## BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

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

JULY, 1942.

#### I.—SUB-ATOMICS.

Absorption spectra of gases in the extreme ultra-violet, T. Takamine and Y. Tanaka (Astrophys. J., 1941, 93, 386—390).—Absorption spectra of H, He, Ne, and A are photographed with a 20-cm, grating at grazing incidence in vac. Results are discussed. E. R. R.

Blank and background effect on photographed spectral lines.—See A., 1942, I, 249.

Improved source for the Lyman continuum in the vacuum ultraviolet.—See A., 1942, I, 212.

Rydberg corrections for D terms in He I. L. Pincherle (*Physical Rev.*, 1942, [ii], **61**, 156—157).—The interaction between the normal 1snd- and the 2p2p-configurations in He I is evaluated. Its contribution to the difference between the Rydberg corrections of the o- and p-terms is very large, and the theoretical vals. of these differences are too small.

Influence of sample composition on magnesium, cadmium, and lead intensity ratios as radiated from a spark source. G. O. Langstroth and K. B. Newbound (Canad. J. Res., 1942, 20, A, 39—47).— Addition of foreign substances can cause marked variations.

First spectrum of antimony. W. F. Meggers and C. J. Humphreys (J. Res. Nat. Bur. Stand., 1942, 28, 463—478).—λλ and measured intensities are given for 466 neutral Sb lines between 1388·91 and 12466·75 A. Almost 80% of the lines are classified as combinations of 60 even energy levels arising from 5s²5p²ns, 5s²5p²nd, and 5s5p⁴ configurations and 31 odd levels from 5s²5p³n, 5s²5p²np, and possibly 5s²5p²nf. The scarcity of visible lines and the high intense ultraviolet and infra-red radiations are due to the relative vals. of various groups of levels. Several spectral series of the type 5s²5p³-5s²5p²ns. groups of leveis. Several spectral series of the type  $5s^25p^3-5s^25p^2ns$  are proposed and an abs. val. of 69700 cm. is deduced for the ground state,  $5s^25p^3.4S_4$ . The principal ionisation potential of Sb is 8.64 v.

Zeeman effects in the arc spectrum of nickel. C. H. Lindsley (J. Opt. Soc. Amer., 1942, 32, 94—97).—Zeeman data for 171 lines of Ni 1 in fields of 85700 and 81300 gauss are tabulated. g vals. are of Ni I in fields of 85700 and 81300 gauss are tabulated. 5 and  $3d^84s^2$  and  $3d^84s^2$  and  $3d^84s^3$  and  $3d^84s^4$  and  $3d^8s^4$ 

First spark spectrum of neodymium; preliminary classification and Zeeman effect data. W. E. Albertson, G. R. Harrison, and J. R. McNally, jun. (*Physical Rev.*, 1942, [ii], 61, 167—174).—Classifications from the combination principle are tabulated for 367 lines of Nd II arising from 30 lower and 57 upper levels and are checked by Zeeman-effect measurements at fields up to 87180 cersteds, and by other data. Quantum nos. are assigned to the levels having approx. LS coupling, and g vals. of all known levels are determined. The lowest term is  $4f^4(^5I)6s - a^6I$ . All low terms found arise from 4f<sup>4</sup>6s and 4f<sup>4</sup>5d, and all identified upper terms probably arise from 4f<sup>6</sup>6p. The strongest lines belong to the sextet and quartet super-multiplets arising from  $4f^4(5I)6p-6s$ . Curves are given showing the variation, in the progression La II, Ce II, Pr II, and Nd II, of the binding of terms arising from the configurations  $f^n s$ ,  $f^n p$ ,  $f^n d$ , and, where known,  $f^{n+1}$ . N. M. B.

Theory of complex spectra. I. G. Racah (Physical Rev., 1942, [ii], 61, 186—197; cf. Slater, A., 1930, 126).—Mathematical. A closed formula is developed which, for two-electron spectra, entirely replaces the previous lengthy calculations by the diagonal-sum method. Applications are made to some configurations with three or more electrons and to the p" configurations of the nuclei.

N. M. B. Results with the Coudé spectrograph of the Mount Wilson Observatory. W. S. Adams (Astrophys. J., 1941, 93, 11-23). E. R. R.

Solar hydrogen vortices. R. S. Richardson (Astrophys. J., 1941, 93, 24—28). E. R. R.

Ultra-violet emission lines in spectra of Me variables. P. W. Merrill (Astrophys. J., 1941, 93, 40—46). E. R. R.

Continuous spectrum of stellar atmospheres consisting of atoms and negative ions of H. R. Wildt (Astrophys. J., 1941, 93, 47—51). E. R. R. 221

Spectroscopic binary 29 Canis Majoris. O. Struve and F. Sherman (Astrophys. J., 1941, 93, 84-91).

J. R. Gill E. R. R. Some line intensities in [the spectrum of]  $\beta$  Lyrae. (Astrophys. J., 1941, 93, 118—127).

T. L. Page (Astrophys. J., 1941, 93, 128—132).

F. R. R.

Luminosities of the non-variable c-stars. R. E. Wilson (Astrophys. J., 1941, 93, 212-229).

Physical processes in gaseous nebulæ. XI. Strengths of forbidden lines as a function of coupling. G. H. Shortley, L. H. Aller, J. G. Baker, and D. H. Menzel. XII. Electron densities of some bright planetary nebulæ. D. H. Menzel and L. H. Aller. XIII. Electron temperatures of typical planetary nebulæ. D. H. Menzel, L. H. Aller, and M. H. Hebb. XIV. Spectrophotometry of typical planetary nebulæ. L. H. Aller. XV. Statistical equilibrium of neutral He. L. Goldberg (Astrophys. J., 1941, 93, 178—193, 195—201, 230—235, 236—243, 244—249).

E. R. R.

Recent shell spectrum of γ-Cassiopeiæ. R. B. Baldwin (Astrophys. J., 1941, 93, 333—336). E. R. R.

Spectrum of the night sky. C. T. Elvey, P. Swings, and W. Linke (Astrophys. J., 1941, 93, 337—348). E. R. R.

Spectra of two peculiar stars [MWC 17 and CD—27° 11944]. P. Swings and O. Struve (Astrophys. J., 1941, 93, 349—355).

Evolution of a peculiar stellar spectrum: Z andromedæ. P. Swings and O. Struve (Astrophys. J., 1941, 93, 356—367).

E. R. R.

Planetary atmospheres and water-cell temperatures. A. Adel and C. O. Lampland (Astrophys. J., 1941, 93, 391-396). E. R. R.

1914 shell spectrum of & Tauri. R. B. Baldwin (Astrophys. E. R. R. 1941, 93, 420-424).

New type of emission in the  $L_a$  group of heavy elements. (MIle.) Y. Cauchois (Compt. rend., 1941, 213, 121—124).—Certain new satellites are observed in the  $L_a$  spectra of elements of at. no. 62—92. These are not due to impurities or to multiple reflexions. The difference in  $\nu$  between the satellite  $(a_i)$  and the main line  $(a_i)$  decreases approx. linearly with increase of at. no. The  $a_i$  lines are decreases approx. Integrity with interest of the relatively intense for Th, Bi, Hg, Au, and Pt, but are less intense for lighter elements. The existence of lines of lower frequency than the principal line suggests a type of internal Raman effect. A. J. M.

Precise determination of the fine structure constant from X-ray spin doublet splitting. R. F. Christy and J. M. Keller (Physical Rev., 1942, [ii], 61, 147—152; cf. A., 1941, I, 2).—Mathematical. Corrections to the Sommerfeld formula for the LII-LIII X-ray spindoublet splitting, taking account of departures from a pure Coulomb field for heavy elements, are calc. By using Dirac wave functions to a Coulomb field and determining the terms in the electron interaction of order  $e^2$ , i.e., of relative order 1/Z, compared with the Sommerfeld splitting. Application to experimental data for elements Z=60-92 gives the fine structure const. as  $1/a=hc/e^2=136\cdot93\pm0\cdot18$ . N. M. B. field for heavy elements, are calc. by using Dirac wave functions for

Optical properties of thick magnetic lenses and application of the lenses to  $\beta$ -ray spectrometry. R. E. Siday (*Proc. Physical Soc.*, 1942, 54, 266—277).—Mathematical. The validity of expressions giving the focussing properties is examined, a method of ray tracing for good image formation is developed and appropriate positions of the principal planes are deduced, and results are general-N. M. B. for good image formation is developed and applied, focal lengths and

Electron microscope.—See A., 1942, I, 213.

Photophoresis and its interpretation by electric and magnetic ions. F. Ehrenhaft (J. Franklin Inst., 1942, 233, 235—256).—Experimental data regarding longitudinal, electro-, and magneto-photo-phoresis and the "trembling effect" are summarised, and the inadequacy of existent theories to explain these phenomena is pointed out. It is shown that irradiated particles behave as if charged and magnetised, and hence it is postulated that light causes or induces magnetism as well as heat and electricity. J. W. S.

Electron polarisation. C. G. Shull (Physical Rev., 1942, [ii], 61, 198).—400-ke.v. electrons scattered through 90° by Au foils (suffi-

ciently thin to ensure single scattering) were counted in parallel and anti-parallel directions to the incident beam. Corr. results showed an asymmetry of 8%, the reality being confirmed by a val. of 1% in the opposite direction when an Al foil was substituted for the second Au foil. The reflexion transmission asymmetry (cf. Chase, A., 1940, I, 387) was 1.56 for the Au foils. There is a transmission polarisation asymmetry  $\sim\!\!2\%$  > the 8% asymmetry as distinct from a reflexion polarisation asymmetry which is  $\ll$  either (cf. Bartlett, A., 1939, I, 594).

Threshold field studies of various positive-corona phenomena. K. E. Fitzsimmons (*Physical Rev.*, 1942, [ii], **61**, 175—182).

Investigation of isotopes in 1941. S. Flügge and J. Mattauch (Physikal. Z., 1942, 43, 1—5).—A review.

N. M. B.
A. J. M.

Depolarisation of neutron beams by magnetic fields. O. Halpern and T. Holstein (*Proc. Nat. Acad. Sci.*, 1942, 28, 112—118).—The quantum-mechanical method described enables the average no. of neutrons in individual spin states to be calc. in transmission through ferromagnets, and shows that the depolarisation depends on ratio of magnetic moment to spin.

L. J. J.

Elastic and inelastic scattering of fast neutrons. H. H. Barschall and R. Ladenburg (*Physical Rev.*, 1942, [ii], **61**, 129—137; cf. Dunlap, A., 1942, I, 127).—The 45° and 90° scattering of 2·5-Me.v. d-d neutrons by C, Al, Fe, Cu, Zn, and Pb is studied by analysing energy distribution of recoiling a-particles in an ionisation chambing is roughly the same for 45° and 90°. The ratio of elastic scattering is roughly the same for 45° and 90°. The ratio of elastic to inelastic scattering in C, Al, and Pb exceeds that in Fe and Cu. N. M. B.

Mean life of neutrons in water and the hydrogen capture cross-section. J. H. Manley, L. J. Haworth, and E. A. Luebke (Physical Rev., 1942, [ii], 61, 152—155).—Observations of the time variation of slow-neutron density in a large vol. of  $\rm H_2O$  during and after irradiation by D–D neutrons show an exponential growth and decay. Analysis of results and of data on the spatial density distribution, which determines the effect of diffusion, gives  $205\pm10~\mu$ -sec. as the mean life of neutrons in  $\rm H_2O$ . This leads to a cross-section of  $0.33\times10^{-24}$  sq. cm. for the capture of slow neutrons by H.

Rupture of homopolar bonds under the influence of particular emissions in selenium compounds. R. Daudel (Compt. rend., 1941, 213, 479—481).—When radioactive Se is produced by neutron bombardment of Na<sub>2</sub>SeO<sub>3</sub> the activity can be conc. by pptn. with a variety of carriers, indicating that it is present as free atoms.

F. J. G.

Resonance scattering of neutrons in helium. W. E. Stephens and H. Staub (*Physical Rev.*, 1939, [ii], 55, 235).—The nos. of forward recoil particles produced in He and C₂H₂ by neutrons from Be bombarded by 0·6- and 0·9-Me.v. deuterons have been determined in a cloud-chamber. For ∼1-Me.v. neutrons there is a relatively large probability of backward scattering in He. This supports evidence for a 0·8-Me.v. unstable state in He (Williams *et al.*, A., 1937, I, 389, 593; Staub and Stephens, A., 1940, I, 383).

Structure of the electronic bands of OD. III. M. G. Sastry (Indian J. Physics, 1941, 15, 455—474).—At 3105—3295 A., approx. 360 lines of the (1,1), (2,2), and (3,3) bands of OD have been measured, and the six main branches of each band have been identified. Rotational consts. in good agreement with existing vals. have been calc. and those for v' = 3 are given for the first time. W. R. A.

β-Ray spectrum of <sup>13</sup>N and mass of the neutrino. E. M. Lyman (Physical Rev., 1939, [ii], 55, 234).—The positron spectrum of <sup>13</sup>N (produced by bombarding graphite with 5·3-Me.v. deuterons) is studied with a highly resolving magnetic spectrometer. Its endpoint energy (E) is  $1\cdot198\pm0\cdot006$  Me.v.; since nuclear disintegration and mass-spectrographic data give <sup>13</sup>N  $\rightarrow$  <sup>13</sup>C +  $e^+$  +  $(e^-)$  +  $\nu$  +  $1\cdot21\pm0\cdot09$  Me.v., the fastest  $\beta$ -particles have the total available energy, and the observed is the true end-point. The mass of the neutrino is  $0\pm0\cdot2m$ . A Konopinski–Uhlenbeck curve consistent with most of the data predicts too many high-energy positrons and an E val. 25% > the observed val. A. J. E. W.

Production of penetrating cosmic-ray particles by photons. M. Schein and V. C. Wilson (*Physical Rev.*, 1939, [ii], **55**, 233—234).— Experiments at 25,000 ft. show that an average of two penetrating particles (barytrons?) per min. are ejected in the forward direction from a Pb plate ( $38 \times 5.2 \times 2.2$  cm.) by non-ionising rays (photons?). At 25,000 ft. the electron (and hence the photon) intensity is 37 times, and the intensity of penetrating rays is 2.9 times, that at sea level. The derived cross-section for barytron production by photons in Pb agrees approx. with Heitler's theory.

A. J. E. W.

Transition curves for electron- and photon-produced showers. N. Nereson (*Physical Rev.*, 1942, [ii], 61, 111—115).—Air-to-Pb transition curves show that the max, for photon-produced showers is displaced to ~3 mm, greater thickness of Pb relative to the max, for electron-produced showers. This agrees with shower theory. The

max. for large showers lies at a greater thickness than that for small showers. No second max. (cf. Altmann, A., 1941, I, 69) is indicated.

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Shapiro (Physical Rev., 1942, [ii], 61, 115—120; cf. A., 1942, I, 80).—>90% of the "star" tracks on a photographic plate kept at 4300 m. for 239 days are produced by protons, and most of the remainder are probably due to α-particles of energy < 9 Me.v.

N. M. B.

Cosmic-ray theory. B. Rossi and K. Greisen (Rev. Mod. Physics, 1941, 13, 240—309).—A quant. theory of cosmic-ray effects is developed by the extrapolation of the ordinary laws of quantum electrodynamics to cosmic-ray energies. Collision processes, the Compton effect, radiation processes, pair production, and scattering are considered and the results applied to a detailed discussion of the production of showers.

O. D. S.

Origin of the soft component of cosmic rays. B. Rossi and K. Greisen (*Physical Rev.*, 1942, [ii], 61, 121—128; cf. A., 1940, I, 187).—Mathematical. The no. of electrons from mesotron decay (cf. Schein, A., 1941, I, 289) is calc.

N. M. B.

Second maximum in the Rossi curve. C. B. O. Mohr and G. H. Stafford (*Nature*, 1942, 149, 385—386).—Evidence for the existence of the second max. has been obtained.

A. A. E.

Introduction to wave mechanics. G. Glockler (*J. Chem. Educ.*, 1941, 18, 418—423).—A treatment of at, structure problems on the basis of the Bohr theory is outlined. It gives a consistent development for such cases as the H atom, the linear harmonic oscillator, and H<sub>2</sub>.

L. S. T.

Theory of the electric charge and the quantum theory. III. H. T. Flint (Phil. Mag., 1942, [vii], 33, 369—383; cf. A., 1940, I, 280).—The author's classical field equations (Fisher and Flint, Proc. Roy. Soc., 1929, A., 126, 645) are used as the basis for quantisation. A notation is developed for the expression of differentiation of matrices and extension of the concept of various operators.

Tensor forces and the theory of light nuclei. E. Gerjuoy and J. Schwinger (Physical Rev., 1942, [ii], 61, 138—146; cf. Rarita, A., 1941, I, 236, 289).—Mathematical. A treatment of the influence of the existence of non-central tensor forces in nuclei on the binding energies of <sup>3</sup>H and <sup>4</sup>He. The tensor forces which produce all the binding in the deuteron are relatively ineffective in binding <sup>3</sup>H and <sup>4</sup>He. The assumption of ordinary and tensor forces of the same range does not represent the properties of <sup>3</sup>H and <sup>4</sup>He. N. M. B.

Reynolds' number for extragalactic nebulæ. F. Zwicky (Astro-phys. J., 1941, 93, 411—416).—Analysis of structures and internal motions of nebulæ, in terms of hydrodynamics of models composed of viscous, compressible fluids, is outlined, and the application of statistical and particle mechanics is discussed.

E. R. R.

#### II.—MOLECULAR STRUCTURE.

Electron diffraction method of determining the structure of gas molecules. R. Spurr and L. Pauling (J. Chem. Educ., 1941, 18, 458—465).—A review. L. S. T.

Secondary K absorption spectra of ferric oxide in the solid and colloidal states. S. Sen (Indian J. Physics, 1941, 15, 433—436).—Both states exhibit extended secondary structure but the positions of succeeding max, and min. are not identical for the two states, nor are the position and width of the primary edges. Evidence is not sufficient to decide the structure of the colloidal particles.

