ -particle a val. calc. from the faraday and the at. wt. of He, the velocity (1.921  $\times$  10<sup>9</sup> cm. per sec.) and the energy have been calc. L. B.

Influence of pressure and temperature on the recombination coefficient and ionisation by  $\gamma$ -rays in air and carbon dioxide. W. MÄCHLER (Z. Physik, 1936, 104, 1—33).—A continuation of earlier work (A., 1936, 541) with special reference to the influence of field strength and pressure on the temp. coeff. of the ionic current. L. G. G.

Absorption of hard  $\gamma$ -rays by light elements. J. C. JACOBSEN (Z. Physik, 1936, 103, 747—755).— With  $\gamma$ -rays from Ra-Th ( $h\nu = 2.6 \times 10^6$  volts) the absorption coeff. per electron is given by  $\mu = 3.8 \times 10^{-28} \times$  at. no., in good agreement with calculations of Bethe. Photo-absorption is very small for light elements, but measurements with heavy elements agree with calc. vals. A. E. M.

Absorption and diffusion of slow neutrons. E. AMALDI and E. FERMI (Physical Rev., 1936, [ii], 50, 899—928).—A detailed study of the absorption properties of slow neutrons establishes the existence of absorption bands which correspond with energy intervals sufficiently narrow to allow the isolation of relatively homogeneous neutron groups. Experiments and considerations to disclose the characteristics of the absorption and scattering properties of the various groups are described. N. M. B.

Diffusion of slow neutrons. G. C. WICK (Atti R. Accad. Lincei, 1936, [vi], 23, 774-782).-Mathematical. O. J. W.

Slowing down of neutrons in water. G. HOR-VAY (Physical Rev., 1936, [ii], 50, 897–898).—A simple method is given for estimating initial neutron energies from final energy and mean square distance of travel, using Fermi's expression for diffusion of neutrons in  $H_2O$ . N. M. B.

Scattering of neutrons by protons. E. T. BOOTH and C. HURST (Nature, 1936, 138, 1011).— The mean free path found for 2.4-m.e.v. neutrons in paraffin wax is  $4.6 \pm 0.9$  cm., corresponding with a cross-section of  $1.8 \pm 0.4 \times 10^{-24}$  cm.<sup>2</sup> for 2.4-m.e.v. neutrons scattered by protons. This val., together with those found by other investigators for neutrons of different energies, is compared with the theoretical curve derived from Wigner's formula. L. S. T.

Neutron-proton interaction: scattering of neutrons by protons. W. D. HARKINS, M. D. KAMEN, H. W. NEWSON, and D. M. GANS (Physical Rev., 1936, [ii], 50, 980-991).—The angular distribution in intensity of recoil protons has been

investigated in  $H_2$ ,  $C_2H_4$ , and  $H_2S$ , and the divergence of available data is discussed. Present theories are shown to be inadequate. N. M. P.

Scattering of neutrons in matter. III. L. S. ORNSTEIN (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 1049—1053; cf. this vol., 5).—Mathematical. O. D. S.

Production of spaces with high neutron concentration. H. R. VON TRAUBENBERG and H. ADAM (Naturwiss., 1936, 24, 797).—The strong backscattering of neutrons at Fe (and weaker at Pb) observed by Mitchell *et al.* (A., 1936, 1045) has been confirmed, and the effect has been used to obtain a high concn. of neutrons in enclosed spaces with Fe or Pb walls. A. J. M.

Atomic disintegration by particles of low energy. E. H. S. BURHOF (Proc. Camb. Phil. Soc., 1936, 32, 643-647).—A method of producing homogeneous ion beams of energies up to 20 kv. from a low-voltage arc is described. Ion currents up to 0.5 milliamp. are obtainable. The reactions  ${}_{1}^{2}H + {}_{1}^{2}H \rightarrow$  ${}_{1}^{3}H + {}_{1}^{1}H$  and  ${}_{3}^{2}Li + {}_{1}^{1}H \rightarrow {}_{2}^{4}He + {}_{2}^{4}He$  were detected using bombarding deuterons or protons of energies 8 and 17 kv., respectively. A. J. E. W.

Efficiency of the  $D \rightarrow D$  nuclear reaction. R. DÖPEL (Ann. Physik, 1937, [v], 28, 87–96).—A new type of apparatus for studying at. disintegration is described and the efficiency of the processes  ${}^{2}D + {}^{2}D \rightarrow {}^{1}H + {}^{1}H$  and  ${}^{2}D + {}^{2}D \rightarrow {}^{3}He + {}^{1}n$  has been re-determined between 10 and 200 kv. The val. at 100 kv. is about 10<sup>-9</sup>, being considerably < the vals. obtained by other workers. A. J. M.

Scattering of protons by protons. T. SEXL (Naturwiss., 1936, 24, 795—796).—Results of experiments on scattering of protons by protons at a const. scattering angle of 45° are compared with theory (A., 1936, 774). A. J. M.

Negative proton and some artificial radioactivities. R. J. WALEN and M. E. NAHMIAS (Compt. rend., 1936, 203, 1149—1151).—The reactions  ${}^{1}_{6}B + {}^{1}_{6}n \rightarrow {}^{1}_{6}C + {}^{1}_{7}\pi$  and  ${}^{22}_{12}Mg + {}^{1}_{6}n \rightarrow {}^{1}_{13}Al + {}^{1}_{7}\pi$  ( ${}^{1}_{7}\pi =$  "negative proton") could not be detected. Neutron bombardment of B induces activity of period I sec.; probably  ${}^{11}B + {}^{1}_{6}n \rightarrow {}^{3}_{5}Li + {}^{4}_{2}He$ . A period of 0.75 sec. was also observed in Li, involving neutron capture. A. J. E. W.

Disintegration of nitrogen by slow neutrons. W. E. BURCHAM and M. GOLDHABER (Proc. Camb. Phil. Soc., 1936, 32, 632—636).—A method of distinguishing the emission of  $\alpha$ -particles and protons, using photographic emulsions of different sensitivity, shows the reaction to be  ${}^{1}_{7}N + {}^{1}_{0}n \rightarrow {}^{1}_{4}C + {}^{1}_{1}H$ . The cross-section is approx.  $10^{-24}$  sq. cm. A. J. E. W.

Transmutation of potassium, chlorine, and phosphorus by Th-C'  $\alpha$ -particles. E. POLLARD and C. J. BRASEFIELD (Physical Rev., 1936, [ii], 50, 890—894; cf. May, A., 1936, 1173).—Observation of the energy distribution of emitted protons shows that these occur in groups corresponding with discrete vals. of the nuclear energy changes. Similarity of behaviour for the three (4n + 3) type elements is found; each gives groups with average energy change difference

J. S. A.

1.5 m.e.v. The vals.  $33.9799\pm0.0015$  and  $37.9753\pm0.0016$  are deduced for the masses of <sup>34</sup>S and <sup>38</sup>A, respectively. N. M. B.

Period of radioactive phosphorus  $^{15}_{15}$ P. G. J. SIZOO and C. P. KOENE (Physica, 1936, 3, 1053— 1056).—A method for the relative measurement of weak activities, eliminating "background ionisation" corrections, is described. The period of  $^{22}_{15}$ P is 15.0 $\pm$ 0.1 days. A. J. E. W.

Radiations emitted from artificially produced y-Rays radioactive substances. II. from several elements. J. R. RICHARDSON and F. N. D. KURIE (Physical Rev., 1936, [ii], 50, 999-1006; cf. A., 1936, 542).-Depending on the measurement of the momentum distribution of the Compton recoil electrons from thin mica in a cloud chamber traversed by a magnetic field, a method for measuring energy and relative intensity of  $\gamma$ -rays from light elements in the energy range 0.5-5 m.e.v. is discussed. The radiation from <sup>41</sup>A appears to be monochromatic and of energy 1.37 m.e.v.; <sup>24</sup>Na emits lines at 0.95, 1.93, and 3.08 m.e.v.; the two guanta annihilation radiation from the positrons of <sup>13</sup>N corresponds with 0.51 m.e.v. Results are in agreement with theory.

N. M. B.

Artificial radioactivity of copper, a branch reaction. S. N. VAN VOORHIS (Physical Rev., 1936, [ii], 50, 895—897; cf. Lawrence, A., 1935, 1296).—The radioactive product of longer half-life produced in Cu by deuteron bombardment emits electrons and positrons in the ratio 1.6 to 1. The half-life is  $12.8\pm0.1$  hr. The excitation curve of positrons and electrons for deuterons of different energies agrees with Oppenheimer's theoretical expression (cf. *ibid.*, 1296). The upper limits of the energy distribution of the positrons and electrons, as found by cloud chamber photographs, are 0.79 and 0.83 m.e.v., respectively, indicating that the activity is due to <sup>64</sup>Cu which branches in disintegrating, going either to Zn or Ni. N. M. B.

Nuclear reactions. S. WESTIN (Tids. Kjemi, 1936, 16, 151–155).—A lecture. M. H. M. A.

Constitution of matter and artificial radioactivity. F. JOLIOT (Bull. Acad. Sci. U.R.S.S., 1936, 613-628).—A lecture.

Heavy particle component of the cosmic radiation. C. G. MONTGOMERY and D. D. MONT-GOMERY (Physical Rev., 1936, [ii], 50, 975—976; cf. A., 1936, 1315).—The results of Brode (cf. *ibid.*, 1441) are examined on the theory developed by Swann (cf. *ibid.*, 542). N. M. B.

Cosmic-ray shower production and absorption in various materials. J. E. MORGAN and W. M. NIELSEN (Physical Rev., 1936, [ii], 50, 882—889).— Measurements of shower production in thin pieces of C, Al, Cu, Sn, and Pb indicate that the increase in counting rate associated with each atom in the producing material  $\propto \text{the } 2 \cdot 0 \pm 0 \cdot 2$  power of the at. no. Z of the element concerned, and for heavy elements increases faster than the first power of the thickness of the producing material. Absorption per atom of showers from Pb, in Pb, Sn, Cu, Al, and C varies over

 $Z^{1-2}$ . Rossi transition curves for Pb, Fe, and Al are given. N. M. B.

Precision cosmic-ray measurements up to within 1—2% of the top of the atmosphere. R. A. MILLIKAN, H. V. NEHEE, and S. K. HAYNES (Physical Rev., 1936, [ii], 50, 992—998, 1191).—The ionisation in self-recording electroscopes sent by balloon into the stratosphere shows a max. at 47.6 mm. atm. pressure and falls 22% at 12.9 mm. pressure (92,000 ft., or 98.3% atm. altitude). Results indicate that atm. cosmic-ray ionisation is not appreciably due to incoming protons, and that the Oppenheimer–Bethe– Heitler law of nuclear absorption is not valid for incoming electrons of a few billion c.v. energy.

N. M. B.

Atom nucleus problem. I. E. TAMM (Bull. Acad. Sci. U.R.S.S., 1936, 301-323).—A lecture. J. J. B.

Nuclear physics. S. FLÜCGE and A. KREBS (Physikal. Z., 1937, 38, 13-36).-A summary.

Fock equations for complex configurations. G. H. SHORTLEY (Physical Rev., 1936, [ii], **50**, 1072— 1075; cf. Brown, A., 1933, 996).—Mathematical. N. M. B.

Atomic wave functions for two stages of ionisation of silicon. H. L. DONLEY (Physical Rev., 1936, [ii], 50, 1012—1016).—Full data calc. by the self-consistent field method are tabulated for Si<sup>+2</sup> and Si<sup>+3</sup>. N. M. B.

Properties of matter at very high pressures and temperatures. F. HUND (Physikal. Z., 1936, 37, 853).—The variations in the properties of matter as the pressure is increased to  $10^{26}$  atm. and the temp. to  $10^{12^{\circ}}$  are discussed. A. J. M.

Metastable states of atomic nuclei. C. F. von WEIZSÄCKER (Naturwiss., 1936, 24, 813—814).— The theory of the "isomerism" of at. nuclei breaking up with liberation of  $\beta$ -rays is discussed. A. J. M.

Regularities in the structure of atomic nuclei. H. SCHÜLER and H. KORSCHING (Naturwiss., 1936, 24, 796—797; cf. A., 1936, 1316).—Comparison of mechanical and magnetic moments of isotopes of elements which have only two isotopes (elements containing an odd no. of protons besides paired neutrons) makes it possible to discover how the at. nucleus changes when two neutrons are introduced. This brings about no change in the mechanical moment, but for some nuclei (Ga, Eu) the magnetic moment is considerably increased, whilst for others (Cu, Re, Tl) there is little change. In the latter case the magnetic moment is greater for the heavier nucleus, and the relative increase is equal to the relative increase in mass of the nucleus. A. J. M.

Bothe-Geiger experiment. W. E. BURCHAM and W. B. LEWIS (Proc. Camb. Phil. Soc., 1936, 32, 637—642; cf. A., 1925, ii, 1).—Coincident emission of electrons and photons during scattering of X-rays by a 50% H<sub>2</sub>-He mixture has been shown, using counters enclosing a large solid angle, and an electrical method for recording coincidences. A. J. E. W.

Fermi's theory of  $\beta$ -decay. E. GORA (Proc. Indian Acad. Sci., 1936, 4, A, 551-554).—Theoretical. R. S. Theory of the  $\beta$ -transformation and nuclear forces. I. G. WENTZEL (Z. Physik, 1936, 104, 34-47).—Mathematical. L. G. G.

Impossibility of a neutrino theory of light. V. FOCK (Compt. rend. Acad. Sci. U.R.S.S., 1936, 4, 229—231).—It is shown that any neutrino theory of light is incompatible with the superposition principle. The theory of Jordan is criticised. O. D. S.

Relativistically invariant formulation of the neutrino theory of light. R. DE L. KRONIG (Physica, 1936, 3, 1120–1132).—Mathematical. A. J. E. W.

Binding of neutrons and protons. J. B. FISK, L. I. SCHIFF, and W. SHOCKLEY (Physical Rev., 1936, [ii], 50, 1090—1091, 1191; cf. this vol., 6; Present, A., 1935, 1442).—Mathematical. N. M. B.

Nuclear radius and many-body problem. H. A. BETHE (Physical Rev., 1936, [ii], 50, 977— 979).—Mathematical. Radioactive  $\alpha$ -decay as a many-body problem gives  $13 \times 10^{-13}$  cm. $\pm 10\%$  for the nuclear radius, agreeing with the experimental cross-section for the disintegration of heavy nuclei by deuterons. N. M. B.

Geometrical theory of matter. G. FOURNIER (Compt. rend., 1936, 203, 1138—1140).—At. nuclei are supposed built up of octahedral and tetrahedral units, corresponding with He nuclei, and protons or neutrons, respectively. A. J. E. W.

Polarisation effects in quartz spectrographs. G. BOLLA (Z. Physik, 1936, 103, 756—767).—Quartz spectrography of continuous spectra with a Glan– Foucault prism between the light source and slit is shown to give an alternating fluctuation in intensity in the resultant spectrogram. This phenomenon is discussed with reference to the components of the spectrograph. L. G. G.

Spectral absorption of neodymium glasses. F. WEIDERT (Oesterr. Chem.-Ztg., 1936, 39, 187).— Changes in absorption spectra of glasses of const. Nd content are related to the variations in composition of the glass. Interference with the normal Nd absorption is greatest for cations of small radius, *i.e.*, development of the full absorption spectrum occurs progressively on replacement of  $\text{Li}_2\text{O}$  by  $\text{Na}_2\text{O}$  by  $\text{K}_2\text{O}$  etc. J. S. A.

Equilibrium  $2H_2+O_2 \longrightarrow 2H_2O$  in the glow discharge. A. GUNTHER-SCHULZE and H. SCHNIT-GER (Z. Physik, 1936, 103, 627-632).—A glow discharge in H<sub>2</sub>O vapour causes decomp. to H<sub>2</sub> and O<sub>2</sub>. The cathodic portion of the discharge appears to act as a catalyst of which the apparent temp. rises from 1900° abs. to 2800° abs. as the pressure of H<sub>2</sub>O vapour increases from 0.04 to 20.0 mm. Hg. H. C. G.

Intensities in the  ${}^{3}\Pi, {}^{3}\Sigma$  band of PH. P. NOLAN and F. A. JENKINS (Physical Rev., 1936, [ii], 50, 943—949).—Measurements of relative intensities of the lines in the (0, 0) band of PH at  $\lambda$  3400, excited by a high-voltage discharge through H<sub>2</sub> and P vapour, are given. The distribution of mols. in the initial states, evaluated by the sum rule, corresponds with thermal equilibrium at 696° abs. Calc. and experimental intensity factors are tabulated and discussed. N. M. B.

Band spectrum of gold hydride. T. HEIMER (Z. Physik, 1937, 104, 303—308).—From an analysis of the arc emission spectrum of AuH, at a dispersion of 1.95 A. per mm., new vibration levels have been assigned to the  $1\Sigma^* - 1\Sigma$  band system. L. G. G.

Band spectrum of bismuth deuteride. A. HEIMER (Z. Physik, 1936, 103, 621-626).—The band system  ${}^{1}\Sigma^{*} - {}^{1}\Sigma$  has been obtained and analysed. Three nuclear vibration levels have been determined, both for initial and final states, and dissociation vals. are given. A. E. M.

Calculation of the ultra-violet absorption frequencies of the alkali halides. T. NEUGE-BAUER (Z. Physik, 1937, 104, 207-218).—Mathematical. The energies of the absorption frequencies are calc. L. G. G.

Spectrum of calcium oxide. P. H. BRODERSEN (Z. Physik, 1936, 104, 135—156).—The band spectrum of CaO in the region 3700-4900 A. has been photographed by means of a hollow cathode at a dispersion of 0.2 mm. per A. The consts. of the electron terms and the energy levels of the dissociation products are derived and discussed. L. G. G.

Spectra of SeO and SeO<sub>2</sub>. R. K. ASUNDI, M. JAN-KHAN, and R. SAMUEL (Proc. Roy. Soc., 1936, A, 157, 28—49; cf. A., 1935, 1188).—Analyses have been made of the emission spectrum of SeO and the absorption spectrum of SeO<sub>2</sub>. The energies of excitation and the energies of the SeO linkings are almost equal in the two mols. The frequency of the symmetric valency vibration of SeO<sub>2</sub> is nearly identical with the vibrational frequency of SeO, both in the normal and excited states. The results indicate strong localisation of the SeO linkings in SeO<sub>2</sub>.

L. L. B.

Absorption and emission spectra of ions of the rare-earths in the solid state. H. GOBREOHT (Physikal. Z., 1936, 37, 851—852).—A study of the infra-red spectra of some rare-earth salts, particularly salts of Eu<sup>+++</sup>, shows that there are certain transitions for which it is possible to observe the Stark separation brought about by the field of the crystal.

A. J. M.

Emission spectra of free radicals produced by photo-dissociation of polyatomic molecules in the Schumann ultra-violet. H. NEUJMIN and A. TERENIN (Acta Physicochim. U.R.S.S., 1936, 5, 465-490).—Excited radicals formed during photodissociation are I from  $I_2$ ; OH from  $H_2O$ , MeOH, EtOH, HCO<sub>2</sub>H, and AcOH; CN from MeCN; NH<sub>2</sub> from NH<sub>3</sub> and N<sub>2</sub>H<sub>4</sub>. In the case of HCO<sub>2</sub>H there is some evidence of the formation of HCO. The relative quenching efficiencies of CO, H<sub>2</sub>, N<sub>2</sub>, and A for OH are 1.0, 0.2, 0.04, and 0.01. The high activity of CO or H<sub>2</sub> towards OH is attributed to a redistribution of the electronic energy in one of the pairs leading to degradation of energy without, however, the completion of a chemical reaction. The rotational structure of the OH band is completely changed by H<sub>2</sub> and He, though He shows no quenching action. The emissions due to CN and  $NH_2$  are quenched by  $N_2$  and, in the case of  $NH_2$ , by  $H_2$  and A. C. R. H.

Band displacement as a consequence of intermolecular forces. G. KORTÜM (Naturwiss., 1936, 24, 780-781).-The displacement of absorption bands on dissolution of substances producing ions has been investigated for the picrate and 2:4-dinitrophenoxide ions in  $H_2O$ , EtOH, and  $H_2O$ -EtOH. In passing from solutions in H<sub>2</sub>O to those in EtOH there is not a simple variation of band displacement. In 40% EtOH the band does not lie between those of the two pure components. If an EtOH solution containing the above ions is added to H<sub>2</sub>O the band is first displaced towards the red, but at a definite [H<sub>2</sub>O] a displacement towards the violet occurs. This inversion is not found in the dielectric const.-composition curve of EtOH-H2O: it is concluded that the band displacement is not necessarily connected with dipole moment. This is supported by the effect of temp. on band displacement in different solvents. A. J. M.

Ultra-violet absorption spectra of simple hydrocarbons. I.  $\Delta^{\tilde{\gamma}}$ -n-Heptene and tetramethylethylene. (MISS) E. P. CARR and (MISS) M. K. WALKER. II. In liquid and solid solution phase. (MISS) E. P. CARR and (MISS) G. P. WALTER. III. In vapour phase in the Schumann region. (MISS) E. P. CARB and (MISS) H. STUCKLEN (J. Chem. Physics, 1936, 4, 751-755, 756-760, 760-768).-I. The ultra-violet absorption spectra of  $\Delta^{\gamma}$ -n-heptene and (:CMe2)2 have been measured in liquid and hexane solution phases between 4000 and 2100 A. and in the vapour phase between 2300 and 1500 A. As the H in  $C_2H_4$  are replaced by alkyl there is a progressive shift of the absorption bands in the Schumann region towards the visible. Comparison with recorded data reveals a parallelism between the spectra of different hydrocarbons having the same configuration with respect to the double linking.

II. Mol. extinction coeffs. of 12 olefine hydrocarbons have been determined between 3300 and 2100 A. The beginning of the absorption curve is characteristic of the no. of alkyls bound to the C of the double linking and is only slightly affected by the nature of the alkyl.

III. Absorption spectra measurements between 2300 and 1500 A. were made for 4 butenes, 5 pentenes, 1 hexene, 2 heptenes, and 2 octenes. For the spectra of all ethylenic derivatives certain general relationships exist, viz., the no. of alkyls bound to the C of the CC groups determines the wave no. of the first absorption band; a progressive shift towards the visible occurs when increasing no. of alkyls are added, but the nature of the alkyl has practically no influence on the position of the first band; where two alkyls are bound to the same C (unsymmetrical substitution) or to different C (symmetrical substitution) the wave no. of the first band is only slightly altered. The bands are analysed and discussed. W. R. A.

Chemical warfare materials. II. Absorption of light in relation to chemical constitution. III. Spectroscopic identification. H. MOHLER and J. PÓLYA (Helv. Chim. Acta, 1936, 19, 1222-1239, 1239-1242; cf. A., 1936, 545).—II. Absorption spectra of pure COMe<sub>2</sub>, COMe·CH<sub>2</sub>Br, COEt·CH<sub>2</sub>Br, COPhMe, COPh·CH<sub>2</sub>Cl, COPh·CH<sub>2</sub>Br, C<sub>6</sub>H<sub>6</sub>, CH<sub>2</sub>Ph·CN, CH<sub>2</sub>Ph·OH, CHPhBr·CN, C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>Br)<sub>2</sub>, CH<sub>2</sub>PhBr, CH<sub>2</sub>PhCl, AsCl<sub>3</sub>, AsEtCl<sub>2</sub>, lewisite I, II, and III, phenarsazine chloride, Clark I and II, Lost, EtSH, Et<sub>2</sub>S, CS<sub>2</sub>, and chloropicrin, alone or in cyclohexane are detailed and discussed. Halogen, particularly Br, shifts the absorption max. towards the red and tends to obscure the fine structure of the C<sub>6</sub>H<sub>6</sub> spectrum.

III. Means of identifying spectrographically Adamsite, Perstoff, and poisons mentioned above are described. R. S. C.

Absorption spectra of dihydropyridine compounds.—See A., III, 68.

Relationship between constitution and spectra of porphyrins. [Energy] level scheme for the porphyrin molecule. H. HELLSTROM (Arkiv Kemi, Min., Geol., 1936, 12, B, No. 13, 6 pp.).—The fluorescence and absorption spectra of the porphyrins are discussed on the basis of a suggested scheme of energy levels and sub-levels in both the gaseous and excited states. A detailed scheme for deuteroporphyrin is given and the  $\lambda$  so calc. are in good agreement with experiment (cf. Hausser *et al.*, A., 1935, 1443).

J. W. B.

Spectra of adsorbed porphyrin. F. BANDOW (Z. physikal. Chem., 1936, B, 34, 323-334; cf. A., 1936, 346, 1048).—The absorption and fluorescence spectra of porphyrins adsorbed on org. and inorg. substances have similar spectral forms to those of solutions of the porphyrins, but there are some differences in the relative intensities of the bands, which are influenced by the nature of the adsorbent and the solvent from which adsorption occurs. The fluorescence and phosphorescence spectra of various porphyrin phosphors are identical. Several complex porphyrin Zn salts have the same spectrum in afterphosphorescence and in phosphorescence during excitation as in solution. R. C.

Absorption spectra of nitroglycerin. K. MASAKI (Bull. Chem. Soc. Japan, 1936, 11, 712—715). —The absorption of nitroglycerin, pure and in EtOH solution, has been measured from 2105 to 4227 A., and bands of some nitroparaffins are enumerated. O.D.S.

Absorption of polar crystals in the infra-red. M. BLACKMAN (Phil. Trans., 1936, A, 236, 103— 131).—The theory of the vibrational spectrum of a plane lattice with one and two particles per cell, and of a cubic lattice of the NaCl type, is derived. Results agree with the infra-red spectrum of NaCl, but with KCl discrepancies occur; the origin of these is discussed. R. S. B.

Absorption spectra of saturated acyclic alcohols in the very near infra-red (6000-9500 A.). The OH band. P. BAROHEWITZ (Compt. rend., 1936, 203, 1244—1247).—Data are given for 20 aliphatic alcohols and halides, and the position and nature of the CH bands discussed. The third harmonic of the OH band at approx. 7400 A. is found in six alcohols at their crit. temp.

A. J. E. W.

Vibration spectra and molecular structure. I. General. Spectrum of the OH group. R. B. BARNES, L. G. BONNER, and E. U. CONDON (J. Chem. Physics, 1936, 4, 772-778).—After a brief discussion of the underlying principles in the interpretation of mol. vibration spectra in problems of mol. structure, the reasons for the appearance or non-appearance of the 3400 cm.-1 frequency in various mols. containing the OH group are discussed. The non-appearance in the Raman spectra of certain alcohols and glycols is attributed to experimental difficulties. This frequency is absent both from the infra-red and Raman spectra of carboxylic acids and certain aromatic compounds containing OH, and the rôle of the H linking in association and chelation is discussed in connexion with these cases. W. R. A.

Infra-red absorption spectra of dioxan-water mixtures. W. GORDY (J. Chem. Physics, 1936, 4, 769—771).—The absorption spectra of various dioxan- $H_2O$  mixtures have been studied between 2.5 and  $6.5 \mu$  and marked changes in the spectrum of  $H_2O$  were observed, especially at low  $[H_2O]$ . Association of the  $H_2O$  and dioxan is suggested as a possible explanation of the observed effects. W. R. A.

Absorption spectra of four aldehydes in the near infra-red. L. KELLNER (Proc. Roy. Soc., 1936, A, 157, 100—113).—A study has been made of the absorption of EtCHO, Pr<sup> $\circ$ </sup>CHO, Bu<sup> $\circ$ </sup>CHO, and Bu<sup> $\beta$ </sup>CHO in the liquid state between 1·1 and 2·1  $\mu$ . The wave-nos. and absorption coeffs. are compared with those of previous investigators. An attempt is made to interpret the absorption frequencies as overtones and combination frequencies of some fundamental vibrations. L. L. B.

Fine structure and perturbation in the rotation-vibration spectrum of acetylene. G. W. FUNKE (Z. Physik, 1937, 104, 169—187).—A repetition of earlier work (A., 1936, 662) with dispersion of 1.8 A. per mm. Two new bands are recorded at 8628 and 8640 A., and the energy scheme is given. L. G. G.

Alleged curvilinear spreading of light rays in scattering media. M. KATALINIC (Kolloid-Z., 1936, 77, 295—298).—The effect obtained by Čoban (Acta phys. Polon., 1935, 4, 7) is due to the formation of haloes on the photographic plate. E. S. H.

Raman investigations with glasses. R. LAN-GENBERG (Ann. Physik, 1937, [v], 28, 104—113).— New results on the Raman spectra of B, Ba, F, Al, and PO<sub>4</sub><sup>'''</sup> glasses are reported. The frequencies due to the lighter oxides (except alkali oxides) in the glasses could be traced, but those due to heavier oxides (BaO, PbO) and the alkali oxides are missing. BO<sub>3</sub><sup>'''</sup> in the glasses has a plane structure as in borates. A. J. M.

Raman spectra of light and heavy phosphine and arsine. M. DE HEMPTINNE and J. M. DELFOSSE (Ann. Soc. Sci. Bruxelles, 1936, 56, B, 373–383; cf. A., 1935, 1445).—The Raman spectra of  $PH_3$ ,  $PD_3$ , AsH<sub>3</sub>, and AsD<sub>3</sub> have been measured. AsD<sub>3</sub> gives lines 1508, 645, and 707 cm.<sup>-1</sup> The consts. of mol. vibration formulæ are calc. Anharmonic vibrations and energies of dissociation are considered.

N. M. B.

Raman spectra of azoimide and carbon suboxide. W. ENGLER and K. W. F. KOHLRAUSCH (Z. physikal. Chem., 1936, B, 34, 214—224).—Force consts. have been calc. from the Raman spectra, and lead to the structures O:C:C:C:O (whole mol. linear) and H·N:N:N (straight N chain), which also agree with the results of electron diffraction experiments.

R. C. Raman effect in electrolytes. I. Raman spectra and electrolytic dissociation. II. Raman effect and the chemical bond. H. J. BERNSTEIN, R. G. ROMANS, O. H. HOWDEN, and W. H. MARTIN (Trans. Roy. Soc. Canada, 1936, [iii], 30, III, 49-57, 57-64).-I. The Raman spectra of conc. aq. solutions of a no. of electrolytes have been investigated. No Raman lines were observed for the electrolytes giving monat. ions. The Raman spectra of those electrolytes which give complex ions are ascribed to complex ions. Variations in the Raman spectra of H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, and AcOH on dilution are ascribed to changes in the degree of hydration and not to varying degrees of dissociation. No lines due to KI are observed in the Raman spectrum of a saturated solution of KI in MeOH.

II. The line due to the OH group has been observed in the Raman spectra of NaOH, MeOH,  $H_2O$ , PhOH, octoic acid, and AcOH. The sharpness and intensity of the line decrease in the above order. The OH line is absent in spectra of CCl<sub>3</sub>·CO<sub>2</sub>H,  $H_2SO_4$ , and HNO<sub>3</sub>. O. D. S.

Raman spectrum of deuterosulphuric acid. A. H. LECKIE (Trans. Faraday Soc., 1936, 32, 1700— 1705; cf. A., 1936, 136).—Raman spectra of  $D_2SO_4$ (from 99.6%  $D_2O$ ), conc. and dil., have been determined. In the case of lines at 570 and 905 cm.<sup>-1</sup> there are isotope shifts in the conc. but not in the dil. acid, affording evidence that these lines are composite, one part being due to  $D_2SO_4$  and the other to one of the ions. F. L. U.

Raman spectra of amines and methylated ammonium ions. J. T. EDSALL (Science, 1936, 84, 423—424).—The relation between the two sets of compounds, as revealed by their Raman spectra, is discussed. L. S. T.

Raman effect and molecular structure. I. Structure of the guanidinium ion. J. GUPTA (J. Indian Chem. Soc., 1936, 13, 575—579).—The principal Raman line occurs at 995 cm.<sup>-1</sup>, whilst there are subsidiary lines at 520 and 1620 cm.<sup>-1</sup> It is inferred that the NH<sub>2</sub> are arranged symmetrically in one plane about the C atom. R. S.

Structure of organic molecules determined by spectral methods. G. ALLARD (Helv. Chim. Acta, 1936, 19, 1270—1287).—The interpretation of the Raman spectra and ultra-violet absorption spectra of org. compounds is discussed theoretically.

J. W. S.

Raman spectrum of deuteromethanol. S. MIZUSHIMA, Y. MORINO, and G. OKAMOTO (Bull. Chem. Soc. Japan, 1936, 11, 698—699).—Raman frequencies 3270—3480 and 1107 of MeOH, attributed to the vibration of H, are shifted to 2420—2560 and 955, respectively, in MeOD, whilst the frequencies associated with MeO are unchanged. R. S. Structure of methyl and ethyl selenides. P. DONZELOT (Compt. rend., 1936, 203, 1069—1070).— Raman and infra-red absorption spectrum data are given, and vibration frequencies deduced. The Se valency angle in Me<sub>2</sub>Se is approx. 99.3°.

A. J. E. W.

Raman effect in dibasic acids in crystalline state. B. ANAND (Proc. Indian Acad. Sci., 1936, 4, A, 603—609).—An apparatus for the study of the Raman spectra of cryst. powders is described, and the Raman spectra of  $H_2C_2O_4, 2H_2O$ ,  $CH_2(CO_2H)_2$ , and  $(CH_2 \cdot CO_2H)_2$  have been determined. Possible modes of vibration, corresponding with the observed frequencies, are discussed and it is inferred that both  $CO_2H$  possess normal structure in the cryst. state.

R. S.

Raman spectrum of keten. H. KOPPER (Z. physikal. Chem., 1936, B, 34, 396-401).—The frequencies of the Raman spectrum, which has been measured at  $-80^{\circ}$  to  $-90^{\circ}$ , correspond with what would be expected for the structure H<sub>2</sub>C:C:O.

R. C.

Raman effect of organic substances. VII. Raman effect of furan derivatives. K. HAN (Bull. Chem. Soc. Japan, 1936, 11, 701—711; cf. A., 1934, 1155).—The Raman spectra have been measured of 2-furfuryl Me and Et ether, 2-furfurylacetone, 2-furylethylene, 2-furonitrile, 2:5-dimethylfuran, 5-methyl-2-furonitrile, and Et 2-methyl-3-furoate. The frequencies of the 2-furfuryl radical are characterised and constitutive effects in the region 1400—1600 cm.<sup>-1</sup> are discussed. O. D. S.

Raman spectrum of decahydronaphthalene. S. M. MITRA (Z. Physik, 1936, 103, 542—545).—52 lines excited by  $\lambda$  4047 and 4358 are given and compared with those obtained for C<sub>10</sub>H<sub>8</sub> and cyclohexane. A. E. M.

Raman spectra of some substituted triphenols and of tannin. B. SUSZ, S. FRIED, and E. BRINER (Helv. Chim. Acta, 1936, 19, 1359—1371; cf. A., 1935, 1446; 1936, 1359).—Additional Raman data are recorded for Me triacetylgallate and acetyltannin, and the results for this class of compound are compared and discussed. J. W. S.

Ionisation of air by irradiated cholesterol. A. H. Roffo and A. E. Roffo (Compt. rend., 1936, 203, 1190-1191).—Cholesterol irradiated for 240 hr. with a Hg-vapour lamp caused ionisation of air.

A. J. E. W.

Influence of temperature on fading time of fluorescence of uranin solutions. S. W. CRAM (Z. Physik, 1936, 103, 551-559).—In EtOH-H<sub>2</sub>O solutions of low concn.  $(1 \times 10^{-4} \text{ g. of uranin per c.c.})$ , the fluorescence resonance time decreases considerably with rise in temp. from 0° to 30°; further rise in temp. has little effect. This temp. effect disappears as concn. of dye increases and is negligible at  $6 \times 10^{-3}$  g. per c.e. Increase in viscosity of solvent also decreases the effect. The theories of Franck and Vavilov do not explain the results. H. C. G.

Rules for fading of polarised fluorescence. II. A. JABŁONSKI (Z. Physik, 1936, 103, 526-535; cf. A., 1935, 915).—Mathematical. Previous work on the depolarising effect due to the Brownian rota-

tional movement of cylindrical mols. is extended to take other depolarising processes into account. It is shown that where fluorescence is unaffected by Brownian rotation, other depolarising processes are also inoperative. H. C. G.

Spectral absorption and fluorescence of dyes in the molecular state. E. E. JELLEY (Nature, 1936, 138, 1009—1010).—Suspensions of many dyes in solids and liquids, possessing a very narrow absorption band associated with fluorescence of slightly longer  $\lambda$ , parallel to the case of the ruby, have been prepared. The fluorescence is a resonance effect and is not light scattered by small solid particles of dye. Both fluorescence and the absorption band disappear when the dye passes into the cryst. state. Details for the prep. of such suspensions of 1: 1'-diethyl- $\psi$ -cyanine chloride and for obtaining the mol. absorption spectrum are given. L. S. T.

Quenching of fluorescence and photo-sensitisation in solutions. Investigation of photosensitisation in solutions. III. E. V. SCHPOLSKI and G. D. SHEREMETIEV (Acta Physicochim. U.R.S.S., 1936, 5, 575-592).-The intensity of fluorescence of solutions of rhodamin G extra (I), uranin (II), eosin B extra (III), and erythrosin in H<sub>o</sub>O, EtOH, and COMe<sub>2</sub> remains unchanged on saturating the solutions with O<sub>2</sub>. Na<sub>2</sub>SO<sub>3</sub> possesses small but distinct quenching power on aq. solutions of (I), (II), and (III), and the effect of temp. on the intensity of luminescence is increased by its presence. Na<sub>2</sub>SO<sub>2</sub> is considered to quench by causing increased association of the dye rather than transferring energy through collisions of the second kind. The intensity of fluorescence of (III) in presence of Na<sub>2</sub>SO<sub>3</sub> is unchanged on oxidising the latter by passing  $O_2$ , indicating that the quenching power of Na<sub>2</sub>SO<sub>4</sub> is the same as that of Na<sub>2</sub>SO<sub>3</sub>. These is no evidence of connexion between quenching by, and photo-sensitised oxidation of, Na<sub>2</sub>SO<sub>3</sub>. HgCl<sub>2</sub> quenches and (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> increases the fluorescence of aq. solutions of (III). Possible causes for this, and the behaviour when both salts are present, are discussed. C. R. H.

Excitation of phosphors in the neon discharge tube. A. RÜTTENAUER (Physikal. Z., 1936, 37, 810– 813).—A Ne discharge tube in which phosphors may be excited by  $\lambda 4000$ —2500 A. and the resonance lines  $\lambda 736$  and 744 is described. It is possible to separate the phosphorescent radiation due to the two  $\lambda$  regions. ZnS phosphors are excited in both the ultra-violet and Schumann ranges, the phosphorescence due to the former increasing in intensity with increasing c.d., whilst that due to the latter decreases in intensity with increasing c.d. and pressure. Commercial ZnSiO<sub>3</sub> phosphors were not excited in either range, but ZnSiO<sub>3</sub> phosphors could be prepared which were very powerfully excited in the Schumann range, but not in the ultra-violet. The excitation of phosphors in Ne discharge tubes may be of industrial importance. A. J. M.

Luminescence phenomena relative to the production of sensibly white light. M. SERVIGNE (Compt. rend., 1936, 203, 1247—1249).—The effect of traces of Sm on the photo-luminescence of Ca molybdate and tungstate, containing traces of Ag, is described. Addition of synthetic willemite to such a mixture enables radiation of the spectral character of sunlight to be produced. A. J. E. W.

Photo-effect at selenium barrier layers. P. GÖRLICH (Z. tech. Physik, 1935, 16, 268–271; Chem. Zentr., 1936, i, 1188).—The Se layer should be  $0.08\pm$ 0.01 mm. thick and formed at 218°. The sputtered Pt layer on the electrode should be 3–4 mµ thick. H. J. E.

Explanation of photo-electric effect with cuprous oxide. W. BEHRENDT (Physikal. Z., 1936, 37, 886-901).—The photoelectric properties of  $Cu_2O$  have been investigated to decide between the kinematic theories of the process put forward by Schottky et al. and the conen. theory of Teichmann et al. which regards the photo-effect as analogous to a thermo-electric effect. The photo-current and potential of the pre-wall effect increase with increasing thickness of the metal electrode up to a saturation val., making an absorption of electrons in the metal probable. This is in agreement with the Schottky theory. The photo-current with zero external resistance is independent of the presence of a barrier layer. Determinations of thermo-electric power show that there is no analogy between it and photo-potential and no qual. or quant. explanation of the latter is possible on the assumption of concn. elements. The views of Wolff on the mechanism of the crystal photoeffect are used to obtain formulæ for the shortcircuit current for the various photo-effects in the Cu<sub>2</sub>O cell, which are in agreement with experiment. The effect of temp. on the short-circuit current was also considered. For the pre-wall effect it is unaffected by temp. The effect of temp. on the hinder-wall effect depends on the change of light absorption and not on any change in electron absorption.

A. J. M.

Artificial rectifying layers with electronic semi-conductors of different conducting types. W. HARTMANN (Physikal. Z., 1936, 37, 862-865).— The rectifying properties of Cu<sub>2</sub>O with artificial "barrier" layers have been investigated. Similar experiments with ZnO (an electron-excess semi-conductor) showed a considerable rectifying effect, the rectifier working in the opposite sense to Cu<sub>2</sub>O. A. J. M.

Effect of light and heavy hydrogen on the selective photo-effect with the alkali metals. W. KLUGE and W. UHLMANN (Physikal Z., 1936, 37, 857—862).—The selective photo-effect was investigated for cells containing composite cathodes of the type M-MH-M and M-MD-M (M = Li, Na, K). The substitution of D for H results in a displacement of the spectral sensitivity curve towards the violet in the case of Li and Na, but with K there was no effect. The displacement is larger for Li than for Na, and is connected with the smaller lattice consts. of NaD and LiD compared with those of the hydrides. A. J. M.

Factors in the ionisation of carbon disulphide by X-rays. L. S. TAYLOR (J. Res. Nat. Bur. Stand., 1936, 17, 557-576; cf. A., 1935, 148; 1936, 1321).--The electrical conductivity of liquid CS<sub>2</sub> exposed to X-rays has been measured with application of a d.c. field or of a square wave-form a.c. The phenomena observed can be explained by barrier potentials due to space charge. J. W. S.

Ionisation potentials of free radicals. R. G. J. FRASER and T. N. JEWITT (Physical Rev., 1936, [ii], 50, 1091).—Measurements previously described (cf. A., 1934, 1290) are extended, with improved technique, to Me and Et, and give ionisation potentials  $11\cdot 1 \pm 0.5$  and  $10\cdot 6 \pm 0.5$  volts, respectively. Results are compared with indirect estimations. N. M. B.

Born effect of ionic mobility. Walden's rule. Influence of concentration on electrolytic conductivity. J. J. HERMANS (Z. Physik, 1936, 104, 100—112).—A mathematical discussion of the Born effect from which is derived a formula explaining experimentally observed deviations from Walden's rule. L. G. G.

Influence of pressure of ionic conductivity of solids. W. JOST and G. NEHLEP (Z. physikal. Chem., 1936, B, 34, 348—356).—The theory previously advanced (A., 1936, 666) to account for the abnormally high vals. found experimentally for A in the conductivity equation  $\kappa = Ae^{-Q/RT}$  indicates that the conductivity will be influenced by pressure. AgCl and AgBr prove to have (negative) temp. coeffs. of  $\kappa$  with approx. the predicted vals.  $\beta$ -AgI exhibits an anomalous positive temp. coeff., which falls rapidly with increasing pressure. R. C.

Conduction phenomena in semi-conductors. J. A. V. FAIRBROTHER (Proc. Roy. Soc., 1936, A, 157, 50-66).—Using a W wire coated with a layer of insulating material, Langmuir probe methods of measurement in a low-pressure Hg discharge are used to study the electrical behaviour of the insulating material (A., 1929, 1359). The electrical conductivity of pure  $Al_2O_3$  varies with temp. according to Wilson's theory of electronic semi-conductors. The observed phenomenon of electron diffusion through  $Al_2O_3$  supports the theory advanced by Lowry to explain the mechanism of the thermionic emission from oxidecoated filaments. L. B.

Grotthus conductivity of molten electrolytes. T. ERDEY-GRÓZ (Z. physikal. Chem., 1936, 178, 138— 142).—The equiv. conductivity of most molten electrolytes near the m.p. is  $\gg$  that calc. by Walden's rule (A., 1932, 111), assuming complete dissociation into simple ions. This may be explained by supposing that the electrolyte is only partly dissociated into simple or complex ions and that there is conduction by a Grotthus mechanism in addition to normal electrolytic conduction. R. C.

Electrical conductivity of dielectric liquids ionised by X-rays. I. ADAMCZEWSKI (Acta phys. polon., 3, 235—260; Chem. Zentr., 1936, i, 1575).— The ionisation current rises linearly from zero, falls off at higher currents, and finally follows a straight line of small slope. Saturation was not attained (using saturated hydrocarbons as dielectrics) with field strengths up to 17,000 volts per cm.

J. S. A.

Dissociation in electric field, and insulating liquids. K. H. REISZ (Z. physikal. Chem., 1936, 178, 37-42).—The similarity between conduction of the current in gases and conduction in insulating liquids is probably only superficial. Onsager's theory of dissociation in an electric field (A., 1934, 1176) yields a semiquant. explanation of the relation between the conductivity of such liquids at high field strengths and their physical properties. R. C.

Absolute determination of dielectric loss at high frequencies by the condenser-thermometer method. C. SCHMELZER (Ann. Physik, 1937, [v], 28, 35-53).—The condenser-thermometer method of determining the abs. dielectric loss of liquids gives results accurate to  $\pm 5\%$ . The transition  $\lambda$  ( $\lambda_s$ ) was determined for H<sub>2</sub>O, MeOH, EtOH, Pr<sup>a</sup>OH, Bu<sup>a</sup>OH, and Et<sub>2</sub>O. Considerable differences are found between the mol. vol. of  $H_2O$ , EtOH, and  $Et_2O$  calc. from the van der Waals const. b, and the "apparent" mol. vol. calc. from  $\lambda_s$ . The differences for  $H_2O$  and EtOH can be explained by assuming a quasi-cryst. structure for these liquids. That for  $Et_2O$  is due to the use of a val. of  $\eta$  obtained from Stokes' law, which is not sufficiently accurate for particles of mol. dimensions. The high-frequency conductivity of solutions of HgCl<sub>2</sub> and AcOH in COMe<sub>2</sub>, tetraiso-amylammonium iodide in dioxan, and NBu<sup>a</sup><sub>4</sub>Br in  $C_6H_6$  increases more rapidly with increasing frequency than indicated by theory. This is ascribed to the dipole loss of ion pairs. The high-frequency conductivity also increases with increasing field strength, explained as due to a kind of dissociation-potential A. J. M. effect.

High-frequency loss and quasi-crystalline structure of liquids. P. DEBYE and W. RAMM (Ann. Physik, 1937, [v], 28, 28—34).—The variation of dielectric const. of polar liquids with frequency is considered in connexion with the hypothetical quasicryst. structure (hindered rotation of mols.) of liquids. The dielectric loss is considered as a function of y = E/kT (E is the "hindrance" energy, kT the thermal energy). Deviations from the val. of the loss calc. by the usual theory are to be expected where y is specially great, *i.e.*, for strongly associated or very viscous liquids. A. J. M.

Dispersion determinations in the region of decimetre waves. M. WIEN (Physikal. Z., 1936, 37, 869-871).—It is possible to calculate from the results of von Ardenne *et al.* (A., 1936, 1182) the transition  $\lambda$  ( $\lambda_s$ ) of a no. of dipole liquids, the results being in agreement with those obtained by other methods. For PhNO<sub>2</sub> and glycerol,  $\lambda_s$  varies with the  $\lambda$  at which the dispersion is measured. The Debye theory does not hold for viscous solutions of sucrose. A. J. M.

Dielectric constants of gases and vapours. VII. M. KUBO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 30, 238—243; cf. this vol., 12).—The dielectric const. of 1:4-dioxan vapour has been determined. It is inferred from the val. of the dipole moment (0.43—0.49 D) that < 5% of the symmetrical *cis*-form is present. R. S.

Dipole moment of tetrachloroethylene. C. L. TSENG, C. LIU, and C. E. SUN (J. Chinese Chem. Soc., 1936, 4, 473—476).—The dipole moment was zero, indicating symmetry. C. R. H.

Dielectric constants of the ozonides of ethyl fumarate, ethyl maleate, and methylisoeugenol, and the variation of these constants with time. E. BRINER, E. PERROTTET, H. PAILLARD, and B. SUSZ (Helv. Chim. Acta, 1936, 19, 1354—1358).— The dielectric consts. of Et maleate, Et fumarate, and methylisoeugenol and their ozonides have been determined at 23° and 168 m. The vals. for the ozonides are  $\gg$  those of the parent compounds and increase with time, probably owing to changes producing H<sub>2</sub>O and org. acids. J. W. S.

Refraction and dispersion of gases and vapours. X. Effect of temperature on refractivity of iodine, and refractivity of atomic iodine. A. BRAUN and P. HOLEMANN (Z. physikal. Chem., 1936, B, 34, 357-380).-The mol. refractivity, R, of I vapour for  $\lambda$  656.3 mµ has been determined at 150—1030° at concns. of  $1-4 \times 10^{-5}$  g. per c.c. Between 400° and 600° R begins to fall with rising temp., due to dissociation into atoms. From the variation with concn. of R at the highest temp. the at. refractivity of at. I is calc. to be  $13.4 \pm 0.2$  c.c. From this val., R for  $I_2$  has been calc., the variation of this val. with concn. and temp. being due to damping effects and the variation of the optical absorption with temp., respectively. The at. refractivity of at. I for  $\lambda \infty$  is  $12.5 \pm 0.3$  c.c. Comparison of this val. with the at. and ionic refractivities of neighbouring elements shows that completion of the outer electron shell causes a considerable fall in refractivity. The refractivity of various iodides is compared with the sum of the at. and ionic refractivities of the con-R. C. stituent elements.

Refraction in solutions. V. Complete refractivity curve of carbamide. J. M. SCHER-SCHEVER and A. E. BRODSKI (Z. physikal. Chem., 1936, B, 34, 145—150; cf. A., 1936, 424).—n has been determined for aq.  $CO(NH_2)_2$  at conces., c, of 0.003—  $4\cdot 1M$  at 25°. The graph of the apparent mol. refraction, R, of the solution against  $\sqrt{c}$  is similar to that for an electrolyte, so that the form of the latter curve cannot be explained by interaction of the ionic fields and throws no light on the degree of dissociation of the solute. The  $\Phi$  and II curves of  $CO(NH_2)_2$ , however, differ characteristically from those of KCI. R. C.

Anomalous dispersion in dipole liquids. J. MALSCH (Physikal. Z., 1936, 37, 849—851).—Recent determinations of anomalous dispersion in glycerol solutions can be explained by assuming that there is a relaxation time for the dipole structure >, and distinct from, that for the dipole itself. Experiments with solutions of electrolytes in glycerol indicate the existence of characteristic vibrations of ion complexes in the range of short electric waves. A. J. M.

Solvent action on optical rotatory power. C. O. BECKMANN and K. COHEN (J. Chem. Physics, 1936, 4, 784—804).—The theoretical method of Darwin (A., 1925, ii, 2) is extended to the field of mol. optics and account is taken of the effect of intermol. forces on the optical const. On the basis of the concept of deformation a relation between the rotivity and the average mol. field of the mol. is developed. An expression for the average field is derived for the limiting case of a continuous medium, and a more general derivation from statistical mechanics is given for a simple mol. model. For gases the expression is related to the dielectric const., and for liquids an analogous expression in terms of molar polarisations is obtained. By experimental verification of these theoretical results the validity of the use of change of rotivity as a measure of the mol. field is established. W. R. A.

Optical rotatory power of hydrogen and deuterium compounds. H. ERLENMEYER and H. SCHENKEL (Helv. Chim. Acta, 1936, 19, 1199–1200). —The vals. of  $[\alpha]_{D}^{20}$  for *l*-OD·CHPh·CO<sub>2</sub>D and *d*-OD·CPhMe·CO<sub>2</sub>D are  $-179\cdot10^{\circ}$  and  $+36\cdot69^{\circ}$ , respectively, compared with  $-173\cdot27^{\circ}$  and  $+37\cdot98^{\circ}$ , respectively, for the corresponding H-compounds.

J. W. S.

Mechanical double refraction of oils in relation to molecular structure and association. D. VORLANDER and P. SPECHT (Z. physikal. Chem., 1936, 178, 93-112).- Experiments on the production of mechanical double refraction with the Maxwell-Kundt cylinder apparatus are described. The min. speed of rotation required to produce double refraction in an amorphous liquid is not inversely proportional to the viscosity, and is influenced by constitutive factors. The double refraction of Et cinnamate (I) increases proportionately to the speed of rotation, u, up to a certain point, then tends towards a limit corresponding with equilibrium between the directive mechanical forces and the random mol. movements. The sp. double refraction of (I) and some other liquids passes through a max. with increasing u. Observations are impossible beyond a certain val. of u owing to darkening of the field of vision, a phenomenon apparently due to fine suspended solids in the liquids. The mixture rule is not valid for the double refraction of mixtures of PhMe and p-C<sub>6</sub>H<sub>4</sub>Me COMe. The angle of extinction increases with u towards a limit or max. val. which is near 45° but depends on the nature and double refraction of the oil, a result which agrees with Haller's theory (A., 1932, 1201). R. C.

Magnetic rotation and magnetic birefringence of benzene derivatives, pure and in solution. J. RABINOVITCH (Compt. rend., 1936, 203, 1249—1252). —Data are recorded for o-, m-, and p-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>, p-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub>, and (CH<sub>2</sub>Ph)<sub>2</sub> in COMe<sub>2</sub> solution, o-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub>, in CCl<sub>4</sub> solution, and pure m-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub>. The effect of orientation is discussed. A. J. E. W.

Magneto-optical properties of liquids. Application to the analysis of hydrocarbons. M. SCHERER (Publ. Sci. tech. Min. de l'Air, 1934, No. 50, 1—91; Chem. Zentr., 1936, i, 1189—1190).—The Verdet const. (C) of the paraffins up to  $C_{16}H_{34}$  follows an additive law ( $\rho_m$  for  $CH_2 = 1.02$ ). In the corresponding olefines C is smaller. Measurements for alkyl-benzenes and -naphthalenes are also recorded. Calc. vals. are generally < observed vals. of C, the differences increasing with decreasing  $\lambda$  and being independent of the length of the org. chain. Paraffins have a very small negative double refraction, which increases with the no. of C atoms. The first members of the olefines have a small positive val., which becomes negative for higher members. The acetylenes are more negative than the paraffins. The alkylbenzenes have large positive vals. The application of these results to the analysis of mixtures is discussed. Measurements with solutions of Co, Cu, and Fe salts in  $H_2O$  and MeOH show anomalies in the dispersion curves near the absorption bands. In most cases circular magnetic dichroism was observed.

H. J. E.

Nature of hydrate binding for the ions of the transition elements, particularly Co<sup>...</sup>. G. Joos (Ann. Physik, 1937, [v], 28, 54–58).—  $Co_2(SO_4)_3$ , Rb<sub>2</sub>SO<sub>4</sub>, 24H<sub>2</sub>O shows a very weak paramagnetic susceptibility ( $\chi$ ) determined by the weighing method in an inhomogeneous field.  $\chi$  varies with temp. in the normal way. In this compound, hydrate formation of the Co<sup>...</sup> ion is brought about by a rebuilding of the electron shell with true complex formation. The complex is, however, much less stable than [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>...</sup>. For all other ions of the Fe group the H<sub>2</sub>O is bound by electrostatic forces. A. J. M.

Resonance structures of carbon dioxide, carbonyl sulphide, and carbon disulphide. A. CLOW and J. M. C. THOMPSON (Nature, 1936, 138, 802-803).—A resonance  $+O \equiv C - O^- \Longrightarrow O \cdot \overline{C} \equiv O^+$ gives a val. for the magnetic susceptibility of CO<sub>2</sub> in agreement with that observed. Introduction of S is accompanied by a fall in resonance energy, and the experimental val. can be accounted for by the existence of an intermediate state,  $+S \equiv C - O^- \Longrightarrow$  $S = C = O \Longrightarrow S - \overline{C} \equiv O^+$ . A further fall occurs with  $CS_2$  and the calc. and observed diamagnetic susceptibilities indicate resonance between  $S \cdot \overline{C} \equiv S^+ \Longrightarrow$ S = C = S. L. S. T.

Maximum valency of elements and atomic structure. IX. Physical properties and reactivity of molecules in the co-ordination sphere. B. ORMONT (Acta Physicochim. U.R.S.S., 1936, 5, 593-603).—A discussion. A preliminary investigation is recorded in which MgCl<sub>2</sub> di- (I) and tri-allyl alcoholates (II) were brominated with a Br-air mixture at 10°. (I) reacted slowly, but (II) reacted vigorously, one alcohol mol. being brominated.

C. R. H.

Stereochemistry of metallic phthalocyanines. --See A., II, 78.

Low electronic states of simple heteropolar diatomic molecules. I. General survey. II. Alkali-metal hydrides. R. S. MULLIKEN (Physical Rev., 1936, [ii], 50, 1017—1027, 1028—1040; cf. A., 1934, 1288).—Theoretical. N. M. B.

General calculation of characteristic frequencies of polyatomic molecules. R. MECKE (Z. Physik, 1937, 104, 291—302).—A discussion of the usefulness and validity of mol. models in the evaluation of characteristic frequencies of polyat. mols. Formulæ are developed applicable to many org. compounds.

L. G. G. Appraisal of empirical formulæ relating equilibrium vibration frequency and distance in **non-hydride di-atom nuclei.** C. H. D. CLARK and J. L. STOVES (Phil. Mag., 1936, [vii], **22**, 1137—1157; cf. A., 1935, 1448).—The formulæ of Allen *et al.* (*ibid.*, 685), Badger (A., 1934, 477), and Clark (*ibid.*, 833) connecting fundamental vibration frequency and internuclear distance have been compared in respect of their agreement with experimental data for 70 ground and excited states of 33 non-hydride di-atoms. Clark's formulæ are in best agreement for both the simple di-atoms containing one atom of the K-series and for the more complex di-atoms. A. J. M.

Recombination of diatomic molecules with emission of radiation. R. ROMPE (Physikal. Z., 1936, 37, 807—808).—The efficiency coeff. for a process involving collision between an excited and an unexcited atom to form a diat. mol. with emission of radiation is very small, being about  $10^{-4}$  for  $H^* +$  $H \rightarrow H_2$ , and  $10^{-3}$  for  $Te^* + Te \rightarrow Te_2$ . The process can be expected to occur only when the conen. of excited atoms is great, e.g., at high temp. or in the electric discharge. The spectral intensity distribution in the recombination continuum of the Te<sub>2</sub> discharge was determined. The velocity distribution of the recombining particles follows the Boltzmann law. The temp. of the recombining particles, estimated from the intensity distribution, is  $1300-2000^{\circ}$  abs. A. J. M.

C·C linking in hexaphenylethane. E. HUCKEL (Z. physikal. Chem., 1936, B, 34, 335—338).—The theory that the weakness of the above linking compared with an ordinary C·C linking is due half to the gain in resonance energy of the double-linking electron on dissociation and half to steric hindrance of the substituents (A., 1936, 291) is criticised. It is shown that the resonance effect cannot be separated experimentally from steric and other effects, so that only the total weakening can be measured. R. C.

Fundamental vibration frequencies of the molecules  $C_2H_4$ ,  $C_2D_4$ , and  $C_2H_2D_2$ . C. MANNE-BACK and A. VERLEYSEN (Ann. Soc. Sci. Bruxelles, 1936, 56, B, 349—372).—Mathematical. Using Bonner's experimental data (cf. A., 1936, 269) the potential function and vibration frequencies are calc. Intensities and polarisations of Raman and infra-red spectra of  $C_2D_4$  and  $C_2H_2D_2$  are predicted and discussed.

N. M. B.

Ionisation, excitation, and chemical reaction in uniform electric fields. II. Energy balance and energy efficiencies for the principal electron processes in hydrogen. R. W. LUNT and C. A. MEEK (Proc. Roy. Soc., 1936, A, 157, 146—166; cf. this vol., 7).—The abs. vals. of the energy efficiencies and fractional energy losses for the principal collision processes effected by an electron swarm moving through mol. H<sub>2</sub> in a uniform electric field are calc. The only assumption involved in the calculations not based on experiment or theory is that the form of the electron distribution is Maxwellian. The energy efficiencies for the excitation of the two lowest triplet states are in good agreement with experiment. Over a wide range of  $Xp^{-1}$ , the total fractional energy loss is approx. const. The main conclusion reached is that the Maxwellian distribution represents the actual distribution to a close approximation. L. L. B. Coulomb's law of force between charges. S. J. PLIMPTON and W. E. LAWTON (Physical Rev., 1936, [ii], 50, 1066–1071).—A very accurate experimental test is described. If the exponent in the law of force is not exactly 2, but is  $2 \pm q$ , then  $q < 2 \times 10^{-9}$ in space remote from matter. N. M. B.

**Parachor. II.** R. LAUTIÉ (Bull. Soc. chim., 1936, [v], 3, 2367–2371; cf. A., 1936, 1325).— The relation between the parachor [P] and the crit. const. of a normal liquid is given by  $[P] = \phi T_c/P_c^{\frac{3}{2}}$ . F. L. U.

Calculation of specific surface and edge and corner energies of small crystals. I. N. STRANSKI (Monatsh., 1936, 69, 234-242).—Mathematical.

R. S.

Two-dimensional gases, liquids, and solids. I. LANGMUIR (Science, 1936, 84, 379-383).—An address. L. S. T.

Lattice theory of alkaline-earth carbonates. II. Elasticity constants of aragonite. III. Lattice energy of the crystals of calcite and its thermochemical applications. B. Y. OKE (Proc. Indian Acad. Sci., 1936, 4, A, 514-524, 525-530; cf. A., 1936, 1185).—II. The elasticity const. of aragonite consists of an electrostatic part and a part due to repulsive forces, both of which have been calc.

III. The lattice energy of calcite has been calc. and verified by a thermochemical cyclic process.

R. S.

Formation of dehydration nuclei on crystals of chrome alum. J. A. COOPER and W. E. GARNER (Trans. Faraday Soc., 1936, 32, 1739–1744; cf. A., 1935, 151; 1936, 175).—Dehydration nuclei formed on crystals of chrome alum are spherical. Their rate of growth increases up to 0.01 cm., beyond which it is const. On the assumption that the retarding effect at small sizes is due to depression of the dissociation pressure by a surface tension, the latter is calc. to be  $7.49 \times 10^{6}$  dynes per cm. F. L. U.

Transformations produced in certain metals by heating in a vacuum or in air. J. J. TRILLAT and S. OKETANI (Compt. rend., 1936, 203, 1064— 1066).—Au leaf 50—70 m $\mu$  thick, after heating to 500° in a vac. or in inert gas, gives electron-diffraction patterns corresponding with a hexagonal structure (*a* 5·28 A.) having the *c*-axis perpendicular to the plane of the leaf. Ag is similar. A. J. E. W.

Lattice constant of purest aluminium. A. IEVINŠ and M. STRAUMANIS (Z. physikal. Chem., 1936, B, 34, 402–403; cf. A., 1936, 1186).—The val. is  $4.04145\pm0.00002$  A. at 25°. R. C.

Texture of thinly rolled tungsten foil. W. G. BURGERS and J. J. A. PLOOS VAN AMSTEL (Physica, 1936, 3, 1064—1066).—Electron-diffraction photographs show that the crystallites in rolled W foil have a cube plane parallel to the plane of the foil, and a cube edge at 45° to the direction of rolling. The oxide layer formed on heating in air has the crystallites oriented at random. A. J. E. W.

Structure and magnetic properties of manganese boride, MnB. R. HOGART and M. FALLOT (Compt. rend., 1936, 203, 1062-1064).-MnB is orthorhombic; a 2.95, b 11.5, c 4.10 A.; 8 mols. in unit ccll. The space-group is  $D_{2h}^{0}$ —Pnna. Relative at. parameters are given. The magnetic moment of Mn is 9.65 Weiss magnetons. A. J. E. W.

"Oriented " oxidation of barium. W. G. BURGERS and J. J. A. PLOOS VAN AMSTEL (Physica, 1936, 3, 1057—1063).—Ba volatilised on Cu at high temp. gives electron-diffraction patterns showing a preferential orientation of the crystallites with the [111] direction perpendicular to the surface. Oxidation of such oriented layers gives BaO layers with the [110] direction nearly normal to the surface. The directions of closest packing of Ba atoms in the two structures are thus approx. parallel. This result is correlated with similar observations on Fe and FeO (cf. A., 1935, 161). A. J. E. W.

Wüstite phase. H. NOWOTNY and F. HALLA (Z. anorg. Chem., 1936, 230, 95–96).—A mixture of very pure Fe powder with  $Fe_3O_4$ , heated for 2 hr. at 700—750° and quenched in Sn, gives an X-ray diagram showing the wüstite lines. The change does not occur below 550°. Wüstite is decomposed slowly at room temp., as shown by the gradual appearance of  $Fe_3O_4$  lines. F. L. U.

Crystal structure of  $H_3PW_{12}O_{40}, 29H_2O$ . A. J. BRADLEY and J. W. ILLINGWORTH (Proc. Roy. Soc., 1936, A, 157, 113—131).— $H_3PW_{12}O_{40}, 29H_2O$  is cubic, with 8 mols. in the unit cell and the length of the edge 23.28 A. The structure has been determined entirely from one powder photograph taken by J. F. KEGGIN. In conformity with the space-group  $O_h^3$ , the structure is composed of two interpenetrating diamond lattice-complexes, one consisting of 8 anions  $(PW_{12}O_{40})^{-3}$ , the other of 8 clusters of  $H_2O$  mols. together with the acidic H  $(H_3, 29 H_2O)^{+3}$ . Each anion is identical with that found by Keggin in the pentahydrate (A., 1934, 479). The positions of all the atoms, except the H atoms, have been found. The 29  $H_2O$  mols. are divided up into six groups, 12 + 6 +6 + 4 + 1. Their interat. distances all lie between  $2\cdot 8$  and  $2\cdot 9$  A. L. B.

Constitution of platinum compounds of cacodyl oxide. K. A. JENSEN and E. FREDERIKSEN (Z. anorg. Chem., 1936, 230, 34-40).—Compounds of the type  $PtX_{2}$ ,  $(AsMe_2)_2O, H_2O$  (X = Cl, Br, I) (described, shortly, by Bunsen) have been prepared and their properties studied. They lose 1/ mol. of  $H_2O$  on heating and form more highly coloured compounds. The aq. solutions are acid, in agreement with  $[PtX_2, (AsMe_2)_2O, H_2O] \implies [PtX_2, (AsMe_2)_2O, OH]' +$ H. The I compound (others too insol.) in  $C_6H_6$  shows a high dipole moment, from which a *cis*-configuration is inferred. The anhyd. compound is bimol. (in CHBr<sub>3</sub>) and has a very small dipole moment. It has therefore a uniplanar *trans*-structure. F. L. U.

Structure of the carbonyl group. Quantitative investigation of oxalic acid dihydrate by Fourier synthesis from X-ray crystal data. J. M. ROBERTSON and I. WOODWARD (J.C.S., 1936, 1817—1824).—Abs. intensity determinations have been carried out for the two principal zones of reflexions from  $H_2C_2O_4, 2H_2O$  (I). The preliminary structure assigned by Zachariasen (A., 1935, 152) was confirmed, and the results were used to calculate the phase consts. for most of the reflexions. A double Fourier synthesis was made, giving fairly sharp resolution of all the atoms in the mol. in a projection along the b-axis, and of four of the atoms in a projection along the a-axis. Vals are given for the 12 parameters of the structure. The C—O distances in the CO<sub>2</sub>H groups differ slightly (1.24 and 1.30 A.). The O of  $H_2O$  is at 2.52 A. from one of the O of  $CO_2H$ , showing the formation of a true H linking. The other O of  $CO_2H$  is almost equidistant from two O of H<sub>2</sub>O mols. (2.87 and 2.84 A.), indicating OH linkings. The C-C distance in (I) (1.43-1.45 A.), is definitely < that in diamond (1.54 A.), indicating 23-30% of This double linking property in the C-C linking. linking in (I) is not a true single linking probably because of conjugation of double linkings in adjacent CO<sub>2</sub>H. This fact explains the invariance of structure of the  $C_2O_4$  group in the different cryst. forms of (I), and in many oxalates, which show a planar or nearly planar configuration of the group. A. J. M.

Structure of resorcinol. Quantitative X-ray investigation. J. M. ROBERTSON (Proc. Roy. Soc., 1936, A, 157, 79—99).—The unit cell contains 4 asymmetric mols., and has a  $10.53 \pm 0.03$ , b  $9.53 \pm 0.03$ , c  $5.66 \pm 0.02$  A.; space-group  $C_{2x}^{9}$  (Pna). A quant. X-ray investigation has led to a complete determination of the structure. The  $C_{6}H_{6}$  rings are regular plane hexagons, the distance C—C being  $1.39 \pm$ 0.01 A. The orientation of the mol. and the coordinates of the atoms are given. In the crystal the mols. are grouped in spiral arrays about alternate twofold screw axes, the OH of successive pairs of mols. approaching each other to within about 2.7 A., indicating the presence of OH linkings. The min. distances of approach between the other atoms on adjoining mols. (C to O, and C to C) are all about 3.5 A. L. B.

p-Azoxyanisole in the solid, anisotropic liquid, and isotropic liquid states. P. CHATELAIN (Compt. rend., 1936, 203, 1169—1171).—The solid is monoclinic with holohedral symmetry; a:b:c =1.988:1:2.590,  $\beta = 108^{\circ}20'$ . Vals. of *n* for the anisotropic and isotropic liquids, for different  $\lambda\lambda$  and temp., are given and discussed. A. J. E. W.

Structure of cellulose acetate soluble in acetone or "cellite." G. CENTOLA (Atti R. Accad. Lincei, 1936, [vi], 23, 788—793).—X-Ray measurements indicate that the mol. of cellite consists of chains of glucose residues, some of which may be completely or partly acetylated and others entirely unchanged. Cellite is not merely a mixture of cellulose triacetate and cellulose. O. J. W.

Submicroscopic roughness of metallic surfaces and its effect on the electron interference pattern. F. KIRCHNER (Ann. Physik, 1937, [v], 28, 21-27).—The effect of submicroscopic roughness on the electron interference pattern for large single crystals, or surfaces containing many small crystals with parallel orientation, and surfaces with small block-like projections is considered. The case of ordinary metallic surfaces and thin layers is also discussed. For Ag of thickness 10—50 m $\mu$  the interference ring is wider for reflexion than transmission. It is shown that this widening is determined by the roughness of the surface, indicating projections to the extent of 100 m $\mu$  downwards. The greater is the widening the smoother is the surface. The application of these results to polished metal surfaces is considered. The fact that, with polishing, the sharp interference rings are replaced by two wide rings having practically the same diameter for all metals does not indicate the existence of a monat. "liquid" or a Beilby layer on the surface of the metal. It is due to the reduction in height, by polishing, of the crystal blocks projecting from the surface, a refraction effect due to the high polish, and the deformation of the crystal lattice in the process of polishing. A. J. M.

Beilby layer on non-metals. G. I. FINCH (Nature, 1936, 138, 1010).—Polished plane surfaces cut in arbitrary directions from many types of single crystals, e.g., quartz, diamond, garnets, topaz, etc., yield electron diffraction patterns of spots and lines and thus provide irrefutable evidence of the cryst. structure of the polish layer. Other crystals, notably beryl, zircon, tourmaline, cassiterite, and hæmatite, give patterns of diffuse haloes typical of liquid Hg and various glasses. Etching restores the cryst. pattern. The results establish the validity of Beilby's view of the formation of an amorphous polish layer which may, however, subsequently recrystallise.

L. S. T. Electronic diffraction study of bromochloroform. P. CAPRON and M. DE HEMPTINNE (Ann. Soc. Sci. Bruxelles, 1936, 56, B, 342-348).—Using Pauling's method (cf. A., 1936, 272), interat. distances calc. from electron diffraction photographs are : C-Br 2.01, Br-Cl 3.00, C-Cl 1.76, Cl-Cl 2.95 A. Possible structural arrangements are discussed.

N. M. B.

Electronic analysis of surfaces by means of slow electrons. R. J. MOON and W. D. HARKINS (J. Physical Chem., 1936, 40, 941-957).-Apparatus for the study of surfaces by electron diffraction is described. Using a const. angle of incidence = angle of reflexion and a varying accelerating potential (P), the collector current-P curve for liquid oleic acid in bulk shows three max. A pronounced fatigue effect is observed. The (100) cleavage plane of NaCl gives max. corresponding with an inner potential 0 and one of about 10 volts. The (100) plane of galena gives no distinct max. at room temp., but several at 206° corresponding with an inner potential of 16.9 volts. In presence of a trace of org. vapour the grating properties of a galena surface are permanently destroyed by slow electrons at  $206^{\circ}$ . F. L. U.

Changes in resistance, with time, of thin sputtered metal layers. V. VAND (Z. Physik, 1936, 104, 48—67).—The electrical resistance in vac. of sputtered films of Ag and Au is shown to decrease hyperbolically with time and approach a fixed min. val. asymptotically. The resistance-time curve after admission of air to the film is also hyperbolic but in this case the asymptotic part of the curve increases to a val. slightly > that in vac. The resistance changes are not due to diffusion in the film, but to local disintegration of the lattice structure. This theory is elaborated mathematically. L. G. G.

Magnetic anisotropy of single crystals of iron and nickel. H. SCHLECHTWEG (Ann. Physik, 1936, [v], 27, 573—596).—A discussion of the interpretation of magnetic experiments at large field strengths where the magnetisation process can be considered as a rotation of the magnetic vector of the crystal. The case of a crystal disc suspended from a torsion wire with its plane parallel to a magnetic field is considered in detail. From the variation in the moment of rotation of a suspended disc of Krupp "Hyperm 4" containing  $4\cdot4\%$  Si with the direction of the magnetic field it is deduced that the anisotropy const. of the metal is  $2\cdot56 \times 10^5$  ergs per cm.<sup>3</sup> O. D. S.

Variation with temperature of the magnetostriction of nickel. W. DÖRING (Z. Physik, 1936, 103, 560—582).—The magnetostriction of polycryst. Ni has been measured for temp. up to 400°. With increasing magnetic field the effect quickly reaches saturation at all temp., but the saturation val. falls with rising temp. to a very small quantity above  $360^\circ$ . The saturation magnetostriction  $\propto$  the square of the saturation magnetisation over the temp. range. A. E. M.

Ferromagnetic anisotropy in single crystals and in polycrystalline sheets. R. M. BOZORTH (Physical Rev., 1936, [ii], 50, 1076—1081).—It is shown theoretically that the (110) direction may under certain conditions be the direction for easiest magnetisation. Magnetisation curves for single crystals of Fe, Ni, and Fe-50% Ni are calc. and discussed. The anisotropy const. for an Fe single crystal is calc. from experimental data. N. M. B.

Reversible and irreversible magnetisation processes with change of temperature. N. EMBIRIKOS and H. BITTEL (Physikal. Z., 1936, 37, 901-906).—The hysteresis loops of Ni + 1% Mn, Ni + 1% Cr, and Ni + 2% Cr are decreased in area by shaking the test-piece. The effect of temp. on magnetisation may be divided into a reversible and an irreversible part. The reversible part decreases with rise of temp., and increases with increasing field strength. The theory of the process is considered. Variation of electrical conductivity with magnetisation is determined only by the reversible process.

A. J. M. Temperature dependence of the intensity of magnetisation of ferromagnetic substances in weak magnetic fields. K. HONDA and T. NISHINA (Z. Physik, 1936, 103, 728—737).—This is studied on Fe single crystals and polycryst. electrolytic Fe and Ni in the light of the Honda–Okubo theory. L. G. G.

Optical constants of fluorite in the extreme ultra-violet. R. TOUSEY (Physical Rev., 1936, [ii], 50, 1057—1066).—Using the method of photographic photometry with a vac. spectrograph, high-precision measurements of the reflecting power of a polished fluorite surface were obtained at nineteen  $\lambda\lambda$  over 1605—927 A. for 45°, 60°, 75°, and 85° incidence. Curves for *n* and extinction coeff. are calc. The extinction curve shows an absorption band of approx. 100 A. half-width, with max. near 1115 A. The absorption increases again below 1060 A. There is evidence of a surface layer having a higher absorption coeff. and reflecting power than fluorite itself.

N. M. B.

Theory of rupture of brittle bodies. A. SMEKAL (Z. Physik, 1936, 103, 495—525).—A theory is developed to explain the processes involved in the breakage of homogeneous and inhomogeneous bodies, with one or more eracks on the surface or inside the body. A. E. M.

Strength of rock-salt crystals. I. Influence of temperature and internal impurities. II. High-vacuum strength and influence of adsorbed impurities. W. BURGSMULLER (Z. Physik, 1936, 103, 633-654, 655-670).—I. The breaking strength of rock-salt and of synthetic NaCl crystals with and without uniformly distributed impurities has been studied between -271.8° and 500°.

II. The breaking strength of synthetic NaCl crystals in vac. between  $-90^{\circ}$  and  $500^{\circ}$ , together with the influence of adsorbed gases, is studied. The effect of adsorbed impurities as compared with uniformly distributed impurities (see above) on crystal cohesion and plasticity is discussed. L. G. G.

Effect of temperature on the strength of rocksalt crystals. K. KRUGEL (Z. Physik, 1937, 104, 194-196).—The breaking strength of synthetic NaCl crystals increases regularly between room temp. and 350°. Above 350° fluctuations in strength due to constriction and lattice rotation occur. L. G. G.