Importance of certain carbon dioxide bands in the temperature radiation of Venus. A. Adel (Astrophys. J., 1941, 93, 397—400).— CO<sub>2</sub> in the earth's atm. absorbs completely the fundamental emissions  $\nu_2$  (14-97  $\mu$ .) and  $\nu_3$  (4-27  $\mu$ .) from the large CO<sub>2</sub> component of the atm. of Venus. Thus the upper-stage bands of the types  $\nu_3 \rightarrow (\nu_1, 2\nu_2)$  (near 10  $\mu$ .) and  $(\nu_1, 2\nu_2) \rightarrow \nu_2$  (near 13  $\mu$ .) determine the quality of radiation received from the atm. of Venus. E. R. R.

Resonance bands of NH in spectra of class R. R. Wildt (Astrophys. J., 1941, 93, 502—504).—Intensities of ultra-violet resonance bands of NH, identified in R-type stars, are compared with those of  $C_2$ , CN, and CH. Scattering of these intensities suggests large differences in the relative abundances of H, C, and N. E, R, R.

Grating infra-red solar spectrum. I. Rotational structure of HDO band  $\nu_2$ . II. Rotational structure of NNO band  $\nu_1$ . A. Adel (Astrophys. J., 1941, 93, 506—509, 509—510; cf. A., 1941, I, 319).— The absorption band  $\nu_2$  of HDO at 7·12  $\mu$ ., which appears in the grating infra-red solar spectrum, is rarely observed since it lies in a region reduced to zero intensity by HHO vapour in the atm. The rotational structure of the atm. band  $\nu_1$  of NNO at 7·78  $\mu$ . is obtained with a 2400-line echelette grating.

Continuous spectra of hydrogen and deuterium, H. M. James and A. S. Coolidge (*Physical Rev.*, 1939, [ii], **55**, 234).—H<sub>2</sub> and D<sub>2</sub> continua arising from transitions from the lower v levels of the

 $1s\sigma^2 s\sigma^3 \Sigma_a$  state to the unstable  $1s\sigma^2 p\sigma^3 \Sigma_a$  state have been completely calc. Franck-Condon approximation is avoided by direct calculation of electric moments of the transitions as functions of r; the moments decrease rapidly as r increases. Spectra are computed for transitions from each of the v levels, and abs. mean lives for the levels are determined. Relative probabilities of excitation from the ground-state by electron impact are estimated, and the spectral intensity due to such excitation is determined for a range of electron energies. Results disagree with observations by Smith (A., 1936, 537) but agree with those of Finkelnberg and Weizel (cf. A., 1931, 779). A. J. E. W.

Infra-red absorption of  $^{13}$ Cl\*0 at 4.66  $\mu$ . R. T. Lagemann (J. Chem. Physics, 1942, 10, 193—194).—The absorption curve of CO shows weaker lines belonging to the R branch of the fundamental band of 18C16O interspersed among the lines of the fundamental band of 12C16O at 4.66 μ. L. J. J.

C-H bond spectrum in relation to molecular structure. N. R. Tawde (J. Univ. Bombay, 1941, 10, Part 3, 137—138).—Variations in vals. of the C-H frequency correspond with a classification into linear, tetrahedral, and planar mols. (~3290, 3020, and 2980 cm.-1, respectively).

Reversible discharge tube.—See A., 1942, I, 213.

Clean-up of mercury vapour in discharges through hydrogen, helium, and nitrogen.—See A., 1942, I, 213.

Optical transmissibility of quartz glass. A. Schraub (*Physikal. Z.*, 1942, 43, 64—69).—Fused quartz, in contrast to cryst. quartz, begins to absorb strongly at 260 m $\mu$ . The fluorescence radiation lies in the violet. A. J. M.

Absorption spectra of potassium permanganate in different media. M. P. Murthy and J. Singh (Current Sci., 1942, 11, 52).—The absorption bands of the MnO<sub>4</sub> ion at 5495, 5255, 5060, and 4900 A. disappear suddenly on adding H<sub>2</sub>SO<sub>4</sub> (>11·2N.) or KOH (>1·0N.).

W. R. A.

Vibrational structure of electronic transitions for some complex ions. M. L. Schultz (*J. Chem. Physics*, 1942, **10**, 194).—Groups of equidistant absorption bands of Co, Ni, and Fe<sup>++</sup> aquo- and amminocomplex ions are ascribed to electronic transitions in which the vibrational structure characteristic of the complex ion is resolved. The separation of the bands is characteristic of the ion and is approx. the same in aq. solutions and in the solid hydrates at liquid-air temp. Raman spectra of Cu(NH<sub>3</sub>)<sub>4</sub><sup>++</sup>, Zn(NH<sub>3</sub>)<sub>6</sub><sup>++</sup>, and Cd(NH<sub>3</sub>)<sub>6</sub><sup>++</sup> give displacements of the same order as the vibrational separations of Ni<sup>++</sup> aquo- and ammino-complexes. Solid CoCl<sub>2</sub>,6H<sub>2</sub>O gives a series of 5 bands the separation of which leads to a val. 22 kg.-cal. for the heat of dissociation of Co(OH2)6++.

Light absorption of the cobaltic complexes. II. Cyanide and thiosulphate complexes. A. von Kiss [with G. Auer and G. Major] (Z. anorg. Chem., 1941, 246, 28—34).—Extinction curves from 200 to 700 m $\mu$ . are recorded for the following complex salts in H<sub>2</sub>O at room temp.: [Co(NH<sub>3</sub>)<sub>5</sub>(S<sub>2</sub>O<sub>3</sub>]Cl, trans-Na[Co(en)<sub>2</sub>(S<sub>2</sub>O<sub>3</sub>)<sub>2</sub>], room temp.:  $[Co(NH_3)_5(S_2O_3)]CI$ ,  $trans-Na[Co(en)_2(S_2O_3)_2]$ ,  $Na_5[Co(SO_3)_2(CN)_4]$ ,  $K[Co(H_2O)_2(CN)_4]$ ,  $K_4[Co(CN)_5(S_2O_3)_2]$ ,  $Ag_2[Co(H_2O)(CN)_5]$  (in presence of KCN),  $K_4[Co(CN)_5(S_2O_3)_3]$  (in presence of Na $_2$ S $_2O_3$ ), and  $tso-H_4[Co(CN)_5(S_2O_3)]$ . Possible interpretations are discussed pretations are discussed. F. J. G.

Light absorption by unsaturated compounds in the near ultraviolet and visible due to electron cloud oscillations. A. Henrici (Z. physikal. Chem., 1940, B, 47, 93—126).—An attempt is made to calculate the characteristic vibrations of the p-electron cloud, associated with the mol. as a whole, in mols. containing conjugated double bonds, and to calculate the red shift with increasing no. of conjugated double bonds. The calc. long- $\lambda$  limit of absorption of  $C_6H_6$  is 3000 A. Fair agreement with known absorption vals. is obtained for hydrocarbons from anthracene to pentacene, and for dephenylpolyenes. Agreement is improved by taking polarisability and dielectric const. into account. In C6H6 the bands at 2000 and 2500 A. correspond with electron vibrations perpendicular and parallel, respectively, to the ring plane. The band 1785 A. is an overtone parallel to the ring plane. L. J. J.

Association of electron bands in solution spectra. V. Light absorption of aliphatic and aromatic azo- and diazo-compounds. G. Kortüm (Z. physikal. Chem., 1941, B, 50, 361—381).—Data for absorption spectra of aq. and EtOH solutions of several azo- and diazo-compounds are discussed with reference to electromeric formulæ for the compounds based on resonance theories.

Analysis of absorption spectra. V. Effect of substituents at the Analysis of absorption spectra. V. Effect of substituents at the olefinic carbon atoms on the physico-chemical properties of chromophoric vinylene and divinylene groups. E. Hertel and K. A. Hoffmann (Z. physikal. Chem., 1941, B, 50, 382—402).—The induced effect of substituents on the basicity, the reactivity towards MeI, and the absorption characteristics of a no. of NH<sub>2</sub>, NO<sub>2</sub>-, and CN-substituted derivatives of (CHPh.)<sub>2</sub> and (CHPh.CH)<sub>2</sub> is investigated. No simple relation between absorption and the other properties appears to exist. The prep. and solubilities in org. solvents of p-dimethylaminocinnamylidene-, m.p. 150—151°, p-nitrobenzylidene-,

m.p. 160—161°, and p-nitrocinnamylidene-malononitrile, m.p. 184°, p-dimethylaminocinnamylidenephenylacetonitrile, m.p. 187—188°, and p-dimethylaminobenzylidenenitromethane, m.p. 174°, are described.

Investigation of organic substances with the aid of electron excitation in the glow discharge. H. Schüler and A. Woeldike (*Physikal. Z.*, 1942, 43, 17—22).—The ultra-violet emission spectra of PhMe, PhEt, PhPra, PhPra, and o-, m-, and p-xylene excited by electron collision in a discharge tube are similar to their absorption spectra. New emission bands are found at 3900—5700 A. The spectra do not change in intensity if Kr is used instead of H<sub>2</sub> as the carrier of the discharge, and are therefore a primary result of the excitation of the mol. by electron collision. The various mono-derivatives of C<sub>6</sub>H<sub>6</sub> give the same spectra, and two spectra, green and blue, are obtained for each substance in the visible. This is explained by supposing that these mols. can fall back from the excited state, and still leave the CoH5 radical excited. Purely spectroscopic data give 2.48 e.v. the C<sub>6</sub>H<sub>5</sub> radical excited. Purely spectroscopic data give 2.48 e.v. or 57,000 g.-cal. per g.-mol. as the upper limit of the work of separation of Me from the C<sub>6</sub>H<sub>6</sub> ring. Comparison of intensities shows that the efficiency of the electron collision process depends on the positions of substituents in di-derivatives. No visible spectrum is obtained in the case of C<sub>6</sub>H<sub>6</sub>, PhCl, PhBr, PhOH, PhCN, or NH<sub>2</sub>Ph, since the falling back of these mols. from the excited state does not set force well substituted are set to excite the Ph radical. set free sufficient energy to excite the Ph radical.

Reversible quenching by oxygen of the fluorescence of polycyclic hydrocarbons. H. Weil-Malherbe and J. Weiss (*Nature*, 1942, 149, 471—472).—Differences in fluorescence intensity exhibited by 3: 4-benzpyrene dissolved in tetralin or  $C_6H_{14}$  are attributed to the quenching effect of dissolved  $O_2$ . Other polycyclic hydrocarbons behave similarly. Self-quenching is interpreted by an elementary process:  $(HC)^* + (HC) \rightarrow (HC)^+ (HC)^- \rightleftharpoons (HC)_2$ . A. A. E.

Loss of efficiency of strontium sulphide [phosphors]. E. Streck (Z. physikal. Chem., 1940, B, 47, 220—226).—The discoloration of SrS phosphors, with consequent loss of efficiency, is investigated. Pure SrS gives no coloration when irradiated with ultra-violet light or when kept in the light for several weeks. Light affects inght of when kept in the light for several weeks. Eight anects SrS-Bi phosphors if traces of  $H_2O$  are present. The effect of dry gases is investigated; only  $CO_2$  has a slight effect, which is more marked in the presence of  $H_2O$ . The phosphor is also affected by  $H_2O$  even in the dark. The reaction occurring is  $SrS + 2H_2O = Sr(OH)_2 + H_2S$ ; the  $H_2S$  may be oxidised and the Sformed may give rise to polysulphides. The prep. of varnishes to prevent decomp. of the phosphors is discussed; they must preserve the phosphor against  $H_2O$  and must not give rise to acids by hydrolysis. phosphor against H<sub>2</sub>O, and must not give rise to acids by hydrolysis. Two varnishes which satisfy these conditions are a polystyrene varnish and (better) a natural resin.

Application of new method of analysis of molecular spectra to saturated aliphatic hydrocarbons. H. Deslandres (Compt. rend., 1941, 213, 98—102; cf. A., 1940, I, 8, 55).—The Raman spectra of hydrocarbons  $C_nH_{2n+2}$  up to n=12 are analysed by using the formula  $\nu=qd_1/s'r'$  ( $\nu=$  frequency, s'= no. of energised electrons,  $d_1=$  const. =1062, q and r' are integers).  $C_{12}H_{26}$  is taken as an example.

Thermal energy of crystalline solids. (a) Basic ideas. (Sir) C. V. Raman. (b) White phosphorus. R. Norris. (c) Lithium, tungsten, gold, silicon, and grey tin. B. Dayal. (d) Diamond. V. B. Anand. (e) Magnesium, zinc, and cadmium. B. Dayal. (f) Quartz. R. Norris. (g) Alkali halides. C. S. Venkateswaran (Proc. Indian Acad. Sci., 1941, 14, A. 459—467, 468—472, 473—483, 484—491, 492—498, 499—505, 506—515).—(a) The thermal energy of cryst. solids is considered from the viewpoint of at. vibrations. The energy associated with elastic vibrations negligible. Most of the energy is associated with lattice frequencies vibrations. The energy associated with elastic vibrations is negligible. Most of the energy is associated with lattice frequencies appearing as monochromatic infra-red lines. The residues with superlattice frequencies of different orders, which appear monochromatically in the far infra-red, become increasingly important at low temp. The theories of Debye and Born lack theoretical justification and observational verification.

(b) The sp. heat has been calc. by considering the unit cell of four P<sub>4</sub> mols. Of the 48 degrees of freedom, 24 are identified with internal vibrations of the P4 mol. characterised by Raman vv, 12 are associated with the inactive  $\nu$  of a triply degenerate rotational oscillation of each of  $P_4$  mol., 9 with the observed low- $\nu$  vibration due to the hindered translations of P<sub>4</sub> mols, in the unit cell, and 3 with simple translations of the unit cell in the lattice. The Einstein terms of each have been evaluated and the calc. vals. of C, agree well with observed vals.

(c) Applying the theory of (a) the nos. of lattice frequencies associated with body-centred cubic lattices, face-centred cubic lattices, and diamond-like structures are 1, 3, and 7, respectively. The calc. sp. heats of Li, W. Au, Si, and grey Sn agree well with experimental vals. Lattice frequencies ≈ those given by Lindemann's m.p. formula.

(d) The at. heat data of Pitzer (A., 1938, I, 184) agree satisfactorily with a formula containing Einstein terms corresponding with

observed vv.

(e) Monochromatic Einstein frequencies must be present to

explain the shape of sp. heat curves of metals having hexagonal structure. One, the smaller, corresponds with vibrations of the atoms parallel to the hexagonal axis, and the other is associated with movements of the atoms in the basal plane. Terms corresponding with superlattice frequencies must also be included. Vals. for Mg, Zn, and Cd in good accord with experimental data are obtained.

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(f) The Debye limiting frequency of quartz is calc., from ultrasonic-vibration data, as 189 cm. A Debye function for this limiting frequency, even after allowing for monochromatic lattice vibrations, does not agree with sp. heat data. Re-examination of Raman spectra of quartz revealed lines corresponding with superlattice frequencies of 145 and 69 cm.-1 Inclusion of Einstein terms

for these yields acceptable sp. heat vals. for the range 53—296° K.

(g) The character table for rock-salt, derived by group theory, gives 8 triply degenerate normal modes of vibration; 1 corresponds with translation of the cell as a whole, 2 are active in the infra-red but inactive in Raman effect, and 5 are inactive in both but their overtones appear in Raman spectra. A general expression for the thermal energy of cubic crystals, developed in terms of lattice and superlattice frequencies, gives vals. for Cp in reasonable agreement with experimental data.

Raman spectrum of mercuric chloride in relation to its structure. K. V. K. Rao (*Proc. Indian Acad. Sci.*, 1941, **14**, **A**, 521—528).—Raman spectra of solid, liquid, gaseous, and dissolved HgCl<sub>2</sub> all contain a displacement of 314 cm.<sup>-1</sup> indicating that HgCl<sub>2</sub> is a non-polar, linear mol. A displacement of 377 cm.-1 in the spectra for the solid and liquid is attributed to an overtone of the forbidden frequency. Lattice oscillations give rise to displacements of 73, 95, and 124 cm.-1 The effects of temp. on the spectrum are discussed.

Effect of temperature on the intensities of Raman lines. I. Crystals. K. Venkateswarlu (Proc. Indian Acad. Sci., 1941, 14, A, 529-534).—The intensity ratio of the Stokes and anti-Stokes lines at different temp. is investigated for quartz, NaNO<sub>3</sub>, and HgCl<sub>2</sub> crystals, and agrees with that predicted by existing theories.

Raman effect and hydrogen bonds. I. Mixtures of esters and acceptor molecules. G. V. L. N. Murty and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1941, 14, A, 593—603).—H-bond formation between esters as donor mols. and PhOH, EtOH, MeOH, and CHCl<sub>3</sub> as acceptor mols. is studied by Raman effect, particularly changes in the C:O frequencies. Four groups are distinguished: (i) the C:O frequency is displaced; (ii) the appearance of a modified C:O frequency with the original one; (iii) diffuseness of C:O frequency; and (iv) no change. The strengths of H-bonds depend on the anionoid power of the donor and the cationoid power of the acceptor

Raman spectra of acetylenes. VI.  $\Delta^a$ -Butine, -pentine, and -hexine,  $\Delta^{\gamma}$ -hexine,  $\Delta^{\delta}$ -octine, and  $\alpha$ -chloro- $\Delta^{\alpha}$ -heptine. F. F. Cleveland, M. J. Murray, and H. J. Taufen (J. Chem. Physics, 1942, 10, 172—176; cf. A., 1942, I, 83).—Data are recorded for the 2200 cm.<sup>-1</sup> region.  $\Delta^a$ -Butine shows a second strong line at 2158 cm.<sup>-1</sup>, and  $\Delta^b$ -octine shows no line near 2245 cm.<sup>-1</sup> Introduction of Clark regions. radically modifies the spectrum of  $\Delta^{\delta}$ -octine.

Raman spectra of sugars in the solid state and in solution. I. Raman spectra of α- and β-d-glucose. F. H. Spedding and R. F. Stamm (J. Chem. Physics, 1942, 10, 176—183).—A method is described of photographing Raman spectra of cryst. org. powders and solutions of poor scattering power, involving the use of saturated (CH<sub>2</sub>-CO<sub>2</sub>H)<sub>2</sub> solution and a Hg vapour absorption cell as filters for  $\lambda\lambda < 2300$  A. and for  $\lambda\,2537$  A., respectively. 36 lines are recorded for a- and 32 for  $\beta$ -d-glucose, as well as a no. of new bands.

for a- and 32 for β-d-glucose, as wen as a no. of hear L. J. J.

Spectrophotometric terms and symbols. Anon. (Analyst, 1942, 67, 164).—Report of a Panel appointed by the Publication Committee.

T. F. W.

Spectrophotometric studies. Reaction of cyanide with nitrogenous derivatives of ferriprotoporphyrin.—See A., 1942, II, 208.

Electric strength of dielectrics. (A) A. E. W. Austen and S. Whitehead. (B) A. von Hippel, R. J. Maurer, and G. M. Lee (Physical Rev., 1942, [ii], 61, 199—200, 200).—(A) A discussion of, and enquiries concerning, work reported by von Hippel (cf. A., 1941, I, 328), with reference to available data.
(B) A brief reply to the above.

Electric breakdown of ionic crystals. H. Fröhlich (*Physical Rev.*, 1942, [ii], **61**, 200—201).—Mathematical. von Hippel's experiments (cf. A., 1941, I, 328) confirm Fröhlich's theory of dielectric strength of ionic crystals and the behaviour of mixed crystals (cf. A., 1939, I, 551, 1941, I, 454). I, 551; 1941, I, 454).

Dipole moment and molecular structure. I. Dipole moments of ethyl esters of phenyl-substituted acetic, malonic, and glutaric acids. N. L. Phalnikar, B. V. Bhide, and K. S. Nargund. II. Dipole moments of ethyl esters of p-substituted benzoic acids. A. H. Dipole moments of ethyl esters of p-substituted benzoic acids. A. H. Bhatkhande, N. L. Phalnikar, and B. V. Bhide (J. Univ. Bombay, 1941, 10, Part 3, 48—52, 53—55).—I. Dipole moments are recorded as follows: CH<sub>2</sub>Ph·CO<sub>2</sub>Et, 1·82 D.; CHPhMe·CO<sub>2</sub>Et, 1·818 D.;

II. Dipole moments are recorded as follows: EtOBz, 1-93 d.; p-C<sub>6</sub>H<sub>4</sub>Cl·CO<sub>2</sub>Et, 2·24 d.; p-C<sub>6</sub>H<sub>4</sub>Br·CO<sub>2</sub>Et, 2·31 d.; p-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>Et, 4·05 d.; p-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>Et, 3·41 d.; these vals. indicate that the average angle between the moment of the CO2Et

group and the C-C line is 79°. F. J. G. Molal volume nomographs for aliphatic hydrocarbons. D. S. Davis (Ind. Eng. Chem., 1942, 34, 351).—From Egloff and Kuder's data (A., 1941, I, 329) nomographs relating the mol. vol. of a liquid

mol. have been constructed. Indirect estimation of critical temperature and of molar refractivity. R. Livingston (J. Physical Chem., 1942, 46, 341—343),—For members of a homologous series and over restricted ranges the crit. temp. and mol. refractivity vary linearly with b.p.

hydrocarbon at its b.p. with its b.p. and the no. of C atoms in the

Optical properties of diffusing materials. S. Q. Duntley (J. Opt. Soc. Amer., 1942, 32, 61—70).—A general theory of the optical properties of non-homogeneous non-isotropic materials bounded by reflecting surfaces is developed. These properties may be defined by an equation containing eight consts., namely, two surface reflexion factors, two absorption coeffis, and four scattering coeffis. The necessary optical measurements and a graphical derivation of the optical consts. are described. The method allows complete specification of the optical properties of diffusing materials, e.g.

Dispersion of optical glass. M. Herzberger (J. Opt. Soc. Amer., 1942, 32, 70—77).—An empirical dispersion formula is developed which closely fits published data for many silicate glasses for  $\lambda\lambda$  down to 2.6  $\mu$ . The formula suggests that silicate glasses have two absorption bands in the near ultra-violet, probably ~2000 and 1600 A. A more complex formula is developed for the dispersion curves of certain extraordinary glasses, e.g., dense flint glasses. O. D. S

Far ultra-violet reflectivities of metallic films. M. Banning (J. Opt. Soc. Amer., 1942, 32, 98—102).—Reflectivities of evaporated films of Al, Cu, Ag, and Be were measured spectrographically in the region 1200—2200 A. before exposure of the films to air. The reflectivity of Cu films falls on exposure to air but the other metals show no effect. The min. in the reflectivity of Be previously reported (A., 1939, I, 407) is not confirmed; it was probably due to a thin film of W evaporated over the Be surface.

O. D. S.

Polarisation of light diffused by mercury vapour. R. Lennuier (Compt. rend., 1941, 213, 120-121).-Determination of the polarisation of light diffused by Hg vapour shows that the isotropy of the Hg atom is comparable with that of the inert gas atoms.

Rotation of the plane of polarisation by organic compounds. Optical activity of terpene compounds. Influence of solvent on the rotation of the plane of polarisation. W. Hückel [with K. Kümmerle, G. Legutke, C. Kühn, H. Niggemeyer, F. Nerdel, S. Eskola, H. Pietsch, H. Weidner, W. Doll, I. Schneider, F. Neumann, W. Tappe, and H. Sowal (Annalen, 1941, 549, 95—186).—Cyclic terpens of the compound of the compoun penes are selected as possessing non-mobile structures, and the optical activity of camphane derivatives (camphor, epicamphor, fenchocamphorone, etc.) containing C.O, 'CH'2, and other groupings to confer asymmetry is studied. Effects ascribed to stereoisomerism (e.g., in the menthols and menthylamines), induced asymmetry in C:C bonds, the effect of primary, sec., and tert. nature of OH groups and their attachment to primary, sec., and tert. C atoms, are described. Kuhn's calculation of optical activity by assigning individual contributions to each centre of asymmetry is examined; it appears to be satisfactory for CO: and unsaturated compounds, of doubtful val. for saturated alcohols, and inapplicable to saturated hydrocarbons. The influence of solvent on optical activity of terpenes is discussed. General influences are difficult to trace but variation is marked among alcohols in C<sub>6</sub>H<sub>8</sub> or EtOH and other solvents (PhCN, PhNO<sub>2</sub>, C<sub>8</sub>H<sub>8</sub>, C<sub>10</sub>H<sub>12</sub>, etc.); an intimate spatial relation or a no. of alternative spatial relations between solvent and solute is assumed. and solute is assumed.

Modern valency formulæ and the elementary student. J. C. Speakman (Chem. and Ind., 1942, 227).—Copley's rule for the abs. valency of an atom in an electronic formula (A., 1942, I, 196) is unsatisfactory.

A. J. M.

Flow of energy in thermal transpiration for a Bose-Einstein and a Fermi-Dirac gas. D. V. Gogate and D. S. Kothari (*Physical Rev.*, 1942, [ii], 61, 349—358).—Mathematical. Two chambers at different temp, are connected by an effusion orifice. The energy flow for a relativistic and non-relativistic gas is considered in the three possible cases when the chambers are assumed to contain a gas non-degenerate in both, degenerate in both, and degenerate in one and non-degenerate in the other.

Effusion phenomena in a degenerate Bose-Einstein gas. D. V. Gogate and Y. V. Kathavate (Phil. Mag., 1942, [vii], 33, 310—

314).—The expressions for effusion of no., mass, and energy of particles are shown to depend only on temp. in degenerate Bose-Einstein statistics, whilst in the non-degenerate case they depend on concn. as well. The effusion of a single gas between two chambers at different temp. is calc.

Quantum theory of the chemical bond. C. A. Coulson (Proc. Roy. Soc. Edin., 1941—42, 61, A, 115—139).—A survey of the mol. orbital aspect of the problem. An explanation of the Hartree theory of at. electron motion leads to an account of the normal single bond, illustrated by H<sub>2</sub>, HCl, and H<sub>2</sub>O, the double bond (C<sub>3</sub>H<sub>4</sub> and its double-streamer orbit), and conjugated compounds (allyl, C<sub>6</sub>H<sub>8</sub>, and aromatic compounds). Other applications considered are rotation about a conjugated single bond, vibrations, and polymerisation.

N. M. B.

Quantum mechanical calculations on the theory of organic dyes. I. T. Förster (Z. physikal. Chem., 1940, B, 47, 245—268).—The electronic terms of org. dye ions, and hence the  $\lambda$  of light they absorb, are calc. from valency theory for two types of mol.: (1) a conjugated chain with an odd no. of CH groups, and auxochrome groups (NH<sub>2</sub>, OH, etc.) at the two ends; (2) a similar mol. but branched in the middle. The theory accounts for the observed properties of dye ions. Absorption is displaced to longer λλ with increasing length of chain, and with increasing power of the auxo-chrome. The connexion between constitution and chemical stability, e.g., towards hydrolysis, is also satisfactorily accounted for.

Structure of the heteropoly-acids. B. V. Nekrassov (J. Gen. Chem. Russ., 1941, 11, 373—375).—A discussion of the structure of the phosphotungstic and phosphomolybdic acids and their salts, with special reference to the work of Keggin (A., 1934, 479) and Nikitina (A., 1941, I, 56, 88). The formula  $Na_3[P(MoO_4)_4,(8-x)MoO_3]_*xNaHMoO_4$  is suggested as being fundamental for both sets of acids. N. G.

Electrical contact between solids. H. Y. Fan (Physical Rev., 1942, [ii], 61, 365—371).—A mathematical treatment of contact between two metals and between a metal and a semi-conductor.

Study of mobility spectrum of large atmospheric ions. P. Queney (Compt. rend., 1941, 213, 498—500).—Apparatus is described and numerical results of observations are tabulated. F. J. G.

Linear effect of the electric field in molecular beam investigations with ammonia. H. Scheffers ( $Physikal.\ Z.$ , 1942, 43, 6—10).— Deviation of a mol. beam of NH<sub>3</sub> by an electric field is  $\infty$  field strength; with other mols, the effect is  $\infty$  (field strength)? This result requires for NH<sub>3</sub> a moment  $\sim \frac{1}{3}$  of that deduced from accurate determinations of the dielectric const. This discrepancy is further investigated. The effect of translational and rotational motion of the mol. is discussed. Consideration of nuclear spin does not affect the result. If the solid pyramidal structure of the does not affect the result. If the solid pyramidal structure of the  $\mathrm{NH_3}$  mol. is accepted the discrepancy cannot be explained, but if it is supposed that the N atom can vibrate through the plane of the H atoms, the moment of the mol. is comparable with that deduced from the effect of the electric field on mol. rays.

#### III.—CRYSTAL STRUCTURE.

New casette for X-ray diffraction patterns.—See A., 1942, I, 212. New method in X-ray crystallography.—See A., 1942, I, 212

Quantum theory and diffuse X-ray reflexions. G. D. Preston (Nature, 1942, 149, 373—374).—Differences in interpretation as between Raman and others regarding the origin of non-Laue diffuse reflexions are defined and briefly discussed.

A. A. E.

Quantum theory and diffuse X-ray reflexions. M. Born, (Mrs.) K. Lonsdale, and H. Smith (Nature, 1942, 149, 402—403).—Polemical (cf. preceding abstract).

Quantum theory and diffuse X-ray reflexions. M. Born (Nature, 1942, 149, 403—404).—Raman's theory of the origin of extra spots on Laue photographs is contested. The spots are not contradictory to lattice dynamics, but provide a powerful method of checking it.

Quantum theory and diffuse X-ray reflexions. (Mrs.) K. Lonsdale and H. Smith (Nature, 1942, 149, 404—405; cf. Pisharoty, A., 1942, I, 86).—In the diamond the "forbidden" 222 reflexion is similar to a Bragg reflexion, the {220} planes give extra reflexions, and there are no reflexions from the (200) planes of intensity comparable with that predicted. Pisharoty and Subrahmanian's contentions (ibid.) regarding the absence of 111 extra reflexions in type II diamonds are rejected. A. A. E.

Temperature-diffuse scattering of X-rays by potassium chloride and potassium bromide crystals. (Miss) J. H. Hall (Physical Rev., 1942, [ii], 61, 158—167; cf. Siegel, A., 1941, I, 195).—Cu Ka radiation is used, and the displacement of the tempe-diffuse max. from the Brayer scattering angle is determined for parious settings of the the Bragg scattering angle is determined for various settings of the crystal near the 400, 420, and 440 Bragg reflexions. The theoretical

displacement curve for KCl, calc. from the relative effects of the  $\alpha_1$  and  $\alpha_2$   $\lambda$  at the angles of incidence used, agrees well with experiment. Half-widths and relative intensities found experimentally are corr, for the vertical divergence of the slit system. An attempt is made to determine the elastic consts. of KBr from diffuse N. M. B. scattering data.

X-Ray interference in partially-ordered layer lattices. S. Hendricks and E. Teller (J. Chem. Physics, 1942, 10, 147—167).—Mathematical. The effect of lattice irregularities on intensity and sharpness of X-ray patterns is calc. for different types of irregularity in layer lattices. The results obtained are applied to partially ordered stacking of layers in micas, and to irregularities in closepacked structures of spheres and in graphite. L. J. J.

New concepts of the solid state. (Sir) C. V. Raman (Current Sci., 1942, 11, 85—92).—A lecture. W. R. A.

Structure of evaporated films of chromium and aluminium on glass. (Miss) A. R. Oliver (*Physical Rev.*, 1942, [ii], **61**, 313—314).— Electron-diffraction study of films of Al on glass, and of Al on Cr deposited on glass, shows no indication of the nature of the hardening produced in Al films by using a Cr base or by washing with H<sub>2</sub>O (cf. Sabine, A., 1939, I, 407). The oxide film on Al, if present, is very thin and amorphous.

X-Ray study of selenium in the liquid and colloidal states. K. Das Gupta and S. R. Das (Indian J. Physics, 1941, 15, 401—409).—X-Ray diffraction by liquid Se from 220° to 430° reveals a single broad band with band spacing > for amorphous varieties. Band spacing increases with rise of temp, and gives a similar curve to  $\rho^{\dagger}$ , when plotted against temp. Colloidal Se is stable at 100° for several hr. but when allowed to evaporate yields a sticky mass. The X-ray diffraction (i) of coagulum slowly coagulated indicates a sharp monoclinic pattern, (ii) of rapidly coagulated ppt. gives broad bands, (iii) of the sticky mass from evaporated sol gives one broad band with spacing 4.07 A., the same as for liquid Se near its m.p. but 0.57 A. > that in amorphous Se. It is concluded that similar arrangements of atoms exist in liquid and colloidal Se.

Lattice spacings and crystal structure of cementite. W. Hume-Rothery, G. V. Raynor, and A. T. Little (Iron & Steel Inst., March, 1942, Advance copy, 7 pp.).—Cementite isolated from three steels by electrolytic dissolution of the Fe in HCl is found by X-ray examination to have an orthorhombic structure with a 4.5155, b 5.0773, c 6.7265 A. at 25°. It may be formed from martensite by simple shear in the central layer of a block of three superimposed cubes, the top and bottom layers being displaced relative to each other by ~0.5a in the [100] direction, and by subsequent minor adjustments of angles and distances with expulsion of certain C atoms to just inside or outside the plane of Fe atoms.

Structures of complex fluorides. Ammonium hexafluosilicate-ammonium fluoride,  $(NH_4)_2SiF_6,NH_4F$ . J. L. Hoard and M. B. Williams (J. Amer. Chem. Soc., 1942, 64, 633—637).—From X-ray investigation the structure is  $D_4^5h-P4|mbm$ , which is an ordered aggregate of  $NH_4$ , octahedral  $SiF_6$ , and "extra" F' ions. Parameters are deduced, and their vals. are discussed in relation to expectal stability. crystal stability.

Chromic oxide hydrates. II. S. I. Djatschkovski and V. M. Ofitzerov (J. Gen. Chem. Russ., 1941, 11, 371—372; cf. A., 1941, I, 19).—The changes in % of H<sub>2</sub>O, colour, and X-ray diffraction pattern of Cr<sub>2</sub>O<sub>3</sub> hydrate are followed when this is heated to temp. varying from 250° to 850°. The temp. of transition from brown varying from 250° to 850°. The temp. of transition from brown the colour of the colour amorphous Cr<sub>2</sub>O<sub>3</sub>,4H<sub>2</sub>O to light green cryst. Cr<sub>2</sub>O<sub>3</sub> is between 400° and 450°. The hydrate can exist only in the amorphous colloidal state. Cryst. Cr.O. has an interplanar spacing of 5.33 A.

Determination of parameters in potassium dihydrogen arsenate and silver arsenate. L. Helmholz and R. Levine (J. Amer. Chem. Soc., 1942, 64, 354—358).—The X-ray structures of KH<sub>2</sub>AsO<sub>4</sub> and Ag<sub>3</sub>AsO<sub>4</sub> are determined. The As—O distances in both are 1.75 A. The Ag—O distance of 2.34 A. is discussed in relation to the colours of Ag<sub>3</sub>AsO<sub>4</sub>, Ag<sub>2</sub>PO<sub>4</sub>, Ag<sub>2</sub>SO<sub>4</sub>, and Ag<sub>2</sub>O. Random distribution of H<sub>2</sub>AsO<sub>4</sub>' ions and its influence on the determination of parameters of KH<sub>2</sub>AsO<sub>4</sub> are discussed. The H-bond distance (O—H—O) is 2.54 A., equal to that in Ag<sub>3</sub>PO<sub>4</sub>.

X-Ray analysis of some organic compounds. R. H. Joshi and M. R. Kapadia (J. Univ. Bombay, 1941, 10, Part 3, 35—39).—NHPhAc has a 7.95, b 9.48, c 19.56 a., with 8 mols. in the unit cell, space-group  $Q_h^{15}$ . NPhMeAc has a 6.56, b 7.06, c 16.56 A., with 4 mols. in the unit cell. p-OMe·C<sub>6</sub>H<sub>4</sub>·NHAc has a 24·4, b 9·08, c 7·54 A., with 8 mols. in the unit cell, space-group  $Q_h^{15}$ .