Method of estimating the distribution of molecules of different sizes in macro-molecular systems. H. DOSTAL and H. MARK (Naturwiss., 1936, 24, 796).—A method of estimating the no. of mols. of different mol. wts. in a system is based on determinations of viscosity and osmotic pressure.

A. J. M.

Thermal resistance of bismuth single crystals at low temperatures, and in a magnetic field. W. J. DE HAAS, A. N. GERRITSEN, and W. H. CAPEL (Physica, 1936, 3, 1143—1158).—Data for the thermal and electrical resistances are recorded; the apparatus and technique are described. The thermal conductivity at low temp. is largely affected by the purity of the lattice; its dependence on a transverse magnetic field was followed up to a saturation val. at each temp. investigated. The results are discussed in relation to the electronic and lattice conductivities, and the Wiedemann-Franz-Lorenz const. A. J. E. W.

Translatory effect of deformation on metallic conduction. A. PERRIER (Helv. phys. Acta, 1935, 8, 494-497; Chem. Zentr., 1936, i, 1188).

H. J. E.

Diamagnetic susceptibility of thallium compounds. V. C. G. TREW (Trans. Faraday Soc., 1936, 32, 1658—1667).—Measuremonts of the mass suscoptibility of 27 Tl<sup>I</sup> compounds gives  $-38.4 \times 10^{-6}$ for the susceptibility ( $\chi$ ) of the Tl<sup>\*</sup> ion. The val. of  $\chi$  calc. by Slater's method (A., 1930, 1234) is considerably > the observed val., and comparison with the data for Hg and Pb indicate that the discrepancy is due to too high a val. for the screening const. of the 5d and 6s levels given by this method. From the observed val. of  $\chi$  1.36 A. is deduced for the ionic radius of Tl<sup>\*</sup>, compared with 1.49 A. from X-ray data. F. L. U.

Paramagnetic rotatory power of hydrated dysprosium ethyl sulphate: paramagnetic saturation. J. BECQUEREL, W. J. DE HAAS, and J. VAN DEN HANDEL (Physica, 1936, 3, 1133— 1142).—Measurements on Dy(EtSO<sub>4</sub>)<sub>3</sub>,9H<sub>2</sub>O are recorded. At liquid He temp., the paramagnetic rotation in the direction of the optic axis is  $\rho_p = A \times$ tanh ( $\mu H_a/kT$ ) +  $BH_a$  ( $H_a$  = effective magnetic field strength, k = Boltzmann const.). The first term indicates the occurrence of only one doubly degenerate energy level at low temp.; the second term, of much smaller magnitude, represents a distinct type of paramagnetism. Paramagnetic saturation was observed at 1.62° abs., with  $H_a = 25,000$  gauss. The relation given does not apply at liquid H<sub>2</sub> or higher temp., where more than one energy level occurs.

A. J. E. W. Magnetism of diradicals. E. HUCKEL (Z. physikal. Chem., 1936, B, 34, 339—347).—A quantum theory interpretation is given of the fact that if two CPh<sub>3</sub> are linked by removal of two H atoms the product formed by linking in the p-p'-position is diamagnetic, whilst linking in the m-m'-position yields a paramagnetic product (A., 1935, 689). The second compound must be capable of existing also in a diamagnetic state with only slightly different energy.

R.C.

Diffraction of light by ultrasonic waves : a test for polarisation. S. PARTHASARATHY (Current Sci., 1936, 5, 243).—Tests made on *m*-xylene for incidences of the light beam normal and oblique to the sound wave front at frequencies of  $7\cdot164 \times 10^6$  and  $20\cdot00 \times 10^6$  cycles per sec. and different light  $\lambda\lambda$  showed no polarisation. N. M. B.

Visibility of ultrasonic waves in liquids. S. PARTHASARATHY [with N. S. N. NATH] (Proc. Indian Acad. Sci., 1936, 4, A, 555—561; cf. A., 1936, 1453).— When a beam of monochromatic light is passed through a liquid subjected to stationary ultrasonic waves, and focussed by a microscope, a pattern appears periodically when the distance between the microscope and the cell is increased. Multiplication of the fringes occurs at intermediate distances. The influence of ultrasonic amplitude and obliquity of light waves to sound waves has been investigated and a theory is advanced.

R. S.

Optical examination of supersonic wave fields in liquids and glasses. E. HIEDERMANN (Z. Physik, 1937, 104, 197—206).—The amplitude distribution in supersonic wave fields in liquids and glasses has been studied by an improved method. The results are illustrated and compared with other similar work. L. G. G.

Calculation of latent heats of evaporation. P. GUARESCHI (Atti R. Accad. Lincei, 1936, [vi], 23, 783-787; cf. this vol., 72).—A relationship for the latent heat of evaporation of liquids as a function of the coeff. of association is derived. O. J. W.

Specific heat of paramagnetic crystals at low temperatures. I. WALLER (Z. Physik, 1936, 104, 132-134).—A formula is derived for the contribution to the sp. heat of energy from the magnetic field. L. G. G.

Specific heats of metal electrons. A. SOMMER-FELD (Ann. Physik, 1937, [v], 28, 1-10).—A review of recent theoretical and experimental work.

A. J. M. Specific heat of iron. (MME.) E. LAPP (Ann. Physique, 1936, [xi], 6, 826-855).—High-precision data and correction terms, for the temp. range 18— 960°, are reported. Magnetic and calorimetric data are compared. N. M. B.

Heat capacities of silver, nickel, zinc, cadmium, and lead from  $-80^{\circ}$  to  $120^{\circ}$ . H. L. BRON-SON and A. J. C. WILSON (Canad. J. Res., 1936, 14, A, 181–193; cf. A., 1933, 559).—Mean heat capacities over 10° intervals from  $-80^{\circ}$  to 120° have been determined. Vals. of  $C_p$  calc. from Debye's expression and involving no calorimetric data show an average deviation of 0.7% from the experimental vals. Equations fitting the experimental curves are given.

F. L. U.

Heat capacity of silver and nickel between 100° and 500°. H. L. BRONSON, E. W. HEWSON, and A. J. C. WILSON (Canad. J. Res., 1936, 14, A, 194—199; cf. preceding abstract).—Mean heat capacities between 0° and various temp. between 100° and 500° have been determined, and vals. corresponding with the higher temp. calc. F. L. U.

Intensity of orbital interaction in metals. R. FORRER (Compt. rend., 1936, 203, 1268—1270).— The m.p. of a solid is given by  $T = F\sqrt{N}$ , where F is a temp. about 300°, and N is the no. of "contacts" between electronic orbits. Vals. of F obtained for the elements are discussed in relation to the electronic configurations of their atoms. A. J. E. W.

Approximate correction of b.p. for variation in barometric pressure. R. LIVINGSTON (Science, 1936, 84, 459).—The relation  $\Delta T = 0.1T_{b.p.} \times \Delta P_{atm.}$ holds to 0.1° for normal liquids for changes in pressure of 15 to 20 mm. L. S. T.

Determination of velocity of fusion. G. TAM-MANN and H. HARTMANN (Z. anorg. Chem., 1936, 230, 53-64).—A method is described whereby the rate of melting of a cylindrical rod of material maintained at a const. temp. near its m.p. may be measured when heat is supplied at a known rate to one end. The rate of flow of heat deduced from the observed rate of melting is compared with that calc. theoretically for the experimental conditions. The same method is applied to the rate of melting at the surface of contact between rods of different materials [Sn-Pb, Cd-Zn, Ag-Cu, NHAcPh-C<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub>, and Fe-C] which form a eutectic. F. L. U.

Heat movement in solids and liquids and the theory of melting, J. I. FRENKEL (Bull. Acad. Sci. U.R.S.S., 1936, 371–393).—A review with particular reference to the author's own work (cf. A., 1936, 1189). J. J. B.

Critical temperature of normal liquids. R. LAUTIÉ (Bull. Soc. chim., 1936, [v], 3, 2337-2343; cf. A., 1936, 149).—The abs. crit. temp. of a normal liquid is related to its mol. wt. best by the expression  $T_c/\sqrt{M} + 2500\sqrt{M}/T_c = 101$ , provided that  $T_c/\sqrt{M}$  lies between 36 and 68. The alternative expression  $T_c = 1 \cdot 2T_b + 10\sqrt{M} + 20$  ( $T_b = abs. b.p.$ ) takes account of the difference between isomerides. The range of validity of these expressions is illustrated. F. L. U.

Density of liquid and solid bodies. A. BREIT-WIESER (Suddeuts. Apoth.-Ztg., 1936, 16 pp.).-Abridgement of a monograph, giving methods. R. S.

Empirical expression for the specific volume of superheated water vapour. P. TONGAS (Compt. rend., 1936, 203, 1134–1136).—The sp. vol.  $v = 47.07T/p - 10^{(0.00292T - 1.455)}/\{10^{(0.00439T - 0.0345)} - 33 - p/10^4\}$  cu. m. per kg., for p = 1 - 300 kg. per sq. cm. and  $T = 373 - 823^\circ$  abs. A. J. E. W.

Vapour pressures of liquid krypton. J. J. MEIHUIZEN and C. A. CROMMELIN (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 1088—1089).—The v.p. of liquid Kr between the triple point (115.97° abs., p 0.7204 atm.) and the crit. point (209.39° abs., p 54.182 atm.) is expressed by log  $p_{\text{atm.}} = -$  899.979/T - 12.55400 log T + 31.50311 + 0.0175105T. The b.p. of Kr is 119.93° abs. O. D. S.

Temperature distribution in boiling water. W. FRITZ and F. HOMANN (Physikal. Z., 1936, 37, 873—878).—The variation of temp. with height of a column of boiling  $H_2O$  was determined by means of thermo-elements, the  $H_2O$  being heated by a polished metal hot-plate. The temp. deviates considerably from that calc. from the hydrostatic pressure within the liquid. The phenomenon of superheating is considered. A. J. M.

Recent advances in physical science. E. T. JONES (Proc. Roy. Phil. Soc. Glasgow, 1936, 62, 114-122).—The approach to abs. zero of temp. and the nature of electrostatic force are discussed.

N. M. B. Range of validity of Nernst heat theorem. H. SCHMOLKE (Z. Physik, 1937, 104, 221-227).—It is shown that, with insufficient theoretical foundation, the limit of validity of Nernst's heat theorem is often exceeded. L. G. G.

Complete equation of state of one-, two-, and three-dimensional gases of hard elastic spheres. L. TONKS (Physical Rev., 1936, [ii], 50, 955-963).— Mathematical. For a linear gas the equation is fl = NkT/(1-0), where f = the force, and l the length of the gas, N the total no. of atoms, and  $\theta$  the fraction of the gas length occupied by the atoms. A linear gas consisting of a single atom obeys, on a time average, statistical laws. For a plane gas  $\tau a =$  $NkT/(1-\theta^{1})$ , where  $\tau$  is the surface tension, a the area of the gas, and 0 has vals. near 1. For three dimensions  $pv = NkT(1-\theta^{1})$ . N. M. B.

Quantum theory of the equation of state at low temperatures. L. GROPPER (Physical Rev., 1936, [ii], 50, 963-974; cf. Slater, A., 1931, 1117).---Mathematical. The quantum formulæ for the second virial coeff. *B* are derived for the case of Boltzmann, Einstein-Bose, and Fermi-Dirac statistics, and are expressed in terms of the phases of the Schrödinger wave function. For low temp. the expression for *B* 

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is developed in a power series of T, the temp. which gives agreement in the case of the experimental formula for He. N. M. B.

Heat conduction by rarified gases. II. Thermal accommodation coefficient of helium, neon, and nitrogen on glass at 70° to 90° abs. W. H. KEESOM and G. SCHMIDT (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 1048-1049, and Physica, 1936, 3, 1085-1092; cf. A., 1936, 1059).-The accommodation coeffs. of the gases on glass increase with decreasing temp. At 70° to 90° abs. the coeffs. of He, Ne, H, and N are respectively 0.383, 0.555, 0.803, and 1.02. O. D. S.

Viscosity of gases. P. GUARESCHI (Atti R. Accad. Lincei, 1936, [vi], 23, 603-609).-The viscosity of gases is discussed from the point of view of the kinetic theory.  $\eta$  is a function of the coeff. of association,  $\alpha$ , of the gas, and when  $\alpha = 1$  the val. of  $\eta$  for all gases is  $1125 \times 10^{-7}$ . The temp. at which  $\alpha = 1$  is given by  $\sqrt{(MT)}/\sigma^2 = 3.95 \times 10^{16}$ , where  $\sigma$ is the mol. diameter. O. J. W.

Viscosity of liquids. II. P. GUARESCHI (Atti R. Accad. Lincei, 1936, [vi], 23, 690-695; cf. preceding abstract).-The author's relationship for the viscosity of gases as a function of the mol. vol. and the coeff. of association holds also for liquids.

O. J. W.

Oiliness of liquids. I. Determination of the static friction coefficients. J. SAMESHIMA, M. KIDOKORO, and H. AKAMATU (Bull. Chem. Soc. Japan, 1936, 11,659-666).—Static friction coeffs.have been determined for Mo, Et, Pra, Bua, n-, sec.-, and tert.-amyl, n-hexyl, heptyl, and octyl alcohol, acetic, propionic, butyric, valeric, hexoic, heptoic, octoic, and nonoic acid,  $C_n H_{2n+2}$  (n = 6-9),  $C_6 H_6$ , PhMe, liquid paraffin, (CH2.OH)2, EtOAc, oleic acid, and lubricating oil. Amonton's law does not hold when the wt. moved is small. R. S.

Viscosity of gas mixtures and its representation by gas-kinetic mixture formula. SCHRÖER (Z. physikal. Chem., 1936, B, 34, 161-180).-A review of existing data shows that Sutherland's viscosity equation,  $\eta_{12} = \eta_1/(1 + n_2A_1/n_1) +$  $\eta_2/(1 + n_1 A_2/n_2)$  is valid for mixtures of permanent gases, whilst for other gases the deviations are not so great as to warrant making any supplementary assumptions, such as polymerisation, association, or dipole-quadrupole effects. London's theory of van der Waals forces leads to a val. of  $\sim 0.95$  for f in the equation  $C_{12} = f \sqrt{(C_1 C_2)}$  for the Sutherland const. of the mixture, and this figure agrees with the experimental data (cf. A., 1930, 536). The viscosities of mixtures of  $SO_2$  with MeCl and with Me<sub>2</sub>O have been measured; there are positive deviations from the above equation which fall with rising temp.

**R**. C.

Viscosity of binary mixtures. A. J. A. VAN DER WYK (Nature, 1936, 138, 845-846).-A formula is given which expresses the results obtained for CH<sub>2</sub>Ph·OBz-PhMe and C<sub>6</sub>H<sub>14</sub>-CCl<sub>4</sub> mixtures.

L. S. T.

Range of accuracy and values of the constants in the various formulæ of Lichteneckers for mixtures. D. A. G. BRUGGEMAN (Physikal. Z., 1936, 37, 906-912).-The formulæ put forward by Lichteneckers for the properties of mixtures in terms of those of their components have been tested in the case of vol., n, dielectric const., and conductivity. A. J. M.

Ultra-violet absorption and orientation polarisation of binary mixtures : allylthiocarbimide and piperidine. R. KREMANN and O. FRUHWIRTH (Monatsh., 1936, 69, 319-341; cf. A., 1933, 885).-Absorption is a max. in the 50 mol.-% mixture, but on either side of the max. the curve deviates from linearity owing to (dipole) association between the compound and each of the components; the orientation polarisation curve shows the same effect. The calc. dipole moment for C<sub>5</sub>H<sub>10</sub>N·CS·NH·CH<sub>2</sub>·CH:CH<sub>2</sub> is in good agreement with that obtained for the 50% mixture. An apparatus for the determination of dielectric consts. is described and the equilibrium diagram for  $CH_2$ :CH- $CH_2$ ·NCS,  $C_5H_{11}N$ , and  $C_6H_{14}$ is given. R. S.

Diamagnetism of mixtures of organic liquids. J. F. SPENCER and V. C. G. TREW (Nature, 1936, 138, 974-975; cf. A., 1932, 216).-Remeasurement of the magnetic susceptibilities of  $CHCl_3-COMe_2$ ,  $COMe_2-CHCl:CCl_2$ , and  $CHCl_3-Et_2O$  by the Gouy method show that deviations from linearity are  $\geq 4\%$ . For many pairs of org. substances the deviations are small, rarely >0.5%, when the constitutions and mol. wts. of the constituents are similar; they amount to 1-4% when the constitutions or the mol. wts. are markedly different. L. S. T.

Equilibrium of liquid and vapour in the system argon-oxygen. P. BOURBO and I. ISCHKIN (Physica, 1936, 3, 1067-1081).—The total pressure (p) has been determined for four mixtures between  $87^{\circ}$  and  $96 \cdot 5^{\circ}$  abs. The relation log p = A + B/T is confirmed. The mixtures form "regular" solutions (cf. A., 1929, 266), the Hildebrand equation applying accurately to the results. A. J. E. W.

Control of composition in the application of the Debye-Scherrer method of X-ray crystal analysis to the study of alloys. W. HUME-ROTHERY and P. W. REYNOLDS (J. Inst. Metals, 1937, 60, Advance copy, 541-550).-The lump specimen must be annealed to remove coring at a suitable temp. bearing a definite relation to the temp. at which the filings are to be annealed. Filings should be taken with a new file and washed with  $C_6H_6$  or  $CCl_4$  to remove grease, light impurities (dust etc.) being simultaneously removed by elutriation. The filings used for the X-ray work should be analysed, both metals of binary alloys being determined; analysis of the original lump is liable to give misleading results owing to segregation effects.

A. R. P.

Lattice spacings of certain primary solid solutions in silver and copper. W. HUME-ROTHERY, G. F. LEWIN, and P. W. REYNOLDS (Proc. Roy. Soc., 1936, A, 157, 167-183; cf. A., 1934, 725).-Measurements have been made of the mean lattice spacings of primary solid solutions of Cd, In, Sn, and Sb in Ag, and of Zn, Ga, and Ge in Cu. In each series of alloys increasing valency of the solute produces an increased lattice distortion at equiat. compositions. In dil. solid solutions in Ag, equal at. percentages of Cd, In, Sn, and Sb expand the lattice of Ag by amounts  $\infty 2:3:4:6$ , respectively. For the Cu alloys the relative factors for Zn and Ga are as 3:4, but the corresponding factor for Ge is  $4\cdot8$ . It is suggested that in both series increasing valency tends to expand the lattice, but that this expansion is opposed by some factor which is relatively more important in the Cu series. L. B.

Metals and alloys. XX. X-Ray analysis of gallium bronzes. E. ZINTL and O. TREUSCH. XXI. Stoicheiometry of binary sodium compounds. E. ZINTL and A. HARDER (Z. physikal. Chem., 1936, B, 34, 225–237, 238–254; cf. A., 1936, 1193).—XX. X-Ray analysis shows the existence of three intermediate phases at room temp. Cu takes up ~15 at.-% Ga with distension of the lattice ( $\alpha$ -phase). Alloys with 20-24 at.-% Ga show the presence of the  $\alpha$ -phase, a  $\mu$ -phase (probably having closest hexagonal spherical packing with a 2.594, c 4.229 A.), and a  $\delta$ -phase (cubic, with a 8.711 A., formula  $Cu_9Ga_4$ , and the same type of crystal as  $\gamma$ brass) (cf. Å., 1935, 22). The intermediate phase  $\phi$ , which has a narrow region of homogeneity at  $\sim 58$ at.-% Ga, has a tetragonal layer lattice with a 2.830, c 5.831 A., and represents the compound CuGa<sub>2</sub>, which does not exist in the pure state but is stabilised by mixed crystal formation with Cu.

XXI. By fusing Pb or Sn with Na and extracting the excess of Na with liquid NH<sub>3</sub> the compounds richest in Na have been found to be Na<sub>15</sub>Pb<sub>4</sub> (cubie, a 13·29 A., space-group  $T_4^a$ ) and Na<sub>15</sub>Sn<sub>4</sub> (rhombic,  $a_1$  9·79,  $a_2$  22·78,  $a_3$  5·56 A., and 38 atoms in the unit cell). It is inferred that the max. Na content permitted by the valency rules for binary compounds of Na with elements 1—4 places before the inert gases having a completely ordered distribution of atoms is not always reached when the negative atom ion is more readily polarised. R. C.

X-Ray investigation of system manganeseantimony. F. HALLA and H. NOWOTNY (Z. physikal. Chem., 1936, B, 34, 141—144).—In the above system there is a tetragonal solid phase, Mn<sub>2</sub>Sb, with a 4.08, c 6.56 A., and space-group  $D_{4A}^{7}$ ; it is isomorphous with Fe<sub>2</sub>As and Cu<sub>2</sub>Sb. R. C.

Nature of the solid solution of antimony in lead. N. V. AGEEV and I. V. KROTOV (J. Inst. Metals, 1936, 59, Advance copy, 493—500).—Evidence from X-ray analysis and determinations of d indicates that the solid solution of Sb in Pb is of the monat. type; this is confirmed by thermodynamic analysis if it is assumed that the accepted solubility line in the equilibrium diagram may be in error to the extent of  $\pm 2^{\circ}$ . A. R. P.

Solubility of silver and gold in solid magnesium. W. HUME-ROTHERY and E. BUTCHERS (J. Inst. Metals, 1937, 60, Advance copy, 551-556).— Mg dissolves a max. of  $15\cdot3\%$  Ag at the eutectic temp. (471°) and the solubility decreases with fall in temp. to  $3\cdot9\%$  Ag at  $300^\circ$ . The solubility of Au in Mg increases with rise in temp. to a max. of  $0\cdot1$  at.-% at  $575^\circ$ . A. R. P. Alloys of magnesium. IV. Constitution of magnesium-rich alloys of magnesium and silver. R. J. M. PAYNE and J. L. HAUGHTON. V. Constitution of magnesium-rich alloys of magnesium and cerium. J. L. HAUGHTON and T. H. SCHO-FIELD (J. Inst. Metals, 1937, 60, Advance copy, 557—562, 605—612).—IV. The system has been examined by thermal and micrographic analysis. The eutectic is at  $472^{\circ}$  (48.6% Ag) and the solid solubility falls from 15% at this temp. to <1% at 200° (cf. preceding abstract). Mg<sub>3</sub>Ag is formed by a peritectic reaction at  $495.5^{\circ}$ .

V. Thermal and micrographic analysis shows a eutectic at  $590^{\circ}$ ,  $21^{\circ}$  Ce, the solid solubility increasing from  $<0.15^{\circ}$  Ce at  $337^{\circ}$  to about  $1.6^{\circ}$  at  $590^{\circ}$ , and a peritectic reaction at  $614^{\circ}$  in alloys with  $>30^{\circ}$  Ce. A. R. P.

Constitution of silver-rich antimony-silver alloys. P. W. REYNOLDS and W. HUME-ROTHERY (J. Inst. Metals, 1937, 60, 645—654).—Examination of the system by thermal and micrographic methods up to 25 at.-% Sb has shown that the system closely resembles the Sn-Ag system. A peritectic horizontal occurs at 702.5° in alloys with 7.2—17.0 at.-% Sb due to the reaction liquid  $+ \alpha \Longrightarrow \beta$ . The  $\beta$ -phase is a close-packed hexagonal solid solution which reacts with liquid at 558.2° to form  $\gamma$  (Ag<sub>3</sub>Sb), the peritectic horizontal starting at 16.3 at.-% Sb. The range of  $\alpha$  solid solution decreases by about 1.6 at.-% Sb between 700° and 300° and the composition of the  $\beta$ phase at 702.5° is 8.8 at.-% Sb. A. R. P.

Mercury-thallium alloys and their use for thermometric purposes. H. MOSER (Physikal. Z., 1936, 37, 885-886).—The Hg-Tl system shows two eutectics at 8.5% and 40.4% Tl, respectively. The physical properties of these alloys have been examined with special reference to their possible use in thermometry. The 8.5% Tl alloy has m.p.  $-60.0\pm0.2^{\circ}$ , and may therefore be useful as a thermometric liquid at low temp. Thermometers filled with it behave in all other respects like Hg thermometers. The 40.4% Tl alloy has m.p.  $-0.8^{\circ}$ , and its v.p. at  $500^{\circ}$  is about half that of Hg. It may therefore be used at higher temp. although the difficulty of filling an instrument with the alloy is a disadvantage.

A. J. M.

Magnetic investigation of the system zincaluminium. H. AUER and K. E. MANN (Z. Metallk., 1936, 28, 323-326).—The vals. of the diamagnetic susceptibility of Al-Zn alloys indicate that the solubility of Al in Zn is 0.1% at 100°, 0.38% at 200°, and 1.1% at the eutectic temp. (370°). The  $\beta =$  $\alpha + \gamma$  eutectoid horizontal is at 270° and begins at 0.65% Al. The solubility of Fe in Zn is small at room temp. but increases slightly with rise in temp.

A. R. P. Ternary system aluminium-magnesium-zinc. II. Section Al-Al<sub>3</sub>Mg<sub>4</sub>-Al<sub>2</sub>Mg<sub>3</sub>Zn<sub>3</sub>-Al. W. Kös-TER and W. DULLENKOFF (Z. Metallk., 1936, 28, 309-312; cf. A., 1936, 1194).—Al<sub>3</sub>Mg<sub>4</sub> ( $\delta$ ) and Al<sub>2</sub>Mg<sub>3</sub>Zn<sub>3</sub> (T) form a pseudo-binary system with a eutectic at 450°, Al 36, Mg 44, Zn 20%, the two constituents of which are solid solutions with Al 41, Mg 48, Zn 11, and Al 22, Mg 28, Zn 50%, respectively. A ternary eutectic occurs at 447°, Al 57, Mg 31, Zn 12% between the  $\alpha$ ,  $\beta$ , and T phases of the ternary system. The four-phase reaction: liquid (Al 51, Mg 39, Zn 10%) +  $\delta$  (Al 50, Mg 45, Zn 5%)  $\Longrightarrow$  $\gamma$  + T (Al 44, Mg 33, Zn 23%) occurs at 449° and the four-phase reaction: liquid +  $\gamma$  (Al 55, Mg 40, Zn 5%)  $\Longrightarrow$   $\beta$  + T at 448°. A. R. P.

System aluminium-magnesium-zinc. K. RIE-DERER (Z. Metallk., 1936, 28, 312—317; cf. preceding abstract).—The various phases have been examined by X-rays;  $\beta$  is hexagonal a 11.38 A., c/a 1.57,  $\delta$  is body-centred cubic, a 10.45—10.56 A., 58 atoms in the unit cell, and T (Al<sub>2</sub>Mg<sub>3</sub>Zn<sub>3</sub>) is also body-centred cubic with 160 atoms in the unit cell, a 14.29—14.27 A. along the section T- $\beta$  and 14.29—14.60 A. along the section T- $\delta$ . The limits of homogeneity of T in these directions are Al 44.6, Mg 31.7, Zn 23.7% and Al 27.5, Mg 32.5, Zn 40%, respectively. A. R. P.

Hume-Rothery binding forces in metallic compounds. F. LAVES (Naturwiss., 1936, 24, 742). —It is possible to prepare a continuous series of mixed crystals of Mg and AgCd<sub>3</sub> (a "Hume-Rothery" compound). Debye-Scherrer diagrams show a continuous displacement of lines as the amount of Mg is increased. This indicates that there is no essential difference between the "Hume-Rothery" binding and that which is found in the elements. A. J. M.

Atomic rearrangement process in the alloy  $Cu_3Au$ . C. SYKES and F. W. JONES (Proc. Roy. Soc., 1936, A, 157, 213-233).—Experimental data relating to the effect of at. rearrangement on the energy content of  $Cu_3Au$  are compared with those predicted by the theories of Bragg and Williams (A., 1934, 954) and of Bethe (A., 1935, 1193) and Peierls (A., 1936, 782, 1196). The last-named theory gives the best approximation. From the deduction that the energy of any atom is fixed only by the identity of its neighbours within two at. distances, it follows that a large proportion of the energy of the ordering process is released when the regions of consistent order have reached a length of  $5 \times 10^{-7}$  cm. On the other hand, the electrical resistance of the alloy begins to diminish when the ordered regions are about  $5 \times 10^{-7}$  cm. long. L. L. B.

Methods for the examination of thermal effects due to order-disorder transformations [in alloys]. C. SYKES and F. W. JONES (J. Inst. Metals, 1936, 59, Advance copy, 469-492; cf. A., 1935, 576). -Apparatus is described for making measurements while the temp. is continuously varied. The specimon in the form of a hollow cylinder is mounted inside and thermally insulated from a Cu cylinder and can be heated independently by means of an internal nichrome coil. The whole is placed in an evacuated SiO<sub>2</sub> tube and by suitable adjustment of the current the temp. of the specimen is made to follow a definite wavy curve which intersects the heating curve of the Cu at a no. of points. In this way a sp. heat-temp. curve is obtained which includes the heat effects of any transformation superimposed on the normal  $C_p - \tilde{T}$  curve. Values of sp. heat at any temp. and of the direct energy content may be obtained. Examples of its use with  $Cu_3Au$  and  $\beta$ -brass are given. A. R. P.

Influence of temperature on potential-concentration relations for binary alloys. G. TAM-MANN and H. WARRENTRUP (Z. anorg. Chem., 1936, 230, 41-42).—In alloys forming continuous series of mixed crystals the electrode potential is independent of the composition of the electrode over a wide range, if the temp. is below that at which internal diffusion can occur (Ag-Au, Tl-Pb at room temp.). At temp. high enough to permit diffusion (>300° for Ag-Au, >250° for Tl-Pb) the potential varies continuously with composition. Curves are given to illustrate tho effect of temp. in the case of alloys yielding a eutectic, those giving intermetallic compounds, and for the special cases of Zn-Cu and Cu-Ag-Au. F. L. U.

Reactivity of alloys during transformations in solid state. II. J. A. HEDVALL and U. ROSEN (Z. anorg. Chem., 1936, 229, 413—417; cf. A., 1932, 574).—The rate of oxidation of CoSn undergoes a sudden increase at 517—519°, corresponding with the temp. of phase transformation. AgCd similarly shows a max. rate at 432—434°. J. S. A.

Stability of solid solutions of ferrous and cobaltous oxides. J. BÉNARD (Compt. rend., 1936, 203, 1356—1359).—FeO and CoO form a complete series of solid solutions, with a linear variation of the X-ray parameter. The temp. at which the reaction  $4\text{FeO} = \text{Fe} + \text{Fe}_3\text{O}_4$  is reversible (570°) increases to 880° for 3FeO + CoO, remains approx. const. with increasing [CoO], and then falls. Mixtures richer in CoO form solid solutions of  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ , and CoO, together with Co. H. J. E.

Investigation by emanation method of changes in mixtures of oxides during transition to compounds. H. KITTEL (Z. physikal. Chem., 1936, 178, 81-92).—The effect of continued heating on the emanating power, E, of Fe<sub>2</sub>O<sub>3</sub> and equimol. mixtures with ZnO, MgO, BeO, and CuO, all rendered radioactive by addition of radio-Th, has been examined. In the temp. region in which active intermediate reaction products are formed (cf. A., 1936, 1216) E rises, but on crystallisation of the final product falls again. The reactivity of the Fe<sub>2</sub>O<sub>3</sub> is greater the lower the temp. at which it has been prepared. E is considerably affected by the expulsion of traces of H<sub>2</sub>O at the higher temp. If Fe<sub>2</sub>O<sub>3</sub> or a ZnO-Fe<sub>2</sub>O<sub>3</sub> mixture is heated at const. temp. below 700° E remains steady but fluctuates at higher temp.

R. C.

Lower limit of the formation of mixed crystals of the new type. A. POLESICKI (Compt. rend. Acad. Sci. U.R.S.S., 1936, 4, 65—66; cf. Chlopin and Nikitin, A., 1930, 149).—No mixed crystals of  $KClO_4$ – PbSO<sub>4</sub> are formed when  $KClO_4$  is crystallised from saturated solutions of PbSO<sub>4</sub> in NaNO<sub>3</sub>. O. D. S.

Molecular heat of methane in solid mixtures of methane and krypton. A. EUCKEN and H. VEITH (Z. physikal. Chem., 1936, B, 34, 275–299).—From measurements of the mol. heat of  $CH_4$ -Kr mixed crystals at 12—80° abs. the mol. and rotational heats of  $CH_4$  in the crystals have been calc. The anomaly exhibited by pure  $CH_4$  at 20.6° decreases with increasing proportion of Kr and for 30—50% Kr the rotational heat rises continually with temp.; for the

the surface, forming mols. which evaporate into the gas phase. In terms of this and the reverse process certain apparent anomalies in experimental data can be explained. A. J. E. W.

Rate-determining step in the diffusion of hydrogen through palladium. A. FARKAS (Trans. Faraday Soc., 1936, 32, 1667—1679; cf. A., 1933, 1260).—The rate of diffusion of  $H_2$  through a Pd disc into a vac. has been measured at different temp. between 20° and 320°. By using para- $H_2$  and measuring the rate of para-ortho conversion on both sides of the disc, it is shown that although the two sides may have entirely different catalytic activities, the rate of diffusion is independent of its direction. The primary processes occurring are (1) sorption of  $H_2$  involving dissociation, (2) transfer of at. H through the Pd, (3) desorption of  $H_2$ . Heats of activation for these processes are cale. Under the experimental conditions used, sorption is the rate-determining process.  $H_2$  diffuses slightly more rapidly than  $D_2$ . F. L. U.

Solubility of deuterium and hydrogen in solid palladium. II. A. SIEVERTS and W. DANZ (Z. physikal. Chem., 1936, B, 34, 158–159; cf. A., 1936, 25).—The solubilities have been determined at 1 atm. between 20° and 350°. R. C.

Adsorption of carbon monoxide on zinc oxide. W. E. GARNER and J. MAGGS (Trans. Faraday Soc., 1936, 32, 1744—1748).—Adsorption isotherms for CO on ZnO have been determined between —78° and 35° and heats of adsorption calc. The adsorption isobar shows no discontinuity, and the conclusion is reached that discontinuities occur only in the case of adsorbents where capillary flow is present.

F. L. U. Adsorption of molecular and atomic iodine on quartz glass. P. HÖLEMANN and A. BRAUN (Z. physikal. Chem., 1936, B, 34, 381-395).-The adsorption of I vapour has been measured at 150-1000° and conens. of  $1.7 \times 10^{-5}$  and  $3.3 \times 10^{-5}$  g. per c.c. The adsorption falls with rising temp., and at a given temp.  $\propto d$  of the vapour. From the variation with temp. at 150-400° the calc. mol. heat of adsorption of mol. I is 1.2 kg.-cal. Above 850° the I is adsorbed almost exclusively as atoms, the lower limit of the heat of adsorption being  $\sim 15$ kg.-cal. The active surface for at. adsorption is  $\ll$  than for mol. adsorption, showing that the atoms are mainly adsorbed at special centres, whilst mol. adsorption occurs fairly uniformly over the whole surface. The v.p. of I at 15.21° is 0.120 mm.

R. C. Adsorption on ionic lattices. I. M. KOLTHOFF (J. Physical Chem., 1936, 40, 1027—1040).—Various types of adsorption on ionic ppts. are discussed.

F. L. U. Adsorption of complex [metal-]ammine ions by silica gel. L. H. REYERSON and R. E. CLARK (J. Physical Chem., 1936, 40, 1055—1062; cf. A., 1930, 991).—Adsorption isotherms for complex Ag-NH<sub>3</sub> and Cu-NH<sub>3</sub> ions on undialysed and electro-dialysed SiO<sub>2</sub> gel have been determined. Adsorption increases with rise of  $p_{\pi}$  from 8 to 9.6, and is strong at very low concns. F. L. U.

highest proportion of Kr (72%) there is a max. again at about 22°. Above 30° for all the mixtures and for pure  $CH_4$  the rotational heat is approx. 3R/2. The results indicate that in the solid state, but not in the gaseous state, the three modifications of CH4 are able to pass directly one into another. It appears that the potential energy of CH4 rotating in the crystal is negative relative to that of the corresponding free rotator and rises numerically with temp.; an explanation is suggested. Light is thrown on the anomaly at 20.6° by supposing that instead of ascribing independent rotational degrees of freedom to the individual mols. torsional waves, resulting from the coupling of the rotators, may be assumed to be propagated through the whole solid, taking over the role of individual degrees of freedom. This furnishes a possible mechanism for the transformation of potential into rotational energy when a certain temp. is reached. R. C.

Demixing in aqueous salt solutions. H. G. B. DE JONG and L. T. VAN ZIJP (Proc. K. Akad. Wetensch. Amsterdam, 1936, **39**, 1103—1106; cf. A., 1935, 1320).—Demixing has been observed in a no. of solutions in which double decomp. is involved. O. D. S.

Solubility in alkalis of some phenolic derivatives.—See A., II, 21.

 $D_2O$  and  $H_2O$  as solvents for optically active materials. H. ERLENMEYER and H. SCHENKEL (Helv. Chim. Acta, 1936, 19, 1381–1382).—The val. of  $[\alpha]_{20}^{\infty}$  for NMePr<sup>\$PhBz\*NO\_3\$</sup> is slightly greater for aq. solutions than for solutions in  $D_2O$  (90.8%).

J. W. S.

Theory of concentrated solutions. XIV. Solubilities in mixtures of two miscible solvents. J. MAHIEU (Bull. Soc. chim. Belg., 1936, 45, 667-675).-The solubilities of picric acid, anthracene, anthraquinone, C10H8, NHAcPh, aceto-p-toluidide, and I have been determined (mainly at 25°) in various complete series of homogeneous binary mixtures. These mixtures involve the solvents  $C_6H_6$ , PhMe, PhCl, PhBr, CCl<sub>4</sub>, CS<sub>2</sub>, Et<sub>2</sub>O, COMe<sub>2</sub>, CHCl<sub>2</sub>,  $C_6H_{14}$ , PhNO<sub>2</sub>, NH<sub>2</sub>Ph, *cyclohexane*, H<sub>2</sub>O, EtOH, MeOH, and PrOH. Some of the results obtained afford no evidence of a parallelism between the solubility curves and the saturated v.p. curves for the corresponding mixtures. Solubility curves with maxima, minima, points of inflexion, etc. have been obtained and are interpreted in terms of compound formation between the solvents or between the solute and one of the solvents. Solubility curves for binary mixtures which are characterised by a crit. solution temp. (T) generally exhibit max., irrespective of whether the solute raises or lowers T. J. G. A. G.

Solubility of gases in molten metals. H. VON WARTENBERG (Z. Elektrochem., 1936, 42, 841-845).—Published work is reviewed and evidence for the formation of gas-metal compounds adduced.