Crystal structure of diphenylselenium dichloride. J. D. McCullough and G. Hamburger (J. Amer. Chem. Soc., 1942, 64, 508—513).—Orthorhombic crystals of SePh<sub>2</sub>Cl<sub>2</sub> have space-group symmetry  $D_{25}^{15}$ —Pbca, 8 mols. per unit cell,  $a_0$  7.59,  $b_0$  17.97,  $c_0$  17.77, all  $\pm 0.03$  A., i.e., the same as for SePh<sub>2</sub>Br<sub>2</sub> (A., 1941, I, 196). The Se—Cl distance is  $2.30\pm0.05$  A. and the Cl-Se-Cl angle is  $180\pm5^{\circ}$ . Micellar structure and deformation processes in fibrous materials. IX. Supra-molecular structure of cellulose hydrate. Introduction of laminar micelles into the theory of deformation processes. B. Baule, O. Kratky, and R. Treer (Z. physikal. Chem., 1941, B. 50, 255—297).—Consideration of the properties, e.g., mobility and crystallisation tendency, of thread-like mols. throws light on the changes, e.g., micellar formation, which may occur during pptn. A modified theory based on deformable elongated laminar micelles is discussed and developed mathematically. C. R. H.

Long X-ray diffraction spacings of collagen. R. S. Bear (J. Amer. Chem. Soc., 1942, 64, 727).—The structural period for large fibreaxis collagenous tissues from dried beef tendon is 640 A.

W. R. A.

X-Rays and stoicheiometry of proteins with special reference to the structure of the keratin-myosin group. W. T. Astbury (J.C.S., 1942, 337—347).—A lecture.

Extra spots in electron diffraction patterns. A. Charlesby and H. Wilman (Nature, 1942, 149, 411—412).—Apparently anomalous features in certain electron-diffraction patterns are now found to correspond closely with X-ray extra spots. Streaks given by anthracene crystals indicate that the mols. vibrate with max. amplitude at right angles to their length. A. A. E.

Resistivity of antimony-tin single crystals at low temperatures. C. T. Lane and W. A. Dodd (*Physical Rev.*, 1942, [ii], **61**, 183—186; cf. A., 1942, I, 169).—Resistivity-temp, curves are plotted for single crystals of pure Sb and alloys of Sb with 0—3 at.-% Sn in the temp, range 300—4·2° K. Crystals were oriented so that the [111] plane was perpendicular to the electric field. Resistivity decreases normally as temp, is lowered, but the average temp, coeff. of resistance between 4·2° and 77·3° K. decreases sharply with increasing Sn content to a small const. val. at 3 at.-% Sn. Addition of Sn at room temp, only slightly changes resistivity, but the effect at liquid-He temp, is very large. "Residual" resistivity is approx. a parabolic function of [Sn]. Results are compared qualitatively with Bloch's theory.

N. M. B.

Phenomena of conical refraction. (Sir) C. V. Raman (Current Sci., 1942, 11, 44—46).—Conical refraction by a crystal of  $C_{10}H_8$  is discussed. W. R. A.

Optical properties of crystals of conicine hydrochloride. J Jaffray (Compt. rend., 1941, 213, 132—133).—The crystals are orthorhombic, and investigation of birefringence shows that they are uniaxial at 6160 A. at room temp.

A. J. M.

Transition state theory of diffusion in crystals. R. M. Barrer (Trans. Faraday Soc., 1942, 38, 214).—Correction (cf. A., 1942, I, 199).

# IV.—PHYSICAL PROPERTIES OF PURE SUBSTANCES.

Determination of mol. wt. of macromolecular substances. VIII. Distribution function of multimolecular substances and its determination by fractionation. G. V. Schulz (Z. physikal. Chem., 1940, B, 47, 155—193).—Expressions are derived for mean mol. wt. on the basis of frequency distribution, mass distribution, and integral distribution; corresponding distribution functions are defined. The distribution function of a multimol. substance can be determined by separation into fractions of decreasing solubility and increasing ease of pptn. with increasing mol. wt. The sources and limits of error in fractionation methods of determining mean mol. wt. and the degree of variation of mol. wt. in a multimol. substance are discussed theoretically.

L. I. I.

Magnetism of strontium. S. R. Rao and (Miss) K. Savithri (Proc. Indian Acad. Sci., 1941, 14, A, 584—592).—The sp. magnetic susceptibility of Sr, determined by the Curie method, is  $1\cdot02\times10^{-6}$  at  $0^{\circ}$ ,  $1\cdot09\times10^{-6}$  at  $65^{\circ}$ , and thereafter decreases to  $0\cdot73\times10^{-6}$  at  $260^{\circ}$ . The significance of these results from the Fermi distribution of energy of the valency electrons is discussed. W. R. A.

Magnetic susceptibilities of metal oxides and their molecular structures with special reference to those of cobalt. S. S. Bhatnagar, B. Prakash, and M. A. Qayyum (J. Indian Chem. Soc., 1941, 18, 540—554).—The magnetic susceptibilities of CoO, Co<sub>3</sub>O<sub>4</sub>, and Co<sub>2</sub>O<sub>3</sub> and their variation with temp. are determined with specimens prepared by different methods, and concordant vals. of  $\chi$  are obtained for all three oxides. The vals. of the Bohr magneton nos. are utilised in a discussion of the mol. constitution of the oxides. The effect on  $\chi$  of adsorption of O<sub>2</sub> by CoO is examined. Very slight amounts of impurity completely vitiate conclusions drawn from magnetic measurements.

Magnetic susceptibilities of cis- and trans-decalin. W. Byerly and P. W. Selwood (J. Amer. Chem. Soc., 1942, 64, 717—718).— $\chi_{\rm p}$ , are (cis) -0.774 and (trans)  $-0.779 \times 10^{-6}$ . The slight difference is considered to be significant and indicative of the greater paramagnetism arising from the more distorted cis-structure.

W. R. A.

Diamagnetic susceptibility of butyl alcohols. B. Cabrera and (Mlle.) H. Colson (Compt. rend., 1941, 213, 108—111).—There are small but definite differences in the vals. of  $\chi$  for the four BuOH isomerides. These probably arise from a deformation of the C atom due to substitution of Me for an attached H, the resulting increase in  $\chi$  being independent of the positions of the H substituted. General dissymmetry of the mol. may also produce an increase in  $\chi$ .

Temperature and frequency effects on ultrasonic velocities in carbon dioxide. C. J. Overbeck and H. C. Kendall (J. Acoust. Soc. Amer., 1941, 13, 26—32).—Ultrasonic velocity in pure CO<sub>2</sub> is measured from 25° to 530°, with νν from 27 to 147 kc. Earlier discrepancies are ascribed to impurities and temp. gradients. Velocity depends on temp. and ν, and the variation with ν is greater at high temp.

O. D. S.

Origin of the absorption of ultrasonic waves in liquids. K. F. Herzfeld (J. Acoust. Soc. Amer., 1941, 13, 33–35).—Theoretical. The absorption coeff. of ultrasonic waves in  $\rm H_2O$ ,  $\rm C_6H_6$ ,  $\rm CCl_4$ , and MeOH is  $\propto \nu^2$  for  $\nu\nu$  up to 50 Mc. but is > expected from viscosity and heat conduction of the liquids. The hypothesis that the high absorption is due to a slow energy exchange between internal and external degrees of freedom agrees with the data for all except  $\rm H_2O$ .

Absorption of ultrasonic waves in highly viscous liquids. J. L. Hunter (J. Acoust. Soc. Amer., 1941, 13, 36—40).—The absorption coeff. of ultrasonic waves in glycerol, castor oil, linseed oil, and olive oil at temp. from 0° to 50° and  $\nu\nu$  3-157 and 3-95 Mc. is measured with Fox's apparatus (A., 1938, I, 20). Vals. exceed those calc. from the viscosity and heat conduction of the liquids but the difference is  $\Rightarrow$  experimental error. The temp. coeff. agrees with the val. calc. from viscosity and heat conduction. O. D. S.

Supersonic measurement of the heat capacity of propylene. D. Telfair (J. Chem. Physics., 1942, 10, 167—171).— $C_v$  vals. from 12·30 g.-cal. per mol. at 270°  $\kappa$ . to 21·00 g.-cal. per mol. at 510°  $\kappa$ . are recorded, obtained by acoustical velocity measurements in  $C_3H_6$  by means of a Pierce acoustic interferometer used well on the low-v side of the intramol. dispersive region. Max. absorption would occur at 80—100 Mc., corresponding with a relaxation time  $\sim 10^{-8}$  sec. The vals. obtained agree with an assumed potential restricting rotation  $\sim 2000$  g.-cal. per mol. L. J. J.

Resonance method of measuring the ratio of the specific heats of a gas,  $C_p/C_v$ . III. Sulphur dioxide and nitrous oxide. A. L. Clark and R. Katz (Canad. J. Res., 1941, 19, A, 111—115; cf. A., 1940, I, 248, 271).—By the method previously described, the vals. of  $\gamma$  for SO<sub>2</sub> and N<sub>2</sub>O have been found to follow the relations  $1\cdot 2642 + 0\cdot 0169P + 0\cdot 0026P^2$  and  $1\cdot 2783 + 6\cdot 320 \times 10^{-3}P + 1\cdot 22 \times 10^{-4}F^2 + 6\cdot 80 \times 10^{-8}P^4$ , respectively, where P = pressure in atm.

Heat capacities of red and yellow lead monoxides at high temperatures. H. M. Spencer and W. M. Spicer  $(J.\ Amex.\ Chem.\ Soc., 1942, 64, 617-621)$ .—An aneroid calorimeter is described. Heat contents and vals. of  $C_p$  for yellow and red PbO are given.

Phase transitions. I. Heat capacity of nickel nitrate hexammoniate from  $54^{\circ}$  to  $300^{\circ}$  K. Transition at  $243^{\circ}$  K. E. A. Long and F. C. Toettcher (J. Amer. Chem. Soc., 1942, 64, 629-632).— $C_p$  for Ni(NO<sub>3</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub> (I), determined from  $54^{\circ}$  to  $300^{\circ}$  K., has max. val. at  $243\cdot 3^{\circ}$ . There is a gradual transition from  $173^{\circ}$  to  $247^{\circ}$ , the heat of transition being 1818 g.-cal. per mol., and the corresponding entropy is  $7\cdot 65\pm 0\cdot 5$  entropy units. There is an additional region of anomalous thermal behaviour at  $<80^{\circ}$  K. The transition at  $243^{\circ}$  is discussed from the viewpoint of order-disorder in the orientation of NO<sub>3</sub> groups in the crystal lattice. W. R. A.

System correlating molecular structure of organic compounds with their b.p. VI. Monohalogen derivatives of the hydrocarbons. C. R. Kinney (J. Org. Chem., 1942, 7, 111—116; cf. A., 1939, I, 134).—Observed b.p., of 437 organohalides show an average deviation of 4·18° from the vals. calc. from the equation, b.p. = 230·14 × (b.p. no.)<sup>1/3</sup> — 543, in which b.p. no. for the mol. is obtained by summing the at. and structural b.p. nos. for the various atoms and structural groups in the mol. Different b.p. nos. must be assigned to primary, sec., and tert. halogen and structural differences in the arrangement of the C atoms must be considered. Characteristic b.p. nos. are assigned to halogen attached to doubly or trebly linked C. Until more reliable data are available the influence of cis.-trans-isomerism on the b.p. nos. for the halogens are used as in analogous open-chain derivatives. Unusually high b.p. are always observed for unsubstituted alicyclic halides, R·[CH<sub>2</sub>]<sub>n</sub>, X, in which R is a further unsubstituted alicyclic ring and n may be any integer or 0, and for the similarly constituted dicyclo-derivatives R[CH<sub>2</sub>]<sub>2</sub>R. This structure seems to affect the b.p. uniformly. Characteristic b.p. nos. are used for halogen attached to the C<sub>6</sub>H<sub>6</sub> or C<sub>10</sub>H<sub>8</sub> rings; these give satisfactory results regardless of the presence or absence of alkyl groups. The best agreement is obtained with fluorides and chlorides.

Freezing point of phenothiazine. L. E. Smith and O. A. Nelson (J. Amer. Chem. Soc., 1942, 64, 461—462).—Phenothiazine, prepared by sublimation, has f.p.  $185\cdot11\pm0\cdot02^{\circ}$ . W. R. A.

Entropy of vaporisation and density of liquids at their b.p. J. H. Simons and R. K. Smith (J. Physical Chem., 1942, 46, 380—387).— The total entropy of vaporisation ( $\Delta S$ ) is considered as being the sum of the entropy of conversion of liquid into perfect gas ( $\Delta S_c$ ) and the entropy of gaseous expansion ( $\Delta S_x$ ). Vals. of  $\Delta S$ ,  $\Delta S_c$ , and  $\Delta S_x$  for 126, substances are tabulated, and empirical equations connecting  $\Delta S$  with b.p. are discussed.

C. R. H.

Vapour pressure of monatomic vapours. R. W. Ditchburn and J. C. Gilmour (*Rev. Mod. Physics*, 1941, 13, 310—327).—Methods of measurement of the v.p. of monat. vapours from 10<sup>-8</sup> to 10<sup>3</sup> mm. are discussed critically. The theoretical significance of such measurements is indicated. Published data for the v.p. of monat. vapours are correlated and discussed critically. The best vals. are tabulated.

O. D. S.

Vapour pressure and vapour density measurements on gallium trichloride. W. Fischer and C. Jübermann (Z. anorg. Chem., 1940, 245, 254—256; cf. A., 1936, 787).—A reply to Laubengayer and Schirmer (A., 1940, I, 369).

J. W. S.

Vapour pressure and critical constants of isobutene. J. A. Beattie, H. G. Ingersoll, and W. H. Stockmayer (J. Amer. Chem. Soc., 1942, 64, 546—548).—The v.p. of iso- $C_4H_8$ , measured from 30° to 125°, is satisfactorily represented by  $\log \rho$  (atm.) =  $4\cdot3759-1163\cdot34/T$ . Crit. consts. are determined by the compressibility method:  $\theta_e=144\cdot73\pm0\cdot05^\circ$  c.;  $\rho_e=39\cdot48\pm0\cdot05$  normal atm.;  $v_e=0\cdot240$  l. per mol.;  $\rho_e=4\cdot17$  mols. per l. W. R. A.

Vapour pressures of tritium liquid hydrogens. Dependence of hydrogen vapour pressure on mass of molecule. W. F. Libby and C. A. Barter (J. Chem. Physics, 1942, 10, 184—186).—Distillation and radioactivity measurements on the distillate gas from ~10-9M. solutions of HT in H<sub>2</sub> and DT in n-D<sub>2</sub> give the following vals. for v.p. of the different kinds of mol. at 20-4° k., as derived from Henry's law consts. assuming H<sub>2</sub> and D<sub>2</sub> to form nearly perfect solutions: H<sub>2</sub> 760 mm., HD 438 mm., D<sub>2</sub> 256 mm., HT 254±16 mm., DT 123±6 mm., T<sub>2</sub>45±10 mm.

Joule-Thomson effect in carbon dioxide. J. R. Roebuck, T. A. Murrell, and E. E. Miller  $(J.\,Amer.\,Chem.\,Soc.,\,1942,\,64,\,400-411).-$  Iso-enthalpic curves of CO<sub>2</sub> are measured between  $-55^\circ$  and 300 and between 1 and 200 atm. The Joule-Thomson coeff. is calc. as a function of temp. at a series of const. pressures. The inversion curve in the liquid region and the contact point of a particular isenthalp with the v.p. curve are located. W. R. A.

Compressibility of and an equation of state for gaseous isobutene. J. A. Beattie, H. G. Ingersoll, and W. H. Stockmayer (J. Amer. Chem. Soc., 1942, 64, 548—549).—The compressibility of gaseous iso-C<sub>4</sub>H<sub>8</sub> is measured from 150° to 275° and from  $\rho=1$ ·0 to 9·0 mols. per l., the max. pressure being 250 atm. The consts. of an equation of state are determined from the data up to crit.  $\rho$ , and vals. of the second virial coeff. are given from 150° to 275°. In a glass-lined bomb iso-C<sub>4</sub>H<sub>8</sub> does not polymerise markedly during a 10-hr. period until 275° is reached. W. R. A.

Variation of viscosity of liquids with temperature. M. K. Srinivasan and B. Prasad (Phil. Mag., 1942, [vii], 33, 258—271).— Known viscosity data are used to compare the applicability of a no. of published formulæ connecting  $\eta$  and temp., for a no. of org. liquids and liquid metals. The best for unassociated liquids is Andrade's simple formula  $\eta = Ae^{b|T}$ , which is as accurate as the modified formula  $\eta v^{\dagger} = Ae^{v|T}$ . For liquid metals,  $\eta v^{\dagger}/\sqrt{T} = B/(v-v_0)$  (Macleod),  $\eta = K^1vT^{-1}eQ/RT$  (Silverman), and  $\eta = Ae^{\beta T}/(T-v_0)$  (Madge) hold, though the last is theoretically unsound. For org. liquids, Silverman's and Madge's formulæ are applicable. Irany's function of  $\eta$  is not linear for liquid metals. L. J. J.

Effect of laminar and turbulent flow on X-ray diffraction diagrams of water and nitrobenzene. W. R. Dubs (Z. Ver. deut. Ing., 1941, 85, 50—52).—The Debye-Scherrer patterns of jets of  $\rm H_2O$  and PhNO2 in free air are studied. The degree of stability (laminar or turbulent flow) of a jet ~0.81 mm. in diameter is determined from corresponding experiments with coloured filaments on a model 11 times the scale. The laminar resistance law still holds when the filaments depart appreciably from strictly laminar flow. Diffraction diagrams showed no effect definitely attributable to change from laminar to turbulent flow. Small effects in intensity distribution noted in the case of PhNO2 can be attributed to temp. changes accompanying change of type of flow. There is no evidence of any change in the quasi-cryst, structure with breakdown of laminar flow.

R. B. C.

# V.—SOLUTIONS AND MIXTURES (INCLUDING COLLOIDS).

Graph for preparing binary systems of approximate mol. fractions. W. Byerly (J. Chem. Educ., 1941, 18, 465).

L. S. T.

Volatility of silicic acid in steam.—See B., 1942, I, 249.

Apparent volumes of individual ions in aqueous solution. K. Fajans and O. Johnson (J. Amer. Chem. Soc., 1942, 64, 668—678).—A partition of the apparent mol. vol. ( $\Phi_0$ ) of strong electrolytes into vals. of individual ions has been made on the basis of the behaviour of NH<sub>4</sub>Cl near 35°. Vals. of  $\Phi_0$  for electrolytes have been obtained by extrapolation from measurements of  $\rho$  at >N. Near 35° NH<sub>4</sub>Cl closely resembles H<sub>2</sub>O in several properties and it is concluded that NH<sub>4</sub>, and Cl' ions fit into the structure of liquid H<sub>2</sub>O and that the apparent vol. of each is equal to the vol. of 1 mol. of H<sub>2</sub>O. For ions which are larger or smaller than H<sub>4</sub>O mols. the thermal expansibility of their aq. solutions is influenced greatly by the breaking of the loose H<sub>2</sub>O structure. Displacement of protons within H<sub>2</sub>O mols. and H<sub>3</sub>O and NH<sub>4</sub> ions is brought into relation with the mechanism of hydration of ions and mols. Comparison of anions with cations and of ions of different structures shows that the gradation of their apparent vols. in aq. solution may be very different from that of their size in crystals.

Densities and specific heats of aqueous solutions of dl-a-alanine,  $\beta$ -alanine, and lactamide. F. T. Gucker, jun., and T. W. Allen (J. Amer. Chem. Soc., 1942, 64, 191—199).—Vals. of sp. heats and of  $\rho$  for aq. solutions of lactamide (I), dl-a-alanine (II), and  $\beta$ -alanine (III) have been determined from 0·1 or 0·2m. to approx. saturated solution at 5°, 25°, and 40°. The apparent molal heat capacities of solutes  $\alpha$  concn., and the slopes increase in the order (I), (II), (III). Vals. at infinite dilution are (I) > (II) by 25 and > (III) by 40 g.-cal. per degree per mol. Apparent molal vol.  $\alpha$  molarity and the limiting val. of (I) is > that of (II) by 12·90 and > that of (III) by 14·78 ml.; these vals. are considered to be the electrostriction of the solvent. The limiting slopes of the partial molal heat capacities and vols. for (II) and (III) have been calc. The calc. differences in the heat capacities and vols. at different temp, are  $\sim_k$  of those observed. W. R. A.

Specific heats of morpholine and its aqueous solutions. H. M. Trimble, C. J. Engle, R. A. Brown, and R. F. Schmuck (J. Amer. Chem. Soc., 1942, 64, 679—681).—The sp. heats of morpholine and its aq. solutions between 0° and 130° and between 0 and 100°, H<sub>2</sub>O have been determined, and the partial molal heat capacities of the components of the system have been calc. at 25°, 50°, 75°, 100°, and 130°.

W. R. A. \*

Diffraction pattern of sulphuric acid at different concentrations. H. N. Bose (Indian J. Physics, 1941, 15, 411—415).—X-Ray diffraction of aq.  $\rm H_2SO_4$  (21·4—99·2 wt.-%  $\rm H_2SO_4$ ) has been measured with a view to establishing hydrate formation. Pure  $\rm H_2SO_4$  gives two sharp bands with spacings of 4·07 and 7·98 a., of which the former is more pronounced. With dilution the spacing diminishes from 4·07 to 3·6 a. for  $\rm H_2SO_4$ ,  $\rm H_2O$ , and for all concuss is between 4·07 and 3·24 a., the val. for  $\rm H_2O$ . The possible existence of hydrates and the application of the idea of Lennard-Jones relating band-spacing and particle size are discussed. W. R. A.

Light absorption of cobalt thiosulphate solutions.—See A., 1942, I, 194.

Electric moments of inorganic halides in dioxan. I. Phosphorus, arsenic, and antimony trihalides. P. A. McCusker and B. C. Curran (J. Amer. Chem. Soc., 1942, 64, 614—617).—Vals. of dielectric const. ( $\epsilon$ ) and  $\rho$  for dioxan solutions of PCl<sub>3</sub>, PBr<sub>3</sub>, AsCl<sub>3</sub>, AsBr<sub>3</sub>, AsI<sub>3</sub>, SbCl<sub>3</sub>, and SbBr<sub>3</sub> have been measured at various concns. ( $\epsilon$ ) at 25°. The  $\Delta\epsilon/\epsilon$  ratios for PCl<sub>3</sub> and PBr<sub>3</sub> decrease with increasing solute concn. Vals. of  $\mu$  are AsCl<sub>3</sub> 3·11, AsBr<sub>3</sub> 2·90, AsI<sub>3</sub> 1·83, SbCl<sub>3</sub> 5·16, SbBr<sub>3</sub> 5·01 D. W. R. A.

Magnetic rotation of cerium salts in aqueous solutions. W. K. Wilson, C. M. Mason, J. W. Hickey, and J. H. Mack (J. Amer. Chem. Soc., 1942, 64, 412—416).—The magnetic rotation and n of aq. CeCl<sub>3</sub> have been determined at  $10^\circ$  intervals from  $20^\circ$  to  $50^\circ$  and up to 2.753m. Verdet consts.  $\alpha$  concn. and temp. Mol. rotations show variation with concn. but are const. at low concn. The vals. recorded by Slack et al. (A., 1934, 1293) are disproved.

Solid solutions of alkali halides. A. V. Tobolsky (J. Chem. Physics, 1942, 10, 187—192).—X-Ray studies of solid solutions of alkali halide pairs with a common ion at room temp. and at 550° show that the miscibility is determined by the difference (8) between their lattice parameters. For  $\delta < 6\%$  miscibility is complete at room temp. For  $\delta$  6—13% miscibility is complete at 550°, whilst for  $\delta > 13\%$  two phases result for all temp. up to the m.p. On the basis of the Born theory of ionic lattices, free energy of mixing, and Vegard's law, the expression  $9\delta^2/T(1-2x) + \log_e x - \log_6 (1-x) = 0$  is derived for the mol. fraction (x) of one component dissolved by the other in a typical alkali halide pair with electrostatic energy 180 kg.-cal. per mol. at  $0^\circ$  K. Miscibility is complete above  $T=4\cdot5\delta^2$  and the heat of mixing is  $\sim -9\delta^2$  g.-cal. per mol. L. J. J.

Cation field strengths and their relation to the devitrification, combination, and m.p. of silicates. A. Dietzel (Z. Elektrochen., 1942, 48, 9—23).—If the field strength of a cation be defined as  $z/a^2$  (z = valency, a = cation-anion distance), the cations which

are important in glass technology can be usefully arranged in a series of increasing  $z/a^2$ , viz., K (=0·13) < Na < Li < Ba < Pb < Sr < Ca < Mn < Fe<sup>II</sup> < Zn < Mg < Zr < Be < Fe<sup>III</sup> < Al < Ti < B < Si < P (=2·1). The relation between  $z/a^2$  and the tendency to devitrification is discussed. Large differences between  $z/a^2$  for the foreign cation and  $z/a^2$  for Si<sup>III</sup>, B<sup>III</sup>, or P<sup>IIII</sup> make for stable binary systems. Ternary systems are possible where  $\Delta z/a^2$  for the two primary cations is >0·05. Where  $\Delta z/a^2$  is <0·05 eutectics or mixed crystals are formed. The val. of  $\Delta z/a^2$  affords an indication of whether ternary compounds are likely; e.g., they would not be expected in the system Li<sub>2</sub>O-BaO-SiO<sub>2</sub> where  $\Delta z/a^2$ LIBa = 0·015; on the other hand they would be expected in the system Li<sub>2</sub>O-K<sub>2</sub>O-SiO<sub>2</sub> where  $\Delta z/a^2$ LIB = 0·10. The greater is the val. of  $\Delta z/a^2$ , the larger is the no. of possible ternary systems. The greatest degree of combination  $(y_{\text{max}})$  of a metallic oxide with SiO<sub>2</sub> (no. of mols of SiO<sub>2</sub> per 1/n mol. of  $R_m$ O<sub>n</sub>) can be represented by  $y_{\text{max}} = (0·36a^2/z) + C$ . If  $C \sim 0$  the compound melts congruently; if C = 0·3 - 0·5 it melts incongruently. With the exception of K, which ought to form K<sub>2</sub>O<sub>3</sub>SiO<sub>2</sub>, the binary systems examined conform to the requirements of the formula. The formula is applicable to ternary systems, the  $y_{\text{max}}$  vals. for each cation being added together. The relation between  $y_{\text{max}}$  and m,p. is discussed. C. R. H.

Magnesium and its alloys.—See B., 1942, I, 272.

Solubility of aluminium in mercury. W. Klemm and P. Weiss (Z. anorg. Chem., 1940, 245, 285—287).—The solubility of Al in Hg at 422—595° has been redetermined. The results confirm those of Smits and de Gruyter (A., 1921, ii, 371) and indicate that ocompound is formed but that Hg and Al form a eutectic system with eutectic composition of very low Al content.

J. W. S.

Effect of small iron and silicon contents on the magnetic susceptibility of aluminium. P. Weiss and W. Klemm (Z. anorg. Chem., 1940, 245, 288—294).—The magnetic susceptibility ( $\chi$ ) of Al is increased only slightly when the Fe content is increased from 0·11 to 3·22%, so determination of the Fe content from  $\chi$  determination is impossible. For the Al-rich limit of the  $\theta$  (FeAl<sub>3</sub>) phase  $\chi=+1$  × 10°, and the data obtained suggest that this phase extends to higher Al contents than hitherto believed. Increase in the Si content from 0·05 to 1·19% decreases the  $\chi$  of Al very slightly.

Ternary alloy system: aluminium-lead-silver. A. N. Campbell, L. Yaffe, W. G. Wallace, and R. W. Ashley (Canad. J. Res., 1941, 19, B, 212—230).—The system has been studied by thermal analysis followed by chemical analysis of the separated layers. The region of partial miscibility extends from the binary system Al-Pb to alloys containing \$85.58% of Ag and 4.71% of Pb. No ternary compounds are formed and the ternary eutectic almost coincides with the eutectic of the system Ag-Pb.

J. W. S.

Solubility of a hydrogen-nitrogen mixture in liquid carbon dioxide. I. A. Abdulaev (J. Appl. Chem. Russ., 1941, 14, 302—304).—The solubility of a  $3H_2+N_2$  mixture (I) was investigated at 0°, 10°, and 20° and at pressures varying from 20 to 203 atm. The solubility of (I) in liquid  $CO_2$  rises with increasing temp. at const. pressure and with increasing pressure at const. temp. N. G.

Solubility of carbon disulphide vapour in body fluids and tissues.—See A., 1942, III, 417.

Solubility of stannous oxide in perchloric acid. M. Gorman and P. A. Leighton (J. Amer. Chem. Soc., 1942, **64**, 719—720).—The solubility of SnO in  $HClO_4$  is the same as in HCl for conens. up to 0.04M-acid and 0.017M-Sn<sup>II</sup>. W. R. A.

Distribution of benzoic acid between water and benzene. F. T. Wall (J. Amer. Chem. Soc., 1942, 64, 472—473).—The distribution const.  $K_1 = C_W/C_B^{1/2}$  ( $C_W = \text{concn. of BzOH in } H_2\text{O}$ ;  $C_B = \text{concn. of BzOH in } C_8H_8$ ) is modified to  $K_2 = C_W(1-\alpha)/\sqrt{\{C_B(1-\beta)\}}$  where  $\alpha$  is the degree of ionisation of BzOH and  $\beta$  is the degree of dissociation of dimerides. This equation fits experimental data very satisfactorily.

W. R. A.

Adsorption of dihydroxybenzenes by sugar charcoal. Discontinuities in the adsorption of phenol, resorcinol, and quinol from aqueous solutions. K. D. Jain and J. B. Jha (J. Indian Chem. Soc., 1941, 18, 535—539; cf. A., 1941, I, 255).—Data are tabulated for the adsorption of PhOH, o-, m-, and p-cresol, m- and p-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub> on sugar C from aq. solutions. The cresols give regular curves, whilst the others show periodic max. and min.

F. L. U.

Reactions of solids. CXXV. Sintering phenomena in copper powders as revealed by their adsorptive power towards dissolved dyestuffs. J. Hampel (Z. Elektrochem., 1942, 48, 82—84).—Max. adsorption by Cu powder of Congo-red from MeOH solutions and of eosin, methylene-blue, and rhodamine from aq. solutions takes place at ~200°. As temp. increases above 200° adsorption decreases fairly regularly except for a period of const. adsorption at ~400—500°. Below 200° adsorption is more irregular, with a tendency towards min. adsorption at 100—150° which is very pronounced in the case of eosin. The data are discussed on the basis of Hüttig's theory. The adsorption is divided into six ranges corresponding with alternate activation and deactivation with rise of temp, as a

result of changes in mol. grouping on the Cu surface at lower temp. and in the crystal interior at higher temp. C. R. H.

Reproducible contact angles on reproducible metal surfaces. I. Contact angles of water against silver and gold. F. E. Bartell and P. H. Cardwell (J. Amer. Chem. Soc., 1942, 64, 494—497).—Solid surfaces with reproducible properties have been prepared by vaporising the solid in a vac., condensing the vapours as a film on a supporting medium, and by controlling adsorption. The max. advancing H<sub>2</sub>O contact angle was 95±0.5° for Ag and 92.5±0.5° for Au and the corresponding max. receding angles were 38±1° and 34±1°. Adsorption of air on the surfaces made them more hydrophobic and relatively large max. advancing angles were obtained. W. R. A.

Direct measurement of the spreading pressures of volatile organic liquids on water. L. F. Transue, E. R. Washburn, and F. H. Kahler (J. Amer. Chem. Soc., 1942, 64, 274—276).—Using a modification of the direct method (A., 1940, I, 356) the spreading pressures of iso-C<sub>5</sub>H<sub>11</sub>·OH, C<sub>6</sub>H<sub>8</sub>, PhMe, and COPhMe have been measured. Vals. of γ, interfacial tensions of the org. liquid-H<sub>2</sub>O interface, and spreading coeffs. have been measured for each liquid. W. R. A.

High-mol. wt. aliphatic amines and their salts. V. Soluble and insoluble films of the amine hydrochlorides. E. J. Hoffman, G. E. Boyd, and A. W. Ralston (J. Amer. Chem. Soc., 1942, 64, 498—503).—The variation of γ of solutions of C<sub>12</sub>H<sub>25</sub>·NH<sub>2</sub>,HCl with concn. has been investigated at various temp. by the ring method and at < the crit. concn. for micelle formation. Time effects of long duration were encountered. Insol. monolayers of C<sub>18</sub>H<sub>37</sub>·NH<sub>2</sub>.HCl on various sub-solutions become more expanded with increase in temp. and also with increase in the size of the anion. The behaviour of O-acid salts of C<sub>18</sub>H<sub>37</sub>·NH<sub>2</sub> has been studied. W. R. A.

Membrane permeability. III. Preferential ionic permeability of membranes of cupric ferrocyanide and of parchment. G. M. Willis (Trans. Faraday Soc., 1942, 38, 169—179).—E.m.f. of the cell S|electrolyte  $c_1$ |membrane|electrolyte  $c_2$ |S, in which S is a saturated Hg<sub>2</sub>Cl<sub>2</sub> electrode, were measured for different vals. of  $c_1$  and  $c_2$ , the ratio  $c_1/c_2$  being always 10. The apparent mobilities of anions in their K salts for membranes of  $\text{Cu}_2\text{Fe}(\text{CN})_6$  are in the order Br',  $\text{NO}_3' > \text{Cl'} > \text{I'} > \text{CNS'}$ ;  $\text{SO}_4'' > \text{Fe}(\text{CN})_6''''$  (=0), and are quite unrelated to their mobilities in free solution. This order is the same as for the adsorption of these ions, and it is inferred that the membrane potentials are largely determined by the adsorption. With parchment membranes the differences are less marked and the adsorption effects are smaller, but increase in valency reduces the apparent mobility of an ion, the more strongly and at a concn. that is the higher, the higher is the valency. F. L. U.

Derivation of laws of ideal dilute solutions. H. Gehlen (Z. Elektrochem., 1942, 48, 110—112).—Mathematical. Equations for the b.p. elevation, f.p. and v.p. lowering, and osmotic pressure of dil. solutions have been derived from a consideration of chemical potential.

C. R. H.

Derivation and biological implications of the general membrane equilibrium equation.—See A., 1942, III, 416.

Germicidal aërosols.—See A., 1942, III, 417.

Paraffin oil emulsions.—See B., 1942, III, 155.

Absorption of light by gold sols containing acacia gum and sodium chloride. R. V. Lloyd and D. P. Evans (Trans. Faraday Soc., 1942, 38, 179—186).—A method is described for preparing a standard red Au sol suitable for measurements of light absorption. Such a standard sol can be used to determine with accuracy the efficiency of different protective agents, by measuring the % absorption of red light (for which the observed changes are greatest) by sols 0.083N. in NaCl and containing varying amounts of protective. At a certain crit. concn. of protective the sols break and Au is pptd., and at this same point the curves connecting % light absorption with protective concn. exhibit a break the position of which can be determined with an exactness that increases with the duration of the experiment. This method provides a means of drawing finer distinctions between closely similar protectives than is possible by Zsigmondy's "Au no." method. F. L. U.