E. S. H.

Diffusion of gases through metals. J. S. WANG (Proc. Camb. Phil. Soc., 1936, 32, 657-662; cf. A., 1936, 281, 1062).—Consideration is given to a surface process in which atoms diffusing to the surface from inside the metal combine with atoms adsorbed on

▼ (a-c)

Sorption properties of mixed catalysts. I. Sorption of ammonia on ammonia catalyst and the rôle of the promoter. M. J. KAGAN, N. M. MOROZOV, and O. M. PODUROVSKAJA (Acta Physicochim. U.R.S.S., 1936, 5, 491-508).—NH<sub>3</sub> is adsorbed by  $Al_2O_3$  at 400-740°, the amount adsorbed decreasing with rise of temp. The heats of adsorption are 30,000 and 18,000 g.-cal when the adsorbed NH<sub>3</sub> amounts to 2 and 6 c.c. per g. of  $Al_2O_3$ , respectively. Above 500° the adsorbed NH<sub>3</sub> decomposes into H and NH<sub>2</sub>, which is retained in the adsorbed layer. The addition of K<sub>2</sub>O to  $Al_2O_3$  reduces the heat of adsorption and the adsorption capacity. From data for mixtures of Fe and  $Al_2O_3$ , with and without K<sub>2</sub>O, it is inferred that  $Al_2O_3$ , by adsorbing NH<sub>3</sub>, inhibits, and that K<sub>2</sub>O, by reducing the adsorption capacity of  $Al_2O_3$ , promotes, the catalytic action of Fe in the synthesis of NH<sub>3</sub>. C. R. H.

Adsorption layers in disperse systems. XIV. Surface phenomena in processes of crystallisation. Effect of adsorption layers on the localised crystallisation of silver. N. N. SERB-SERBINA. XV. Effect of adsorbed layers on the crystallisation of calcium sulphate. N. N. SERB-SERBINA and V. G. DUBINSKI (J. Phys. Chem. U.S.S.R., 1934, 5, 1186—1189, 1190—1198).—XIV. The relative quantities of Ag formed in the reduction of ammoniacal AgNO<sub>3</sub> by glucose in presence of surface-active substances and hydrophilic colloids were measured. Surface-activo substances (e.g., o-cresol and aq. NH<sub>3</sub>) do not affect the localised crystallisation. Hydrophilic colloids decrease the amount. Adsorption layers of such colloids render the nuclei passive and decrease the rate of crystallisation. Adsorption of ions on the micelles increases the no. of crystal nuclei and the dispersity.

XV. The crystallisation of  $CaSO_4$  in glass, Ag, and paraffin-coated vessels in presence of surface-active substances and hydrophilic colloids was studied.  $CaSO_4$  crystallises in greater quantity on a hydrophobic than on a hydrophilic surface under conditions of quiet growth. Almost all additions increase the local crystallisation. Hydrophilic colloids raise the limit of supersaturation and, under the above conditions, decrease the dispersity. CH. Abs. (e)

Theory of negative adsorption of Debye-Hückel electrolytes. K. ARIYAMA (Bull. Chem. Soc. Japan, 1936, 11, 687—691).—Mathematical.

R. S.

Chemisorption on charcoal. VIII. Influence of temperature on (a) catalytic oxidation of salts, (b) catalytic decomposition of hydrogen peroxide. A. KING (J.C.S., 1936, 1688—1692; cf. A., 1935, 1069).—C activated in  $O_2$  exerts a max. catalytic effect on the oxidation of  $K_4$ Fe(CN)<sub>6</sub>, Na<sub>3</sub>AsO<sub>3</sub>, KNO<sub>2</sub>, and quinol when the temp. of activation (t) is in the region of 450°, and a min. effect when t = about 850°. In the catalytic decomp. of  $H_2O_2$  the activity is max. for t = 900° and min. for t = 450°. The results are interpreted on the assumption of the existence of at least two surface oxides of C. F. L. U.

Effect of dilute hydrochloric acid on surface tensions of aqueous salt solutions. J. W. BELTON (Trans. Faraday Soc., 1936, 32, 1717-1721; cf. A., 1935, 1317).—The presence of HCl at 0.1M produces a lowering of the surface tension of aq. solutions of LiCl, CaCl<sub>2</sub>, SrCl<sub>2</sub>, BaCl<sub>2</sub>, NaClO<sub>4</sub>, and Na<sub>2</sub>S<sub>2</sub>O<sub>6</sub>. The effect increases with increasing salt concn. The amount of H<sub>2</sub>O adsorbed at the surface of the ternary solutions is calc. from the Gibbs equation. F. L. U.

Effects of sodium chloride and aniline hydrochloride on surface tensions and partial vapour pressures of aqueous aniline solutions. J. C. SPEAKMAN (J.C.S., 1936, 1662—1668; cf. A., 1935, 930).—Surface tensions and partial v.p. of NH<sub>2</sub>Ph have been measured for aq. solutions of NH<sub>2</sub>Ph containing NaCl, NH<sub>2</sub>Ph,HCl, and NaCl + NH<sub>2</sub>Ph,HCl, and surface adsorptions have been estimated. The max. adsorption of NH<sub>2</sub>Ph is not affected by NaCl, but is diminished by NH<sub>2</sub>Ph,HCl. The results are discussed from the point of view of the influence of the salts on the solubility of NH<sub>2</sub>Ph. F. L. U.

Surface films of resinols and allied substances. F. A. ASKEW (J.C.S., 1936, 1585-1592; cf. A., 1935, 974).—Surface pressure and surface potential measurements of 18 compounds of, or related to, the resinol group have been made, and the results compared with similar data for compounds of known structure. The amyrins and other mono-OH compounds give mol. areas consistent with accepted formulæ with OH in the position corresponding with the 3-position in the sterol formula. Data for CO- and  $CO_2H$ -sub-stituted compounds are also consistent with their allotted formulæ. The behaviour of  $(OH)_2$ -compounds, especially those related to betulin, is difficult to interpret. Compounds having two or more widely separated polar groups may be attached to H<sub>2</sub>O by only one of them if it possesses a much greater H<sub>2</sub>Oattracting power than the others, but may be caused to lie flat in the surface if the former is weakened, e.g., by acetylation. The phenomenon of contraction, shown by many of the films, is discussed. F. L. U.

Surface energy in saturated phases. N. F. LASCHKO and B. G. PETRENKO (Ukrain. Chem. J., 1936, 11, 270–273).—Theoretical. R. T.

Unimolecular films of nerve proteins.—See A., III, 56.

Multimolecular films : mixed films with two or more components. I. Fatty acids and nonpolar substances. R. J. MYERS and W. D. HARKINS (J. Physical Chem., 1936, 40, 959-971).-By means of apparatus previously described (this vol., 26) surface pressure-mol. area curves for films of myristic (I), pentadecoic (II), stearic (III), and oleic (IV) acids mixed with varying amounts of C14H30 or Nujol on 0 01 N-HCl have been determined. Addition of Nujol to (III) facilitates collapse at a lower pressure, but the areas at zero compression are not affected. On the other hand, for (I), (II), and (IV) areas at zero compression are considerably larger than those of the pure acids, and the form of the curves is markedly F. L. U. changed.

Unsupported starch films. W. SECK and R. BREM (Kolloid-Beih., 1936, 45, 99-148).—The properties of starch films have been studied with special reference to anisotropy. In general the films consist of an inner unoriented mass enclosed between oriented outer layers. The degree of orientation is decreased with increasing conen. and increasing thickness of the film. The influence of  $\eta$  and of the method of prep. has also been studied. E. S. H.

Quantitative spreading of fibrinogen in unimolecular films. L. FOURT and A. M. PERLEY (Proc. Soc. Exp. Biol. Med., 1935, 33, 201-203).-By the use of solutions of fibrinogen containing 9.5% of EtOH, quant. spreading of the protein films on the surface of aq. buffer solutions is obtained, the area per mg. being approx. independent of the amount of protein spread. W. O. K.

Pore diameter of collodion membranes used in ultrafiltration. P. GRABAR and S. NIKITINE (J. Chim. phys., 1936, 33, 721-741; cf. A., 1933, 672; 1932, 691).—The size distribution of the pores has been calc. from the rates of flow of a liquid, under various pressures, through each membrane saturated with an immiscible liquid having a very small interfacial tension with respect to the first. The difference between the min. and the max. pore diameters for membranes from different batches prepared by Elford's method is approx. cc the mean pore diameter, d. The pore distribution for membranes with small vals. of d is irregular, but with large vals. of d, the distributions are regular. The dispersion curves generally show two or more max. J. G. A. G.

Cryoscopic studies of solutions in formamide. II. F. H. GETMAN (Rec. trav. chim., 1936, 55, 969-978; cf. A., 1936, 561).-F.-p. data for MeOH, EtOH, Pr<sup> $\circ$ </sup>OH, Bu<sup> $\circ$ </sup>OH, Bu<sup> $\beta$ </sup>OH, Bu<sup> $\circ$ </sup>OH, CH<sub>2</sub>·CH·CH<sub>2</sub>·OH, (CH<sub>2</sub>·OH)<sub>2</sub>, glycerol, and CH<sub>2</sub>Ph·OH show that, with the exception of Bu<sup> $\circ$ </sup>OH and glycerol, which undergo solvation, the alcohols are slightly associated in the more conc. solutions. In dil. solutions the solutes have normal mol. wts. E. S. H.

Present ideas on the conditions of electrolytes in aqueous solutions. J. J. VAN LAAR (Chem. Weekblad, 1936, 33, 759—768).—A presentation of views associated with the author and Ghosh as distinct from those of Debye and Hückel. S. C.

Variation with concentration of apparent molecular volume of certain strong electrolytes. A. KRUIS (Z. physikal. Chem., 1936, B, 34, 1–12).— By d and dilatometric measurements the apparent mol. vol.,  $\phi$ , of NaCl, SrCl<sub>2</sub>, KCl, and NH<sub>4</sub>NO<sub>3</sub> in aq. solution has been determined at 25° for a series of conces. The graphs of  $\phi$  against  $\sqrt{c}$  are slightly sigmoid, but at the lower conces. the slopes agree with the Redlich-Rosenfeld theory (A., 1931, 1122). R. C.

Equivalent dispersion of strong electrolytes in solution. I. Variation with concentration of equivalent refraction in the visible. A. KRUIS [with W. GEFFCKEN]. II. Physical interpretation of observed effects. III. Variation with concentration of equivalent dispersion in ultraviolet. A. KRUIS and W. GEFFCKEN (Z. physikal. Chem., 1936, B, 34, 13-50, 51-69, 70-81).-I. *n* has been measured for aq. NaCl, KCl, SrCl<sub>2</sub>, NH<sub>4</sub>NO<sub>3</sub>, and Na<sub>2</sub>SO<sub>4</sub> at concn., *c*, of 0.01-2N at 25° for several  $\lambda\lambda$  in the visible. The apparent equiv. refraction, *R*, for NaCl, KCl, and SrCl<sub>2</sub> passes through a max. with increasing c, whilst for  $NH_4NO_3 R$  decreases almost linearly with increase in c from 0.01N to 3N. The equiv. dispersion, D, increases almost linearly with c for  $Na_2SO_4$  and decreases linearly with increasing c for NaCl, KCl,  $SrCl_2$ , and  $NH_4NO_3$ . Apart from the max. on the R-c curves the change of D with c tends to run parallel with that of R with c at conens. >1.5N. The change in D in passing from the dissolved to the cryst. state is the same in sign as that accompanying increasing c.

II. The above variation of D with c is due to the variation with c of the characteristic frequency, v, and the probability of transition of the long- $\lambda$  ultraviolet halogen band, whilst the dependence of Ron c arises chiefly from the variation of the parameters of bands in the farther ultra-violet. Since the rate of change of the band parameters with increasing cappears to vary with the cation and since, also, the position of the long- $\lambda$  ultra-violet absorption max. of the halogen ion does not vary with c or the cation there must be a red shift of the absorption max. towards v by an amount which increases with c. This shift must be ascribed to the Lorentz-Lorenz force increasing with c. For NaCl the val. of D extrapolated to infinite dilution,  $D_{\infty}$ , may be represented by a three-term formula, the positive infrared term of which is to be attributed to the ions reducing the infra-red part of the refraction of the  $H_2O$ . The refractometric solution effect is not, however, due solely to the effect of the ions on the infra-red bands of  $H_2O$ . Vals. of  $D_{\infty}$  have been calc. for various ions. The results show that D and R run parallel with each other; both are smaller for cations of the noble gas type than for the isosteric noble gases and anions.

III. As c increases, D in the infra-red increases for  $\text{Li}_2\text{SO}_4$ ,  $\text{NaClO}_4$ , and  $\text{NH}_4\text{F}$ , falls for LiCl, NaCl, CsCl,  $\text{MnCl}_2$ ,  $\text{NiCl}_2$ , LiOAc, LiBr, RbBr, NaI, and LiCNS, and remains const. for  $\text{LiClO}_3$  and  $\text{NaClO}_3$ . For a given cation the rate of variation of D with c falls in the order CNS', I' > Br' > Cl', OAc'; the effect of varying the cation is uncertain. R. C.

Interpretation of variation with concentration of equivalent refraction of strong electrolytes. A. KRUIS (Z. physikal. Chem., 1936, B, 34, 82—95).— The change in slope of the equiv. refraction-concn. curve of aq. NaBr, NaCl, KCl, SrCl<sub>2</sub>, and Na<sub>2</sub>SO<sub>4</sub> at 25° at concns. <N is attributed to an effect of the ions on H<sub>2</sub>O mols. which are not in their immediate vicinity. This depresses their refractive power by altering their quasicryst. arrangement or degree of polymerisation. R. C.

Optical behaviour of dissolved ions and its significance for the structure of solutions of electrolytes. V. Optical absorption and dispersity of organic dye ions in aqueous solution. G. KORTÜM (Z. physikal. Chem., 1936, B, 34, 255–274; cf. A., 1936, 1197).—Measurements of the absorption of various dyes at conens. of  $1-3 \times 10^{-5}M$  for several  $\lambda\lambda$  have been made to test the validity of Beer's law. Deviations from the law in such dil. solutions are due to micelle formation by the dye ions, which is more marked and more rapidly established the larger are the ions and the less their surfaces are

shielded by hydrophilic groups. The bearing of these results on the connexion between degree of dispersity and the tinctorial properties of dyes is discussed. R. C.

Physico-chemical properties of electrolytes. I. Relation between physico-chemical and spectral properties of electrolytes. F. VLES (Arch. Phys. biol., 1935, 12, 57-73; Chem. Zentr., 1936, i, 1190).—A discussion (cf. A., 1935, 444). H. J. E.

Dielectric constants of some dilute solutions of salts. W. M. MAZEE (Physikal. Z., 1936, 37, 914-916).—The dielectric consts. of dil. aq. solutions of KI, MgSO<sub>4</sub>, BeSO<sub>4</sub>, K<sub>3</sub>Fe(CN)<sub>6</sub>, K<sub>4</sub>Fe(CN)<sub>6</sub>, and Ba<sub>2</sub>Fe(CN)<sub>6</sub> were determined. The results agree with the Debye-Falkenhagen equation. In very dil. solutions MgSO<sub>4</sub> and BeSO<sub>4</sub> have the same dielectric const. A. J. M.

Rotatory power and structure of electrolytic solutions. I. PEYCHES (Ann. Physique, 1936, [xi], 6, 856—993).—Ionic interaction in electrolytes has been examined over a wide concn. range by a study of the optical activity of the tartrate ion in the alkali and substituted  $NH_4$  tartrates. Data are recorded for conductivity, ultra-violet absorption, and Raman effect from which conclusions are reached relative to the nature and extent of the ionisation. A new effect arising from the difference of size of the anion and cation has been observed and this is discussed in relation to the Debye-Hückel theory. The variation of rotatory power is said to be a linear function of the ionic potential. N. M. B.

Optical absorption and association of stannous halides in aqueous solution. H. FROMHERZ and H. J. WALLS (Z. physikal. Chem., 1936, 178, 29— 36).—The absorption curves have been determined. At sufficiently high concess or in presence of a sufficient excess of halogen ions the solutions exhibit absorption bands corresponding with co-ordinatively saturated complex ions of the type  $SnX_4''$ . These are less stable than the complexes formed in solutions of Pb halides and with increasing dilution change continuously through unstable intermediate products containing less halogen to simple ions. R. C.

Complex aquo-arsenate ions with several shells [of solvent molecules]. H. BRINTZINGER and C. RATANARAT (Z. anorg. Chem., 1936, 230, 28—30; cf. A., 1936, 1066).—The ionic wt. of arsenate ions, calc. from dialysis coeffs. determined at different  $p_{\rm H}$  vals., indicates that the no. of H<sub>2</sub>O mols. associated with AsO<sub>4</sub><sup>'''</sup> is 18, with HAsO<sub>4</sub><sup>'''</sup> 6, and with H<sub>2</sub>AsO<sub>4</sub>' 2 or 3. In the bi- and ter-valent ion the central ion is considered to be surrounded by two and three shells of H<sub>2</sub>O mols., respectively. F. L. U.

Development of ideas in colloid chemistry. H. R. KRUYT (Natuurwetensch. Tijds., 1937, 19, 17—19).—A brief discussion of the similarity between true and colloidal solutions. S. C.

Colloid chemistry with reference to molecular association. G. MALFITANO and A. HONNELAÎTRE (Rev. gén. Sci., 1935, 46, 456–465; Chem. Zentr., 1936, i, 1585).—Theoretical. J. S. A. General theory of lyophobic colloids. I. H. C. HAMAKER (Rec. trav. chim., 1936, 55, 1015-1026).—Theoretical. The stability of colloids is discussed in terms of the forces of attraction and repulsion between the disperse particles. E. S. H.

Structure of water envelope of micelles of organic colloids. K. HESS and J. GUNDERMANN (Z. physikal. Chem., 1936, B, 34, 151-157).— Reasons are advanced for rejecting the view that the X-ray diagrams of cellulose and starch are actually the diagrams of a H<sub>2</sub>O envelope surrounding the micelles and having the ice structure (A., 1934, 1162). R. C.

Colloids and the biological effect of radiation. F. ELLINGER (Nature, 1936, 138, 1014-1015).---Results obtained by the action of ultra-violet light on various colloidal substances are recorded. The effect of ultra-violet light on colloids is purely photochemical; it is independent of the electrical charge on the colloids, and when no photochemical action occurs there is no change in this charge. Postulation of a special colloid-chemical theory of the biological action of radiation is unnecessary. L. S. T.

Colloid structure and infra-red absorption spectra. S. S. BHATNAGAR, P. L. KAPUR, and M. D. RAJPAL (Kolloid-Z., 1936, 37, 281–286).—The infra-red absorption spectra of Fe<sub>2</sub>O<sub>3</sub>, As<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, SnO<sub>2</sub>, and Au hydrosols have been determined. Sols having particle diameters  $0.9-1.3 \mu$  and  $1.55-1.75 \mu$ are less and those of diameter  $1.3-1.55 \mu$  and  $>1.75 \mu$ more transparent than H<sub>2</sub>O. These differences and the displacement of the absorption bands of H<sub>2</sub>O are traced to disturbance of the equilibrium between H<sub>2</sub>O, (H<sub>2</sub>O)<sub>2</sub>, and (H<sub>2</sub>O)<sub>3</sub> by the hydrated colloid particles. E. S. H.

Absorption and scattering of light in hydrophobic colloids. I. F. B. GRIBNAU (Kolloid-Z., 1936, 77, 289-294).—Theoretical. E. S. H.

Viscosity problem in organic colloids. Influence of solvent and temperature on the viscosity of cellulose nitrate solutions. W. PHILIPPOFF (Angew. Chem., 1936, 49, 855-857).--Viscosity data are given for solutions of four different kinds of cellulose nitrate in COMe<sub>2</sub>, PhNO<sub>2</sub>, and BuOAc over the range --75° to 60°. The results are discussed in relation to solvation. E. S. H.

Aerosols. I. Conditions of formation. N. N. ANDREEV and S. G. KIBIRKSCHTIS (Kolloid-Z., 1936, 77, 299–301).—Aerosols require a stabiliser as well as disperse phase and dispersion medium. E. S. H.

Constitution of dilute soap solutions. I. Turbidity phenomenon of soap solutions. P. EKWALL (Kolloid-Z., 1936, 77, 320-333).—Nephelometric investigations of aq. Na stearate, palmitate, myristate, laurate, and oleate show that with increasing concn. the solutions pass through two regions of turbidity; the first is caused by particles of free fatty acid and the second by particles of acid soap. At still higher concns. particles of alkali-rich soap are formed and the turbidity diminishes. With rising temp. the particles lose their cryst. structure; this transformation occurs at temp. < the m.p. of the corresponding fatty acid. E. S. H. Electrophoretic mobility of purified tristearin. I. The acid region,  $p_{\rm H}$  2 to 7. A. L. ROBERTS (Trans. Faraday Soc., 1936, 32, 1705–1717).—The mobility of the particles in an emulsion of tristearin at 25° in phosphate, phthalate, citrate, and acetate buffers increases continuously with rise of  $p_{\rm H}$  from 2 to 7, the curve being steepest between 6 and 7. At const.  $p_{\rm H}$  the effect of added anions is determined by conen. rather than the nature of the ions, and in solutions of alkali metal chlorides the lyotropic effect is slight. In the absence of extraneous salts, the electrokinetic charge density decreases with increasing  $p_{\rm H}$ , but increases if added salt is present. Explanations are offered. F. L. U.

Fundamental system of organic micelles. P. A. THIESSEN (Naturwiss., 1936, 24, 763).-It is suggested that the alkali salts of the normal higher fatty acids provide a simple system for studying the properties of org. micelles. Such compounds exist in rhombic and monoclinic forms, the latter being that usually present in colloidal systems. The behaviour towards polarised light and X-rays leads to information concerning the fine structure of the micelles. The sol  $\implies$  gel transition is due to a movement of the long C chains in a crystallographically defined plane, resulting in a loosening of the micelle structure, and a sudden change in the state of aggregation of the micelle. The application of electron diffraction to the study of surface conditions of the micelle shows that the surface is occupied to a large extent by polar groups. The results of such investigations with soaps are readily applied to other org. substances containing both polar and non-polar groups. A. J. M.

Condition of dissolved highly polymerised organic compounds, especially cellulose. I, II. G. SAITO (J. Soc. Chem. Ind. Japan, 1936, 39, 351— 353B).—The assumption that long-chain mols. behave independently of one other in dil. solution is subjected to criticism. A. G.

Diffusion of compounds of high mol. wt. and related compounds. V—IX. M. TANIGUCHI and I. SAKURADA (J. Soc. Chem. Ind. Japan, 1936, 39, 333B, 333—335B, 335—336B, 336—337B, 337—338B; cf. A., 1936, 286).—V. The diffusion coeff. (D) of mixtures is discussed from a theoretical point of view.

VI. The relation derived in V is shown to hold for solutions containing two or more of glucose pentaacetate, cellobiose octa-acetate, quinol, cellulosedextrin acetate (I), and secondary cellulose acetate (II) in MeOAc at  $23^{\circ}$ .

VII. D for two fractions of (I) in MeOAc has been determined at  $24.7-25^{\circ}$ . The same val. is obtained when cellulose nitrate is dissolved in the solvent to an extent such that  $\eta$  is increased 30 times.

VIII. D has been determined for fractions of (II) in MeOAc at  $16.5-21.5^{\circ}$ .

IX. If a spherical mol. is assumed, the mol. radius (r) of fractions of (II) = 53-60.5 A. and the mol. wt. = 9400-10,000, *i.e.*, a polymerisation of approx. 40 glucose residues. These vals. are approx. 0.5-0.33 of those derived from osmotic data. If the mol. is regarded as a fibril with the long axis = 12 A. (Staudinger), the degree of polymerisation = 90-120, in agreement with osmotic data. R. S. B.

Study of the solute state of natural high polymerides. M. ULMANN (Angew. Chem., 1936, 49, 926—928).—An isothermal distillation method for determining osmotic pressure is described which gives results in agreement with those obtained by the membrane method and may be used with very dil. solutions where the membrane method fails. The method enables a distinction to be drawn between normal association, when the mols. are grouped together, and special association, due to the formation of a new type of mol. entity. F. C. B. M.

Deformation of dissolved polystyrene molecules on streaming. R. SIGNER and C. SADRON (Helv. Chim. Acta, 1936, **19**, 1324—1327; cf. A., 1933, 902).— The streaming anisotropy and extinction angle of solutions of polystyrene in *cyclo*hexanone and tetralin show a discontinuous increase at a certain val. of the streaming gradient (G), which depends on the concn. and solvent. The discontinuity occurs at a const. val. of the product  $G_{\eta}$ . The phenomenon is attributed to a deformation of the chain-like solute mols., superposed on their orientation in the streaming liquid.

H. J. E. Structure of platinum sols. II. The platinum hydroxosols. W. PAULI and A. BACZEW-SKI (Monatsh., 1936, 69, 204-233; cf. A., 1935, 1202). -The conductivity,  $\kappa$ , and the NaOH and Ba(OH)<sub>2</sub> conductometric titration vals. for Pt hydroxosols increase towards equilibrium vals. with time. Boiling accelerates the process. The difference between the observed conductivity and that calc. from the [H'] is ascribed to the formation of complex Pt acids and Pt platinates on the colloid surface. Pure cone. Pt hydroxosols prepared by electro-decantation, and also the supernatant liquid and coagulate obtained therefrom by freezing, have been similarly investigated. When two such sols are mixed,  $\kappa$  etc. increase towards new equilibrium vals. owing to the formation of ionogenic groups and reactive oxides on the particle surface. Pt hydroxosol is completely coagulated by reduction with H, or by long boiling, but is unaffected by CO<sub>2</sub>, whilst treatment with HHal does not yield R. S. halogen-sols.

Viscosimetric investigation of the structure of ferric hydroxide sols. IV. Influence of alcohols. I. B. REVUT (Acta Physicochim. U.R.S.S., 1936, 5, 537—548).—Alcohols lower the conductivity and [Fe<sup>TT</sup>] of FeCl<sub>3</sub> solutions without affecting the  $p_{\rm ff}$  to any great extent; the extent of the lowering increases with the no. of C atoms. The coagulating effect of alcohols on Fe(OH)<sub>3</sub> sols is attributed to a reduction in [Fe<sup>TT</sup>] in the intermicellar liquid, followed by a lowering of the  $\varepsilon$ - and  $\zeta$ -potentials. C. R. H.

Transference numbers of colloidal "ferric hydroxide." J. W. MCBAIN and W. M. THOMAS (J. Physical Chem., 1936, 40, 997—1004).—Transport nos. of a " $Fe(OH)_3$ " sol, previously described (A., 1932, 994; 1933, 567), have been determined by the analytical and moving boundary methods, which give the same results. In the sol used, only 10.5% of the total Cl functioned as anion, the remainder travelling with the Fe. The physicochemical properties of the sol are summarised. F. L. U.

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Coagulation of sols by electrolytes. VI. Cupric ferrocyanide sol. H. B. WEISER and W. O. MILLIGAN (J. Physical Chem., 1936, 40, 1071– 1082; cf. A., 1936, 157).—Both above and below the pptn. concn., adsorption of cations is  $\geq$  the displacement of H ions in a Cu<sub>2</sub>Fe(CN)<sub>6</sub> sol stabilised by H<sub>4</sub>Fe(CN)<sub>6</sub>; this appears to be due to the fact that most of the H ions of the diffuse outer layer are in the intermicellar liquid. The adsorption of cations is largely an exchange adsorption. The behaviour of Cu<sub>2</sub>Fe(CN)<sub>6</sub> sol towards electrolytes is essentially similar to that of sols of S, As<sub>2</sub>S<sub>3</sub>, and hydrous oxides. F. L. U.

Perfection and agglomeration of crystalline precipitates on ageing. I. M. KOLTHOFF (Science, 1936, 84, 376-377).-The ageing of BaSO<sub>4</sub> and AgCl at room temp. substantiates the view that the classical type of ageing (so-called Ostwald ripening) is of subordinate significance at room temp. Fresh ppts., although cryst., are highly imperfect, and, especially during the early stages of ageing in the motherliquor, a very fast perfection process occurs as a result of recrystallisation without always being accompanied by pronounced changes of the external surface (Ostwald ripening). All factors which decrease the solubility of the ppt. inhibit the speed of perfection and vice versa. This recrystallisation occurs in a liquid film around the primary particles, the surface of which is very irregular and contains spots of various activities, and results in a self-digestion and self-perfec-tion of the primary particles. The speed of perfection is determined not by the solubility of the ppt. in the bulk of the solution but also by the solubility in the liquid film around the particle. Agglomeration and a cementing process, which is irreversible and results in a decrease of total surface of the ppt., also accompany recrystallisation. L. S. T.

Hydration and structure of starch. G. CEN-TOLA (Atti R. Accad. Lincei, 1936, [vi], 617—622).— Aq. v.p.-temp. curves have been measured for two samples of starch in which the moisture content varied from 0 to 30%. Two stages of dehydration are observed. The H<sub>2</sub>O lost in the second slower stage is supposed to enter into the crystal lattice, but since the v.p. varies continuously with the composition of the solid phase, it cannot be H<sub>2</sub>O of crystallisation. O. J. W.

Colloidal copper and alcoholic aluminium oxide gel. M. A. MILLER (Kolloid-Z., 1936, 77, 310-312).—Finely-divided Cu, reduced from aq. CuCl<sub>2</sub> by Al, is peptised to a sol by 95% EtOH; the particles are slowly transformed into Cu(OH)<sub>2</sub>. Al and Cu in contact in 95% EtOH form Al(OH)<sub>3</sub> gel. E. S. H.

Ionic exchange produced by the addition of nitrates of thorium, hexol, and cerium to the negative sol of silver iodide. J. GHLIS and J. EECKHOUT (Proc. K. Akad. Wetensch. Amsterdam, 1936, **39**, 1099—1103).—After coagulation of an AgI sol by the addition of  $Th(NO_3)_4$  or hexol nitrate part of the  $NO_3'$  ions is removed with the ppt. The amount removed is < in the case of lyophilic sols. After coagulation with Ce( $NO_3$ )<sub>3</sub> the whole of the  $NO_3'$  is found in the solution. O. D. S.

Intramicellar swelling of cellulose in water. I. SAKURADA and K. HUTINO (Kolloid-Z., 1936, 77, 346—351).—The formation of " $H_2O$ -cellulose" (I) by treating Na-cellulose-I with  $H_2O$  is described. The lattice consts. of (I) have been determined and it appears that  $H_2O$  penetrates into the lattice. (I) is stable in  $H_2O$  and mineral acids at room temp., but when dried at 25° it is converted into cellulose hydrate (II). (I) swells in  $H_2O$  more strongly than (II). E. S. H.

Hydrophilic properties of cellulose. I. Hydration problem. K. KANAMARU. II. Hydrophilic properties of electropositive cellulose fibres. K. KANAMARU and T. NAKAMURA (Kolloid-Z., 1936, 77, 351-356, 357-365).—I. When cellulose and its derivatives are kept in H<sub>2</sub>O the  $\zeta$ -potential falls in accordance with  $-d\zeta/dt = a(\zeta - \zeta_{\infty})$ , where  $\zeta_{\infty}$  is the value of  $\zeta$  which is asymptotically approached. The results show that  $\zeta_0 - \zeta_{\infty}$  is a measure of the capacity,  $\zeta_0 - \zeta$  of the degree, and  $-d\zeta/dt$  of the velocity of hydration.

II. Čellulose treated with adsorbed  $Al(OH)_3$  gives reduced hygroscopicity and enhanced electrical insulating properties. The best conditions for treating cellulose so as to improve these properties without impairing mechanical strength have been determined. E. S. H.

Heterogeneous equilibrium of protein solutions. I. Activity coefficients and membrane equilibrium in mixtures of gelatin and salts. N. R. JOSEPH (J. Biol. Chem., 1936, 116, 353-370).— The effect of gelatin and other proteins on the activity coeff. of ZnCl<sub>2</sub> has been determined electrometrically and also on the basis of data relating to membrane equilibria and solubility. P. G. M.

Digestion of peptised silver bromide. A. RANDOLPH (Z. Physik, 1936, 103, 414—420).—AgBr in gelatin solution was submitted simultaneously to peptising and ripening processes. Emulsions of different grain size were produced, superior to those obtained by ordinary methods. The sensitivity of an emulsion depends not only on the AgBr grain size but also on the physico-chemical state of the grains.

A. E. M.

Retardation of thixotropic solidification by amino-acids. W. HELLER (Compt. rend., 1936, 203, 1507—1509).—Changes occurring during the centrifuging of thixotropic  $Fe_2O_3$  sols, with and without added glycine or glucose, are described and discussed. A.J.E.W.

Perchlorates and the lyotropic series. P. GIBERT and A. DURAND-GASSELIN (Bull. Soc. chim., 1936, [v], 3, 2237—2239).—The proximity of ClO<sub>4</sub>' to I' and CNS' in the lyotropic series is illustrated by the fact that aq. solutions of Mg(ClO<sub>4</sub>)<sub>2</sub> dissolve gelatin, agar, sol. starch, glycogen, gluten, gliadin, and (in part) edestin, and form mucilages with rice and carob starch, in the cold. Silk is dissolved slowly on heating, whilst fibrin, casein, ovalbumin, and wool are unaffected. COMEEt is completely miscible with dil. aq. Mg(ClO<sub>4</sub>)<sub>2</sub>. F. L. U.

Gelation of bentonite suspensions. G. BROUGH-TON and L. SQUIRES (J. Physical Chem., 1936, 40, 1041—1053).—The influence of concn., temp., and addition of EtOH on the rate of gelation of bentonite suspensions has been studied. The results are consistent with the view that setting is due to the formation of random structures by direct aggregation of the particles without any solvent sheath.

F. L. U.

Electrodialysed gels of silica, alumina, ferric hydroxide, and their mixtures. II. Moisture retention capacity of the gels saturated with different cations. P. B. BHATTACHARYYA and K. GANGULY (J. Indian Chem. Soc., 1936, 13, 547— 554; cf. A., 1936, 796).—The pure gels take up most H<sub>2</sub>O when saturated with Na', whereas binary mixtures have the greatest capacity when saturated with Mg<sup>\*\*</sup>. The absorption accords with the Freundlich isotherm and retention of H<sub>2</sub>O is a max. at SiO<sub>2</sub>/ Fe<sub>2</sub>O<sub>3</sub>(Al<sub>2</sub>O<sub>3</sub>) = 1.4. R. S.

Diffusion of water through agar jellies. L. ZOBRIST and M. GRUBER (Kolloid-Z., 1936, 77, 333— 342).—The influence of  $H_2O$ -v.p., temp., concn. of agar, and relative positions of agar and  $H_2O$  has been determined. Diffusion increases at a rate which is  $> \infty$  the saturation deficiency; with rising temp. the diffusion decreases for const. saturation deficiency. The influence of agar concn. varies according to the direction of diffusion of the  $H_2O$ . E. S. H.

Liquefying of sodium hydroxide-albumin gels. J. L. DONNELLY (Kolloid-Z., 1936, 77, 343-345).--When egg-white is treated with NaOH the electrical conductivity rises and then falls; the viscosity and surface tension are lowered, the vol. increases, the temp. rises, and the basic reaction towards phenolphthalein diminishes. These changes are traced to hydrolysis of the hydrated proteinates and dissolution of the Na salts of the degradation products.

E. S. H.

Determination of equilibrium in deuterium exchange reactions in which molecules with numerous atoms are involved. K. WIRTZ (Z. physikal. Chem., 1936, **B**, 34, 121-140).—Theoretical. The equilibrium consts., K, of exchange reactions such as  $A + B \Longrightarrow C + D$  and their variation with temp., T, can be calc. from the vibrational spectra and structure of the mole. statistically by using the relation  $\log_e K = RT \log_e (\Sigma_C \Sigma_D / \Sigma_A \Sigma_B)$ , where  $\Sigma$  are partition functions, assuming that for polyat. mols. translation and rotation are fully excited and vibration not excited at all, and that the changes in the moments of inertia and masses of the heavy mols. caused by interchange of H and D can be neglected; the zeropoint energy of vibration is taken to be  $h\nu/2$ . A method of calculating the contribution to K of the symmetry nos. of complex mols. is described. Calculation of the distribution ratios of H and D for various interchange reactions on these lines has given results agreeing with published data. R. C.

Dissociation constants. A. G. OGSTON (J.C.S., 1936, 1713; cf. A., 1936, 765).—Dissociation consts. of the following have been determined:  $C_6H_2Cl_3$ ·OH,  $C_6Cl_5$ ·OH,  $C_6H_2Br_3$ ·OH,  $C_6Br_5$ ·OH, hypoxanthine, 7- and 9-methylhypoxanthine, inosine, adenine, adenosine,  $\alpha$ -bromopropionyltyrosine, tyramine. Physico-chemical properties of solutions of sulphite-chromium complexes. A. L. ZAIDES (J. Gen. Chem. Russ., 1936, 6, 1325—1334).—The sp. conductivity  $\kappa$  and the intensity of coloration I of violet  $\operatorname{Cr}_2(\operatorname{SO}_4)_3$  solutions increase with rising  $[\operatorname{Na}_2\operatorname{SO}_3]$ ; the Cr is present chiefly as cation with low, and as anion with high,  $[\operatorname{Na}_2\operatorname{SO}_3]$ . In the case of green  $\operatorname{Cr}_2(\operatorname{SO}_4)_3$  solutions the vals. of  $\kappa$  and I pass through a min. at 0.7 mol. of  $\operatorname{Na}_2\operatorname{SO}_3$  per Cr atom. The conversion of violet into green  $\operatorname{Cr}_2(\operatorname{SO}_4)_3$  solutions is represented as  $[\operatorname{Cr}(\operatorname{H}_2\operatorname{O})_6]_2(\operatorname{SO}_4)_3 + \operatorname{H}_2\operatorname{O} \rightarrow$  $[\operatorname{Cr}(\operatorname{H}_2\operatorname{O})_4(\operatorname{SO}_4)_2]' + \operatorname{H}^* + [\operatorname{Cr}(\operatorname{H}_2\operatorname{O})_5\operatorname{OH}]^* + \operatorname{SO}_4''.$ R. T.

Capacity of complex cations to form double shell complex compounds. Single and double shell complex ions of triferric-, tricobaltic-, and trichromic-hexa-acetate-dihydroxy-ions in solution. H. BRINTZINGER and F. JAHN (Z. anorg. Chem., 1936, 230, 176–180; cf. this vol., 94).— The existence of cations of the type  $[M_3(ACO)_6(OH)_2]^*$ (M = Fe, Co, Cr), and of double shell anions  $\{[M_3(ACO)_6(OH)_2]Z_4\}^{\prime\prime\prime\prime\prime\prime}$  (Z = SO<sub>4</sub>, HPO<sub>4</sub>, HASO<sub>4</sub>) in aq. solution is inferred from measurements of dialysis coeffs. F. L. U.

Chemistry in liquid sulphur dioxide. G. JANDER and K. WICKERT (Z. physikal. Chem., 1936, 178, 57—73).—The solubilities and conductivities of solutions in SO<sub>2</sub> of various inorg. substances are recorded. Assuming that the solvent dissociates in accordance with the scheme  $2SO_2 \implies O \cdot SO_2'' +$ SO''  $\implies SO_3'' + SO''$ , thionyl compounds, giving the SO'' ion, should in SO<sub>2</sub> be analogous to acids, whilst sulphites, giving the SO<sub>3</sub>'' ion, should be analogous to bases. Such reactions as Na<sub>2</sub>SO<sub>3</sub> + SOCl<sub>2</sub> = 2NaCl + 2SO<sub>2</sub> are then comparable with neutralisation. Precipitation, solvolytic, and oxidation-reduction reactions have also been studied. The compounds [(NEt<sub>3</sub>)<sub>2</sub>SO]SO<sub>3</sub> and [(NHEt)<sub>2</sub>SO]SO<sub>3</sub> have been obtained by reaction of liquid SO<sub>2</sub> with NEt<sub>3</sub> and NHEt<sub>2</sub>, respectively. R. C.