Gold sol. II. Chain formation in alternating electric field. H. R. Kruyt and J. G. Vogel (Kolloid-Z., 1941, 95, 2—20).—The formation in a Au sol of chains of particles by the action of an alternating field (cf. Pauli and Russer, A., 1932, 225; 1935, 1073) has been confirmed by the ultramicroscope. Accompanying changes in the electrical conductivity ( $\kappa$ ) of the sol are satisfactorily accounted for by the occurrence of metallic conduction along the chains. Such changes, which may amount to a 25-fold increase in  $\kappa$ , can be prevented by decreasing the voltage, increasing the separation of the electrodes, or stirring. Chain formation is best seen in sols of the noble metals, and as a rule does not occur in hydrophobic sols of non-metallic substances. It is favoured by high dispersity, high particle concn., low concn. of intermicellar electrolyte, high potential gradient, and high frequency. The chains tend to set along the lines of force, and are usually branched; they break up spon-

taneously in the absence of an electric field. The phenomenon is attributed to incipient coagulation starting in the immediate neighbourhood of the electrodes.

F. L. U.

Effect of autoclave treatment on the condition of hydroxides of beryllium, magnesium, and aluminium. T. Katsurai and T. Kita (Kolloid-Z., 1941, 95, 41—43).—Aq. suspensions of Be(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> free from alkali but containing some Cl' do not form sols when heated in an autoclave for 2 hr. at 190°, and the structure of the particles remains amorphous. Under similar conditions 0·1N-BeCl<sub>2</sub> is hydrolysed and forms a stable sol. An aq. suspension of Al(OH)<sub>3</sub> heated for 1 hr. at 190° gives a very stable sol, the properties of which are described.

Hydrous cupric hydroxide and basic cupric sulphates. H. B. Weiser, W. O. Milligan, and E. L. Cook (J. Amer. Chem. Soc., 1942, 64, 503—508).—The data from X-ray diffraction and from isothermal and isobaric dehydration indicate that Cu(OH)₂ is the only compound formed by the system CuO-H₂O. Spontaneous decomposible Cu(OH)₂ gel to brownish-black CuO is accelerated by dilalkali and is much more rapid than the decomp. of large crystals of Cu(OH)₂. If the ratio of equivs. of CuSO₄ (0·1—1·0n.) to alkali (0·1—1·0n.) in a mixture is ≡1 blue Cu(OH)₂ is formed; if ≡1·3, 4CuO,SO₂,3H₂O (I) is formed; if 1·25, 5CuO,SO₂,xH₂O (II) is obtained; if from 1 to 1·25, Cu(OH)₂ or CuO and (II) are co-pptd.; and if 1·25—1·33, mixtures of (I) and (II) are given. The identity of (II) has been established by X-ray diffraction data, by electrometric titration, and by analysis. In presence of low concess, of heavy metal sulphates Cu(OH)₂ is converted to (II) and is not stabilised. W. R. A.

Equilibria and changes in metal hydroxide sols. H. Bassett and R. G. Durrant (J.C.S., 1942, 277—303).—Hydroxide sols of Al, Cr, Fe<sup>III</sup>, La, Nd, and Th have been investigated to determine the nature of the stabilising ions, the way they are attached to the micelles, and the cause of the ageing of sols. In all cases Cl' was the contra ion. NaPO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> were the principal coagulants, and conditions under which they are suitable for determining H' and metal ion (M') concn. in sols. have been developed and are discussed. The majority of the MOH sols appear to be emulsions, the second liquid phase having [MOH] so high that it constitutes a viscous "glass" with or without a cryst. core. The micellar charge is due to peptising cations adsorbed at the "glass" surface, in equilibrium with similar ions which are free in the intermicellar liquid. Some cations, accompanied by an equiv. no. of anions, will pass into solution in the "glass." If these are M' there will be a tendency for co-ordinated H<sub>2</sub>O to be replaced by co-ordinated MOH, resulting in the formation of very basic cations. If sufficient peptising cation is available the MOH may be converted into a basic salt which may continue as a sol, pass into true solution, or crystallise. An example of this last has been furnished by the separation of cryst.  $3Th(OH)_4$ ,  $ThCl_4$ ,  $10H_2O$ (probably [Th(Th(OH)4)3]Cl,10H2O) from Th(OH)4 sol after 6 years, and there are indications that basic chlorides of La and Nd will crystallise from sols. Ageing of sols is attributed to one of four causes: (i) micelle coalescence with liberation of adsorbed cations, (ii) dehydration of the MOH constituent of the micelles, (iii) MOH crystallisation, and (iv) crystallisation of the "glass" as a basic salt or its passage into true solution. A no. of cryst. basic Alsulphates have been prepared and formulæ ascribed to four of them, viz.,

[Al(Al(OH) $_3$ {\_1]2[SO\_4]3[H\_2O]\_{17} or 18. [Al(OH){Al(OH) $_3$ }3]Al{Al(OH) $_3$ }4]\_2[SO\_4]7[H\_2O]\_{32} or 33. [Al(H\_2O){Al(OH)}\_3]3[Al{Al(OH)}\_3]3[SO\_4]3[H\_2O]\_{20-5} or 31. [Al(H\_2O){Al(OH)}\_3]3[SO\_4]3[H\_2O]\_{20-5} or 31. [Al(H\_2O){Al(OH)}\_3]3[SO\_4]3. C. R. H.

Dialysis in the study of colloids. VIII. Colloidal ceric hydroxide. V. C. Vora, P. M. Barve, and B. N. Desai (J. Univ. Bombay, 1941, 10, Part 3, 40—47).—The effects of dialysis, dilution, ageing, and exposure to sunlight on the cataphoretic speed, stability, conductivity, and viscosity of Ce(OH)<sub>4</sub> sol are recorded. F. J. G.

Viscosity and mol. wt. of chain polymerides. K. H. Meyer (Kolloid-Z., 1941, 95, 70—74).—Viscosity data for different classes of macromol, substances are reviewed, and it is shown that for unbranched chain polymerides the quotient  $\eta_{sp}/cM$  is not const. but decreases with increasing mol. wt. (M). Staudinger's "viscosity rule" cannot therefore give information about the form of dissolved mols., but is useful for obtaining the mol. wt. of a member of a series of chain polymerides by interpolation. F. L. U.

Relation between viscosity and temperature for cresol solutions of aniline-formaldehyde resins. W. Scheele, L. Steinke, and I. Avisiers (Kolloid-Z., 1941, 95, 74—81).—Data are recorded for the variation of  $\eta$  with temp, over the range  $40-90^\circ$  for cresol solutions of various NH<sub>2</sub>Ph-CH<sub>2</sub>O resins at different concns. The results can be represented with considerable accuracy by  $1/\eta = Ae^{-\epsilon/kT}$ , and the consts. A and  $\epsilon$  are, for a given material, linear functions of the concn. The straight lines obtained by plotting  $\log 1/\eta$  against 1/T for different concns, intersect at a common point corresponding with vals. of  $\eta$  and T the significance of which is discussed. F. L. U.

Viscosities of solutions of polyvinyl chloride. D. J. Mead [with R. M. Fuoss] (J. Amer. Chem. Soc., 1942, 64, 277—282).—Vals. of  $\eta$  for several polyvinyl chloride (I) samples, fractionated and poly-

disperse, have been obtained as a function of concn., temp., rate o shear, and solvent. The equiv.  $\eta \propto \text{concn.}$ , does not vary much with solvent [PhNO<sub>2</sub>, mesityl oxide, cyclohexanone (II), and COMe·C<sub>8</sub>H<sub>11</sub>], and decreases slightly with rising temp. Increase in pressure causes a decrease in the val. of abs.  $\eta$  of solutions of (I) and this effect must be eliminated by extrapolation to zero pressure or by an empirical correction formula. An empirical formula has been derived which permits determination of the limiting equiv.  $\eta$  for zero concn. from a single  $\eta$  measurement at a finite concn. of (I). A fractionated sample, having equiv.  $\eta$  of 7.2 in (II) at 25°, has mol. wt. 102,000.

Cupri-ethylenediamine disperse viscosity of cellulose.—See B., 1942, II, 224.

Electrical properties of solids. XII. Plasticised polyvinyl chloride. D. J. Mead, R. L. Tichenor, and R. M. Fuoss (J. Amer. Chem. Soc., 1942, 64, 283—291).—Data at  $40^\circ$  and  $60^\circ$  at 60, 600, and 6000 cycles per sec. are given for polyvinyl chloride (I) plasticised with 8—30 wt.-% of 14 different plasticisers. Plasticisation causes separation of chain mols. by plasticiser mols. and is accompanied by a rapid decrease in micro- and macro-scopic coeffs, of friction. Concn. of plasticiser and loss factor have been connected empirically;  $\eta$  is inversely  $\alpha$  (relative concn.)  $^3$  or  $^4$ . The concn. of plasticiser required to produce a given internal  $\eta$  depends on the size and shape of the plasticiser mol.; long cylindrical mols, reduce  $\eta$  > spherical mols, of the same mol. wt. Plasticisers of approx. the same size and shape are equally effective, irrespective of chemical structure, but with (I) plasticisers must contain a polar or polarisable group to ensure interaction with the polymeride. W. R. A.

Swelling and dissolution mechanism of xanthated sodium-cellulose fibres. IV. W. Schramek, U. Metzner, and E. Seidel (Z. physikal. Chem., 1941, B, 50, 298—304).—Whan xanthated Na-cellulose is dispersed in dil. NaOH the X-ray interference rings disappear although there is negligible conversion into the amorphous state. The results are compared with those obtained in similar experiments with regenerated cellulose and with natural fibres. C. R. H.

Calculation of protein-anion affinity constants from acid titration data. J. Steinhardt (J. Res. Nat. Bur. Stand., 1942, 28, 191—199; cf. B., 1941, II, 338).—A method based on the following postulated equilibria is described:  $WHA \rightleftharpoons WA^- + H^+; WA^- \rightleftharpoons W^{\pm} + A^-; WH^+ \rightleftharpoons W^{\pm} + H^+; WHA \rightleftharpoons WH^+ + A^-, where W^{\pm}, WH^+, etc. represent ionic states of wool in combination with a strong acid <math>HA$ . C. S. W.

Affinities of anions of strong acids for wool protein. J. Steinhardt, C. H. Fugitt, and M. Harris (J. Res. Nat. Bur. Stand., 1942, 28, 201—216; cf. B., 1941, II, 338).—Titration curves of 18 strong acids (H<sub>3</sub>PO<sub>4</sub>, HPO<sub>3</sub>, H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, H<sub>4</sub>SO<sub>4</sub>, NH<sub>2</sub>SO<sub>3</sub>H, o-OH·C<sub>6</sub>H<sub>4</sub>·SO<sub>3</sub>H, C<sub>1</sub>H<sub>12</sub>·SO<sub>3</sub>H, BuβSO<sub>3</sub>H, C<sub>12</sub>H<sub>25</sub>·SO<sub>3</sub>H, C<sub>12</sub>H<sub>25</sub>·O·SO<sub>3</sub>H, 2-C<sub>16</sub>H<sub>7</sub>·SO<sub>3</sub>H, C<sub>6</sub>H<sub>4</sub>Ph·SO<sub>3</sub>H, p-OH·C<sub>6</sub>H<sub>4</sub>·N·N·C<sub>6</sub>H<sub>4</sub>·SO<sub>3</sub>H-p', OH·C<sub>6</sub>H<sub>3</sub>(CO<sub>2</sub>H)·SO<sub>3</sub>H, anthraquinone-2-sulphonic acid, C<sub>10</sub>H<sub>6</sub>Prβ·SO<sub>3</sub>H, p-Ph·[C<sub>6</sub>H<sub>4</sub>]·SO<sub>3</sub>H, and the free colour acid of Orange II) are determined at 0°, 25°, or 50° by the methods previously described (B., 1940, 660; 1941, II, 77). From the data so obtained (after applying suitable corrections for effects of hydrolytic decomp.) and previously published results (B., 1941, II, 338), the affinities of the acid anions are calc. by the method of Steinhardt (see preceding abstract) and a pronounced tendency for the affinities of anions for wool to rise with increasing mol. wt. is revealed. The average heats of dissociation of several anion-wool complexes are tabulated. C. S. W.

Influence of shaking on the thixotropic sol-gel transformation. W. Heller and H. L. Roeder (Trans. Faraday Soc., 1942, 38, 191—194).—The difference between thixotropic and thixolabile systems is one of degree only, the latter being the more sensitive to mechanical coagulation. Shaking of thixotropic systems for periods varying from a few min. to a few hr. causes an increase in the setting time, examples of which are given for sols of  $V_2O_5$  and of Fe<sub>2</sub>O<sub>3</sub>; the change is attributed to partial mechanical coagulation. The formation of strongly anisometric aggregates by shaking does not result in rheopexy but in an increase in setting time. F. L. U.

Kinetics of sol-gel transformation. V. Influence of different coagulating electrolytes on the setting of ferric phosphate gel. H. L. Dube and S. Prakash (Proc. Indian Acad. Sci., 1941, 14, A, 577—583; cf. A., 1940, I, 321).—The influence of coagulating ions on the setting of FePO<sub>4</sub> gels has been studied by consideration of the variation in vals. of p, the gel characteristic, and R, the rate const., in the equation  $\log S = \log R + p \log C$ . With 'uni-univalent (KCl, KBr, KNO<sub>3</sub>) and multi-univalent (MgCl<sub>2</sub>, CaCl<sub>2</sub>, BaCl<sub>2</sub>) electrolytes neither changes markedly, but with uni-multivalent electrolytes [K<sub>2</sub>SO<sub>4</sub>, K<sub>3</sub>Fe(CN)<sub>6</sub>, and K citrate] marked variations, consistent with Whetham's law, are observed. W. R. A.

Factors influencing flocculation and precipitation. Influence of initial particle size. E. M. Beavers, J. E. Magoffin, and F. K. Cameron (Text. Res., 1941, 11, 139—153).—The rate of settling of 1% bentonite sols, approx. uniform in particle size, after flocculation with  $H_2\mathrm{SO}_4$  has been determined. The data fit the equation  $\log (1-a) = A \log t + D$ , where a is the fraction settling in time t,

and A and D are consts., which is developed from the assumption that the flocs intermesh and are compressed by their own wt., thus affording progressively increased resistance to settling. The initial particle size affects the form of the flocs and hence their rate of settling, the change in the charge, and the absorption of acid; the acid causes floc formation, which promotes settling, but at higher conens. may affect their shape so as to retard settling, and a max. efficiency of pptn. is observed between 0-0117 and 0-0230N.

Rhythmic precipitation of silver chloride in gelatin tanned with chromium chloride. C. S. Narwaini and G. T. Gursahani (J. Indian Chem. Soc., 1941, 18, 531—534).—Liesegang rings of AgCl are obtained when AgNO<sub>3</sub> diffuses into gelatin that has been tanned with CrCl<sub>3</sub> of such concn. that all the available Cl is combined with the gelatin. The effect of varying the conen. of gelatin, CrCl<sub>3</sub>, and AgNO<sub>3</sub> on the character of the rings is described. F. L. U.

Silica and the Liesegang phenomenon. A. C. Copisarow and M. Copisarow (Nature, 1942, 149, 413).—Aq. commercial waterglass (1: b by vol.) covered with conc. HCl at 17° immediately gives a fine network structure which soon becomes a translucent membrane at the interface. White horizontal bands then gradually extend below the membrane and tend to arrange themselves in groups. With more dil. Na<sub>2</sub>SiO<sub>2</sub> the reaction was quicker and the bands were more closely packed. Anomalies attended the substitution of SO<sub>2</sub> or H<sub>2</sub>SO<sub>4</sub> for HCl. The interfacial membrane was never distorted by protuberances etc.

A. A. E.

Electrophoresis of mixtures of ovalbumin and yeast-nucleic acid.— See A., 1942, III, 487.

#### VI.—KINETIC THEORY. THERMODYNAMICS.

Improved values for the equilibrium constants and degrees of dissociation for certain important gas equilibria. H. Zeise (Z. Elektrochem., 1942, 48, 23—26).—New vals, for the energy change, equilibrium const., and degree of dissociation for the reactions  $H_2O \rightarrow 0.5H_2 + OH$  and  $OH \rightarrow O + H$  have been calc. on the basis of Dwyer's val. for the energy change in  $H_2O \rightarrow H + OH$  (cf. Physical Rev., 1941, [ii], 59, 928). C. R. H.

Gas equilibrium  $C_2H_4 \rightleftharpoons C_2H_4 + H_2$ . H. Zeise (Z. Elektrochem., 1942, 48, 30.432).—The author claims to have anticipated Guggenheim (cf. A., 1941, I, 113) in his method of calculating the equilibrium const. for the decomp. of  $C_2H_4$  (cf. A., 1940, I, 321). New vals. calc. on the basis of more accurate data agree more closely with Guggenheim's vals. than did the earlier vals.

C. R. H.

Lead citrate complex ion.—See A., 1942, III, 412.

Spectroscopic investigation of the association of ferric ions with chloride, bromide, and hydroxyl ions. E. Rabinowitch and W. H. Stockmayer (J. Amer. Chem. Soc., 1942, 64, 335—347).—Absorption curves for Fe(ClO<sub>4</sub>)<sub>3</sub> solutions in the presence of different amounts of OH', Cl', and Br' ions have been determined at different temp, and ionic strengths ( $\mu$ ). Curves for the Fe(ClO<sub>4</sub>)<sub>3</sub>-HClO<sub>4</sub> system have been analysed and the absorption curve of free (hydrated) Fe'' ions separated from that of Fe(OH)'' ions. Similarly absorption curves for solutions containing HCl or HBr have been analysed and show successive association steps. Curves for FeCl', FeCl<sub>2</sub>', FeCl<sub>3</sub>, and FeBr'' (all yellow) have been derived. FeCl<sub>4</sub>' ions exist only in very conc. solutions. Equilibrium consts. for the formation of FeCl', FeCl<sub>3</sub>, and FeBr'' at  $\mu = 1$  have been derived and the distribution of FeIII between several ionic species at different chloride concns, has been calc. The heats and entropies of formation of (FeOH)", (FeCl)", and (FeBr)" ions have been evaluated.

Many-acid problem. K. J. Mysels (J. Chem. Educ., 1941, 18, 478—479).—A method for calculating the degree of neutralisation of a mixture of aq. acids when  $p_{\rm H}$  is known is given. L. S. T.

Glass electrode measurements of the  $p_{\rm H}$  of chromic acid solutions. W. H. Hartford (Ind. Eng. Chem. [Anal.], 1942, 14, 174—176).— Except for a small variation with temp. in dil. solutions, the effect of temp., purity of acid, and  ${\rm H_2O}$  on the  $p_{\rm H}$  of aq.  ${\rm CrO_3}$  is negligible. Variations in the measurements occur with different types of instrument at  $p_{\rm H}$  vals. <2; much of this discrepancy is due to liquid junction potentials. Each instrument gives consistent readings, and can be used for control purposes. L. S. T.

Thermodynamics of aqueous solutions of potassium chloride at temperatures from 15° to 45° from e.m.f. measurements on cells with transference. W. J. Hornibrook, G. J. Janz, and A. R. Gordon (J. Amer. Chem. Soc., 1942, 64, 513—516).—Activity and osmotic coeffs, obtained from e.m.f. measurements on the cell Ag, AgCl | KCl(m<sub>1</sub>)|KCl(m<sub>2</sub>)|AgCl,Ag at conens, up to 0·1m. and 10° intervals from 15° to 45°, agree well with recorded vals. W. R. A.

Activity coefficients of rubidium and cæsium sulphates in aqueous solution at 25°. H. H. Cudd and W. A. Felsing (J. Amer. Chem. Soc., 1942, 64, 550—551).—Isopiestic ratios for Na<sub>2</sub>SO<sub>4</sub>-Rb<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>-Cs<sub>2</sub>SO<sub>4</sub> have been determined for aq. solutions (~0-4—1-8M.). The activity coeffs of Rb<sub>2</sub>SO<sub>4</sub> and Cs<sub>2</sub>SO<sub>4</sub> have been calc.

from the observed molalities and ratios by comparison with those of Na<sub>2</sub>SO<sub>4</sub>. W. R. A.

Activity coefficients of strontium chloride by an isopiestic method. B. A. Phillips and G. M. Watson [with W. A. Felsing] (J. Amer. Chem. Soc., 1942, 64, 244—247).—Activity coeffs. of aq. SrCl. (0-05—1-30м.) have been determined by an improved isopiestic method using BaCl. as the reference standard. W. R. A.

Phase-rule experiments with organic compounds. C. M. Mason, B. W. Rosen, and R. M. Swift (J. Chem. Educ., 1941, 18, 473—474). L. S. T.

Binary halide systems. I. System sodium chloride—magnesium chloride. W. Klemm and P. Weiss (Z. anorg. Chem., 1940, 245, 279—284).—Thermal and X-ray analysis shows the existence of the compounds NaCl,MgCl<sub>2</sub> and 2NaCl,MgCl<sub>2</sub>, each with incongruent m.p. The tendency to form compounds with the corresponding Mg halide increases from Li to K halides and from bromides to fluorides.

System ferric chloride—sodium chloride. H. F. Johnstone, H. C. Weingartner, and W. E. Winsche (J. Amer. Chem. Soc., 1942, 64, 241—244).—FeCl<sub>3</sub> and NaCl do not form a compound but form a eutectic (44 mol.-%, NaCl, m.p. 158°). The v.p. of FeCl<sub>3</sub> and of 3 mixtures with NaCl have been determined by a static method. The low v.p. of FeCl<sub>3</sub> in the presence of NaCl at temp. > the b.p. of pure FeCl<sub>3</sub> is due to NaCl (solute) lowering the v.p. Thus, the possibility of volatilising FeCl<sub>3</sub> during chlorination of ores in the presence of excess of NaCl is prevented.

Vapour-liquid equilibria of the system acetone-acetic acid-water. R. York, jun., and R. C. Holmes (Ind. Eng. Chem., 1942, 34, 345—350).—The vapour-liquid equilibria at 760 mm. of the binary systems COMe<sub>2</sub>-H<sub>2</sub>O, COMe<sub>2</sub>-AcOH, and AcOH-H<sub>2</sub>O and of the ternary system COMe<sub>2</sub>-AcOH-H<sub>2</sub>O have been investigated, using a still of the pattern described by Scatchard et al. (A., 1938, I, 400) and utilising d and acidity measurements for analysis of the samples. The ternary system shows considerable deviations from Raoult's law.

J. W. S.

Determination of dineric distribution. W. D. Bancroft and S. S. Hubard (J. Amer. Chem. Soc., 1942, 64, 347—353).—In a system of three liquid components containing two immiscible components each consolute with the third, the composition of the conjugate phases may be conveniently determined, knowing the isothermal diagram for the system at the desired temp., by a graphical method which is described. The method has been applied to the systems  $C_6H_6$ —EtOH— $H_2$ O and CHCl3—COMe2— $H_2$ O, in which the distribution over the entire range of concn. can be expressed by equations of the mass law type which do not ignore increase in the mutual solubility of the slightly miscible liquids on addition of the consolute liquid.

Active substances. LI. Equilibria between  $\text{CO}_2\text{-CO}$  and Ni-NiO and between  $\text{CO}_2\text{-CO}$  and  $(\text{Ni} + \gamma\text{-Al}_2\text{O}_3)\text{-NiAl}_2\text{O}_4$ , and their influence on the physical state of the solid reactants. LII. Boudouard decomposition in the systems Ni-NiO and  $(\text{Ni} + \gamma\text{-Al}_2\text{O}_3)\text{-NiAl}_2\text{O}_4$ . R. Fricke and G. Weitbrecht (Z. Elektrochem., 1942, 48, 87-106, 106-110).—LI. The equilibria have been investigated over a range of temp., and the solid phases have been subjected to X-ray examination. Calculations of the surface energy of the solid phases have been made and applied to a discussion of the data which is concerned chiefly with the influence of particle size of the reactants on surface energy and with heats of reaction, especially of Ni-spinel (I) formation.

LII. The dissolution in Ni of C derived from the decomp. of CO has been examined. Ni obtained by reduction of NiO loses its dissolved C more slowly than does Ni from (I). This is due to the smaller particle size and greater surface activity of Ni from (I), and the consequent ease of diffusion of C through the Ni surface.

Thermodynamic constants of the dithionite (hyposulphite) ion. W. G. McMillan, jun., J. D. Roberts, and C. D. Coryell (J. Amer. Chem. Soc., 1942, 64, 398—399).—The molal heat content in dil. solution of the S<sub>2</sub>O<sub>4</sub>" ion is -178.7 kg.-cal. Re-examination of Jellinek's potentiometric data (A., 1911, ii, 365) gives -178.3 kg.-cal. for the heat content and -143.4 kg.-cal. for the free energy of the ion.

W. R. A.

#### VII.—ELECTROCHEMISTRY.

Conductances of aqueous solutions of lithium, sodium, and potassium hydroxides at 25°. L. S. Darken and H. F. Meier (J. Amer. Chem. Soc., 1942, 64, 621—623).—Vals. of  $\Lambda_0$  have been deduced from the conductances of aq. LiOH, NaOH, and KOH at 25°. At low concn. NaOH and KOH behave as typical strong electrolytes, whereas LiOH shows measurable deviation from complete ionisation.

W. R. A.

Anomalies in conductivity measurements in presence of hydrogen peroxide. M. Bobtelsky and A. E. Simchen (J. Amer. Chem. Soc., 1942, 64, 454—461).—In conductometric titrations in presence of  $H_2O_2$  additional resistances ( $\Delta R$ ) are encountered which reach a max. at small  $[H_2O_2]$  ( $\sim$ 0-02M.) and diminish on further addition of  $H_2O_2$ .

The variation of  $\Delta R_{\rm max}$ , with changes in electrolyte concn., nature of electrolyte, nature of electrodes, temp., stirring velocity, and a.c. frequency has been investigated. The effect depends mainly on  $[{\rm H}_2{\rm O}_2]$ , and on the chemical nature of the electrode (e.g., Sn > Pt) but not on its physical condition (bright Pt = grey platinised Pt). W. R. A.

Determination of the transference numbers of potassium iodide from the electromotive force of iodide-iodine gravity cells. S. W. Grinnell and F. O. Koenig (J. Amer. Chem. Soc., 1942, 64, 682—686).—Precise measurements with a special potentiometer (described) of the e.m.f. of gravity cells using the earth's field with the electrode Pt, KI (excess) + I give vals. for the transference no. of K' in agreement with the best modern vals.

W. R. A.

Standard potential of silver silver bromide electrode in anhydrous methanol at 25°. E. W. Kanning and A. W. Campbell (J. Amer. Chem. Soc., 1942, 64, 517—519).—The potential of the cell (Pt)H<sub>2</sub>| ·HBr, MeOH|AgBr, Ag has been measured at 25° over the concn. range 0.000474—0.0543m. On the molality basis the standard potential of the AgBr electrode in MeOH solution of HBr is -0.1328 v., and -0.1451 v. on the molarity basis. The val. of 1.42 for the const., A, as compared to the theoretical val. of 2.11, shows deviations from the Debye-Hückel limiting law for the solutions studied. W. R. A.

Physico-chemical studies with aqueous fluoride solutions. I. Decomposition and discharge potentials of fluorides in aqueous solution. H. Shrivastava (Proc. Indian Acad. Sci., 1941, 14, A, 535—546).—The decomp. potentials of aq. HF, LiF, NaF, KF, NH<sub>4</sub>F, KHF<sub>2</sub>, AgF, CdF<sub>2</sub>, and SbF<sub>3</sub> and the cathode and anode discharge potentials of aq. NH<sub>4</sub>F, KHF<sub>2</sub>, AgF, CdF<sub>2</sub>, and SbF<sub>3</sub> have been measured at 25° with polished Pt electrodes. Current-voltage curves of LiF, NaF, NH<sub>4</sub>F, KF, and KHF<sub>2</sub> have two breaks, one const. at 1.55±0.5 v. and the other at a higher potential which varies with the metallic ion and with concn. The SbF<sub>3</sub> curve has two breaks, each dependent on concn., but the curves for HF, AgF, and CdF<sub>2</sub> have only one break. Only the current-cathode potential curves for NH<sub>4</sub>F, KHF<sub>2</sub>, and SbF<sub>3</sub> have two breaks corresponding with the breaks in the current-voltage curves, all other current-cathode (anode) potential curves having only one break. It is concluded that alkali fluorides may have a true decomp, potential in aq. solution.

W. R. A.

Electrical activity of acetylcholine. R. Beutner and T. C. Barnes (Science, 1941, 94, 211—212).—Production of negative electrical potential by contact between very dil. solutions of acetylcholine and H<sub>2</sub>O-sol., lipin-like substances is demonstrated. E. R. R.

Preferential ionic permeability of membranes of cupric ferrocyanide and of parchment. [Membrane potentials.]—See A., 1942, I, 236.

Overvoltage. XI. Some unusual overvoltage phenomena. XII. Long time charge and decay phenomena. A. L. Ferguson and H. Bandes (Trans. Electrochem. Soc., 1942, 81, Preprints 10 and 11, 105—122, 123—134).—XI. A resumé of the problems in electrolytic systems and a crit. survey of theories of overvoltage is given. An apparatus for obtaining a photographic record of the variations of the potential of a polarised electrode with time, or rates of polarisation, is described. This has been used to study the decay of polarisation and to measure the IR potential drop of both anodes and cathodes in 2N-H<sub>2</sub>SO<sub>4</sub>, and the effects of previous charge, c.d., time of charge, and rate of agitation have been investigated; charge and decay curves are given.

XII. Long-time charge and decay curves for anode, cathode, and

XII. Long-time charge and decay curves for anode, cathode, and total cell potentials when cells are polarised to different c.d. are given; the fundamental nature of the process appears distinctly different for anode and cathode. The importance of the discharge of ions at the electrodes even at the lowest applied potentials is emphasised, and breaks in both charge and discharge curves at ~1·23 v. and 1·58 v., the theoretical potential of the O<sub>2</sub>-H<sub>2</sub> cell and the observed decomp. potential of H<sub>2</sub>O respectively, have been found.

Structure of the anodic passive layer on zinc. K. Huber (Z. Elektrochem., 1942, 48, 26—29).—The passivity of Zn and in particular the colour changes which a Zn anode undergoes in NaOH solutions of various conens. are discussed. As [NaOH] increases the darkening of the anode is less pronounced when viewed by reflected light, although in diffused light the differences in colour are not so noticeable. At low [NaOH] amorphous Zn(OH), appears on the anode. The passive layer can be removed as thin scales after momentarily reversing the current so as to make the anode active again. The scales, which have a highly disperse structure, are doubly refractive. The structure of the layer as revealed by X-ray analysis is discussed.

C. R. H.

Electrode polarisation in dielectric constant measurements. W. G. Smiley and A. K. Smith (J. Amer. Chem. Soc., 1942, 64, 624—628).— The polarisation capacitance (r) of Pt electrodes in very dil.  $\mathrm{H}_2\mathrm{SO}_{\bullet}$ ,  $\mathrm{H}_2\mathrm{CO}_3$ , and NaCl, alone and with glycine, gelatin, and  $\mathrm{COMe}_2$ , has been measured by an apparatus which is described. An empirical equation connecting variation of r and frequency is advanced. r increases with decreasing  $p_\mathrm{H}$ . W. R. A.

Chemical polarisation in the precipitation of metals from and their dissolution in electrolytes. G. Masing (Z. Elektrochem., 1942, 48, 85–86).—Polarisation curves based on the equations of Le Blanc and Schick are shown to be of limited applicability. C. R: H.

Polarographic study of phthalic acid and phthalates. N. H. Furman and C. E. Bricker (J. Amer. Chem. Soc., 1942, 64, 660—668).—o-C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)<sub>2</sub> (I) and its salts have been investigated polarographically over the  $p_{\rm H}$  range l—8. The distribution of total phthalate between undissociated mols. and H phthalate and phthalate ions has been calc. Three reproducible polarographic waves due to phthalate are found in unbuffered solutions near  $p_{\rm H}$  4 with multivalent cations present. The no. and height of the waves depend on  $p_{\rm H}$  of the buffer, but in buffered solutions the height can be used for quant. measurements. Small successive additions of BaCl<sub>2</sub>, Ba(OAc)<sub>2</sub>, CaCl<sub>2</sub>, and LaCl<sub>3</sub> to well-buffered phthalate solutions at  $p_{\rm H}$  3-6 diminish the first wave systematically but not linearly. The amount of undissociated (I), derived from polarographic data, agrees with the theoretical distribution of the undissociated form as a function of  $p_{\rm H}$ . Approx. half-wave potentials for phthalate waves are given at various  $p_{\rm H}$  vals. The slopes of typical curves have been analysed. W. R. A.

Polarographic examination of water for surface-active substances. K. E. Schwarz, H. J. Schröder, and M. von Stackelberg (Z. Elektrochem., 1942, 48, 6—9).—The dependence of the height of the max of polarographic curves on the relative concns. of electrolyte and reducible substance is discussed and illustrated with data for KCl-O<sub>2</sub> solutions. Surface-active substances have a damping effect on the max. of such curves. A self-recording apparatus, involving a dropping Hg electrode, which makes use of this property and is suitable for determining impurities in H<sub>2</sub>O, is described. C. R. H.

#### VIII.—REACTIONS.

Rate equations for consecutive reactions. T. L. Hill (J. Amer. Chem. Soc., 1942, 64, 465—467).—Mathematical. Procedures for solving the system of the first-order differential equations corresponding with a set of consecutive or chain reactions are discussed. W. R. A.

Thermal reaction between hydrogen and oxygen at higher pressures. O. Oldenberg and H. S. Sommers, jun. (f. Chem. Physics, 1942, 10, 193; cf. A., 1941, I, 302).—A reply to Dainton (A., 1942, I, 101).

Limits of inflammability of acrylonitrile in air. G. W. Jones, R. E. Kennedy, and G. S. Scott (U.S. Bur. Mines, 1941, Rept. Invest. 3597, 1—6).—CH<sub>2</sub>:CH·CN (I) yields inflammable mixtures when air at 745—750 mm. pressure is saturated with its vapour between —6-25° and 29-4°. This temp, range corresponds with mixtures containing 3.05—17.0 vol.-% of (I).

Macromolecular compounds.

Macromolecular compounds. CCLXXV. Kinetics of charpolymerisations. XI. Polymerisation of methyl methacrylate. G. V. Schulz and F. Blaschke (Z. physikal. Chem., 1941, B, 50, 305—322).—
The rate of polymerisation of CH<sub>2</sub>:CMe·CO<sub>2</sub>Me is not influenced by the size of the reaction vessel or by the condition of the vessel walls. At 100° and in presence of air or O<sub>2</sub> the reaction is in two stages, a preliminary slow stage until 20—30% polymerisation has occurred followed by a very rapid stage. At 140° the progress of the reaction is more regular. At 100° there is an induction period which is absent at 140°. The induction period disappears at ~125°. It also disappears in presence of peroxides, suggesting that peroxide formation takes place during the induction period. The reaction is much slower in N<sub>2</sub> than in air or O<sub>2</sub>. A chain mechanism for the reaction is proposed.

Nuclear substitution of benzene derivatives.—See A., 1942, II, 220.

Kinetic study of acidolysis phenomena. A. Chablay (Compt. rend., 1941, 213, 242—244).—Investigations previously reported (cf. A., 1938, I, 522) are extended to the reversible reaction between RCO<sub>2</sub>H and heptoic and octoic acid. The vals. found for the const. k of the mass action law are 1.05 and 1.01, respectively. N. M. B.

Kinetics of the mutarotation of aminomethylene-d-camphor. B. K. Singh and S. C. Sen (Proc. Indian Acad. Sci., 1941, 14, A, 572—576).—Aminomethylene-d-camphor is converted into iminomethylene-d-camphor in glacial AcOH, measurably at 35° and rapidly at higher temp.; the reaction is of the first order. Mutarotation in 75—90% AcOH differs from mutarotation in glacial AcOH in that the initial rise in [a] is followed by a gradual fall, the extent of which varies with [AcOH]. In aq. AcOH the mutarotation is no longer of the first order.