Exchange of hydrogen between ethyl alcohol and calcium deuteroxide. J. C. JUNGERS and K. WIRTZ (Bull. Soc. chim. Belg., 1936, 45, 679-683).--The D content of EtOH vapour after 1-20 hr. contact with Ca(OD)<sub>2</sub> at room temp. has been determined. The observed vals. accord with those calc. on the hypothesis that only the hydroxy-H of EtOH is exchanged. The reaction is complete in <1 hr.

J. G. A. G.

Conditions for a heterogeneous reaction with a gas phase in the case of miscibility of the condensed phases. M. Doné (Compt. rend., 1936, 203, 1359—1361).—An approx. calculation is made of the equilibrium pressure in the gas phase, assuming that the components of the liquid phase form an ideal mixture. The system  $NaNO_{3 liq}$ — $NaNO_{2 liq}$ — $O_{2}$  is discussed. H. J. E.

Blackening of cinnabar. C. BROSSET (Naturwiss., 1936, 24, 813).—The conversion of red cinnabar into black metacinnabarite on heating is probably monotropic between  $380^{\circ}$  and  $700^{\circ}$ . The black substance produced by the action of visible and ultraviolet light on cinnabar, when examined by the X-ray powder method, shows only lines attributable to

F. L. U.

cinnabar. The blackening cannot be due to the formation of metacinnabarite. A. J. M.

Thermal decomposition of calcium carbonates. L. HACKSPILL (Compt. rend., 1936, 203, 1261-1263). -Different pressure-temp curves are obtained for the decomp. of calcite and of artificial cryst. CaCO<sub>3</sub>; the discrepancy is probably due to difference in crystal size. A. J. E. W.

(A) System sodium and thallium nitrates, chlorides, and sulphates. N. P. LUSHNAJA. (B) Ternary system KCl-KNO3-K2SO1. E. I. Kuz-MINA. (C) Physicochemical conditions of crystallisation of KClO<sub>3</sub> at 0° and -10°. A. I. SASLAVSKI. (D) Binary system NH Cl-H O. E. I. ACHUMOV and B. B. VASSILLEV. (E) System KCl-Ca(ClO<sub>3</sub>), at 25° in aqueous solution. V. S. EGOROV. (F) Sodium and potassium carbonates and bicarbonates in aqueous solutions. A. G. BERGMAN, B. B. VASSILIEV, and S. S. SINANI. (G) System Na<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub>-H<sub>2</sub>O at low temperatures. S. S. SINANI and V. N. CHUDJAKOV. (H) System Na<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub>-H<sub>2</sub>O at elevated temperatures. B. B. VASSILIEV. (I) Isotherm of the system Na<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub>-H<sub>2</sub>O at 0°. V. N. KRAT (Trans. State Inst. Appl. Chem. U.S.S.R., 1935, No. 23, 34-63, 63-66, 67-84, 85, 85-96, 97-100, 100-109, 110-117, 117-118).-(A) The equilibrium diagram, based on thermal analysis, is described.

(B) The ternary eutectic is at  $318^{\circ}$  (K<sub>2</sub>SO<sub>4</sub> 1, KCl 16.75, KNO<sub>3</sub> 82.25%). (c) The KClO<sub>3</sub> yield can be increased to 92–93 and

94-95% at 0° and  $-10^{\circ}$ , respectively.

(D) Solubility data (100-215°) are recorded.

(E) Solubility data are given.

(F) Methods of separating Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> from the solutions obtained in the production of Al(OH)<sub>3</sub> from Khibin nephelites have been studied.

(c) Solubility data  $(-30^{\circ} \text{ to } 12.6^{\circ})$  are recorded.

(H) The best method of separating Na<sub>2</sub>CO<sub>3</sub> and  $K_2CO_3$  is by isothermal evaporation at 125°, when anhyd. Na<sub>2</sub>CO<sub>3</sub> separates. CH. ABS. (e)

Ammoniates of uranyl and uranous chlorides. P. SPACU (Z. anorg. Chem., 1936, 230, 181-186; cf. A., 1934, 613).-Tensimetric study of the systems UO2Cl2-NH3 and UCl4-NH3 indicates the existence of compounds of  $UO_2Cl_2$  with 1, 2, 3, 4, and 5 mols., and of  $UCl_4$  with 3, 4, 5, 6, 10, and 12 mols. of  $NH_3$ . The temp. range was  $-78^{\circ}$  to  $184^{\circ}$ . F. L. U.

Pseudo-binary fusion diagram of monomeric and dimeric dihydroxyacetone. D. TOLLENAAR (Z. anorg. Chem., 1936, 229, 418-422).-The complete equilibrium diagram between the monomeric form, m.p. 83°, obtained by distillation, and the dimeric form, m.p. 117°, obtained by crystallisation from MeOH at  $-80^{\circ}$  has been investigated. By crystallisation from MeOH at 0°, the pseudo-unary equilibrium form, m.p. 82°, mol. wt. 95, is obtained.

J. S. A.

Influence of the modifications of ammonium nitrate in the three-component system ammonium nitrate-carbamide-resorcinol. K. HRYNA-KOWSKI and M. SZMYT (Z. Krist., 1936, 94, 358-366).-F.-p. measurements indicate that the org.

components have no marked effect on the polymorphism of the  $NH_4NO_3$ . The system has two ternary cutectics : one at  $74.0^\circ$ , with 16.0, 18.0, and 66.0, and one at  $42.4^{\circ}$  with 52.0, 45.5, and 2.5% of  $NH_4NO_3$ , CO(NH<sub>2</sub>)<sub>2</sub>, and resorcinol, respectively. B. W. R.

Solubility in the system lead chloride-calcium chloride-zinc chloride-water. D. M. TSCHISHI-KOV and A. S. SCHACHOV (J. Appl. Chem. Russ., 1936, 9, 1387–1393).—Solubility data are recorded for the systems  $PbCl_2$ -ZnCl\_2-H<sub>2</sub>O,  $PbCl_2$ -CaCl\_2-H<sub>2</sub>O, and ZnCl\_2-CaCl\_2-H<sub>2</sub>O, at 25<sup>°</sup> and 60<sup>°</sup>. The formation of double salts is suggested by solubility minima in all three systems. R. T.

Double decomposition in absence of a solvent. XXXI. Multi-component mutual systems. A. G. BERGMAN and I. S. DOMBROVSKAJA. XXXII. Stable complex of quinary mutual systems of nine salts. V. P. RADISCHTSCHEV (Bull. Acad. Sci. U.R.S.S., 1936, 133-152, 153-192).-Theoretical. Methods of representation of multi-component sys-R. T. tems are given.

Free energy as basis of thermodynamics. J. E. VERSCHAFFELT (Natuurwetensch. Tijds., 1937, 19, 21-23).-Mathematical. S. C.

Application of thermomechanics to electro-Application of thermometation (Bull, Acad. roy. chemistry. J. E. VERSCHAFFELT (Bull, Acad. roy. Belg., 1936, [v], 22, 1002—1014).—Theoretical. Problems involving the partial molal free energy of electrolytes are considered. R. C. M.

Thermodynamics of the solubility and crystal hydrate formation of the alkali halides. W. D. TREADWELL and A. AMMANN (Helv. Chim. Acta, 1936, 19, 1201-1210).-The solubility (s) of the anhyd. cryst. alkali halides can be calc. from their heats of formation, decomp. potential, and entropy, independently of the degree of dissociation of the solution. A measure of s can also be obtained by assuming that 1/80 of the lattice energy can be transposed into osmotic work, and subtracting from this the osmotic work which is actually obtainable. The differences between the former and the latter vals. observed with KF, RbF, CsF, LiCl, LiBr, LiI, and NaI are said to afford evidence of the formation of crystal hydrates, whilst the divergences of opposite sign observed with LiF and NaF indicate complex formation. The diminution of the solubility of NaCl in D2O as compared with H<sub>2</sub>O is calc. J. W. S.

Free energy of formation of magnesium oxide and magnesium chloride. W. D. TREADWELL, A. AMMANN, and T. ZURRER (Helv. Chim. Acta, 1936, **19**, 1255—1270; cf. A., 1934, 1317).—From the v.-p. curve of Mg, the sp. heat, heat content, and entropy of Mg and MgO have been calc. between 298·1° and 2400° abs. From these data and the equilibrium MgO +  $Cl_2 \implies MgCl_2 + 0.5O_2$  the heat of formation of MgCl<sub>2</sub> at various temp. is calc. The equilibrium in the reaction  $3MgO + 2Al \Longrightarrow Al_2O_3 +$ 3Mgga, has also been calc. for various [Mg]. Various e.m.f. data are shown to be in agreement with the calc. heat of formation of MgO. The e.m.f. of the Mg-Cl<sub>2</sub> combination in molten MgCl, indicates that the Mg ion forms stable complexes therein. Anodes of Au around which  $O_2$  is passed act as  $Cl_2$  electrodes in molten  $MgCl_2$  saturated with MgO. J. W. S.

Structure, heat content, and special properties of active substances. II. Surface and heat content of crystalline magnesium hydroxide. R. FRICKE, R. SCHNABEL, and K. BECK (Z. Elektrochem., 1936, 42, 881—889; cf. A., 1935, 574).—The heat of dissolution of  $Mg(OH)_2$  ppts. in 3.75N-HCl varies with the age and method of prep. of the  $Mg(OH)_2$ . Energy differences of 850 g.-cal. per mol. are observed. X-Ray examination shows that the difference in energy content is related to large differences in surface. By comparison of these quantities an estimate of the mean surface energy of cryst.  $Mg(OH)_2$  has been obtained. E. S. H.

Specific heat of aqueous systems containing sodium, potassium, and magnesium chloride. V. I. NIKOLAEV, A. G. KOTON, and G. F. OGOROD-NIKOV (Bull. Acad. Sci. U.R.S.S., 1936, 193—214).— Min. sp. heat is found for "eutonic" solutions.

R. T. Heats of formation and of dissolution of isomeric cobaltammines. T. C. J. OVENSTON and H. TERREY (J.C.S., 1936, 1660—1662).—Vals. are given for *cis*- and *trans*-[Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]Cl and for *cis*- and *trans*-[Co en<sub>2</sub>Cl<sub>2</sub>]Cl. Heats of formation are calc. from the observed heats of reaction of the respective compounds with aq. Na<sub>2</sub>S. F. L. U.

Heats of combustion of some physiologically important carbohydrate derivatives. H. COL-LATZ (Cellulosechem., 1936, 17, 128–129).—The heats of combustion of Ca  $\alpha$ -glycerophosphate, Ca hexose diphosphate, and lactaldehyde are 1870, 1612, and 5157 g.-cal. per g., respectively. A. G.

Thermochemistry of oxygen-hæmoglobin reaction.—See A., III, 2.

Physico-chemical properties of solutions in liquefied gases. XV. Conductivity of acids and salts in liquid ammonia. E. N. GURJANOVA and V. A. PLESKOV (Acta Physicochim. U.R.S.S., 1936, 5, 509-536).—Vals. of  $\Lambda$  at -40° are recorded for solutions of  $NH_4NO_3$ ,  $NH_4Cl$ , NaCl,  $NH_4Br$ ,  $NH_4ClO_4$ , KClO<sub>4</sub>, AcOH, NaOAc, KOAc, HCO<sub>2</sub>H, HCO<sub>2</sub>Na, BzOH, NaOBz, H<sub>2</sub>S, HCN, Ca(NO<sub>3</sub>)<sub>2</sub>, Ba(NO<sub>3</sub>)<sub>2</sub>, and Sr(NO<sub>3</sub>)<sub>2</sub>. The vals. of  $\Lambda_{\infty}$  for strong electro-lytes obtained by extrapolation are in good agreement with the theory of Fuoss and Kraus; for weak electrolytes the calc. vals. are < the extrapolated vals. The ionic mobilities have been calc., and the low val. for NH4 is attributed to solvation and to the affinity of protons for the  $NH_3$  mol. The val. of  $\Lambda_{\infty}$ for H<sub>2</sub>S suggests that it is monobasic and that in the (NH<sub>4</sub>)<sub>2</sub>S present in solution, one of the NH<sub>3</sub> groups is more weakly bound than the other, the dissociation being  $NH_4SHNH_3 \implies NH_4 + SHNH_3'$ . The dissociation consts. of weak acids are > the corresponding vals. for aq. solutions. The heat of dissociation of acids in liquid NH<sub>3</sub> is small. C. R. H.

Temperature coefficients of electrical conductivity of electrolytes in methyl and ethyl alcohols. A. G. OGSTON (Trans. Faraday Soc., 1936, 32, 1679—1691).—Limiting conductivities ( $\Lambda_0$ ) and dissociation consts. have been determined at 4°, H (A., I.) 15°, and 25° for KCl, AgNO<sub>3</sub>, KMeCO<sub>3</sub>, NEt<sub>4</sub>ClO<sub>4</sub>, NEt<sub>4</sub> picrate, KOMe, and HCl in MeOH, and for KI, LiI, KEtCO<sub>3</sub>, NEt<sub>4</sub>ClO<sub>4</sub>, NEt<sub>4</sub> picrate, KOEt, and HCl in EtOH. The temp. coeffs. of  $\Lambda_{07}$  are the more negative (1) the greater is  $\Lambda_0$ , (2) the lower is the temp., and (3) in the order EtOH < MeOH <H<sub>2</sub>O. Negative coeffs. in hydroxylic solvents are explained by the effect of electrostriction pressure on viscosity in the neighbourhood of the ions. The mobility of OMe' and OEt' is partly abnormal. Heats of dissociation are calc. F. L. U.

Kinetics of complex formation in non-aqueous solutions, in connexion with conductivity. I. E. J. GORENBEIN (J. Gen. Chem. Russ., 1936, 6, 1230—1233).—The increase in the sp. conductivity of the system  $AlBr_3-HgBr_2-EtBr$  with time is said to be due to the reactions  $2AlBr_3 + HgBr_2 \rightarrow 2AlBr_3, HgBr_2$  (+EtBr)  $\rightarrow 2AlBr_3, HgBr_2, EtBr \rightarrow [2AlBr_3, HgBr, EtBr]^* + Br'$ . R. T.

Basic salt concept in the sexavalent uranium series. P. JOLIBOIS and G. FOURETIER (Compt. rend., 1936, 203, 1263—1265).—[H<sup>\*</sup>] and electrical conductivity measurements show  $SO_3, UO_3$  to be the only compound of  $SO_3$  and  $UO_3$  stable in solution. This and other  $UO_3$  compounds may exist in solution as complex acids,  $UO_3$  then having no basic function. A. J. E. W.

Tellurium electrode. O. TOMIČEK and F. POUPE (Coll. Czech. Chem. Comm., 1936, 8, 520—531; cf. A., 1934, 1321).—Electrodes prepared by polishing rods of pure Te with emery give, in presence of  $CO_2$ -free air or  $O_2$ , trustworthy vals. of the [H'] of solutions in the  $p_{\pi}$  range 2—12. Salt effects have been investigated. The H<sub>2</sub> and Te electrodes are in general approx. equally affected by Na<sub>2</sub>SO<sub>4</sub> and NaCl, but at  $p_{\pi} < 5$  the Te electrode is more strongly influenced by NaCl. NaHSO<sub>3</sub> interferes, but NaNO<sub>3</sub>, NaClO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>ClO<sub>4</sub>, and dil. KMnO<sub>4</sub> have only small effects and the electrode is a trustworthy indicator in the electrometric titration of H<sub>3</sub>PO<sub>4</sub>, AcOH, tartaric acid, and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. The electrode reactions in acid and alkaline solutions are indicated. J. G. A. G.

Temperature coefficents of single electrode potentials. J. SKOTNICKÝ (Coll. Czech. Chem. Comm., 1936, 8, 496—519).—Determinations of the e.m.f., at 15°, 25°, 35°, of cells containing the electrodes Ag|AgCl|Cl', Hg|Hg<sub>2</sub>Cl<sub>2</sub>|Cl', Pt|quinhydrone + H', Ag|Ag', and Hg|Hg<sub>2</sub>°, show that the temp. coeff., dE/dT, of the single electrode potentials depends mainly on the activity of the ion controlling the potential of the electrode and on the relative change of this activity with temp. The expression for dE/dT contains a term which is characteristic of the particular electrode and is const. within wide limits of concn. and almost independent of other components of the electrode is  $\pm 0.837$  mv. per 1°, assuming that the thermo-potential of the 3*M*-KCl junction is zero. J. G. A. G.

Effects of corrections for liquid-junction potentials of saturated calomel electrodes on dissociation constants obtained by electrometric titration. W. J. HAMER and S. F. ACREE (J. Res.

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Nat. Bur. Stand., 1936, 17, 605-613).-The potential of the 4.1N-KCl-HgCl electrode free from liquidjunction potentials is 0.2422 volt on the H scale at 25°. From electrometric titrations of 0.1M-malonic acid with 0.1007N-NaOH, an estimate has been made of the errors in  $p_{\rm H}$ , dissociation consts., "salting-out coeff.," ionic strength, ionic concn., and H-ion activity arising from neglect of or only partial correction for the liquid-junction potential between saturated KCl and Na malonate buffer solutions. Partial corrections produce larger errors than no corrections. Small errors in  $p_{\pi}$  produce large errors in dissociation consts. The first and second dissociation consts. (corr.) of malonic acid in Na malonate buffer solutions at 25° are  $1.67 \times 10^{-3}$  and  $2.51 \times 10^{-6}$ , respectively. Their relations to the vals. expected in pure H<sub>2</sub>O are discussed. J. W. S.

Absolute interface potential at an electrode. M. CALVIN (Mem. Manchester Phil. Soc., 1935– 1936, 80, 29–32).—The abs. interface potential at -273° has been calc. for a no. of electrodes by carrying out the electrode reaction through an alternative cycle, the energy changes in each step being known. For the normal H<sub>2</sub> electrode, the energy required to transfer one atom of H from the electrode to a solvated H<sup>\*</sup> is  $-\frac{1}{2}D_{\text{H}_2} - I_{\text{H}} + U_{\text{H}^*} + \phi_{\text{rt}}$ , where  $D_{\text{H}}$ , is the heat of dissociation of H<sub>2</sub> at 25°,  $I_{\text{H}}$  is the heat of ionisation of H at -273°,  $U_{\text{H}^*}$  is the heat of hydration of H<sup>\*</sup> at 25°, and  $\phi_{\text{rt}}$  is the electronic work function of Pt at -273°. The energy, +49,360 g.-cal., is equiv. to an interface potential of +2·14 volts. Analogous cycles for other electrodes are considered. C. R. H.

Potential of iron in hydrochloric acid. L. GUITTON (Compt. rend., 1936, 203, 1254—1257).—A study of the variation of the electrode potential of Fe in aq. HCl solutions with time of immersion indicates that the reaction  $Fe \rightarrow Fe^{**} + 2e$  is slow in dil. solutions. Fe adsorbs H<sup>\*</sup> in conc. solutions, and functions as a H<sub>2</sub> electrode. A. J. E. W.

Polarographic study of complex cyanides of nickel and cobalt. G. SARTORI (Gazzetta, 1936, 66, 688-692).—Deposition potentials for Ni and for Co from solutions of NiCl<sub>2</sub> + KCN and of CoCl<sub>2</sub> + KCN indicate that these solutions contain the complexes  $K_2Ni(CN)_4$  and  $K_4Co(CN)_6$ , respectively. O. J. W.

Downward shift of  $p_{\rm H}$  caused by addition of glucose to boric acid buffer solutions. P. S. TANG and C. Y. LIN (Science, 1936, 84, 315—316).— Data are tabulated. The effect is reversible.

L. S. T.

Anodic potential of chromium in asymmetric alternating-current electrolysis. I. Method and results. A. GELDBACH and M. SOHLÖTTER (Z. Elektrochem., 1936, 42, 889—900).—The influence of superimposed a.c. on the behaviour of a Cr anode in N-HCl and N-H<sub>2</sub>SO<sub>4</sub> during d.c. electrolysis has been determined and is expressed by means of curves.

E. S. H.

Passivity of iron and steel in nitric acid solution. XI, XII. Y. YAMAMOTO (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 64-65, 65-66).—XI. Stirring increases the p.d. between soft steel and a Pt electrode in aq. HNO<sub>3</sub>, particularly if [HNO<sub>3</sub>] is low; it also makes passivation difficult, probably owing to the removal of corrosion product, but with larger  $[\text{HNO}_3]$  stirring does not affect passivation.

XII. The decomp. of aq.  $HNO_3$  between passive Fe electrodes increases with applied p.d., and eventually  $H_2$  is evolved at the cathode and reduction takes place. The p.d. at which reduction occurs rises with [HNO<sub>3</sub>]. J. G. A. G.

Diffusion of cathodically produced hydrogen and deuterium through iron. P. C. BLOKKER (Rec. trav. chim., 1936, 55, 979–988).—The difference between the overpotential vals. for H<sub>2</sub> and D<sub>2</sub> at an Fe cathode in dil. H<sub>2</sub>SO<sub>4</sub> containing As<sub>2</sub>O<sub>3</sub> or HgCl<sub>2</sub> bears no relation to the difference in the diffusion velocities of the two gases in the cathode. E. S. H.

Electrochemical coating of metal surfaces with a monatomic film of nobler metal. O. ERBACHER (Z. physikal. Chem., 1936, 178, 15— 28).—Previous investigations (A., 1933, 468) have been amplified. If a metal is brought in contact with a solution containing ions of a nobler metal and if the less noble metal is such as not to react with the solvent in absence of the nobler ions, then there is no exchange between the electrode and the solution, but only slight adsorption of the nobler ions. If deposited nobler metal redissolves in the liquid more rapidly than it is deposited, then exchange occurs and a monat. film of nobler metal is formed on the electrode.

R. C.

Effect of pretreatment of metal surfaces on electrochemical separation. O. ERBACHER (Z. physikal. Chem., 1936, 178, 43-56; cf. A., 1933, 468).-Mechanical pretreatment of Pb and Bi produces solubility local elements, and when either metal is brought into contact with a solution containing its ions, exchange occurs between the solution and a layer many atoms thick on the surface of the metal. Etching with HNO3 may paralyse the most active local elements and exchange is then confined to a monat. layer. In certain circumstances treatment of Ni with emery-paper does not produce local elements and exchange between the Ni and a solu-tion of Ni" or Bi" ions occurs only in a monat. layer. Polishing or etching renders Ni partly passive, and so gives rise to local elements, and a layer of Bi many atoms thick may be formed on its surface by ex-R. C. change.

Microcoulombmetry and unimolecular oxide films. Theory of adsorptional centres. I. R. KLJATSCHKO (J. Gen. Chem. Russ., 1936, 6, 1179— 1192).—The tenacity with which films of oxide, phosphate, silicate, sulphate, sulphide, or chromate adhere to a Pb anode varies inversely with the val. of  $B_{12}$  (hysteretic wettability, determined from the angle of contact at the boundaries Pb-H<sub>2</sub>O-air). Using very small currents (8—10 microamp.) the amount of O<sub>2</sub> adsorbed at a Pb surface  $\infty$  no. of adsorption centres Z', and not to the no. of atoms or mols., Z; k = Z'/Z = 2.06 for Ag and 0.63 for Pt. The vals. of k are const. only under rigorously fixed conditions, and are not practically reproducible. With increasing current k rises to a max. for given conditions. The val. of  $B_{12}$  of a Ag anode falls after formation of an oxide film, which may partly be removed by washing with org. solvents, the efficiency of which varies in the order  $C_6H_6 < C_2H_4Cl_2 < EtOH < CHCl_3 = CCl_4$ . R. T.

Electrode processes of deposition or dissolution of metals, in relation to the nature of the ions and the concentration. N. A. ISGARISCHEV and E. J. MAJOROVA (J. Gen. Chem. Russ., 1936, 6, 1208-1229).—The cathodic polarisation P in the electrolysis of Cd salts increases in the order  $CdCl_2 =$  $CdBr_2 = CdI_2 < Cd(OAc)_2 < Cd(NO_3)_2$ , and does not appear to be connected with the equilibrium potential  $\varepsilon$ ,  $p_{\rm H}$ , sp. conductivity  $\kappa$ , or ionic activity A of the solutions. The same applies to solutions of CdCl<sub>2</sub> containing alkali or alkaline-earth ions, all of which reduce P; their action increases in the series Na <  $K < NH_4 = Ca = Ba < Sr < Mg.$ Traces of As greatly increase P, whilst Cu and Sb have little action. Addition of Zn salts or gelatin raises or lowers the val. of P, according to the concn. The val. of Pfalls to a min., and then rises as the [CdSO4] is increased from 0.25 to  $4N : \varepsilon$ ,  $p_{\rm u}$ ,  $\kappa$ , and A do not vary parallel with P. At 25° P is > at 50° for 0.25—1N- and lower for 2—4N-CdSO<sub>4</sub>. In all the above cases, anodic polarisation is inconsiderable, and varies independently of the cathode process. In the case of Zn salts  $\tilde{P}$  diminishes in the series  $ZnSO_4 > Zn(OAc)_2$  $> ZnCl_2 > ZnI_2$ , and rises with increasing [Zn"]. R. T.

Protracted change with time of cathodic overvoltage on platinum. G. MASING and G. LAUE (Z. physikal. Chem., 1936, 178, 1-14).-The H overvoltage, ., in aq. KOH rises for some time after the circuit has been closed, but ultimately reaches a const. val., E. If the c.d., I, is kept const.  $dE/d\log I = b = 0.109$ . If the cathode potential,  $\varepsilon$ , is kept const. b = 0.120; Volmer's theory of over-voltage requires b = 0.116. Previous cathodic polarisation accelerates the rise of  $\omega$ , whilst anodic polarisation has the opposite effect; in both cases the same val. of E is reached as when there is no previous polarisation. For Pt recryst. by heating to incandescence with a.c.  $\omega$  changes more slowly, and the const. val. ultimately reached is smaller. It is inferred that Volmer's double-layer theory explains overvoltage even after protracted passage of current, and that the rise of  $\omega$  with time is due to active points on the electrode gradually becoming inactive. The amount of H liberated from the electrode after the circuit is opened  $\infty \epsilon$ . Part of the H appears to be in solid solution within the electrode. R. C.

Dissociation constants in water and deuterium oxide. Measurements with the deuterium electrode. C. SCHWARZENBACH, A. EPFRECHT, and H. ERLENMEYER (Helv. Chim. Acta, 1936, 19, 1292— 1304).—The normal potential of the D<sub>2</sub> electrode is -0.0022 volt. The calc. ionic product of 99.6% D<sub>2</sub>O is 10<sup>-14 801</sup> corresponding with 10<sup>-14 807</sup> for 100% D<sub>2</sub>O as compared with 10<sup>-14 073</sup> for H<sub>2</sub>O. The above results are discussed and the dissociation consts. of various compounds and ions in D<sub>2</sub>O calc. J. W. S.

Dissociation constants of reductic acid and of its product of oxidation by iodine. G. CARPÉNI (Compt. rend., 1936, 203, 1156—1158).—Vals. obtained at 20° using an electrometric titration method,

H\* (A., I.)

Oxidation-reduction potential of thioindigotintetrasulphonate.—See A., II, 30.

Potentiometric study of flavins. L. MICHAELIS, M. P. SCHUBERT, and C. V. SMYTHE (J. Biol. Chem., 1936, 116, 587—607).—Normal potentials of several derivatives of *iso*alloxazine and flavin, including lactoflavin or vitamin- $B_2$ , have been determined. All the dyes on partial reduction form a semiquinone (I) which is red in very acid solution and green at  $p_{\rm fl} 2$ —12. The max. amount of (I) which can exist with the other forms of the dye through a wide  $p_{\rm fl}$ range is approx. 10%, and is practically const. The naturally occurring flavins increase the O<sub>2</sub> consumption of yeast extract only very slightly, but the alloxazine dyes are more active and are comparable with methylene-blue. J. N. A.

Incorporation of thermodynamic variables in chemical kinetics. E. A. MOELWYN-HUGHES (Trans. Faraday Soc., 1936, 32, 1723—1738).— Methods of introducing thermodynamic variables into expressions for reaction velocity are discussed.

F. L. U.

Gas reactions in chemical kinetics. M. BODEN-STEIN (Ber., 1937, 70, [A], 17–34).—A lecture.

Dissociation of hydrogen by tungsten. G. BRYCE (Proc. Camb. Phil. Soc., 1936, 32, 648-652).--The rate of production of at. H on heating a W filament in  $H_2$  has been investigated by observing the pressure change, the at. H produced being absorbed in MoO<sub>3</sub> or WO<sub>3</sub>. With W at const. temp., the rate of dissociation  $\propto$  the square root of the pressure. An expression for the abs. rate of production of H atoms is given. A. J. E. W.

Mechanism of the production of atomic hydrogen by hot tungsten. J. K. ROBERTS and G. BRYCE (Proc. Camb. Phil. Soc., 1936, 32, 653—656; cf. preceding abstract and A., 1936, 422).—Experimental data can be interpreted by assuming either of two possible mechanisms, viz., evaporation of adsorbed atoms from a sparsely-covered surface, or the splitting of an incident  $H_2$  mol. to give two H atoms, one of which is adsorbed, and the other evaporated. In the latter case the surface is almost completely covered.

A. J. E. W.

Kinetics of OH radicals as determined by their absorption spectra. II. Electric discharge through hydrogen peroxide. A. A. FROST and O. OLDENBERG (J. Chem. Physics, 1936, 4, 781-784; cf. this vol., 34).—To study the kinetics of OH radicals in  $H_2O_2$  the concn. of OH as a function of time was measured by the decay of the intensity of the OH absorption bands after interrupting an electric discharge through  $H_2O_2$ . A fresh supply of  $H_2O_2$  was used for each snapshot and was partly decomposed into OH by an electric discharge of short duration. OH radicals disappear more rapidly in  $H_2O_2$  than in  $H_2O$ , indicating a bimol. reaction OH +  $H_2O_2$ . The emission spectrum of OH shows abnormal rotation of OH when excited in  $H_2O_2 >$  in  $H_2O$ , the rotation being determined by the simultaneous dissociation and excitation producing the OH radicals and not by W. R. A. the temp.

Gaseous combustion. W. T. DAVID (Nature, L. S. T. 1936, **138**, 930).—A discussion.

Soap-bubble method of studying the combus-tion of mixtures of CO and  $O_2$ . E. F. FIOCK and C. H. ROEDER (Nat. Adv. Comm. Aeronaut. Rept., Determined to the study of the st 1935, No. 532, 14 pp.).—Data for flame speeds in  $CO-O_2$  mixtures of varied humidity are recorded.

Сп. Авз. (е) Law governing the initial acceleration of slow combustion and the retardation of inflammation of mixtures of pentane, oxygen, and nitrogen. M. PRETTRE (Compt. rend., 1936, 203, 1152-1154).-The pressure increase of mixtures at 260-300° is given by:  $\Delta p = k e^{\phi}$ ; the const.  $\phi$  varies according to the relation  $\phi = \phi_0(1 + \alpha P_n)$ , where  $P_n$  = partial pressure of N<sub>2</sub>,  $\alpha$  = const., and  $\phi = \phi_0$  when  $P_n = 0$ . Also  $\tau(1 + \alpha P_n)$  = const., where  $\tau$  = time after which inflammation occurs. A. J. E. W.

Kinetics of oxidation and ignition of hydrocarbons. I. Ignition delay and slow preoxidation of mixtures of n-pentane and oxygen between 250° and 300°. Laws governing explosion phenomena. M. PRETTRE (Ann. Off. nat. Comb. liq., 1936, 11, 669-718).-The spontaneous ignition of  $C_5H_{12}-O_2$  mixtures, containing  $\geq 20\%$ of C<sub>5</sub>H<sub>12</sub>, under an initial pressure of 100-760 mm. was studied by the static method from 240° to 300°. Ignition delay,  $\tau$ , varied between 1 and 300 sec., and at const. temp. could be expressed by  $\neg P_c P_t^2 =$ const., where  $P_c$  and  $P_i$  are the partial pressure of the fuel and total pressure, respectively. The pressure variation,  $\Delta p$ , caused by slow oxidation corresponded with  $\Delta p = k e^{\phi t}$ , where  $\phi = k_1 P_c P_t^2$ , confirming the relation,  $\phi \tau = \text{const.}$  These results, predicted from the theory of chain reactions, are discussed in relation to the phenomenon of knocking in internal-combustion engines. R. B. C.

Mechanism of thermal change in gaseous organic compounds. M. W. TRAVERS (Nature, 1936, 138, 967-968).—The main process is assumed to be mols.  $\rightarrow$  activated state  $\rightarrow$  complex  $\rightarrow$  unstable intermediate  $\rightarrow$  paired products and the rate of reaction generally measured is the transformation complex  $\rightarrow$  unstable intermediate. Free radicals are not accountable for the processes involved. Thermal decomp. of C2H6 and of C2H6-C2H4-H2 equilibrium mixtures etc. are discussed. J. S. T.

Rate of thermal decomposition of ammonia on a quartz surface. J. A. CHRISTIANSEN and E. KNUTH (Kong. dansk Viden. Selsk., mat.-fys. Medd., 1935, 13, No. 12, 18 pp.; Chem. Zentr., 1936, i, 1172).—Experiments at 789—884°/2—7 cm. con-firmed Hinshelwood and Burk's results (A., 1925, ii, 691). The rate depends on the pretreatment of the walls. The mechanism involves the intermediate formation of NH. On adding  $H_2O$  vapour to the reaction product and cooling in liquid air,  $NH_2OH$ and  $HNO_2$  were detected in the condensate (NH +. H. J. E.  $\mathrm{H_{2}O}=\mathrm{NH_{2}OH}).$ 

Atomic chlorine. G. M. SOHWAB [with H. FRIESS] (Z. physikal. Chem., 1936, 178, 123-137; cf. A.,

1933, 1021).-O<sub>2</sub>, CCl<sub>4</sub>, COCl<sub>2</sub>, and HCl have no effect on at. Cl. CO<sub>2</sub> activates the recombination of the Cl atoms on quartz.  $C_2H_4$  apparently forms with a current of active Cl an explosive substance. The fact that the collision yield for the recombination of Cl atoms on the wall is  $\pm 1$  is usually due to the Cl atoms or atoms of the wall requiring a small energy of activation (~1 kg.-cal. on quartz) to enter into reaction, but is sometimes due to the inertness of parts of the wall. Ag brings about recombination of Cl atoms rather more rapidly than Mg, but its activity may be considerably affected by the formation of AgCl on its surface. R. C.

Thermal decomposition of  $F_2O_2$ . P. FRISCH and H. J. SCHUMACHER (Z. physikal. Chem., 1936, B, 34, 322).—Between  $-25^{\circ}$  and  $-60^{\circ}$  the decomp. is homogeneous, may be represented by  $-d[\mathbf{F}_2\mathbf{O}_2]/dt = 10^{12\cdot4} \times 10^{-17\cdot000/4\cdot57T} [\mathbf{F}_2\mathbf{O}_2]$ , and yields an equimol. mixture of F<sub>2</sub> and O<sub>2</sub>, not FO (cf. A., 1934, 378)

R. C. Effect of helium on the kinetics of the thermal decomposition of acetaldehyde. C.J.M. FLETOHER (J. Amer. Chem. Soc., 1936, 58, 2646-2647).-The presence of He increases the rate of reaction in a way which suggests that the decomp. does not follow a chain mechanism, but involves the direct rearrangement : MeCHO  $\rightarrow$  CH<sub>4</sub> + CO. E. S. H.

Thermal decomposition of crotonaldehyde.-See A., II, 50.

Highly polymerised compounds. CXLVI. Kinetics of chain polymerisation. I. Thermal polymerisation of pure styrene. G. V. SCHULZ and E. HUSEMANN (Z. physikal. Chem., 1936, B, 34, 187–213).—The rate of polymerisation as a whole is determined by that of the primary reaction (activation of the monomeric styrene mol.), which follows the unimol. law, and has a heat of activation of 23,200 g.-cal. and a const. of action of 10<sup>5.35</sup> sec.-1 The distribution of mol. wts. in the product shows that the mean chain length of the resultant mols. is determined by the ratio of the velocities of the chain-breaking reaction (i) and the chain-growth reaction (ii) (cf. A., 1936, 295). Since the mean mol. wt. remains approx. const. during the reaction, (i) as well as (ii) must be bimol. It is probable that chain-breaking consists in the migration of a H from one growing mol. to another, whereby the free terminal valencies become saturated (cf. A., 1935, 740). This view explains the diminution in chain length caused by catalysts and the effect of temp. on the chain length. The velocity of (ii) is  $< 10^{10}$  times that of the primary reaction. R. C.

Kinetics of thermal cis-trans isomerisation. VI. G. B. KISTIAKOWSKY and W. R. SMITH (J. Amer. Chem. Soc., 1936, 58, 2428-2430; cf. A., 1936, 452).—The isomerisation of  $\beta$ -cyanostyrene is a first-order reaction; the velocity coeff. at higher pressures is given by  $k = 10^{11.6 \pm 0.4} e^{-(46,000 \pm 1000)R/T} \sec^{-1}$ The equilibrium mixture at 352° contains 63% of the trans-isomeride. The equilibrium composition is practically independent of temp. E. S. H.

Steric hindrance. W. HÜCKEL (Z. physikal. Chem., 1936, 178, 113-122).-Theoretical. Applic-

viii (a)

 $\nabla$ III (a)

ation of Arrhenius' equation to the temp. coeffs. of numerous reactions exhibiting steric hindrance gives a high val. of both the activation energy, q, and the const. of action, a. Hinshelwood's theory of storic hindrance (A., 1935, 828) affords no adequate explanation. A possible explanation is that  $\alpha \propto$ temp. It may be supposed that before reaction can occur the reacting mols. must assume a favourable orientation, requiring a certain amount of energy. If orientation is an endothermic process  $\alpha$  will rise with temp., and vice versa. If the steric hindrance is due to a protective group having to be forced aside, with a certain expenditure of energy, this is equiv. to orientation, and both  $\alpha$  and q will be large. If, on the other hand, steric hindrance arises from access to the reactive group being largely obstructed by another group  $\alpha$  will be small and q large. The variation of  $\alpha$  with temp. to be expected on this theory is in harmony with the experimental data for temp. coeffs. It is concluded that whilst  $\alpha$  always involves a purely steric factor it may contain energy factors also. R. C.

Periodic reactions. F. M. SCHEMJAKIN (Compt. rend. Acad. Sci. U.R.S.S., 1936, 4, 63-64).—The periodicity const. of periodic reactions increases with decrease in concn. of the exterior and interior components and of the medium, approaching  $\lambda v = hN/M$ ( $\lambda$  = distance between layers, v = velocity of expansion of field of diffusion, M = mol. wt. of the exterior electrolyte, h = Planck's const., N = Avogadro no.). The max. val. is much > that calc. theoretically by Christiansen and Wulff (A., 1934, 955). O. D. S.

Reactivity of hydrogen peroxide in brominebromide solutions. R. O. GRIFFITH and A. MCKEOWN (J. Amer. Chem. Soc., 1936, 58, 2555— 2558).—Observations contrary to those of Bray and Livingston (A., 1923, ii, 473) are reported. E. S. H.

Exchange reactions of heavy water with organic compounds. I. Phenol, acetanilide, and the formate ion. P. A. SMALL and J. H. WOLFENDEN (J.C.S., 1936, 1811—1817).—The H of the OH group of PhOH and of the NH of NHAcPh exchanges rapidly with the D of  $D_2O$ ; the distribution of D between  $H_2O$  and org. compound favours the latter. PhOH undergoes nuclear exchange catalysed by alkali on prolonged heating with  $D_2O$ , but  $s \cdot C_6H_2Cl_2 \cdot OK$  shows no exchange under similar conditions. The exchange of  $D_2O$ with Na and K formates is very slow, which is inconsistent with a structure proposed for  $HCO_2'$  (A., 1936, 663). J. G. A. G.

Ratio between the hydrogen-ion concentration and the velocity of decomposition of ethyl diazoacetate in organic media. M. DUBOUX and R. FAVRE (Helv. Chim. Acta, 1936, **19**, 1177—1190).— The velocity coeff. of the decomp. of  $CHN_2 \cdot CO_2Et$ in presence of dil. org. acids with or without their Na salts is not exactly  $\infty$  [H'] deduced from conductivity measurements, but is relatively the lower the lower is the acid concn., especially in presence of the Na salt. Figures are given for the proportionality factor for acid concns. between 0.1N and 0.0005N, and these permit the use of Bredig and Fraenkel's method of determining the [H']. J. W. S. Influence of solvent on the course of chemical reactions. IX. Kinetics of simple substitution reactions. K. LAUER X. Kinetics of the reaction between allyl bromide and sodium phenoxide in dissociating solvents. K. LAUER and H. SHINGU (Ber., 1936, 69, [B], 2618—2626, 2731—2742).—IX. Measurements of the rate of halogenation of aromatic compounds in solution, of nitration of anthraquinone (I) and PhNO<sub>2</sub> in H<sub>2</sub>SO<sub>4</sub>, and of sulphonation of (I) and benzanthrone show that in general simple substitution reactions do not occur with the velocity expected from the collision theory. The latter is not regarded as disproved since it is satisfactory in many cases and there are sufficient reasons for its breakdown with solutions. A possible relationship between dielectric capacity or conductivity of the solvent and deviations from the expected rates of reaction is indicated.

X. The rate of reaction of  $C_3H_5Br$  with NaOPh giving 98—99% of PhO· $C_3H_5$  and 2—1% of o- $C_3H_5$ · $C_6H_4$ ·OH has been followed kinetically at various temp. in abs. EtOH, MeOH, COMe<sub>2</sub>, EtOH-COMe<sub>2</sub>, and EtOH-H<sub>2</sub>O. It is probable that allylation and other alkylations of alkoxides and phenoxides does not take place through the free ions or mols., but that associates and solvates are present in the solutions and that their composition is greatly altered by dilution. The heterogeneous media are regarded as solutions of electrolytes of medium strength in which the change occurs exclusively with the OPh ion. Change in the rate of reaction with dilution is attributed to the influence of the solvent on the condition of the latter; the more rapid change in COMe<sub>2</sub> than in EtOH is thereby explained. Allylation in alcoholic media occurs approx. in accordance with the collision theory, whereas it is considerably slower in COMe2, H2O, COMe2-EtOH, and H<sub>2</sub>O-EtOH. H. W.

Temperature dependence of the energy of activation in the rearrangement of N-chloroacetanilide. J. O. PERCIVAL and V. K. LA MER (J. Amer. Chem. Soc., 1936, 58, 2413—2418).— The rate of conversion in presence of 0.2M-HCl has been determined at  $0^{\circ}$ ,  $12.5^{\circ}$ ,  $25^{\circ}$ , and  $37.5^{\circ}$ . The energy of activation rises steadily from 19,170 g.-cal. at 0—12.5° to 20,750 g.-cal. at 25—37.5°, corresponding with a mean heat capacity of activation of 63 g.cal. per degree. The action const. *B* varies from 13.2 at 6.33° to 14.45 at 31.3°. Evidence of the inadequacy of the collision theory and of the existence of an appreciable entropy of activation is given.

E. S. H. Rearrangement of N-chloroacetanilide in presence of radioactive hydrochloric acid. A. R. OLSON, C. W. PORTER, F. A. LONG, and R. S. HAL-FORD (J. Amer. Chem. Soc., 1936, 58, 2467—2472).— A kinetic study shows that the rearrangement does not proceed exclusively either by an intramol. rearrangement or by a Cl intermediate, but probably by a combination of these mechanisms. E. S. H.

Rates of alcoholysis of acyl chlorides. G. E. K. BRANCH and A. C. NIXON (J. Amer. Chem. Soc., 1936, 58, 2499—2504).—The rates of alcoholysis of Ac, tri-, di-, and mono-chloroacetyl, *p*-nitro-, -fluoro-, -bromo-, -iodo-, -methyl-, and -methoxy-benzoyl chlorides in  $Et_2O$ -EtOH (60:40) have been determined in very dil. solutions at 25°. The kinetics of reaction and the influence of substituent groups on reactivity are discussed. E. S. H.

Mechanism of formation of ionic compounds of higher order (double salts, spinels, and silicates). C. WAGNER (Z. physikal. Chem., 1936, B, 34, 309— 316).—In the formation of the above compounds by reaction between solid salts and salt-like compounds diffusion processes play the chief part. Assuming that in diffusion it is those ions which are responsible for electrolytic conduction which play the determining part, a formula is derived for the reaction velocity in terms of the work of formation of the reaction, A, the conductivity, and the transport nos. of the ions, or of A and the self-diffusion coeffs. of the ions. Examples of various types of reaction mechanism are discussed. R. C.

Formation of  $Ag_2HgI_4$  by reaction between solid mercuric and silver iodides. E. KOCH and C. WAGNER (Z. physikal. Chem., 1936, B, 34, 317— 321).—Reaction occurs principally by diffusion of Ag' and Hg'' ions and the velocity agrees with the equation previously deduced (cf. preceding abstract). R. C.

Mechanism of diffusion through protective oxides and influence of pressure on the rate of oxidation of nickel. G. VALENSI (Compt. rend., 1936, 203, 1154—1156).—Mainly theoretical. Experimental data for the oxidation of Ni are given.

A. J. E. W. Kinetics of oxidation of metals forming two oxides. G. VALENSI (Compt. rend., 1936, 203, 1252—1254; cf. preceding abstract).—A theoretical discussion of the mechanism of oxidation of metals which form surface layers composed of two different oxide films. The two oxides are formed in const. proportions at const.  $O_2$  pressure. The wt. of  $O_2$ absorbed  $\propto \sqrt{time}$  at const. temp. A. J. E. W.

Laminar systems. IV. Kinetics of the formation of cupric hydroxide layers at the surface of cuprammonium solutions. S. G. MOKRUSCHIN and P. S. KONJAEV (Kolloid-Z., 1936, 77, 301-305; cf. A., 1935, 1317).—The thickness of the film increases linearly with time. The interference colours produced are discussed. The film is permeable to NH<sub>3</sub>. E. S. H.

Dissolution of vacuum films of metals in acids. II. Dissolution of iron and nickel in sulphuric acid. M. A. ROSENBERG and K. E. AVALIANI (Compt. rend. Acad. Sci. U.R.S.S., 1936, 4, 179— 180; cf. this vol., 41).—The films of Fe, whether previously exposed to air or not, dissolved rapidly in 2N-, 0.5N-, and 0.01N-H<sub>2</sub>SO<sub>4</sub>, but relatively slowly in 0.001N, where rusting occurred simultaneously. Brownish-grey films of Ni, 12—100 mµ thick, dissolved very slowly in 2N- and 0.5N-H<sub>2</sub>SO<sub>4</sub>, and not at all in 0.1N. R. C. M.

Velocity of dissolution of comminuted substances. II. W. JACER (Rocz. Chem., 1936, 16, 339-347; cf. A., 1929, 391).—An expression for the velocity of dissolution of solid particles of any shape or size is derived, and shown to hold for the case of NaCl in  $H_2O$ . R. T.

Application of affinity and quantum statistics to catalysis. (MLLE.) G. SCHOULS (Bull. Acad. roy. Belg., 1936, [v], **22**, 1064—1071).—At 273° and 773° abs., the difference in the reaction affinity of  $O_2$  in the  ${}^{1}\Sigma$  (activated) and  ${}^{3}\Sigma$  – electronic levels is  $\approx +36$ kg.-cal. R. C. M.

Influence of added catalysts on the catalytic decomposition of hydrogen peroxide in presence of dichromate. M. BOBTELSKY and L. BOBTELSKY-CHAJKIN (Compt. rend., 1936, 203, 1158—1160).— The decomp. is pseudo-unimol. in absence of catalysts. 3N-NH<sub>4</sub>Cl and  $-(NH_4)_2SO_4$  scarcely affect the reaction. The catalytic effects of the following ions are in the order of magnitude given : Mn<sup>\*\*</sup> > Cu<sup>\*\*</sup> > Fe<sup>\*\*\*</sup> > Co<sup>\*\*</sup> > Ni<sup>\*\*</sup>. The rate of decomp. for low concns. (c)  $\propto$  log c. The temp. coeff. is unaffected by catalysts. A. J. E. W.

Acid catalysis in light and heavy water. O. REITZ (Naturwiss., 1936, 24, 814).—Reactions catalysed by H<sup>\*</sup> proceed more rapidly in D<sub>2</sub>O than in H<sub>2</sub>O, whereas those which are catalysed by proton donors generally proceed more slowly in D<sub>2</sub>O than in H<sub>2</sub>O. A simple connexion between the type of reaction and the effect of D<sub>2</sub>O cannot, however, be derived, since the bromination of COMe<sub>2</sub>, which shows general acid catalysis, proceeds more rapidly in the presence of D<sup>\*</sup> than H<sup>\*</sup>,  $k_{\rm p.}/k_{\rm H}$ . being 1.8 at 25°. A. J. M.

Acid catalysis in non-aqueous solvents. IV. Depolymerisation of paraldehyde. R. P. BELL, O. M. LIDWELL, and M. W. VAUGHAN-JACKSON (J.C.S., 1936, 1792-1799).-The kinetics of the depolymerisation of paraldehyde (I) in C<sub>6</sub>H<sub>6</sub>, PhNO<sub>2</sub>, amyl acetate, and anisole, catalysed by HCl and mono-, di-, and tri-chloroacetic acids, have been investigated dilatometrically and analytically at 0-146°. The reaction is unimol. with respect to (I) and has an apparent order varying between 1.5 and 2.5 with respect to acid. A composite reaction mechanism involving the three O atoms of the (I) mol. is suggested. The catalytic power of the acids is in the same order as the acid strengths, but varies more than the dissociation consts. in H<sub>2</sub>O. The reaction velocity is greatly affected by the solvent, partly owing to varying association of the carboxylic acids and to combination between the acids and solvents. H<sub>o</sub>O is a strong inhibitor. J. G. A. G.

Mechanism of the bromination of aliphatic  $\alpha\alpha$ -disulphones in aqueous acid solutions. L. RAMBERG and E. SAMÉN (Arkiv Kemi, Min., Geol., 1936, **12**, **A**, No. 8, 10 pp.).—Thirty possible mechanisms are discussed, involving the interaction of disulphone (I) or its anion with Br<sub>2</sub>, Br<sub>3</sub>', HOBr, OBr,' or Br', catalysed by H' or OH', or reacting spontaneously. It is considered that of these only two are probable, viz., interaction between (I) and Br<sub>2</sub> catalysed by OH', or a spontaneous reaction between the anion of (I) and Br<sub>2</sub>.

Kinetics of the bromination of aliphatic αα-disulphones in aqueous solutions of hydrobromic acid. E. SAMÉN (Arkiv Kemi, Min., Geol., 1936, 12, A, No. 7, 10 pp.).—Previous work (cf. A., 1934, 1313) has been extended to the determination of the influence of KBr, NaBr, KClO<sub>4</sub>, NaClO<sub>4</sub>, and K<sub>2</sub>SO<sub>4</sub> on the val. for k. For [HBr] < 0.1N and for const. [Br'], k approx.  $\propto 1/[H^*]$ , assuming  $[H^*] = [HBr]$ , except in the presence of K<sub>2</sub>SO<sub>4</sub>. The increased val. for k here observed is due to a reduction in [H<sup>\*</sup>] and the formation of HSO<sub>4</sub>'. The salt effect of perchlorates and the effect of interchanging K with Na are negligible. C. R. H.

Catalysis of ionic oxidation-reduction reactions by dyes and its probable mechanism. P. A. SHAFFER (J. Physical Chem., 1936, 40, 1021-1026; cf. A., 1933, 678).—Naphthaquinones, anthraquinones, indigotin, pyocyanine, flavin, and rosinduline are all markedly catalytic in the  $\text{Ti}^{\cdots} + \text{I}_3'$  reaction, and they also show evidence, on reduction, of an intermediate semiquinone stage. Their ability to catalyse ionic oxidation-reduction reactions in which the reactants accept and donate unequal nos. of electrons (*i.e.*, 1 and 2, respectively) is attributed to the above property. F. L. U.

Heats of activation in the mutarotation of glucose. I. Catalysis in sodium hydroxide solutions. G. F. SMITH (J.C.S., 1936, 1824–1828). The rate of mutarotation of glucose in very dil.  $CO_2$ -free solutions of NaOH has been determined at 0°, 5°, 10°, and 15°. The glucosate ion (I), in addition to OH', is an active catalyst, and in the solutions investigated accounts for 18–41% of the observed velocities. Catalytic coeffs. have been evaluated, and at 15° are 26·3 and 5100 for (I) and OH', respectively. The heats of activation are 17,000 and (probably) 17,700 g.-cal. for catalysis by (I) and OH', respectively. The bearing of the results on Euler's theory of acid and base catalysis is discussed.

J. G. A. G.

Metal ion activation in enzymic catalysis. Arginase. L. HELLERMAN and C. C. STOCK (J. Amer. Chem. Soc., 1936, 58, 2654—2655).—The influence of Mn<sup>\*\*</sup>, Co<sup>\*\*</sup>, Ni<sup>\*\*</sup>, and Fe<sup>\*\*</sup> on the arginasearginine reaction in buffered solutions of different  $p_{\rm II}$  has been studied and compared with the stabilities of corresponding co-ordination complexes of these ions. E. S. H.

Catalysis with fine foam and colloidal metals. III. Comparison of catalytic action of palladium, platinum, and rhodium. G. KAHL and E. BIESALSKI (Z. anorg. Chem., 1936, 230, 88–94; cf. A., 1930, 1133).—In hydrogenation by colloidal metals involving the activation of H<sub>2</sub> only, as with O<sub>2</sub> or C<sub>2</sub>H<sub>4</sub>, the order of decreasing activity is Pd > Pt > Rh, whereas in the reduction of aq. NaClO<sub>3</sub> it is Pt > Rh > Pd, and with KNO<sub>2</sub> Rh > Pt > Pd. Comparison of the foam method with the methods of Skita and of Paal shows that, in the hydrogenation of cinnamic acid, Skita's process is more rapid but less convenient, whilst Paal's is much slower than either of the others. F. L. U.

Dependence of catalytic activity on the amount of promoter. O. BLOCH and N. I. KOBOSEV (Acta Physicochim. U.R.S.S., 1936, 5, 417-432).—The decomp. at 30° of  $H_2O_2$  catalysed by mixtures of  $Fe_3O_4$  and  $Al_2O_3$  has been studied. With increase of  $Al_2O_3$  up to approx. 2 wt.-% the catalytic activity increases, but further addition of  $Al_2O_3$  reduces the activity. The  $Al_2O_3$  owes its promoting action to the formation of  $Fe_3O_4$ ,  $Al_2O_3$  at the surface of the catalyst, the activity of the complex being 3.7 times that of  $Fe_3O_4$ . C. R. H.

Amorphous and crystallised hydrated oxides and oxides. XXIX. Catalytic decomposition of hydrogen peroxide and the "active positions" of the intermediate conditions occurring during the dehydration of natural and artificial ferric hydroxides. Crystallisation of a-Fe<sub>2</sub>O<sub>3</sub>. A. KRAUSE [with H. KRACH] (Ber., 1936, 69, [B], 2708-2719).-The active conditions or active oxides formed by thermal decomp. of Fe<sup>III</sup> hydroxides have cataby thermal decomp. of Fe<sup>111</sup> hydroxides have cata-lytic activity and decompose  $H_2O_2$ . The dehydration products of the röntgenographically amorphous, dark brown orthoferric hydroxide (I) decompose 0.2N·H<sub>2</sub>O<sub>2</sub> relatively easily, although less powerfully than (I).  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, obtained by ignition at 800°, is almost inactive. Dehydration of (I), which when air-dried contains >3H<sub>2</sub>O per Fe<sub>2</sub>O<sub>3</sub>, is a continuous process during which H<sub>2</sub>O present as such (about 2 mols.) is lost; the products [associates of (I)] are re-latively readily sol. in acid and show only weak inter-ferences of  $\alpha$ -Fe<sub>2</sub>O<sub>2</sub>. Finally, dehydration involves ferences of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Finally dehydration involves the OH groups so that active H disappears very late in the process and the dehydrated oxide mols. (nuclei) are formed at a temp. at which the rate of growth of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is great. A coarsely cryst., violet  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> therefore results which is very dense and very sparingly sol. in acids. a-Oxides, obtained by heating the moist gel of (I) under  $H_2O$ , accelerate the decomp. of H<sub>2</sub>O<sub>2</sub> slightly although they appear to have a low d and dissolve readily in boiling  $1.4N-H_2SO_4$ . Artificial, air-dried goethite does not decompose 0.2N- $H_2O_2$  at 20° since it, as hydrate ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, $H_2O$ ), does not contain active H. It becomes catalytically active without suffering decomp. when gently heated at 150°. The oxides obtained by dehydration are more active and the resulting reaction is of the first order. The dehydration, goethite  $\rightarrow \alpha$ -Fe<sub>2</sub>O<sub>3</sub>, is discontinuous since oxide nuclei are formed irregularly owing to breakdown of the goethite mol. or lattice, thus causing the material to appear röntgenographically amorphous. The oxides have a low apparent dand are freely sol. in boiling 1.4N-H<sub>2</sub>SO<sub>4</sub>. The redbrown  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> formed at 800° in consequence of the rapid formation of nuclei and poor recrystallisation is moderately finely-divided and catalytically active but otherwise gives the normal Röntgen diagram of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Catalytic activity appears generally parallel with fineness of division but the relationship is not universal. Dehydration of the very dense natural goethite occurs similarly apart from quant. differences, being discontinuous and giving catalytically active oxide modifications. Recryst. a-Fe<sub>2</sub>O<sub>3</sub> is formed at 800°. Catalytic activity of the active conditions through which goethite passes when dehydrated is caused by active spots which originate during the shattering of the lattice or mol. and are due to increase in the distances between Fe and O atoms. The changes are frequently so subtle that they cannot be detected röntgenographically. H. W.

Study of enzyme action by thermal analysis of reaction velocity. II. Action of inorganic ferment. E. SUITO (Proc. Imp. Acad. Tokyo, 1936, 12, 229-232; cf. A., 1935, 1278).—The catalytic decomp. of aq.  $H_2O_2$  by colloidal Pt takes place in two stages. The duration of the initial process is short, independent of  $[H_2O_2]$ , but decreases with increasing concn. of colloidal Pt. The second process is the chief reaction, and is unimol. The velocity coeff.  $\infty$  [colloidal Pt]<sup>2</sup>, approx. The initial stage is of variable order, and is attributed to adsorption processes. The catalytic activity of the colloidal Pt with respect to time passes through a max. J. G. A. G.

Andrussov's theory of the catalytic preparation of hydrocyanic acid. I. E. ADADUROV (Ukrain. Chem. J., 1936, **11**, 237–249).—The reaction scheme proposed by Andrussov (A., 1935, 1329) for the prep. of HCN by passing  $CH_4$ – $NH_3$ -air through Pt gauze is improbable. The following is proposed:  $NH_2 \rightarrow$  $N + H + H_2$ ;  $CH_4 \rightarrow C + 2H + H_2$ ;  $C + N \rightarrow CN$ ;  $CN + H \rightarrow HCN$ ;  $CN + H_2 \rightarrow HCN + H$ ; H + $O_2 \rightarrow OH + O$ ;  $H_2 + OH \rightarrow H_2O + H$ . R. T.

Thermomagnetic study of iron catalysts used in the synthesis of hydrocarbons by the Fischer process. H. LEFEBVRE and G. LE CLERO (Compt. rend., 1936, 203, 1378—1380).—The thermomagnetic behaviour of a pure Fe oxide catalyst used in treating a CO-H<sub>2</sub> mixture is the same as that of Fe<sub>3</sub>O<sub>4</sub>. When promoted with 0.1-1.0% of K<sub>2</sub>CO<sub>3</sub>, and after a period of use, it shows a Curie point at 575°, due to Fe<sub>3</sub>O<sub>4</sub>, and a second at 250°, due to a solid solution of K ferrite in cubic Fe<sub>2</sub>O<sub>3</sub>. H. J. E.

Molecular orientation and catalysis. Dehydrogenation of cyclohexane catalysed by chromic oxide. A. A. BALANDIN and J. J. BRUSSOV (Z. physikal. Chem., 1936, B, 34, 96-120).-It is deduced from the multiplet theory of catalysis (A., 1929, 519) that there are two kinds of catalysed dehydrogenation. In one the reactant mol. lies flat on the catalyst surface, and for the dehydrogenation of a six-membered ring such as cyclohexane (I) in this way the catalyst must be a cryst. metal with a facecentred cubic or hexagonal lattice, c.g., Pt or Ni. This kind of reaction occurs at ~ 300°. In the second type, the reactant mol. is held by two atoms of the catalyst, which need not have any particular kind of lattice or even be cryst. Reaction occurs at  $\sim 450^{\circ}$ and metal oxides serve as catalysts. Rings other than those with six members will react, and unsaturated intermediate products are formed. As an example of this kind of catalysed reaction the dehydrogenation of (I) to  $C_6H_6$  at  $330-450^\circ$  on microcryst.  $Cr_2O_3$  has been studied (cf. A., 1932, 1095). Langmuir's equation for the velocity of heterogeneous catalysed reactions is valid and at 400° the duration of sojourn of (I) mols. on the catalyst is approx. 2.5 times that of  $C_6H_6$  mols. *cyclo*-Hexene and -hexadiene are formed as intermediate products. A sample of benzine from which mols. with six-membered rings had been removed underwent dehydrogenation on  $Cr_2O_3$ , but not on Pt. MoO<sub>3</sub> acts as a dehydrogenating catalyst, but is less active than Cr2O3. Replacement of a C of a ring by N or S causes the mol. to undergo dehydrogenation more readily. R. C.

Electrostatic phenomena in the catalytic oxidation of ethyl alcohol. A. S. COCOŞINSCHI (Z. Elektrochem., 1936, 42, 876—879).—The production of ions in the catalytic oxidation of EtOH by air in presence of Pt has been confirmed. The effect is not due to thermionic emission. The mechanism is discussed. E. S. H.

Selective properties of (A) platinum, (B) palladium, in the hydrogenation of mixtures of unsaturated compounds. I. F. BOGDANOV and E. I. BASCHKIROVA (Bull. Acad. Sci. U.R.S.S., 1936, 91— 108, 109—121).—(A) Hydrogenation of the components of mixtures of cinnamic acid (I) and oleic acid (II) (in EtOH) proceeds simultancously in presence of Pt catalyst, at 10—20°. Hydrogenation of the second constituent of the pairs  $CH_2:CH:CH_2:OH$ (III)-(I) or -(II) does not commence until that of (III) is complete.

(B) Pd catalyst behaves similarly to Pt with respect to hydrogenation of (III)–(II) mixtures. Hydrogenation of (I) in its mixtures with (III) does not commence until 80% of the latter has been saturated, whilst in mixtures of (I) and (II) hydrogenation of (II) commences only after practically complete hydrogenation of (I). R. T.

Raney's nickel [catalyst]. R. PAUL and G. HILLY (Bull. Soc. chim., 1936, [v], 3, 2330—2332; cf. A., 1935, 844).—Details are given for the prep. of an active Ni catalyst by a modification of Raney's technique. F. L. U.

Anodic formation of manganese dioxide. I. M. GELOSO and (MLLE.) C. ROUILLARD. II. Different modes of oxidation. M. GELOSO (Bull. Soc. chim., 1936, [v], 3, 2221-2230, 2231-2236).--I. In the electrolysis of aq. MnSO<sub>4</sub> the currentanode potential curves consist of two ascending parts joined by a relatively flat portion representing a potential change which may reach 0.6 volt. Deposition of oxides of Mn occurs under conditions corresponding with the first, and evolution of  $O_2$ with the second, of these branches. The influence of [Mn"], acidity, temp., and stirring on the form of the curves has been studied. The composition of the anodic deposit is  $MnO_2, xMnO, x$  being always <1>0.The proportion of MnO<sub>2</sub> increases with decrease of [Mn<sup>"</sup>] and of  $p_{\pi}$ , the max. observed being

96.5%. II. The formation of  $MnO_2$  is due to two mechanisms, viz., (1) (a)  $Mn'' \rightarrow Mn''' + 2e$ , (b)  $Mn''' + 2H_2O \rightarrow MnO_2 + 4H'$ , and (2)  $MnSO_4 + \frac{1}{2}O_2 + H_2O$   $\rightarrow H_2SO_4 + MnO_2$ . F. L. U.

Electrolytic separation of lanthanum and thorium from organic solutions. I. A. ATANASIU and M. BABOR (Bul. Chim. Soc. Romane, 1935— 1936, 38, 83—90).—The separation has been studied in org. solutions free from  $H_2O$ , and from 97% EtOH and MeOH. In the latter case the influence of reducing agents and of the metal composing the cathode has been investigated. D. C. J.

Electrochemical preparation of nitric esters.— See A., II, 45.

Nature of electrode reactions. I. Factors affecting the electrochemical reduction of N-nitrosomethylaniline. J. E. WELLS, D. E. BABCOCK, and W. G. FRANCE (J. Amer. Chem. Soc., 1936, 58, 2630—2632).—The influence of temp., c.d., acid concn., and electrode material has been investigated. The reaction provides a satisfactory method of prep. of NPhMe·NH<sub>2</sub>; the yield is 85%. E. S. H.

Chemical reaction in electric discharges. II. Chemical activity of ions. R. W. LUNT (Trans. Faraday Soc., 1936, 32, 1691-1700; cf. A., 1936, 567).—Theoretical. There are many reasons for believing that chemical reaction in discharges is generally unlikely to be attributable to ions. F. L. U.

Mechanism of chemical reaction in the electric discharge. E. J. B. WILLEY (Nature, 1936, 138, 1054—1055).—Theories that positive ions are the reacting bodies, clusters being formed, are unsatisfactory, but the hypothesis that the positive ions are forerunners of the true reactive species explains many observed facts. L. S. T.

Oxidation of selenium in the glow discharge. II. Study of variables and characterisation of product. III. Striated deposits and possible mechanism. E. OLSON and V. W. MELOCHE (J. Amer. Chem. Soc., 1936, 58, 2511—2514, 2514— 2516; cf. A., 1934, 739).—II. The best conditions of pressure, current, electrode distance, and shape of tubes for the production of  $SeO_2$  and  $SeO_3$  have been determined. The reaction is best initiated in the negative glow.

III. Correlation of voltage measurements with the banded deposits of Se and SeO<sub>2</sub> shows that vaporisation and activation of Se takes place in the luminous regions of the discharge, and combination with  $O_2$  occurs in the dark regions. A mechanism is put forward. E. S. H.

Photo-decomposition of ammonia. H. J. WELCE and A. O. BECKMAN (J. Amer. Chem. Soc., 1936, 58, 2462—2467).—With small amounts of decomp. the quantum yield approaches 1 and the gaseous products approach pure  $H_2$  for the photochemical decomp. For the Hg-photo-sensitised decomp. the quantum yield is 0.12. E. S. H.

Photochemical oxidation of ammonia in seawater. N. W. RAKESTRAW and A. HOLLAENDER (Science, 1936, 84, 442—443; cf. A., 1933, 236).—Data for the photochemical oxidation of  $NH_3$  to  $NO_2'$  in sea-H<sub>2</sub>O are recorded. Oxidation does not occur in distilled H<sub>2</sub>O. Ultra-violet light also slowly destroys nitrite in sea-H<sub>2</sub>O. L. S. T.

Mechanism of the photochemical decomposition of methane. W. GROTH and H. LAUDEN-KLOS (Naturwiss., 1936, 24, 796).—The photochemical decomp. of CH<sub>4</sub> has been investigated using an improved Harteck Xe lamp giving ultra-violet light of high intensity. The decomp. products are H<sub>2</sub> and hydrocarbons, chiefly C<sub>2</sub>H<sub>2</sub> with some C<sub>2</sub>H<sub>6</sub> and traces of C<sub>2</sub>H<sub>4</sub> and hydrocarbons with 3—5 C.  $1\cdot30\pm0\cdot05$ H<sub>2</sub> were produced per quantum absorbed. It is considered that the following reactions occur : CH<sub>4</sub> = CH<sub>3</sub> + H; CH<sub>3</sub> + H = CH<sub>2</sub> + H<sub>2</sub>; 2CH<sub>2</sub> = C<sub>2</sub>H<sub>2</sub> + H<sub>2</sub>. This would give  $0\cdot5$  C<sub>2</sub>H<sub>2</sub> and  $1\cdot5$  H<sub>2</sub> per quantum. A. J. M. Photochemical formation of carbonyl chloride from chloroform, chlorine, and oxygen sensitised by chlorine, and retardation by alcohols and ammonia. H. J. SCHUMACHER and D. SUNDHOFF (Z. physikal. Chem., 1936, B, 34, 300—308).—Reaction occurs according to  $d[\text{COCl}_2]/dt = kI_{abs}.[\text{CHCl}_3]^{\ddagger}$ . Formation of COCl<sub>2</sub> can be almost completely suppressed by added MeOH, EtOH, or NH<sub>3</sub> owing to these substances reacting with Cl atoms propagating the reaction chains. R. C.

Bromination of acetylene in light. W. FRANKE and H. J. SCHUMACHER (Z. physikal. Chem., 1936, B, 34, 181–186; cf. A., 1936, 1228).—Repetition of Booher and Rollefson's experiments (A., 1935, 48) with an improved apparatus has not confirmed their results. The photochemical union of  $C_2H_2$  and  $Br_2$  to give  $C_2H_2Br_2$ , which is a chain reaction with a quantum yield of up to 10,000, is accompanied and vitally influenced by a dark reaction and a polymerisation reaction. The dark reaction seems to be essentially heterogeneous, being considerably affected by the nature and pretreatment of the wall of the vessel, whilst the polymerisation is apparently largely a photochemical reaction. The velocity is approx.  $\infty$ the absorbed light. R. C.

Photodecomposition of aldehydes and ketones. R. G. W. NORRISH and C. H. BAMFORD (Nature, 1936, 138, 1016).—Results obtained in the photodecomp. of COMeBu<sup>a</sup> and COPr<sup>a</sup><sub>2</sub> in cyclohexane solution are described, and the mechanism of the decomps. is discussed in terms of the length of life of the excited mols. L. S. T.

Photo-oxidation of carotene.—See this vol., A., II, 54.

Preparation of very pure conductivity water. P. A. THIESSEN and K. HERRMANN (Chem. Fabr., 1937, 10, 18).—A cheap apparatus for the further purification of H<sub>2</sub>O of conductivity  $1-2 \times 10^{-6} \Omega^{-1}$ consists of a Jena glass flask in which it is treated with a strong current of pure N<sub>2</sub> free from NH<sub>3</sub> and CO<sub>2</sub> at 80—90°. It is then blown into a quartz glass flask having an additional heating coil around its neck and distilled. The product is of conductivity  $<10 \times$  $10^{-8} \Omega^{-1}$  and if again distilled 6—8 ×  $10^{-8} \Omega^{-1}$ . C. I.

Formation of activated water molecules in high vibrational states in the oxy-hydrogen flame. T. KITAGAWA (Proc. Imp. Acad., Tokyo, 1936, 12, 281—284).—Comparison of the emission spectrum of the  $H_2-O_2$  flame with the absorption bands of  $H_2O$ vapour obtained by the author, and isolated from the solar spectrum by Mecke *et al.* (A., 1933, 445, 552) between 5700 and 7000 A., suggests that activated  $H_2O$ mols. are very important intermediate products in the combustion. R. C. M.

Oxidation of halides of alkali metals by molecular oxygen. V. A. PIANKOV (J. Gen. Chem. Russ., 1936, 6, 1295—1297).—The reaction between HgO and aq. KBr may be represented as HgBr<sub>2</sub> +  $2KOH \Longrightarrow HgO + 2KBr + H_2O$ . R. T.

Sodium hydrogen tripolyphosphate. H. HUBER (Z. anorg. Chem., 1936, 230, 123–128).—By adding EtOH to an aq.-AcOH solution of  $Na_5P_3O_{10}$  an oily

layer is obtained which yields crystals of the salt  $Na_5P_3O_{10}, Na_3H_2P_3O_{10}, 3H_2O$ .  $Na_3H_2P_3O_{10}$  is formed as an intermediate product when  $(NaPO_3)_3$  is prepared by rapid dehydration of  $NaH_2PO_4$  or  $Na_2H_2P_2O_7$ . F. L. U

Thiosilicates. I. Cuprous thiosilicates. L. CAMBI and G. G. MONSELISE (Gazzetta, 1936, 66, 696-700).-A thermal study of the system SiS<sub>2</sub>-Cu<sub>2</sub>S shows the existence of the compound 4Cu<sub>2</sub>S,SiS<sub>2</sub>, m.p. 1195°. O. J. W.

Stability of sodium aurichloride solutions. F. REIMERS (Dansk Tidsskr. Farm., 1936, 10, 297-304).—The stability of aq. NaAuCl<sub>4</sub> (I) has been studied. Solutions containing >0.1% (I) cannot be sterilised by heating at 100° owing to deposition of Au. M. H. M. A.

Preparation of beryllium nitrate. A. V. Novo-SELOVA (J. Gen. Chem. Russ., 1936, 6, 1306-1309).-Tensimetric and analytical data suggest the hydrates R. T.  $Be(NO_3)_2, 1, 2, 3, and 4H_2O.$ 

Action of carbon dioxide and of carbon monoxide on compact magnesium at high temperatures. R. DELAVAULT (Bull. Soc. chim., 1936, [v], 3, 2403-2407; cf. A., 1934, 853, 1185).-Below 800° Mg heated in CO reacts only superficially, giving a film of C which does not catalyse the reaction. In dry  $CO_2$  Mg may be heated above 700° without any but a superficial reaction giving rise to CO. If, however, the  $CO_2$  contains either  $O_2$  or  $H_2O_2$ , combustion ensues.

F. L. U.

Calcium alkali phosphates. I. Rhenania phosphate. H. H. FRANK, M. A. BREDIG, and R. FRANK (Z. anorg. Chem., 1936, 230, 1-27).-The sole ternary product obtainable from the system Na<sub>2</sub>O- $CaO-P_2O_5$  at 1000-1400° is NaCaPO<sub>4</sub>, which is present in some specimens of Rhenania phosphate. Specimens of the latter which give an X-ray diagram of "rhenanite" (I) (cf. A., 1932, 1216) contain also combined  $CO_2$ . Starting with pure materials, it is shown that products containing (I) are formed only when CO<sub>2</sub> is present. By heating hydroxyapatite, NaCaPO<sub>4</sub>, or CaHPO<sub>4</sub> with Na<sub>2</sub>CO<sub>3</sub> in an atm. of CO<sub>2</sub> the compound  $Ca_4Na_6(PO_4)_4CO_3$  (II) is obtained in a pure state. On heating at 1400° (II) is decomposed quantitatively into CaO, NaCaPO4, and Na3PO4. The dissociation pressure (CO2) is 1 atm. at 1300°. Heating (II) with CaO in an atm. of  $CO_2$  at temp.  $>800^{\circ}$  gives (11) with CaO in an atm. of  $\operatorname{CO}_2$  at the p. 4000 g. The rise to a carbonatoapatite  $\operatorname{Ca}_{10}(\operatorname{PO}_4)_6\operatorname{Na}_2(\operatorname{CO}_3)_2$ . The Na of (II) can be partly replaced by Ca, and at high temp. the  $\operatorname{CO}_2$  can be replaced by  $\operatorname{SiO}_2$ . The (I) occurring in technical preps. is a Na-(I) of the latter type. The conditions under which (I) is formed, established by experiments with natural phosphorites, are similar to those which apply to the pure system  $CaO-Na_2O-P_2O_5-SiO_2$ . F. L. U.

Combined action of hydrogen and heat on alkaline-earth arsenates. H. GUERIN (Compt. rend., 1936, 203, 1163-1164) .-- Tribasic Ca, Sr, and Ba arsenates at 400-450° are reduced to arsenites, which give the metal oxide, As, and H<sub>2</sub>O simultaneously or at higher temp. A Ba arsenide is formed above 700°. Pyro- and meta-arsenates are first reduced to the corresponding tribasic orthoarsenates,  $As_2O_3$ , and  $H_2O$ . A. J. E. W.

Preparation of zinc and cadmium cyanides. S. C. Woo and T. K. LIU (J. Chinese Chem. Soc., 1936, 4, 518-521).-Zn(CN)2 and Cd(CN)2 are prepared by pptg. MeOH solutions of Zn(OAc)<sub>2</sub> or Cd(OAc)<sub>2</sub> with an Et<sub>2</sub>O solution of HCN. C. R. H.

Precipitation of carbonates. L. CLOUTIER, P. E. PELLETIER, and P. E. GAGNON (Trans. Roy. Soc. Canada, 1936, [iii], 30, III, 149-164).-A study has been made of the variation with the concn. of the composition of ppts. formed at room temp. by the mixing of aq. solutions of Zn, Cu, Cd, Mg, Co, and Ni salts with aq. KHCO<sub>3</sub> or K<sub>2</sub>CO<sub>3</sub>. ZnCO<sub>3</sub> was formed from 0.05M-Zn(NO<sub>3</sub>)<sub>2</sub> by addition of excess of KHCO<sub>3</sub>. By addition of K<sub>2</sub>CO<sub>3</sub> in concn. < approx. 0.15 g.-mol. per litre to 0.05M-Zn(NO<sub>3</sub>)<sub>2</sub>, 2ZnCO<sub>3</sub>,3Zn(OH)<sub>2</sub> was formed. At higher concns. of K<sub>2</sub>CO<sub>3</sub>, 4ZnCO<sub>3</sub>,7Zn(OH)<sub>2</sub> was pptd. 10CdCO<sub>3</sub>,Cd(OH)<sub>2</sub> was formed from 0.05M- $Cd(NO_3)_2$  with equimol. concn. of  $K_2CO_3$ , and  $5CdCO_3, Cd(OH)_2$  with higher concn. of  $K_3CO_3$ .  $3MgCO_3, Mg(OH)_2$  (I) was formed by pptn. from  $0.1M_2$ .  $Mg(NO_3)_2$  by  $K_2CO_3$  in equimol. or higher concess. By stirring in contact with the mother-liquor (I) was converted into MgCO<sub>3</sub> when formed from equimol. solutions and into 4MgCO3,Mg(OH)2 in presence of excess of K<sub>2</sub>CO<sub>3</sub>. 2NiCO<sub>3</sub>,5Ni(OH)<sub>2</sub> was obtained by addition of  $K_2CO_3$  to 0.05M-Ni(NO<sub>3</sub>)<sub>2</sub>. No definite compounds were formed from 0.05M-Co(NO<sub>3</sub>)<sub>2</sub> and  $K_2CO_3$  or from 0.05M-Cu(NO<sub>3</sub>)<sub>2</sub> and KHCO<sub>3</sub> or  $K_2CO_3$ . O. D. S.

Action of ammonium chloride on sulphides. E. MONTIGNIE (Bull. Soc. chim., 1936, [v], 3, 2321-2322; cf. A., 1936, 1080).-CdS, FeS, Sb<sub>2</sub>S<sub>3</sub>, MnS, and  $MoS_3$  are attacked, more or less completely, by conc. aq. NH<sub>4</sub>Cl. No action takes place with other heavy metal sulphides. F. L. U.

Mercury vanadates and xanthates. E. Mon-3, 2322-TIGNIE (Bull. Soc. chim., 1936, [v], 2324).—The prep. and properties of  $Hg_2(VO_3)_2$ ,  $Hg(NO_3)_2$ , 3HgO, and  $Hg^I$  and  $Hg^{II}$  Et xanthates are described. F. L. U.

Complex compounds of mercury and copper halides with aliphatic amines. M. STRAUMANIS and A. CIRULIS (Z. anorg. Chem., 1936, 230, 65-87). -The following compounds are described :

 $[(NH_2Et)_2HgBr_2], m.p. 135^{\circ} (decomp.);$  $[(NHEt_2)HgBr_2], m.p. 145^{\circ} (decomp.);$  $[(NH_2Pr^{\circ})HgBr_2], m.p. 187^{\circ} (decomp.);$ 

 $[(NH_2H^{-})HgBr_2]; [NH_2Et)HgI_2], m.p. 187^{\circ} (decomp.); \\[(NH_2Me)_2HgBr_2]; [NH_2Et)HgI_2], m.p. 14^{\circ}; \\[(NH_2Et)_2HgI_2], m.p. 57-62^{\circ}; [(NH_2Pr^{a})_2HgI_2], m.p. 45-47^{\circ}; [(NH_2Pr^{a})HgI_2], m.p. 0^{\circ}; \\[(NH_2Bu^{\beta})_2HgI_2], m.p. 56^{\circ}; [(NHMe_2)HgI_2], m.p. 83^{\circ}; [(NHEt_2)HgI_2], m.p. 101^{\circ}; [enHgI_2], m.p. 103^{\circ}; \\[Hg(NH_2Et)_4]I_2, m.p. -4^{\circ}; [Cu^{II}(NH_2Et)_4]CI_2; \\[Cu^{II}(NH_2Et)_2]Br_2; [Cu^{II}(NH_2Et)_2(H_2O)_2]I(OH); \\[Cu^{II}(NH_2Et)_4]I_2; [Cu^{II}(NH_2Me)_4][HgI_4]; \\[Cu^{II}(NH_2Me)_{a}]_{a}[HgI_{a}]; 7CuI.HgI_{a}.7NH_{a}Me.$ 

 $[Cu^{I}(NH_{2}Me)_{2}]_{2}[HgI_{4}]; 7CuI,HgI_{2},7NH_{2}Me.$ 

F. L. U.

Autoxidation of the complex metallic compounds of gluconic acid.—See A., II, 49.

Metallic complex salts of aliphatic polyhydroxy-compounds. See A., II, 48.

Crystalline boron. D. P. MELLOR, S. B. COHEN, and E. B. UNDERWOOD (Proc. Austral. Chem. Inst., 1936, 3, 329-333).-Cryst. B was prepared by reducing BBr<sub>3</sub> (synthesised from Br and amorphous B at 700°) with H<sub>2</sub> at a low temp. produced by a W filament; crystallisation of B from molten Cu was unsuccessful. The dark grey solid, containing 0.005% of Si, had mean d 2.36, hardness < 13 (revised Moh scale); 22 spacings obtained from Hull powder photographs are recorded, of which 2.59 and 2.11 A. correspond with the most intense lines. There is evidence that the mol. is three-dimensional. Powder photographs of amorphous B (Moissan's method) showed no evidence of cryst. suboxides, but the most intense band (corresponding with a spacing of approx. 4.9 A.) indicated that a large proportion of the specimen was amorphous. J. G.

Boron hydrides. XXV. Parachor of diborane  $B_2H_6$ . A. STOCK, E. WIBERG, and W. MATHING (Ber., 1936, 69, [B], 2811—2815).—The observed val. (121.9) for the parachor of  $B_2H_6$  harmonises best with Wiberg's formulation  $(B-H_2:B-H_2)H_2^+$  according to which it is composed of 2 single parachors for 2 B atoms (2 × 16.4), 4 H atoms (4 × 17.1), a double linking (23.2), and 2 electrovalencies (-2 × 1.6) = 121.2. Slight uncertainty is introduced with regard to d. H. W.

Present knowledge of the structure of boron hydrides. E. WIBERG (Ber., 1936, 69, [B], 2816-2842).—According to chemical and physical pro-perties the known B hydrides are divisible into two groups,  $B_nH_{n+4}$  ( $B_2H_6$ ,  $B_5H_9$ ,  $B_6H_{10}$ ,  $B_{10}H_{14}$ ) and  $B_nH_{n+6}$  ( $B_4H_{10}$ ,  $B_5H_{11}$ ,  $B_6H_{12}$ ). At present experimentally established structural formulæ can be assigned only to the initial member of each series,  $B_2H_6$  and  $B_4H_{10}$ . They are obtained by comparison of the chemistry of B with that of C and N and are best written BHH2:BHH2 and BHH.BHHBHHBHH2 (simplified  $[B_2H_4]H_2$  and  $[B_4H_6]H_4$  or  $BH_3$  BH<sub>3</sub> and  $BH_3$  BH<sub>2</sub> BH<sub>2</sub> BH<sub>3</sub>), respectively. They are therefore unsaturated, polybasic acids comparable with C<sub>2</sub>H<sub>4</sub> and butadiene in electronic arrangement. The acidic character is established by salt formation with NH<sub>2</sub>. In accordance with the formulæ  $B_2H_6$  and B<sub>4</sub>H<sub>10</sub> unite with 2 and 4 mols. of NH<sub>3</sub>, respectively, giving  $[B_2H_4][NH_4]_2$  and  $[B_4H_6][NH_4]_4$ . As salts, these compounds conduct the current when in solution. The different union of H in B<sub>2</sub>H<sub>6</sub> and B<sub>4</sub>H<sub>10</sub> can also be established from the non-acidic side since in B<sub>2</sub>H<sub>6</sub> a max. of 4 and in  $B_4H_{10}$  of 6 H are replaceable by univalent groups, e.g.,  $[B_2Me_4]H_2$ ,  $[B_4(NH_2)_6]H_4$ . The acidic nature of the substituted products follows from their undiminished power of salt formation with NH<sub>3</sub>. The unsaturated character of boranes is established by their power of adding atoms of alkali metal, giving thus Na[NH<sub>3</sub>·BH<sub>3</sub>]Na, Na[NH<sub>3</sub>·BH<sub>2</sub>:BH<sub>2</sub>·BH<sub>3</sub>]Ba. It is also proved by measurements of the ultra-violet absorption spectrum, which show the analogy of  $B_2H_6$ with  $C_2H_4$  and not  $C_2H_6$  and explain simply the behaviour of the boranes towards H<sub>2</sub>O and H halides :  $BH_3:BH_3 + HX \rightarrow BH_4:BH_3X \rightarrow BH_3:BH_2X + H_2.$ Measurements of dipole and parachor and magnetic observations extend and confirm the chemical evidence. H. W.

Additive product of boron fluoride and potassium sulphate. P. BAUMGARTEN and E. MÜLLER (Ber., 1936, 69, [B], 2688—2690).—Passage of BF<sub>3</sub> over  $K_2SO_4$  at about 240° gives the compound  $K_2SO_4$ , BF<sub>3</sub> which when further heated gives a colourless distillate containing B and F; BF<sub>3</sub> thus resembles  $SO_3$ . H. W.

Preparation of crystalline aluminium orthoarsenate. F. MACHATSCHKI and A. MOSER (Naturwiss., 1936, 24, 743).—Repetition of the work of Goguel (Diss., Paris, 1894) on the prep. of doubly refracting, octahedral crystals of AlAsO<sub>4</sub> gave only cubic crystals of As<sub>2</sub>O<sub>3</sub>. Good crystals of AlAsO<sub>4</sub> of the quartz type were obtained by prolonged heating at 250° in a sealed tube of the ppt. obtained by mixing solutions of  $H_3AsO_4$  and NaAlO<sub>2</sub>, and of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and K<sub>2</sub>HAsO<sub>4</sub>. The physical properties of quartz, AlPO<sub>4</sub>, and AlAsO<sub>4</sub> are compared.

A. J. M.

Measurements on gallium and indium compounds. XI. Fluorides of gallium, indium, and thallium. O. HANNEBOHN and W. KLEMM (Z. anorg. Chem., 1936, 229, 337–351; cf. A., 1934, 1081).—GaF<sub>3</sub> (sublimes at 950°) is obtained by heating  $(NH_4)_3GaF_6$  (I) in F<sub>2</sub> at 250–400°; decomp. of (I) in air leads to ammonolysis, with the successive formation of Ga $(NH_2)F_2$  at 220°, and GaNHF at 400°. The action of F<sub>2</sub> on Ga<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>S<sub>3</sub>, or Ga<sub>2</sub>Tc<sub>3</sub> leads to only partial conversion into GaF<sub>3</sub> at all temp. After ignition at 1000°, and consequent recrystallisation, Ga<sub>2</sub>S<sub>3</sub> is attacked very slowly by F<sub>2</sub>. InF<sub>2</sub> (m.p. 1170°, b.p. 1200°) is obtained by the action of F<sub>2</sub> on the *sall* (NH<sub>4</sub>)<sub>3</sub>InF<sub>6</sub>, or on In<sub>3</sub>O<sub>3</sub>; TIF<sub>3</sub>, m.p. 550°, results similarly from Tl<sub>2</sub>O<sub>3</sub>. GaF<sub>3</sub> is not reducible by H<sub>2</sub>, but InF<sub>2</sub> above 275° forms  $In_2F_4$ , which is shown to be dimeric by its diamagnetic properties. Physical properties, *d*, and mol. vol. increments are discussed. J. S. A.

Combustion of cyanogen. R. DOLIQUE (Bull. Soc. chim., 1936, [v], **3**, 2347–2359).—When the mixture  $(CN)_2 + O_2$  is sparked only 86% of the  $(CN)_2$ reacts according to the usual equation, and small quantities of  $CO_2$ , C, and N<sub>2</sub>O are formed. With  $(CN)_2 + 2O_2$ . CO, NO, and NO<sub>2</sub> are produced in addition to the products of the main reaction. With  $(CN)_2 + 3O_2$  no CO is found after combustion, but 5% of the N appears as NO<sub>2</sub>. F. L. U.

Hydrates of molecular compounds of zirconyl oxalate with oxalic acid and alkali oxalates. (MLLE.) J. BOULANGER (Compt. rend., 1936, 203, 1257—1259).—The dehydration on heating of salts of the type  $ZrO(CO_2)_2, H_2C_2O_4, 2M_2C_2O_4, nH_2O$  (M = Li, Na, K, Rb, Cs, or NH<sub>4</sub>) has been investigated. Vals. of n and heats of dissolution are given for the hydrates observed, and the binding energies of the H<sub>2</sub>O mols. deduced. A. J. E. W.

Basic lead sulphates. G. L. CLARK, J. N. MRGUDICH, and N. C. SCHIELTZ (Z. anorg. Chem., 1936, 229, 401–409).—From an X-ray study of basic Pb sulphates prepared in various ways, the existence of  $4PbO, PbSO_4, 2PbO, PbSO_4$ , and probably  $3PbO, PbSO_4$  is confirmed. The role of  $H_2O$  in the compounds is neglected. J. S. A.

Action of ammonium chloride with nitric acid on various compounds. E. MONTIGNIE (Bull. Soc. chim., 1936, [v], 3, 2320–2321).—A saturated solution of NH<sub>4</sub>Cl to which HNO<sub>3</sub> has been added behaves F. L. U. in many respects like aqua regia.

Constitution of solid phosphorus hydride. P. ROYEN (Z. anorg. Chem., 1936, 229, 369-400).-The solid P hydride (I) obtained by the decomp. of  $P_2H_4$ is variable, and not stoicheiometric in composition, and is not justifiably represented as a definite compound P12H6. (I) is amorphous (X-rays). PH3 is evolved on heating, but no  $H_2$  at temp. below the dissociation temp. of  $PH_3$ . The rate of decomp. falls with decreasing H content, but shows no discon-tinuity at the composition  $P_9H_2$ . The solid hydrides are therefore regarded as sorption complexes of PH<sub>3</sub> in a yellow amorphous form of P; desorption is irreversible, but in liquid NH3, NH3 may be adsorbed, displacing  $PH_3$  and giving an apparent additive compound. Piperidine similarly displaces  $PH_3$  partly, but the black "salt" is not stoicheiometric in composition, and is an adsorption complex. In confirmation, on irradiation of white P in PH<sub>3</sub> under 30-40 atm. pressure, an amorphous product containing up to 14 wt.-% of PH3 is obtained. Amorphous P similarly adsorbs PEt<sub>3</sub> from CS<sub>2</sub> solution; a similar product is obtained by partial displacement of PH<sub>3</sub> from (I) by PEt<sub>3</sub>. J. S. A.

Extraction of sulphur from metallic sulphides. A. SOARE and V. PAVLU (Bul. Chim. Soc. Romane, 1935-1936, 38, 143-144).-Half of the S in FcS<sub>2</sub> is obtained as a sublimate and half as H2S and CS2 by obtained as a sublimate that resence of  $CH_4$ . D. C. J.

Use of chromous sulphate in the removal of oxygen from a stream of gas. Comparison with other oxygen absorbents. H. W. STONE (J. Amer. Chem. Soc., 1936, 58, 2591-2595).-CrSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> solutions rapidly absorb  $O_2$  from a stream of  $N_2$ . The relative rates of absorption of O2 by other reagents. have been determined. E. S. H.

Reaction of hydrogen peroxide with chromic anhydride in dry ethyl acetate. D. G. NICHOLSON (J. Amer. Chem. Soc., 1936, 58, 2525-2526).-The blue compound formed gives an NH4 salt corresponding with  $H_2CrO_5, 2NH_3$ . The blue compound is probably H2CrO5 or CrO3,H2O2. **E**. S. H.

Complex compounds with two co-ordination shells from hexamminechromic and triethylenediaminechromic ions. H. BRINTZINGER and F. JAHN (Z. anorg. Chem., 1936, 229, 410-412).-From measurements of ionic diffusion rates, the existence of the following ions in solutions of 

Attempt to prepare FO : identification of gases resulting from thermal decomposition of F2O2. P. FRISCH and H. J. SCHUMACHER (Z. anorg. Chem., 1936, 229, 423–428).—The products of thermal decomp. of  $F_2O_2$  at  $-60^{\circ}$  to  $-25^{\circ}$  (cf. A., 1934, 378) agree in absorption spectrum, v.p., b.p., m.p., and action on 30% aq. HI with the properties of an equimol.  $F_2-O_2$  mixture. It is concluded that FO has no real existence. J. S. A.

Tervalent manganese chloride. A. CHRETIEN and G. VARGA (Bull. Soc. chim., 1936, [v], 3, 2385-2394).—Mn trichloride, prepared by the action of HCl on  $Mn(OAc)_3$  at  $-100^\circ$ , forms a brown cryst. mass giving green solutions in various org. solvents, e.g., EtOH and AcCl. The formula, from cryoscopic measurements in liquid HCl, is MnCl<sub>3</sub>. MnCl<sub>3</sub> is decomposed irreversibly above -40° into MnCl<sub>2</sub> and F. L. U.  $Cl_2$ .

Active iron. VII. Ferric salt catalase. A. SIMON, W. HAUFE, T. REETZ, and R. PREISSLER. VIII. Prussian-blue reaction. IX. Reactions with 2:2'-dipyridyl and o-phenanthroline. A. SIMON and W. HAUFE (Z. anorg. Chem., 1936, 230, 129-147, 148-159, 160-175; cf. A., 1931, 439).--VII. On the assumption that the catalase activity of Fe salts is due to Fe<sup>\*\*</sup>, which in presence of  $H_2O_2$  is in equilibrium with Fe<sup>\*\*\*</sup>, the relative activity of different Fe<sup>III</sup> salts should increase with the [Fe<sup>\*\*\*</sup>] furnished by them. Velocity coeffs. for the decomp. of  $H_2O_2$  in presence of Fe(ClO<sub>4</sub>)<sub>3</sub>, FeCl<sub>3</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>, NH<sub>4</sub>Fe(SO<sub>4</sub>)<sub>2</sub>,  $Fe_2(SO_4)_3$ ,  $Fe(OAc)_3$ ,  $FePO_4$ , and  $FeF_3$  at  $p_{II}$  1-5 are in the decreasing order given. The same order is found for the [Fe''] in equiv. solutions of the salts named. The activity of any given salt increases with rise in  $p_{\pi}$ . In all cases the velocity of decomp. of  $H_2O_2$  increases rapidly at first, owing to the formation of Fe<sup>\*\*</sup> from Fe<sup>\*\*\*</sup>, whilst it decreases later, increasingly so with increasing  $p_{\rm H}$ , on account of hydrolysis. The Fe<sup>•</sup>  $\Longrightarrow$  Fe<sup>•</sup> equilibrium is influenced by  $p_{\rm H}$  in the sense represented by : Fe<sup>\*\*</sup> + HO<sub>2</sub> ' $\rightarrow$  Fe<sup>\*\*</sup> + HO<sub>2</sub> (high  $p_{\rm H}$ ), Fe<sup>\*\*</sup> + H<sub>2</sub>O<sub>2</sub>  $\rightarrow$  Fe<sup>\*\*</sup> + OH' + OH (low  $p_{\rm H}$ ). VIII. The reaction between Fe<sup>II</sup> salts and

 $K_3Fe(CN)_6$  in aq. solution proceeds in two stages, viz., (1) Fe<sup>\*\*</sup> + [Fe(CN)\_6]'''  $\rightarrow$  Fe<sup>\*\*\*</sup> + [Fe(CN)\_6]'''', (2) 4Fe<sup>\*\*\*</sup> + 3[Fe(CN)\_6]'''  $\rightarrow$  Fe<sup>111</sup><sub>4</sub>[Fe<sup>11</sup>(CN)\_6]\_3. The production of Fe<sup>\*\*</sup> from Fe<sup>111</sup> salts by H<sub>2</sub>O<sub>2</sub> has been followed by adding  $K_3Fe(CN)_6$  to the mixture and measuring the colour change. The salts used were  $Fe(ClO_4)_3$ ,  $FeCl_3$ ,  $Fe(NO_3)_3$ ,  $NH_4Fe(SO_4)_2$ , and  $Fe_2(SO_4)_3$ , all at  $p_{11} 2$ . The initial rate of production of Fe" decreases in the order named, parallel with the initial [Fe ...]. The results show that the catalase effect varies in the same sense as does the [Fe"].

IX. In the production of the red complex [Fe<sup>II</sup> dip<sub>3</sub>]X<sub>2</sub> in a solution of FeX<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, and 2:2'dipyridyl, the rate-determining reaction is Fe" +  $HO_2' \rightarrow Fe^{*} + HO_2$ , and the colour change can therefore be used to follow the formation of Fe<sup>\*</sup>. The results so obtained confirm those given by the use of K<sub>3</sub>Fe(CN)<sub>6</sub>. Similar results are obtained with ophenanthroline, F. L. U.

Iron perchlorates. I. F. LINDSTRAND (Z. anorg. Chem., 1936, 230, 187-208).—The prep. of cryst.  $Fe(ClO_4)_2$  (4, 5, and 6  $H_2O$ ) and  $Fe(ClO_4)_3$  (6, 9, and 10  $H_2O$ ) is described. Solubilities in  $H_2O$ , aq. HClO<sub>4</sub>, and EtOH have been determined, and the sp. gr. of the saturated aq. solutions are given.  $Fe(ClO_4)_2$  is stable in dry air, but deliquesces and becomes oxidised in ordinary air. The aq. solution is less affected by air than is FeCl<sub>2</sub> or FeSO<sub>4</sub>. F. L. U.

Decomposition of cadmium ferrite. H. FORES-TIER and F. REDSLOB (Compt. rend., 1936, 203, 1160-1162).-Ferromagnetism in Fe<sub>2</sub>O<sub>3</sub>,CdO observed on heating depends on the presence of H<sub>2</sub>O, which hydrolyses the ferrite with production of cubic A. J. E. W. Fe<sub>2</sub>O<sub>3</sub>.

Gmelin's reaction. G. SCAGLIARINI (Gazzetta, 1936, 66, 693-695) .- The work of Raurich Sas (cf. A., 1936, 948) is criticised. O. J. W.

Complex heavy metal halides. J. V. DUBSKY and E. WAGENHOFER (Z. anorg. Chem., 1936, 230, 112-122).-Previous work (A., 1935, 946) has been extended by the prep. of the following compounds  $(an = NH_{o}Ph, quin = quinoline)$ :

 $\begin{array}{l} [\text{BiCl}(an,\text{HCl})_5]\text{Cl}_2,5\text{H}_2\text{O}\,;\\ [\text{CrCl}(an,\text{HCl})_5]\text{Cl}_2,7\text{H}_2\text{O}\,;\\ [\text{Cr}(an,\text{HCl})_9]\text{Cl}_3,14\text{H}_2\text{O}\,. \end{array}$ 

[Cr(an,HCl)<sub>6</sub>]Cl<sub>3</sub>,5H<sub>2</sub>O; F. L. U. Spectrographic methods of studying unstable compounds. II. Aquotisation of trans-di-

chlorotetramminocobaltic chloride in aqueous solutions. R. TSUCHIDA (Bull. Chem. Soc. Japan, 1936, 11, 721-734; cf. A., 1935, 446).—Analysis of the absorption spectra of aq. solutions of [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>(1 6)]Cl (I) at intervals after dissolution has been made by comparison with the known spectrum of  $[Co(NH_3)_4ClH_2O(1\ 2)]Cl_2$  (II), which is identical with that of the solution 90 min. after dissolution. It is concluded that an intermediate product,  $[Co(NH_3)_4ClH_2O(1, 6)]Cl_2$  (III), is first formed from (I) and converted through (II) into  $[Co(NH_3)_4(H_2O)_2(1,2)]Cl_3$ . The velocity coeffs. of the first two reactions are calc. The absorption spectra of (I) and (III) are deduced. O. D. S.

Basic salts. XV. Chemistry and morphology of basic salts of bivalent metals. V. Basic cobalt nitrates. W. FEITKNECHT and G. FISCHER (Helv. Chim. Acta, 1936, 19, 1242—1255).—In-complete pptn. of dil.  $(\ge 2M)$  aq. Co(NO<sub>3</sub>)<sub>2</sub> with dil. aq. NaOH yields the bluish-green basic nitrate Co(NO<sub>3</sub>)<sub>2</sub>,6Co(OH)<sub>2</sub> (I). It varies in structure accord-ing to its method of pren. and aga. At nown town ing to its method of prep. and age. At room temp. it is in equilibrium with Co(OH)<sub>2</sub> in 0.35M-solution and at  $100^{\circ}$  in 0.4M-solution. Near the equilibrium concn. the change into Co(OH), is very rapid, but preps. free from Co(OH), can be kept for long periods in more dil. solution. The stability is increased by slight oxidation. At higher concns. (I) passes into the rose-coloured basic nitrate, Co(NO<sub>3</sub>)<sub>2</sub>,3Co(OH)<sub>2</sub> (II). This change is rapid at  $100^{\circ}$  for solutions above 0.6M, but at room temp. the change is observed only with 1.8M solutions, although the equilibrium concn. is <at 100°. Although (II) is formed only in relatively conc. solutions it is only slightly decomposed by H<sub>2</sub>O. J. W. S.

Reaction between ammonium salts and complex nitro-derivatives of cobalt. J. J. PLAKAN

(Ann. Leningrad State Univ., Chem. Ser., 1935, 1, 72-104).—The reaction  $[Co(NH_3)_{z}(NO_2)_{y}]Cl_{z} +$  $yNH_4X = [Co(NH_3)_xX_y]Cl_z + yN_2 + H_2O$  takes place quantitatively when X = I. With different X, the % climination of NO<sub>2</sub>-N rises in the series F < Cl < Br < I;  $H_2PO_4^2 < SO_4$ . The reaction is unaffected by lowering the  $p_{II}$  of the medium or by increasing the reaction time beyond 40 min. R. T.

· Complex salts of phenylhydrazone-oximes [of diketones] and of phenanthraquinone-mono- and -di-oximes.-See A., II, 24.

Action of chlorides on oxides. E. MONTIGNIE (Bull. Soc. chim., 1936, [v], 3, 2319-2320).-Ni(OH)2 with aq. CuCl<sub>2</sub>, ZnCl<sub>2</sub>, or FeCl<sub>3</sub> gives NiCl<sub>2</sub> and the corresponding hydroxide. A similar metathesis occurs with Cu(OH)<sub>2</sub> and FeCl<sub>3</sub>. By suitable choice of proportions oxychlorides of both metals may be F. L. U. formed.

Separation of metallic nickel from solutions of its salts by the action of metallic zinc or iron. S. A. PLETENEV and C. E. FISCHKOVA (J. Appl. Chem., Russ., 1936, 9, 1394-1399).-The following reactions take place when Zn or Fe is added to neutral aq.  $\begin{array}{ll} \mathrm{NiSO}_4: & \mathrm{Zn} + 2\mathrm{H}_2\mathrm{O} \rightarrow \mathrm{Zn}(\mathrm{OH})_2 + \mathrm{H}_2; & \mathrm{Zn}(\mathrm{OH})_2 + \\ \mathrm{NiSO}_4 \rightarrow \mathrm{ZnSO}_4 + \mathrm{Ni}(\mathrm{OH})_2. & \mathrm{If} \ \mathrm{acid} \ \mathrm{in} \ \mathrm{amount} \end{array}$ equiv. to the H, produced is added during the reaction, equiv. to the H<sub>2</sub> produced is actual and  $Ni(OH)_2$ the ppt. consists of a mixture of Ni and  $Ni(OH)_2$ R. T.

Action of nitric oxide on nickel carbonyl. J.S. ANDERSON (Z. anorg. Chem., 1936, 229, 357-368).-NO reacts with  $Ni(CO)_4$ , dissolved in  $C_6H_6$ ,  $Et_2O$ , CHCl<sub>3</sub>, or C<sub>6</sub>H<sub>14</sub>, only in presence of traces of H<sub>2</sub>O, forming small amounts of a deep blue substance, Ni(NO)OH,1.5-2H<sub>2</sub>O (I). (I) is sol. in H<sub>2</sub>O, oxidises rapidly in air, and is decomposed by acids whereby NO, N2, and smaller amounts of N2O are liberated in amounts indicating a reducing power of 1 atom of H per mol. of NO present.  $AgNO_3$  is reduced to Ag, indicating that (I) is a compound of univalent Ni. With  $C_5H_5N$ , (I) forms the compound Ni(NO)OH, $C_5H_5N$ . In MeOH solution, the prolonged action of NO on Ni(CO)<sub>4</sub> gives a green substance (cf. A., 1930, 1539) which gives chiefly N2O with acids, does not reduce  $AgNO_3$ , and is regarded as a hyponitrite,  $[Ni_2(OH)_2(MeOH)_4]N_2O_2$  (II). In the initial stages of the reaction, a blue substance (III) may be isolated, similar in properties to (I), but isomeric with (II), into which it is converted when kept in solution or in the solid state. By analogy with (I), (III) is formulated as Ni(NO)OH,2MeOH or Ni(NO)OMe,MeOH,H2O. EtOH solutions similarly give the stable compound Ni(NO)OH,EtOH or Ni(NO)OEt,H<sub>2</sub>O (IV). (I), (III), and (IV) are con-verted by KCN or  $K_2S_2O_3$  into the known compounds,  $K_2[Ni(NO)(CN)_3]$  and  $K_3[Ni(NO)(S_2O_3)_2],2H_2O$ . The relation of (I) to the Cu<sup>T</sup> carbonyl halides and to the carbonyls is discussed. J. S. A.

Action of ammonia on solutions of rhodium chloride. V. V. LEBEDINSKI (Ann. Sect. Platine, 1936, 13, 9-17).-NH<sub>4</sub>Cl to 20% and 1.5-2 vols. of boiling aq. NH3 are added to boiling aq. RhCl3, when pure [Rh(NH<sub>3</sub>]<sub>5</sub>Cl]Cl<sub>2</sub> is pptd. in good yield. R. T. Separation of rhodium from platinum residues. V. V. LEBEDINSKI (Ann. Sect. Platine, 1936, 13, 73—94).—Rh is pptd. as  $[Rh(NH_3)_5Cl]Cl_2$ , which is purified by dissolving in HNO<sub>3</sub> and repptg. with HCl. The method serves for isolation of Rh from its mixtures with Ir, Pd, and Pt salts. R. T.

Oxidation of cis and trans bivalent platinum non-electrolytes by nitric acid. I. I. TSCHERNIAEV and A. V. BABAEVA (Ann. Sect. Platine, 1936, 13, 59-61).—Pt<sup>II</sup> complexes of the type PtB<sub>2</sub>X<sub>2</sub> [ $B_2 =$  $(NH_3)_2, (C_5H_5N)_2, en; X = Cl, NO_2]$  react with anhyd. HNO<sub>3</sub> as follows: PtB<sub>2</sub>X<sub>2</sub> + 2HNO<sub>3</sub>  $\Rightarrow$  PtB<sub>2</sub>X<sub>2</sub>(OH)<sub>2</sub> (I) + 2NO<sub>2</sub>; (I) + 2HNO<sub>3</sub>  $\Rightarrow$  PtB<sub>2</sub>X<sub>2</sub>NO<sub>2</sub>NO<sub>3</sub> + 2H<sub>2</sub>O + O. Complexes of the type PtB<sub>2</sub>(NO<sub>2</sub>)NO<sub>2</sub>NO<sub>3</sub> are converted by H<sub>2</sub>O into PtB<sub>2</sub>(NO<sub>2</sub>)NO<sub>2</sub>·OH. The configuration of the original complexes (cis or trans) is unaffected by the reaction, except in presence of H<sub>2</sub>O, when migration of the groups occurs to a certain extent. R. T.

Isomerism of ethylene compounds of platinum. —See A., II, 54.

Colorimetric determination of  $p_{\rm H}$ . A. HAHN and A. KRETSCHMANN (Z. Biol., 1936, 97, 585—589).— The  $p_{\rm H}$  of a solution can be calc. from the dissociation const. of an added indicator and from a colorimetric measurement of the extent of dissociation of the indicator. The indicator must be colourless in its undissociated form. The average deviation from the  $p_{\rm H}$  vals. measured electrometrically is 0.05. The method can be modified for urine  $p_{\rm H}$  determinations. E. A. H. R.

Applicability of the antimony electrode to the determination of  $p_{\rm H}$ . H. YOS HIMURA (Japan. J. Med. Sci., 1936, III, 4, 131—141).—The potential of a Sb electrode is higher in McIlvaine's buffer than in a  $PO_4^{\prime\prime\prime}$  buffer of the same  $p_{\rm H}$ . In acid solutions of the former, the time of equilibration is longer and reproducibility is lessened, probably on account of the formation of a sol. complex of Sb with eitrate. The state of deposition of Sb affects the relation between potential and  $p_{\rm H}$ , and except for plated electrodes in  $PO_4^{\prime\prime\prime}$  buffer, where reproducibility is good, the Sb electrode is not suitable for  $p_{\rm H}$  determinations, and cannot be used for biological purposes.

E. A. H. R. Systematic analysis of anions. T. P. CHAO (J. Chinese Chem. Soc., 1936, 4, 443—456).—Twenty-six anions are divided into five groups. Group I: anions pptd. by  $Ca(NO_3)_2$  (I), viz.,  $CO_3''$ ,  $C_2O_4''$ , F', SiO\_3'',  $PO_4'''$ ,  $ASO_2'$  (if in large amount),  $ASO_4''$ ,  $SO_3''$ (partly), and tartrate (if in large amount). Group II: not pptd. by (I) but pptd. by  $Ba(NO_3)_2$  (II), viz.,  $SO_4''$ ,  $SO_3''$ , and  $CrO_4''$ . Group III: not pptd. by (I) or (II) but pptd. by  $Ni(NO_2)_2$  (III), viz., S'', CN',  $Fe(CN)_6'''$ ,  $Fe(CN)_6''''$ , and  $AsO_2'$ . Group IV: not pptd. by (I), (II), or (III) but pptd. by  $AgNO_3$ (IV), viz.,  $S_2O_3''$ , CNS', I', Br', Cl', and  $BO_2'$  (not too trustworthy on account of hydrolysis of  $AgBO_2$ ). Group V: not pptd. by (I), (II), (III), (III), or (IV), viz.,  $ClO_3'$ , OCl', OAc',  $NO_2'$ , and  $BO_2'$ . Tartrate,  $NO_3'$ , and  $CO_3''$  are preferably identified in the original sample. Details are given for separating and identifying the anions in each group. C. R. H.

Properties of the silver electrode and the titration of the total and active chlorine ion in organisms. J. L. TREMBLAY (Natural. Canad., 1936, 63, 269-352).-The potentiometric determination of Cl' by means of a Ag electrode has been investigated. In presence of Br' and I' separate determinations of the ions are possible only if [Cl'], [Br'], and [I'] are of the same order of magnitude. The conditions for stability of different Ag ions for varying degrees of salinity and vals. of  $p_{\rm H}$  have been found, the stable forms indicated being (Ag2), corresponding with Ag<sub>4</sub>O, below  $p_{\pi} 2$ ; Ag at  $p_{\pi} 2-6$ ; Ag<sup>\*</sup> at  $p_{\pi}$  6—10 or 11; and a new ion, corresponding with Ag<sub>4</sub>O<sub>3</sub> or Ag<sub>4</sub>O<sub>5</sub>, above  $p_{\pi}$  11. The theory of the Ag-AgCl electrode is discussed. The e.m.f. is not greatly affected by changes in  $p_{\rm H}$  except for high or low vals. of  $p_{\rm H}$  combined with low [Cl']. The temp. coeff. is 0.42 mv. per 1° between 10° and 40°. A technique has been developed for determining Cl' activity in circulating blood and in other biological liquids, and a series of determinations of Cl' activity in sea-waters is recorded. Data for gelatin solutions have been successfully applied to the confirmation of Donnan's equilibrium theory. C. R. H.

Inaccuracies in micro-iodometry. V. A. PIAN-KOV (J. Gen. Chem. Russ., 1936, 6, 1365–1367).—The amount of I liberated from aq. KI by  $O_2$  varies with the [KI], and is greater in acid than in neutral solutions. Determination of small amounts of oxidising substances (Br,  $K_2Cr_2O_7$ ) should be performed in presence of low [KI] and in an atm. of  $CO_2$ . R. T.

Potentiometric iodide-silver titration at extreme dilutions. I. M. KOLTHOFF and J. J. LINGANE (J. Amer. Chem. Soc., 1936, 58, 2457— 2459).—The procedure is suitable for the determination of as little as 0.05 p.p.m. of Ag' with an error of 3%, using a 500-c.c. sample. Large amounts of Ba(NO<sub>3</sub>)<sub>2</sub> are without influence, but high [SO<sub>4</sub>"] introduces a considerable positive error. E. S. H.

Effect of fluorides on spectral absorption of some iron compounds. Colorimetric determination of fluorine. W. WEYL (Oesterr. Chem.-Ztg., 1936, 39, 187).—The strongly coloured compounds of  $Fe^{III}$  with CNS', thiosalicylic acid, etc. are decolorised by F', owing to the formation of  $[FeF_6]''$ . The reaction is proposed for the determination of small amounts of F. J. S. A.

Spectrographic detection of fluorine. W. PAUL (Angew. Chem., 1936, 49, 901—902).—The sample is heated with  $SiO_2 + H_2SO_4$ , forming  $SiF_4$ , which is distilled over and hydrolysed in a few drops of KOH, contained in a microbeaker, the prep. of which from a PbO-B<sub>2</sub>O<sub>3</sub> glass free from  $SiO_2$  is described. The beaker is melted down in a Pt crucible to a uniform glass, which is coated on Cu electrodes and arced. The presence and approx. amount of F are determined from the occurrence and intensity of Si lines in the spectrum. The limit of detection is <0.1 mg.

J. S. A.

Catalytic determination of oxygen in gas mixtures. O. V. NEKRASOVA and M. S. PLATONOV (J. Appl. Chem. Russ., 1936, 9, 1529—1534).—A known vol. of gas, containing  $O_2$ ,  $CO_2$ ,  $CO_3$ , and excess of  $H_2$ , is passed over fireclay impregnated with Pd (2%), at 150°, and the O<sub>2</sub> content is derived from the vol. change. Catalysts of a higher Pd content, or containing Pt, also catalyse oxidation of CO, leading to fictitious low results. R. T.

Micro-determination of sulphides. A. J. C. HALL (Soc. Chem. Ind. Victoria, 1936, 36, 1113–1117).—Feigl's use of Raschig's reaction of NaN<sub>3</sub> with I (A., 1934, 790; 1935, 711) is described. J. S. A.

Stability of potassium thiocyanate solutions. F. H. CAMPBELL (Soc. Chem. Ind. Victoria, 1936, 36, 1106—1107).—Contrary to published statements, 0.1N-KCNS does not change in titre on keeping, and addition of  $C_5H_{11}$ ·OH has no beneficial effect.

J. S. A.

Co-precipitation of various ions in precipitation of sulphate as barium sulphate. Z. KARAOGLANOV (Z. physikal. Chem., 1936, 178, 143-156).—The pptn. of  $BaSO_4$  from a mixture of  $H_2SO_4$ and a Ba salt in presence of various ions has been examined. The effect of a foreign cation on the wt. of the ppt. is the greater the smaller is the solubility of its sulphate, and the effect of an anion is the greater the smaller is the solubility of its Ba salt. This result may be explained by supposing that concurrently with the pptn. of BaSO4 there occur secondary pptns. in which foreign ions participate, e.g.,  $2\text{KSO}_4' + \text{Ba}'' = \text{Ba}(\text{KSO}_4)_2$ , the solubility of such a secondary product being  $\infty$  the solubility of the electrolyte from which it is formed (cf. A. 1026, 1020). which it is formed (cf. A., 1936, 1220). The observed effects cannot be explained by adsorption, and it seems that the capacity of  $BaSO_4$  to co-ppt. other substances is independent of the sign of the charge on its surface. R. C.

Reduction and volumetric determination of the selenic ion by hydrochloric acid. R. DOLLQUE (Ann. Chim. Analyt., 1936, [iii], **18**, 313–315).—The material is heated with HCl (40 vol.-%), and Cl<sub>2</sub> liberated is carried in a stream of  $CO_2$  into KI. The I liberated is titrated with  $Na_2S_2O_3$ . The accuracy of the method is highly dependent on empirical factors. J. S. A.

Detection and determination of phosphates in presence of salts of arsenic and other acids. I. M. KORENMAN (J. Appl. Chem. Russ., 1936, 9, 1507— 1509).—2 ml. of 2N·H<sub>2</sub>SO<sub>4</sub> and 0·2 ml. each of 6% molybdic acid and 3% strychnine nitrate are added to 3 ml. of solution, when turbidity appears in presence of  $\leq 10^{-6}$  g. of PO<sub>4</sub><sup>'''</sup>. AsO<sub>4</sub><sup>'''</sup>, SiO<sub>3</sub><sup>''</sup>, NO<sub>3</sub><sup>'</sup>, SO<sub>4</sub><sup>''</sup>, Cl', Ca<sup>''</sup>, and NH<sub>4</sub><sup>'</sup> do not interfere, except when present in very great excess. PO<sub>4</sub><sup>'''</sup> can be determined nephelometrically, using the above reaction, with a mean error of 8% for amounts of 4—18  $\times 10^{-6}$  g. R. T.

Sensitive reaction for boric acid. F. P. ZORKIN (J. Appl. Chem. Russ., 1936, 9, 1505—1506).—A drop of the feebly alkaline solution is evaporated to dryness in a crucible, and a drop of 0.05% carmine in conc.  $H_2SO_4$  is added; the colour changes from red to blue in presence of  $<10^{-7}$  g. of B. R. T.

Mineral determination by microchemical methods. L. W. STAPLES (Amer. Min., 1936, 21, 613-634).—A summary of tests, involving the recognition of eryst. ppts. under the microscope, which have given the most satisfactory results in mineral determination. New tests for Fe with  $NH_4Cl$  and for Al and Mn with  $NH_4$  molybdate (cf. A., 1935, 720) are described. L. S. T.

Electrometric titration of carbonic acid and sodium hydrogen carbonate in dilute solution. H. LIANDER (IVA, 1935, 78-83; Chem. Zentr., 1936, i, 1380).— $p_{\rm ff}$  measurements in dil. aq. Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> are compared with the titration curves for CO<sub>2</sub> and NaHCO<sub>3</sub> solutions. An expression is given for the variation with temp. of the equilibrium const. J. S. A.

Qualitative analysis without use of hydrogen sulphide or sulphides. H. EICHLER (Oesterr. Chem.-Ztg., 1936, 39, 185—187).—Sn and Sb are removed as oxides by evaporation with  $HNO_3$ , and Hg, Ag, and Pb are pptd. with HCl.  $NH_4Cl$  and aq.  $NH_3$  are added, pptg. Fe, Mn, Bi, and Hg, together with Al and Cr, which are separated by dissolving the ppt. in acid, and repptg. with NaOH + Br. The filtrate from the  $NH_3$  pptn. is acidified and treated with NaOH, pptg. Ni, Co, Cu, and Cd, and leaving As, Zn, Ba, Sr, Ca, Mg, and Li in solution. In each of the groups so obtained, the metals may be identified by means of sp. tests. J. S. A.

Potentiometric determination of potassium. I. TANANAEV and E. DJAPARIDZE (Z. anal. Chem., 1936, 107, 347—352).—Bivalent metals are titrated potentiometrically with  $\text{Li}_4\text{Fe}(\text{CN})_6$ , alone and in presence of K, when the equivalence point is displaced owing to the formation of  $\text{K}_2\text{M}[\text{Fe}(\text{CN})_6]$ . Using Mn (less suitably Cd or Ni), the [K] may be determined from the magnitude of the displacement, by reference to empirical curves. J. S. A.

Application of picric acid in qualitative microanalysis. A. F. ORLENKO and N. G. FESENKO (J. Appl. Chem. Russ., 1936, 9, 2116—2118).—Characteristic crystals are obtained with picric acid in presence of  $\leq$  the following min. amounts of the cations: K 0.18, Na<sup>\*</sup> 1.1, NH<sub>4</sub><sup>\*</sup> 0.3, Mg<sup>\*\*</sup> and Ba<sup>\*\*</sup> 2.3, Sr<sup>\*\*</sup> 6.1, Ni<sup>\*\*</sup> 7.2, Pb<sup>\*\*</sup> 4.9, Zn<sup>\*\*</sup> 2.1, Hg<sup>\*\*</sup> 3, Ag<sup>\*\*</sup> 2 × 10<sup>-6</sup> g. R. T.

Application of organic redox systems to quantitative analysis. IV. Mechanism of reaction of silver salts with benzidine, and a sensitive new reaction for silver. L. M. KULBERG and S. B. SERE-BRIANI (J. Gen. Chem. Russ., 1936, 6, 1335—1340).— The oxidation of benzidine (I) to benzidine-blue (II) in presence of Ag<sup>\*</sup> proceeds as follows: Ag<sup>\*</sup> + (I) + NO<sub>3</sub>'  $\Longrightarrow$  [Ag(NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·)<sub>2</sub>]NO<sub>3</sub>; 2Ag<sup>\*</sup> + O<sub>2</sub>  $\rightarrow$ Ag<sub>2</sub>O<sub>2</sub>; Ag<sub>2</sub>O<sub>2</sub> + 2HNO<sub>3</sub> + 2H<sup>\*</sup> + 2(I)  $\rightarrow$  2Ag + 2H<sub>2</sub>O + (II),2HNO<sub>3</sub>. An analogous reaction with o-tolidine (III) serves for detection of Ag, as follows: 2—3 drops of HNO<sub>3</sub> are added to 0·1—0·5 ml. of the solution, which is heated to complete elimination of oxides of N, the residue is taken up in H<sub>2</sub>O, and a drop of the extract is placed on a drop of 1% (III) in EtOH, when a blue spot appears in presence of  $<3 \times 10^{-8}$  g. of Ag. R. T.

Detection and determination of zinc by means of diphenylthiocarbazone. H. FISCHER and G. LEOPOLDI (Z. anal. Chem., 1936, 107, 241-269).--- Ag, Cu, Hg, Au, Bi, Cd, and Pb interfere with the detection of Zn by means of diphenylthiocarbazone (I), but their reaction may be suppressed by adding an excess of  $Na_2S_2O_3$  before extracting with a CCl<sub>4</sub> solution of (I). Interference due to Co, Ni, and Pd may be eliminated by adding KCN; Sn<sup>II</sup> may be oxidised to Sn<sup>IV</sup>. The colour produced by Zn with (I) is distinguished from that due to Co, Ni, and Pd in that it is decolorised by addition of  $(NH_4)_2S$ . By addition of  $Na_2S_2O_3$  or KCN where necessary, traces of Zn (0.01-0.001%) may be determined in presence of all other elements, using the colorimetric, mixed colour, direct titration, or indirect titration methods employed in other (I) titrations. J. S. A.

Application of organic redox systems to quantitative analysis. III. Colorimetric determination of traces of copper. L. KULBERG and R. LIRTZMAN (J. Gen. Chem. Russ., 1936, 6, 1251—1255). —The substance is dissolved in acetate buffer at  $p_{\rm H}$ 4, 3 ml. of 0.5% gelatin and 0.3 ml. of 1% o-tolidine are added to 10—25 ml. of the solution, which is then shaken, and 0.5 ml. of 30% NH<sub>4</sub>CNS is added. The blue coloration obtained is compared with that given by standard CuSO<sub>4</sub>. The method serves for the determination of 0.005—0.02 mg. of Cu (error 1—10%) R. T.

Use of copper electrodes in electro-analysis. A. B. SCHACHKELDIAN and F. K. FISCHER (Abh. Staatsuniv. Saratov, 1936, [ii], Chem., 1, 83-91).— Pt cathodes may be replaced by Cu cathodes in the determination of Cu, Zn, Cd, and Ni. J. J. B.

Determination of small amounts of copper, tin, and cadmium in presence of large amounts of zinc, by electrolysis with a constant cathode potential. N. S. KRIVOLUTZKAJA (J. Appl. Chem. Russ., 1936, 9, 1520-1524).-The solution of ZnCl<sub>2</sub> is electrolysed at 40°, maintaining the cathode potential at 0.41 volt, to complete elimination of Cu from solution, when the cathode is washed, dried, and weighed. Electrolysis of the solution is continued at 0.71 volt (35 min.), the cathode is transferred to a solution of HCl and NH2OH, and the current is passed during a further 30 min., at 0.78 volt. The cathode is then washed without interrupting the current, by siphoning. Cd is determined similarly in the residual solution, maintaining the cathode potential at 0.90 R. T. volt.

"Flouring " of mercury as end-point in potassium permanganate titration of impurities in mercury. H. P. MATTHEWS (Soc. Chem. Ind. Victoria, 1936, 36, 1104—1106).—Complete removal of dissolved metals from Hg corresponds with the attainment of max. surface tension, and therefore with the inception of the "flouring" effect. Hg, under 10% H<sub>2</sub>SO<sub>4</sub>, is shaken with successive amounts of standard KMnO<sub>4</sub> until flouring occurs. J. S. A.

Gravimetric determination of aluminium. G. FLUMIANI and M. FERRICH (Rep. III Congr. Slav. Pharm., 1934, 160—169).—In order to avoid the high Al val. obtained from solutions containing Ba, Ca, Sr, and Mg, the Al solution was run slowly into a solution of  $\rm NH_4NO_3$  + slight excess of freshly distilled  $\rm NH_3$  at  $\rm 80-90^\circ$ , maintained at 60° for 20 min., the ppt. being collected and washed with 400-400 c.c. of 0.2-0.3% NH<sub>4</sub>NO<sub>3</sub> to remove the above metals. The filter and ppt. were dried, burnt together, and ignited at 1100-1200° for 10 min. Results are given for known solutions of pure AlCl<sub>3</sub> + Ba, Ca, and Mg chlorides. F. R.

Fractional reaction for Mn<sup>••</sup>. N. A. TANANAEV (J. Appl. Chem. Russ., 1936, 9, 1495—1498, and Z. anal. Chem., 1936, 107, 343—347).—NaOH is added to the solution until it becomes turbid, when aq. KCN is added, in amount sufficient to dissolve the ppt. initially formed (Fe, Ni, Co, Zn, Mn, Hg, Ag, Cd, and Cu cyanides), leaving Al, Pb, and Sb hydroxides undissolved. Na<sub>2</sub>O<sub>2</sub> is then added, and the solution is boiled, when Al(OH)<sub>3</sub> and Pb(OH)<sub>2</sub> dissolve, and a ppt. of MnO<sub>2</sub> forms in presence of  $\leq 0.1$  mg. of Mn. B. T.

Colorimetry of iron and its application to the analysis of phosphorites and apatites. A. B. SCHACHKELDIAN (Abh. Staatsuniv. Saratov, 1936, [ii], Chem., 1, 65—71).—If the solution contains, in addition to Fe,  $P_2O_5$  or F which affect the colour of Fe(SCN)<sub>3</sub>, more Fe(SCN)<sub>3</sub> is added to it, and the [Fe<sup>\*\*\*</sup>] of the original solution is calc. according to Beer's law. The method was used in the analysis of phosphorites and apatites. J. J. B.

Stability of complex compounds of iron and method of detecting iron in a complex ion. A. B. SCHACHKELDIAN (Abh. Staatsuniv. Saratov, 1936, [ii], Chem., 1, 49–63).—K<sub>4</sub>Fe(CN)<sub>6</sub>, CoSO<sub>4</sub>, and traces of Fe<sup>\*\*</sup> afford a bluish-green ppt. of FeCo[Fe(CN)<sub>6</sub>] (I) which may be used for detecting Fe<sup>\*\*</sup>. Dissociation of [Fe(CN)<sub>6</sub>]<sup>\*\*\*</sup> and the presence of Fe<sup>\*\*</sup> in its solutions were proved by formation of (I) and by change of the colour and of the electrical conductivity of the solutions when boiled. J. J. B.

Determination of potassium ferrocyanide in presence of other salts. F. K. FISHER (Abh. Staatsuniv. Saratov, 1936, [ii], Chem., 1, 93—105).— The applicability of various methods is discussed. When large amounts of other salts are present,  $[Fe(CN)_6]'''$  is pptd. by CuSO<sub>4</sub>, Cu<sub>2</sub>[Fe(CN)<sub>6</sub>] is dissolved in KOH, and K<sub>4</sub>Fe(CN)<sub>6</sub> thus regenerated is titrated with KMnO<sub>4</sub>. J. J. B.

Analysis of group II and III cations in presence of  $PO_4^{\prime\prime\prime}$ . M. SCHTSCHIGOL and N. DUBINSKI (J. Appl. Chem. Russ., 1936, 9, 1510— 1513).—Na<sub>2</sub>CO<sub>3</sub> and aq. NH<sub>3</sub> are added, when Fe<sup>III</sup>, Al, Cr<sup>III</sup>, Mn<sup>II</sup>, Ca, Ba, Sr, and Mg carbonates, phosphates, and hydroxides are pptd., whilst Zn, Co, and Ni remain in solution as ammines. The ppt. is treated with AcOH to dissolve salts of Ca, Ba, and Sr. The three fractions thus obtained are further analysed by the ordinary procedures. R. T.

Detection of cobalt with furfuraldehyde in presence of thiocyanates. I. P. RIASANOV (Abh. Staatsuniv. Saratov, 1936, [ii], Chem., 1, 113—116).—  $Co(NO_3)_2$  and furfuraldehyde in a saturated solution of NH<sub>4</sub>CNS give a green colour perceptible in 16,000 parts of H<sub>2</sub>O. Fe if present is pptd. by Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>. Bi must not be present in large quantities.

J. J. B.

Determination of very small quantities of uranium, and uranium content of sea-water. F. HERNEGGER and B. KARLIK (Sitzungsber. Akad. Wiss. Wien, 1935, [iia], 144, 217—225; Chem. Zentr., 1936, i, 1666).—10<sup>-10</sup> g. of U may be detected by means of its fluorescence in NaF. The quant. application of the method is described. Sea-H<sub>2</sub>O contains 0.36—2.3 × 10<sup>-6</sup> per g. of U per litre, according to its origin.

J. S. A.

Determination of polonium content from salts in thick layers. M. HOFFER (Sitzungsber. Akad. Wiss. Wien, 1935, [iia], 144, 131—134; Chem. Zentr., 1936, i, 1566).—The Po content of active Pb salts has been determined. The half-val. period of Po is found to be 138 days. J. S. A.

Analytical chemistry of tantalum, niobium, and their mineral associates. XXXIII. General summary and results. W. R. SCHOELLER (Analyst, 1936, 61, 806—811).—The main results of the 32 papers published in 1921—1936 are summarised and discussed; a classified index to these papers is provided, and suggestions are made for the analysis of rare-earth minerals by the tartaric acid method.

J. G. Stirring mechanism for precision thermostats. S. C. COLLINS (Rev. Sci. Instr., 1936, [ii], 7, 502).—A power-driven impeller maintains centrifugal motion and circulation of the liquid and leaves a max. of space for experimental apparatus.

N. M. B.

Humidity control device for ovens. C. T. WEBSTER (J. Sci. Instr., 1936, 13, 412-413).—Two bulbs, connected by a capillary tube containing Hg, operate on the principle of the wet and dry bulb thermometer, the Hg completing by its movement the heating circuit of a boiler. The difference of pressure between the two bulbs can be maintained at any desired val. C. W. G.

Polarisation prisms. V. A. OSIPOV-KING (Compt. rend. Acad. Sci. U.R.S.S., 1936, 4, 53-56).— The two calcite prisms of a double-image prism are joined by optical contact with a thin, plane-parallel, central plate of optical glass or fused quartz.

0. D. S.

Electron mirrors. G. HOTTENROTH (Z. Physik, 1936, 103, 460—462).—An apparatus employing a specularly reflecting potential field is described.

L. G. G. Colorimetry during the period of development of colour. G. BERGAMI, E. BOERI, and P. BAER (Atti R. Accad. Lincei, 1936, [vi], 23, 610-616).—The colorimetry of solutions which obey Beer's law can be carried out during the period in which the colour is being developed if the reaction which is producing the colour is unimol. With reactions of higher order it is necessary to wait until the colour has been stabilised. O. J. W.

Spectrograph with strong illumination. H. NAGAOKA (Proc. Imp. Acad. Tokyo, 1936, 12, 218— 220).—The intensity of the light to be analysed by an all-quartz instrument is increased several fold by using a collimating system of two lenses, one of which is of short focal length and situated near the slit.

J. G. A. G.

Universal X-ray photogoniometer. R. B. HULL and V. HICKS (Rev. Sci. Instr., 1936, [ii], 7, 464-467).—A compact apparatus for making Laue, rotation, Schiebold–Sauter, and back-reflexion photograms is described. N. M. B.

[Photo-electric] sedimentometer. J. MILBAUER (Sborn. Masary. Akad. Práce, 1935, 9, No. 7, 1—35; Chem. Zentr., 1936, i, 1267).—The transparency is measured with a photo-electric cell. Data for the effect of various factors on the sedimentation of  $Al(OH)_3$  are recorded. H. J. E.

High-speed motion-picture camera in study of surface tension. E. A. HAUSER, H. E. EDGERTON, B. M. HOLT, and J. T. Cox, jun. (J. Physical Chem., 1936, 40, 973-988).-Drops of liquid falling from a circular orifice and films adhering to a circular ring have been photographed at the rate of 1200 and 600 pictures per sec. respectively. The experimental arrangement is described. The photographs show that a drop of liquid in the initial stages of falling remains attached to the main body by a thin neck, the length of which at the time of breaking increases, in the case of pure liquids, as the surface tension decreases. The presence in  $H_2O$  of capillary-active substances, however, diminishes the stem length. H<sub>2</sub>O and glycerol produce stems which on breaking contract to a single secondary drop, whilst the stems of PhNO<sub>2</sub> and  $C_6H_6$  undergo segmentation and finally yield three and from one to five secondary drops respectively. From the frequency of oscillation of the secondary drops satisfactory vals. for the surface tension can be calc. The complexity of the phenomena underlying the drop-wt. and ring methods of determining surface tension suggests that neither method is ideal from the point of view of the accurate measurement of surface tension. F. L. U.

Determination of mean dispersity by means of the photo-cell. E. HOFFMANN (Kolloid-Z., 1936, 77, 286—288).—Technique is described. E. S. H.

Application of electron lamps to determination of  $p_{\rm ff}$  by means of a glass electrode. V. BILININ (J. Appl. Chem. Russ., 1936, 9, 1560—1562).

R. T.

Lamp voltmeter. N. S. DROZDOV and M. K. GOLDABENKOV (J. Appl. Chem. Russ., 1936, 9, 1550-1554). R. T.

Increased  $\gamma$ -ray sensitivity of tube counters and the measurement of the thorium content of ordinary materials. R. D. Evans and R. A. MUGELE (Rev. Sci. Instr., 1936, [ii], 7, 441-449).--The theory and factors affecting sensitivity of tube counters are examined. Sensitivity can be increased by using screen-wire or grooved tube cathodes of greater effective area than the smooth, by the use of cathodes of high at. no., and by selecting the optimum operating voltage and pressure of the filling gas. In this way feeble  $\gamma$ -radiation from granitic rocks may be measured. N. M. B.

Discrimination between partial and total coincidence counts with Geiger-Müller counters. J. C. MOUZON (Rev. Sci. Instr., 1936, [ii], 7, 467-470).—A simple discriminating amplifier, using single pentodes but eliminating the negative bias on the control grids of the amplifier tubes, is described. N. M. B.

Wilson cloud machines for portable use. G. L. LOCHER (Rev. Sci. Instr., 1936, [ii], 7, 471-478).— Two new forms of instrument suitable for portable uses, and with arrangement for optional control by Geiger-Müller counters, are described. N. M. B.

Thyratron-controlled ionisation gauge. J. B. HOAG and N. M. SMITH, jun. (Rev. Sci. Instr., 1936, [ii], 7, 497–499).—A thyratron maintains a const. ionising electron current with line voltage fluctuations of  $\pm 6\%$ . The circuit operates by a.c., and provision is made for outgassing the metal parts of the gauge. N. M. B.

Apparatus for investigating absorption of electric waves on passage through matter. G. PETRUCCI (Nuovo Cim., 1935, [ii], **12**, 361-367; Chem. Zentr., 1936, i, 1461).—Apparatus is described. J. S. A.

Heavy-current discharge tube. A. HUNTER and R. W. B. PEARSE (J. Sci. Instr., 1936, **13**, 403—407).— A  $H_2O$ -cooled cold-cathode 3-kw, discharge tube is described. It is suitable for use with many gases, particularly  $H_2$ , and has the advantages of simplicity robustness, portability, and constancy of intensity. C. W. G.

Technique of electro-osmotic measurements. A. VAŠIČEK (Kolloid-Z., 1936, 77, 305—310).— Apparatus and technique are described. E. S. H.

Electromagnetic piston pump. W. BRENSCH-EDE (Z. physikal. Chem., 1936, 178, 74-75).—A double-acting pump, an improved form of that devised by Livingstone (A., 1929, 903), is described. It is capable of working against pressures up to >100 mm. R. C.

Photo-electric method for recording fast chemical reactions and its application to the study of catalyst-substrate compounds. K. G. STERN and D. DUBOIS (J. Biol. Chem., 1936, 116, 575—586).—A beam of light, of  $\lambda$  selected by a monochromator, traverses the reaction vessel, and falls on a photo-electric cell; the current from this, after amplification, actuates a string galvanometer, the deflexions of which are recorded on sensitised paper film. Rapid and transitory changes in light absorption, resulting from injection of reagent solution into the reaction vessel, are thus recorded. Methæmoglobin and EtO<sub>2</sub>H form an unstable intermediate compound; the formation is half complete in 0 06-0.26 sec., under various conditions. Some preliminary data relating to the liver catalase-EtO<sub>2</sub>H reaction are given. F. A. A.

Vertical micro-electrophoresis cell with nonpolarisable electrodes. H. A. ABRAMSON, L. S. MOYER, and A. VOET (J. Amer. Chem. Soc., 1936, 58, 2362—2364).—Apparatus and technique are described and results for different suspensions reported. E. S. H.

Potentiometry using several electrode pairs connected in series. L. WOLF (Z. anal. Chem., 1936, 107, 338-342).—An assembly is described of four Cu-Ag electrode pairs in the form of a stirrer, so arranged that on removal from the liquid (e.g., during potentiometric titrations), they dip in small, mutually insulated portions of liquid, thereby giving a multiplied e.m.f. J. S. A.

Illuminated matt screen for titration. S. M. STREPKOV (J. Appl. Chem. Russ., 1936, 9, 1427).— Apparatus is described. R. T.

Design and manipulation of the Lunge nitrometer. R. E. SUMMERS and W. H. SUMMERS (Soc. Chem. Ind. Victoria, 1936, 36, 1108–1113).—A modified design is described. J. S. A.

Automatic registration of amount and velocity of sorption. K. V. TSCHMUTOV and V. S. FROLOV (J. Appl. Chem. Russ., 1936, 9, 1555–1559). R. T.

**Pyknometer.** F. G. HOFFMANN (Chem.-Ztg., 1936, 60, 1037).—A 10-c.c. beaker-shaped vessel has an accurately fitting flat cover through the centre of which passes a thermometer. A smaller, similar type (1 c.c.) without thermometer is also described. E. H. S.

Capillary analysis at constant temperature and humidity. C. A. ROJAHN (Arch. Pharm., 1936, 274, 545—547).—An apparatus is described. R. S. C.

Two practical laboratory hints. K LUBER. (Chem-Ztg., 1936, 60, 1006).—(1) For extraction with liquids of low b.p., a Soxhlet extractor, made from a test-tube and glass tubing, is placed inside an ordinary adaptor, connected to a flask and reflux condenser. (2) Small quantities of liquid are cooled in a test-tube covered with cotton-wool, on to which  $Et_2O$  is dropped. E. A. F.

Concrete bases for retort stands. O. H. F. PIERIS (J. Sci. Instr., 1936, 13, 417–418).—Satisfactory bases of any desired shape can be cast.

C. W. G.

Stop-cocks for mechanical operation. C. F. WINCHESTER (Science, 1936, 84, 443-444).

L. S. T.

Modification of Rast's micro-method for mol. wt. determination. Y. P. Liu and T. P. CHOU (J. Chinese Chem. Soc., 1936, 4, 422–428).—Greater accuracy is claimed if a glass stem 2.5 cm. in length and 2 mm. in diameter, at the end of which is a bulb 8 mm. in diameter, is substituted for the usual m.p. tube. C. R. H.

Stopcock substitute. W. C. SCHUMB and H. I. CRANE (J. Amer. Chem. Soc., 1936, 58, 2649).—The tube can be sealed by Hg supported by a fritted glass plate. E. S. H.

Spinning-top ultracentrifuge and the sedimentation of small molecules. J. W. WILLIAMS and C. C. WATSON (J. Amer. Chem. Soc., 1936, 58, 2650—2651).—A criticism of published work (cf. A., 1935, 724). E. S. H.

[Spinning-top ultracentrifuge and the sedimentation of small molecules.] J. W. MoBAIN (J. Amer. Chem. Soc., 1936, 58, 2652).—A reply to criticism (cf. preceding abstract). E. S. H.

Centrifuging in rotating hollow cylinders. E. A. HAUSER and C. E. REED (Nature, 1936, 138, 975; cf. A., 1936, 1355).—The method outlined enables data for the calculation of the particle size distribution curve in a polydisperse system or a particle size fractionation to be obtained. L. S. T.

Micro-viscosimeter for non-Newtonian liquids. G. W. S. BLAIR (Kolloid-Z., 1937, 78, 19-21).-A capillary instrument of 0.5 c.c. capacity is described. F. L. U.

Polygonal presentation of polyphase phenomena. A. H. HUTCHINSON (Trans. Roy. Soc. Canada, 1936, [iii], 30, V, 19—26).—Data which in-Geochemistry.

volve three or more variable factors, conditions, or characters can be represented graphically by the use of polygons. The principles underlying the construction of such graphs are described, and examples of polygonal graphs are given. J. N. A.

Demonstration of phosphorescence. H. WAR-REN (Nature, 1936, 138, 974).—A lecture experiment. L. S. T.

Lecture experiment on electro-capillarity. A. THIEL (Z. Elektrochem., 1936, 42, 879-880).

Radioactivity of mountain air. H. GARRIGUE (Ann. Physique, 1936, [xi], 6, 751 825).-A detailed account of investigations previously reported (cf. A., 1935, 468). The snow-covered mountain-top air may contain a max. of 10-9 curie of Rn per litre, and the liberation to the atm. may reach, on the Pic-du-Midi, the val. of the Rn produced by the snow-capped N. M. B. summit of the mountain (100 g. Ra).

[Radioactive contents of air at Badgastein.] W. KOSMATH and O. GERKE (Sitzungsber. Akad. Wiss. Wien, 1935, IIa, 144, 339-355; Chem. Zentr., 1936, i, 1200).—Data for the Rn content of the air in various localities are recorded. H. J. E.

Determination of the sodium chloride content of air. H. P. GODARD and W. F. SEYER (Trans. Roy. Soc. Canada, 1936, [iii], 30, III, 85-88).—The NaCl content of the air in the neighbourhood of Vancouver has been determined under varying meteorological conditions. 0. D. S.

Upper air. J. KNIGHT (Proc. Roy. Phil. Soc. Glasgow, 1936, 62, 30-46).-An account of the methods and results of observation recording in the upper air and a summary of contemporary knowledge. N. M. B.

Field of thermal water. B. N. FORSCH (Compt. rend. Acad, Sci. U.R.S.S., 1936, 4, 185-186).-On the assumption that thermal H<sub>2</sub>O is saturated with CaCO<sub>3</sub> at a certain stage in its metamorphosis, the expression  $ah = 2 \times 10^4 (C_{\rm R}L/N_2K_2) \approx {\rm const.}$ , is derived (a = alkalinity,  $h = {\rm hardness}$  of the H<sub>2</sub>O;  $L = {\rm solubility}$  product and  $N_2 = {\rm normality}$  of CaCO<sub>3</sub>;  $K_2 = {\rm second}$  dissociation const. of H<sub>2</sub>CO<sub>3</sub>). This yields a family of hyperbolæ, in agreement with the data from 25 springs in the Baikal region, in which the limits for ah are 500 and 50 (mean 160). R. C. M.

Granitisation in the Cross Lake region, Manitoba. H. C. HORWOOD (Trans. Roy. Soc. Canada, 1936, [iii], 30, IV, 99-117).-At contact with intruded granite, andesite shows a gradual transition into granodiorite-gneiss and arkose into granite-gneiss. In the andesite there is a gain of quartz, K-felspar, and biotite, and loss of hornblende; in the arkose K-felspar replaces quartz. The chemical compositions of the rocks (cale. from micrometric analysis of the minerals in thin sections) show in the andesite gain of  $SiO_2$  and  $K_2O_3$ , and loss of  $Fe_2O_3$ , FeO, MgO; and in the arkose gain of  $Al_2O_3$  and  $K_2O$  with loss of  $SiO_2$ . These changes were effected by dil. alkaline solutions containing SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and K<sub>2</sub>O emanating from [the granite at about 600°. L. J. S.

Sudbury nickel irruptive. III. Environ-ment. W. H. COLLINS (Trans. Roy. Soc. Canada, 1936, [iii], 30, IV, 29—53; cf. A., 1935, 602).—A discussion of the relative ages of the "younger granites" (in which some of the ore occurs) and the norite. Further chemical analyses are given of rocks, and ages are computed from the Ra-He ratio. L. J. S.

Knebelite from Bluebell mine, Kootenay Lake, B.C. H. C. GUNNING (Trans. Roy. Soc. Canada, 1936, [iii], 30, IV, 19-22).-Dark green to black patches of knebelite occur in Fe Mn carbonate with pyrrhotine, galena, etc., in limestone intruded by granite. Analysis gave SiO<sub>2</sub> 28.93, Al<sub>2</sub>O<sub>3</sub> nil, Fe<sub>2</sub>O<sub>3</sub> 4.06, FeO 39.15, MnO 24.82, MgO 0.05, CaO 0.68,  $H_2O+ 2.01, H_2O- 0.10 = 99.80\%$ , corresponding with (Fe,Mn)<sub>2</sub>SiO<sub>4</sub>. L. J. S.

High-temperature research on silicates and Bowen (Amer. J. Sci., 1937, [v], 33, 1-21).-A study of the several systems involving SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, study of the several systems involving SiO<sub>2</sub>,  $AI_2O_3$ , FeO, CaO, MgO, Na<sub>2</sub>O, and K<sub>2</sub>O shows that with frac-tional crystallisation the residue consists of alkali Al silicate, NaAlSiO<sub>4</sub>-KAlSiO<sub>4</sub>-SiO<sub>2</sub>, which is referred to as "petrogeny's 'residua' system." Plots of analyses of phonolites, trachytes, and rhyolites from the East African Rift Valley fall within this area. It is suggested that these rocks represent the residual liquids of crystallising magmas. L. J. S.

Monoclinic "hypersthene" from the Cascade lavas. J. VEBHOOGEN (Amer. J. Sci., 1937, [v], 33, 63-69).-Optical data are given for pyroxenes in andesites and dacites from the Cascade Range in Oregon and Washington. These include hypersthene, diopsidic augite, pigeonite, and a monoclinic "hypersthene." The last has the appearance and pleochroism of hypersthene, but gives oblique optical extinction and optical data different from those of clinohypersthene. The approx. chemical composition of this mineral is deduced from the analysis of the containing rock. L. J. S.

Symplectite-bearing nodules in the Ardgour marble, Argyllshire. H. I. DREVER (Geol. Mag., 1936, 73, 448–468). L. S. T.

Shearing phenomena at high pressure of possible importance for geology. P. W. BRIDG-

MAN (J. Geol., 1936, 44, 653-669; cf. A., 1936, 146).—Various phenomena of plastic flow have been studied at confining pressures up to 50,000 kg. per sq. cm. Chalcocite is changed throughout its mass to ordinary cubic Cu<sub>2</sub>S; quartz glass and calcite become more dense, the changes being probably confined to a thin surface layer.  $Bi_2O_3$  is reduced to Bi at the surface and  $SnO_2$  to SnO. Metallic Cu + S is converted into a mixture of chalcocite and cubic Cu<sub>2</sub>S. L. S. T.

Colour changes in zircon (hyacinthe) on heating. K. CHUDOBA (Deuts. Goldschmiede-Ztg., 1935, 38, 474—475; Chem. Zentr., 1936, i, 1199; cf. A., 1936, 1087).—Mongka zircons which have been discoloured by sunlight become red on heating to 110°. This colour disappears on re-exposure to sunlight. Above 110° a brown colour develops and at a higher temp. the specimen becomes colourless and cannot be coloured by subsequent treatment. H. J. E.

Spectrographic examination of Siamese zircons. T. G. KENNARD and D. H. HOWELL (Amer. Min., 1936, 21, 721—726).—Brown, blue, and colourless Siamese zircons from Annam, French Indo-China, show in inclusion-free samples no difference in chemical composition, except for traces of Mg, Na, and Ag. Small amounts of Hf, and traces of Ba and Ca, occur in all the inclusion-free samples, and small amounts or traces of Ag, Mg, or Na were found in one or more specimens. The black inclusions and red spots are markedly different in chemical composition from the inclusion-free material, being much richer in Fe. Al, Cu, and Ti were sometimes present. The blue and brown colours in the inclusion-free zircons are not pigmental. L. S. T.

Outgrowths on zircon. J. A. BUTTERFIELD (Geol. Mag., 1936, 73, 511—516).—Outgrowths in the form of small zircon pyramids growing out from the parent zircons are described. L. S. T.

Osmiridium. IV. O. E. ZVJAGINTZEV (Ann. Sect. Platine, 1936, 13, 123—127).—Native osmiridium from the N. Caucasus and other regions is described (cf. A., 1935, 440). R. T.

Radioactivity of minerals. S. GRABIANKA (Rocz. Chem., 1936, 16, 436–443).—Radioactivity data are recorded for red and black leptinites from Sabeau (France). R. T.

Lead-uranium ratio of Henvey cyrtolite. O. B. MUENCH (J. Amer. Chem. Soc., 1936, 58, 2433— 2434).—An abnormally low ratio was found.

E. S. H.

Spilitic rocks in New Zealand [Great King Island]. J. A. BARTRUM (Geol. Mag., 1936, 73, 414– 423).—Analyses are recorded. L. S. T.

Evolution of the Lower Archæan rocks in Central Sweden and their iron, manganese, and sulphide ores. N. H. MAGNUSSON (Quart. J. Geol. Soc., 1936, 92, 332—359).—The various types of ore are described, and modern views concerning their origin, metamorphism, and relationships to the enclosing rocks are summarised. L. S. T.

Peculiar hydrothermal copper-bearing veins of the N.E. Colorado plateau. R. P. FISCHER (Econ. Geol., 1936, 31, 571—599).—In the Cashin, Cliffdweller, Sunrise, Copper Rivet, and Hoosier (Salt Valley, Utah) mines the ore consists mainly of Cu sulphides, with dolomite, calcite, and barite as the gangue minerals. The deposits are probably of hydrothermal origin, with colloids playing an important rôle in the formation of the ores. Oxidation is negligible in the first two, but abundant in the last three mines. L. S. T.

Hypogene anhydrite from McIntyre mine, Porcupine District, Ontario. G. B. LANGFORD and E. G. HANCOX (Econ. Geol., 1936, 31, 600-609). L. S. T.

Occurrence of minute quantities of mercury in the Chinle shales at Lees Ferry, Arizona. C. LAUSEN (Econ. Geol., 1936, 31, 610-617).—The shales contain from 0.001 to 0.008% Hg (approx.). L. S. T.

Livingstonite. W. E. RICHMOND (Amer. Min., 1936, 21, 719—720).—Livingstonite from Huitzuco, Guerrero, Mexico, is monoclinic, prismatic with  $a:b:c \ 3.7572:1:5.3660, \beta \ 104^{\circ} \ 10';$  space-group  $C_{2A}^{\circ} - P2_1/c$ , cell-content (provisional) Hg<sub>4</sub>Sb<sub>16</sub>S<sub>28</sub>. L. S. T.

Petrologic results of a study of the minerals from the tertiary volcanic rocks of the San Juan region, Colorado. E. S. LARSEN, J. IRVING, F. A. GONYER, and E. S. LARSEN 3rd (Amer. Min., 1936, 21, 679—701).—The occurrence and conditions of formation of quartz, tridymite, and cristobalite are described. Analyses and optical properties of pyroxenes and olivine from the San Juan lavas are recorded and discussed. L. S. T.

X-Ray determination of the silica minerals in submicroscopic intergrowths. C. S. HURLBUT, jun. (Amer. Min., 1936, 21, 727-730).—A method for identifying cristobalite, tridymite, and quartz is outlined. L. S. T.

Geology of the silver deposit at Colquijirca, Peru. H. E. MCKINSTRY (Econ. Geol., 1936, 31, 618-635; cf. A., 1935, 1101).—The ore bodies resulted from the replacement of beds in a folded Tertiary (?) shale-limestone formation. Mineralising solutions entered the limestone along the bedding at a stage later than the folding, silicified and kaolinised the beds, and deposited sulphides. The solutions were high in  $SO_4''$  and were probably acid at certain stages. Comparison of analyses of the overlying gossan and sulphide ore show that oxidation processes were normal, but Ba is leached whereas Zn is retained in the gossan, which also has a ratio of Fe: Si > in the ore. Impervious strata, by preventing dissipation of the descending Ag-bearing waters, may be partly responsible for the exceptional richness of the secondary ore. The ores have been markedly enriched by supergene native Ag. The stromeyerite may also be L. S. T. supergene (cf. loc. cit.).

Diopsides from Southern California. R. MER-RIAM and J. D. LAUDERMILK (Amer. Min., 1936, 21, 715—718).—Chemical analyses and optical properties agree with vals. for artificial diopside. Spectrographic analysis shows the presence of small amounts or traces of Fe, Al, Mn, Cu, Ti, etc. L. S. T.