W. R. A.

Mutarotation of glucose in water-methanol mixtures. H. E. Dyas and D. G. Hill (J. Amer. Chem. Soc., 1942, 64, 236—240).— The rate of mutarotation of glucose has been studied in  $\rm H_2O\text{-}MeOH$  mixtures (0—75% MeOH) at 20° and 29·2°; it changes in the directions to be predicted from the dielectric const. of the mixtures although not quite theoretically. Vals. of [a] of a- and  $\beta$ -glucose and of their solutions in the H<sub>2</sub>O-MeOH mixtures have been determined at 20° and 30°. Equilibrium consts. for the reaction are not

independent of temp. The heats of reaction and of activation change greatly and in parallel with [MeOH], with max. or min. in 60% MeOH. W. R. A.

Hydrolysis. Comparison of the saponification constants of the tolyl and methylcyclohexyl esters of fatty acids. B. E. Mirza and G. D. Advani (J. Univ. Bombay, 1941, 10, Part 3, 72—77).—Velocity coeffs, are recorded for the saponification by EtOH-KOH at 35° of tolyl and methylcyclohexyl esters of AcOH (I), EtCO<sub>2</sub>H (III), and PrCO<sub>2</sub>H (III). For a given acid, the coeff. for the methylcyclohexyl ester is always > that for the corresponding tolyl ester, the ratio being ~10 for p- and m-compounds, and 2—3 for o-compounds. For a given alcohol the ratios of the coeffs, for different acids are (I): (II), 2·8, and (II): (III), 1·6.

Kinetics of hydrolysis of carbamide and arginine. R. C. Warner (J. Biol. Chem., 1942, 142, 705—723).—Experiments at 35°, 66°, and 100° and at  $p_{\rm H} < 1$ —14.5 show that the products of hydrolysis of CO(NH<sub>2</sub>)<sub>2</sub> are NH<sub>3</sub> and HCNO, the reaction being reversible at  $p_{\rm H}$  vals. at which NH<sub>3</sub> is ionised. In acid solution, the rapid hydrolysis of HCNO limits the reversibility of the reaction. HCNO is hydrolysed to NH<sub>3</sub> and CO<sub>2</sub>, the rate of hydrolysis in alkaline solution being independent of  $p_{\rm H}$ . At  $p_{\rm H} < 9$ , the rate increases rapidly. The assumption that HCNO is the only intermediate in CO(NH<sub>2</sub>)<sub>2</sub> hydrolysis quantitatively accounts for the course of the transformation at all  $p_{\rm H}$ . Two simultaneous reactions of the first order with respect to arginine (I) conen., namely, production of NH<sub>3</sub> and citrulline and production of CO(NH<sub>2</sub>)<sub>2</sub> and ornithine, occur during hydrolysis of (I).

Kinetic study of the reactions of n-butyl bromide with the sodium salts of phenol, thiophenol, and n-butyl mercaptan. O. R. Quayle and E. E. Royals (J. Amer. Chem. Soc., 1942, 64, 226—230).—The order of reactivity with Bu^Br is NaSBu^S NaSPh > NaOPh under comparable conditions in MeOH and in EtoH. Rate constst decrease with increasing initial concn. of reactants. Neutral salts exert an effect similar in sign and magnitude to the initial concn. effect. The order of reactivity of NaSBu^S with Bu^Br in different solvents is EtOH > MeOH > C\_8H\_6. A mechanism involving an electron drift from the OR or SR group to the C atom is postulated. W. R. A.

Kinetics of the periodate oxidation of 1:2-glycols. II. Ethylene glycol, pinacol, and cis- and trans-cyclohexene glycols. C. C. Price and M. Knell (J. Amer. Chem. Soc., 1942, 64, 552—554; cf. A., 1939, I, 32).—k are recorded for oxidation of cis- (I) and trans-cyclohexene 1:2-glycol [slower than that of (I) or (CH<sub>2</sub>·OH)<sub>2</sub>] by  $H_5IO_6$  at initial  $p_H$  1—11·5. At initial  $p_H$  7·5—10 the  $p_H$  increases during the reaction. log  $k \propto p_H$ , with none of the irregularities shown by pinacol (loc cit.). The reaction mechanism (discussed) probably involves a cyclic diester of  $H_5IO_6$  formed by a double inversion. R. S. C.

Rate of oxidation of copper at room temperature. A. H. White and L. H. Germer (Trans. Electrochem. Soc., 1942, 81, Preprint 9, 91—104).—Electron diffraction technique is described. In O<sub>2</sub> (20 mm.) at room temp. and for time t > 2 min. the rate of reaction  $\alpha$  1/(t+c), where the const. c is  $\sim 0$  but must be finite. The complete oxidation law can be expressed by  $m/m_0 = 3W/(1+3W) = a+b\log_{10}(t+c)$ , where  $m_0$  is the original mass of Cu per unit area of film, m the mass of Cu per unit area in the Cu<sub>2</sub>O, W the ratio of the integrated intensities of the diffraction rings of Cu<sub>2</sub>O and Cu, and t is measured in min. (>2), a, b, and c being consts.; from this it is estimated that the local thickness, x, of the oxide film increases according to  $x = 4 + 6.5 \log_{10} t$  A., which predicts a limiting film thickness of  $\sim 50$  A.

Influence of electrolytes on ammonolysis by liquid ammonia. J. F. Lemons, P. M. Williamson, R. C. Anderson, and G. W. Watt (J. Amer. Chem. Soc., 1942, 64, 467—468).—The energy of activation for the ammonolysis of 1-chlorobenzthiazole is increased by addition of NH<sub>4</sub>Cl, NH<sub>4</sub>OBz, NH<sub>2</sub>·SO<sub>3</sub>NH<sub>4</sub>, NH<sub>2</sub>·CO<sub>2</sub>NH<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, NaCl, and KCl. Rates of reaction are not appreciably or regularly affected. W. R. A.

Halogen addition to ethylene derivatives. I. Bromine additions in presence of bromide ions. II. Mechanism of the halide ion-catalysed addition reaction. III. Bromine and iodine additions in glacial acetic acid. K. Nozaki and R. A. Ogg, jun. (J. Amer. Chem. Soc., 1942, 64, 697—704, 704—708, 709—716).—I. The equilibrium const. for the dissociation of KBr<sub>3</sub> in glacial AcOH has been determined at 30°, 50°, and 70°. The reaction between Br and maleic and fumaric acids has been studied in glacial AcOH. In presence of LiBr trans additive products are obtained. The reactions are sensitive to the concn. of proton donors and the ionic strength of the reaction between Br and CH<sub>2</sub>:CHBr in glacial AcOH is not affected by the concn. of proton donors or the ionic strength of the solution. LiBr and HBr catalyse the reaction of Br with CH<sub>2</sub>:CH-CH<sub>2</sub>CI (I) to the same extent but for the reaction between Br and CH<sub>2</sub>:CH-CH<sub>2</sub>·OAc (II) HBr is superior to LiBr.

II. The reaction between Br and CH, CHBr in presence of added LiCl in glacial AcOH solution conforms to d[Et]/dt = k[Br][Cl][Et].

The (I)-Br and (II)-I reactions are catalysed by OAc',  $NO_3$ ', and  $HSO_4$ ' ions as well as by halide ions. The most probable mechanism for the halide-ion-catalysed addition of halogen to  $C_2H_4$  derivatives is a termol. reaction between the  $C_2H_4$  derivative, halide ion, and halogen mol.

III. The reaction (a) between Br and (I) in glacial AcOH is complex, yields a mixture of products, and is greatly affected by small amounts of H<sub>2</sub>O but uninfluenced by O<sub>2</sub> or packed reaction vessels. The reactions between Br or I and (II) are similar to reaction (a) but the reaction between I and CH<sub>2</sub>:CH·CH<sub>2</sub>·OH is still more complex. The mechanisms for the reactions are discussed in terms of a complex rate expression.

W. R. A.

Kinetics of the hydrogen fluoride-catalysed reaction between toluene and tert.-butyl chloride. J. W. Sprauer and J. H. Simons (J. Amer. Chem. Soc., 1942, 64, 648—659).—The HF-catalysed reaction between PhMe and Bu<sup>p</sup>Cl is homogeneous and the rate is measurable at 25°. p-C<sub>8</sub>H<sub>4</sub>MeBu<sup>p</sup> is produced in quant. amounts. The reaction is of first order with respect to [Bu<sup>p</sup>Cl] and  $\propto p_{\text{HF}}^{5.5}$ . It is strongly promoted by H<sub>2</sub>O and MeOH, retarded by HCl, but unaffected by O<sub>2</sub>. Tentative mechanisms are advanced and one involving proton transfer or a mutual acid-base catalysis is favoured. W. R. A.

Catalytic action of nickel and copper-thorium in the formation of methane and heavy gases. A. van Itterbeek and W. van Dingenen (Z. physikal. Chem., 1941, B, 50, 341—360).—The adsorption of H<sub>2</sub>-CO mixtures by Ni foil has been determined at low pressures (<2 mm. Hg) and over a wide temp. range. At 167° and 329° H<sub>2</sub> and CO are adsorbed in the ratio 3:1 corresponding with CH<sub>4</sub> formation, and at 125° and 378° they are adsorbed in the ratio 2:1 corresponding with higher paraffin formation. The reaction rates also show max. at these temp. Cu adsorbs H<sub>2</sub> and to a smaller extent CO only if it contains traces of Th. At 250° and 325° H<sub>2</sub> and CO are adsorbed in the ratio 3:1. Similar experiments with D<sub>2</sub> are described. C. R. H.

Catalytic oxidation of ammonia to nitrous oxide in presence of oxides. W. Krauss and A. Neuhaus (Z. physikal. Chem., 1941, B, 50, 323—340).—NH<sub>3</sub>-air and NH<sub>3</sub>-O<sub>2</sub> mixtures were passed over heated oxides of Mn, Bi, Ba, Fe, and Ni, and the yields of N<sub>2</sub>O, NO, and N<sub>3</sub> were determined. On the basis of the results a reaction scheme is discussed in which NH<sub>3</sub> and O unite to form NH<sub>3</sub>O which then reacts with O to form HNO, with HNO to form N<sub>2</sub>, and with O<sub>2</sub> to form HNO<sub>2</sub> which either reacts with NH<sub>3</sub> to form N<sub>2</sub> or decomposes to NO. N<sub>2</sub>O is formed by the union of two HNO. C. R. H.

Zinc-nickel couple in the hydrogenation of organic compounds.— See A., 1942, II, 213.

Hydrogenation with Raney catalysts.—See A., 1942, II, 213.

Protection of ferrous metals by galvanic methods.—See B., 1942, I, 270.

Physical factors in electrodeposition of nickel on iron.—See B., 1942, I, 272.

Photochemical activity of mixtures of vanadic acid and tartaric acid. I. Optical properties of the mixtures. Their reduction in light and in the dark. II. Photocatalysis by colloidal micelle obtained by reduction of vanadic acid and tartaric acid mixtures. Induced optical activity by circularly polarised light. T. L. R. Char (J. Indian Chem. Soc., 1941, 18, 507—522, 563—572).—I. A solution of NaVO<sub>3</sub> to which tartaric acid (I) has been added exhibits an optical rotation opposite in sign to that of the acid used. The rotation of the mixture is diminished by addition of HCl or of (I) to an extent depending only on the  $p_{\rm H}$ . Addition of acid also causes the initial deep red colour to fade, finally to pale yellow, the extinction coeff. for blue light again depending only on the  $p_{\rm H}$ . The dispersed substance in these mixtures is represented by  $[xVO_3',y'][1,zH']$  (II). At  $p_{\rm H} < 4$  reduction of the VO<sub>3</sub>' in this complex occurs in the dark with a velocity that increases with decreasing  $p_{\rm H}$ . The velocity of the dark reaction is the same for d-l-, and an equimol, mixture of d- and l-(I), but a considerably greater velocity is found with racemic acid. In visible or ultraviolet light reduction of VV to VV occurs with the simultaneous formation of dihydroxytartaric acid. The photochemical reaction is small at low  $p_{\rm H}$  but can be conveniently studied at  $p_{\rm H} > 4$ , when the dark reaction does not occur. Velocity data are recorded for red, green, and ultra-violet light, and a reaction mechanism is proposed.

proposed.

II. If the colloid (II) is subjected to complete photochemical reduction to the VIV state the solution obtained is optically inactive and shows no circular dichroism in the visible region when i-(I) is used for the reduction, but is both optically active and circularly dichroic when d- or l-(I) is used. The micelle (III) formed by reduction with d-(I) shows positive rotation and negative ellipticity, and the converse is true for reduction with l-(I). Photo-reduction of persulphate by (I) is catalysed by (III), the velocity being the same whatever variety of (I) is used in its prep. If, however, the  $S_2O_8$ " reduction is carried out in d- or l-circularly polarised light, different velocities are observed according to whether d- or l-reduced

(III) is used as the catalyst. Finally, if the photo-reduction of  $S_2O_8''$  takes place in the presence of dl-reduced (III), the use for this purpose of d- or l-circularly polarised light leads to the production of l- or d-activity, respectively.

Photolysis of methyl acetate. W. L. Roth and G. K. Rollefson (J. Amer. Chem. Soc., 1942, 64, 490—494).—The Hg-sensitised and the non-sensitised photolyses of MeOAc yield Ac2, COMe2, MeOH, CO, CO2, CH4,  $C_2H_8$ , and  $H_2$ . By considering the relative proportions of the products the principal primary process is shown to be a splitting into Ac and OMe radicals, from which other products are formed in secondary reactions. W. R. A.

Production of radicals by the illumination of diacetyl with 4358 A. H. W. Anderson and G. K. Rollefson (J. Amer. Chem. Soc., 1942, 64, 717).—On illumination with 4358 A. an equimol. mixture of Ac<sub>2</sub> and MeCHO reacts at a measurable rate at 100° and seven times as rapidly at 150°, yielding CO, CH<sub>4</sub>, and a small amount of H<sub>2</sub> from decomp. of MeCHO. This indicates that Ac<sub>2</sub> is decomposed into radicals by 4358 A. and is in keeping with the previous result that photo-activated Ac<sub>2</sub> reacts with NO (A., 1941, I, 276).

Luminol light reactions. A. Steigmann (Chem. and Ind., 1941, 889—890).—Cu salts are better and more lasting catalysts for producing light with luminol (I) and H<sub>2</sub>O<sub>2</sub> than is hæmin, hæmoglobin, or blood; excess of (I) paralyses the catalyst and reduces the brightness of the glow and it is best to start the glow by adduces the Cu as (NH<sub>2</sub>·CH<sub>2</sub>·CO<sub>2</sub>)<sub>2</sub>Cu or by immersing a Cu wire in the solution of (I) rendered feebly alkaline by addition of NaBO<sub>3</sub> and NH<sub>4</sub>Cl. Methods of stopping and restarting the glow are described and the use of the reaction in detecting blood, Fe and Co complexes, and Cu is indicated.

A. R. P.

#### IX.—METHODS OF PREPARATION.

Separation of xenon isotopes by rectification. Triple point pressure of xenon. K. Clusius [with L. Staveley and G. Dickel] (Z. physikal. Chem., 1941, B, 50, 403—413).—The triple-point pressure of Xe is 612·2±0·2 mm. Hg at 161·36±03° k. Attempts to separate Xe isotopes by rectification were unsuccessful, although a sample of mixed isotopes was obtained which had an at. wt. ~0·1 > that of normal Xe.

Mechanism of chemical reactions: thermal decomposition of nitrites. K. M. Mehta (J. Univ. Bombay, 1941, 10, Part 3, 135—136).—The decomp. of KNO2 involves the reactions: (1) 2KNO2  $\rightleftharpoons$  K2O + NO2 + NO; (2) K2O + 2NO2  $\rightarrow$  KNO2 + KNO3; (3) KNO2 + NO2  $\rightleftharpoons$  KNO3 + NO; (4) KNO2 + NO  $\rightarrow$  KNO3 + 0.5N2; (5) KNO3  $\rightarrow$  KNO2 + 0.5O2. With AgNO3 the analogous reactions occur, with, in addition, Ag2O + NO  $\rightarrow$  2Ag + NO2, and Ag + 2NO2  $\rightarrow$  AgNO3 + NO.

Copper and nickel complex ions of diethylenetriamine. H. M. Haendler (J. Amer. Chem. Soc., 1942, 64, 686—688).—Vosburgh and Cooper's method of continuous variations (A., 1941, T, 220) is used to show formation of ions,  $[Cu^{II}X]^{++}$ ,  $[Cu^{II}X_2]^{++}$ ,  $[Ni^{II}X]^{++}$ , and  $[Ni^{II}X_2]^{++}$  in  $H_2O$ , X being  $NH([CH_2]_2\cdot NH_2)_2$ , which acts as a tridentate group. R. S. C.

Isomorphous replacement of the elements in alkali alkaline-earth phosphates. R. Klement and F. Steckenreiter (Z. avorg. Chem., 1940, 245, 236—253).—Na Sr, Na Ba, K Sr, and K Ba phosphates have been prepared by sintering stoicheiometric proportions of SrHPO4 or BaHPO4 with Na<sub>2</sub>CO<sub>3</sub> or K<sub>2</sub>CO<sub>3</sub> at 900°. Like NaCaPO4 they exist in high- and low-temp, forms. The P in the high-temp form of NaCaPO4 can be replaced by Si and S without change in the crystal structure but such replacement is possible only to a limited extent in KCaPO4. Silicocarnotite, Ca<sub>5</sub>P<sub>2</sub>SiO<sub>12</sub>, has a similar crystal structure to NaCaPO4.

Reaction between roasted kaolin and lime in aqueous solution. I. Activity of roasted kaolin. W. Strätling and H. zur Strassen. II. Reaction products in relation to the system lime-silica-aluminawater. H. zur Strassen and W. Strätling (Z. anorg. Chem., 1940, 245, 257—266, 267—278).—I. The absorption of Ca(OH)<sub>2</sub> by kaolin, both unheated and after heating at 400—1100°, has been investigated by shaking with aq. Ca(OH)<sub>2</sub> at 20°. The kaolin is most active after heating at 500—700°, when max. absorption [ $\sim$ 3 mols. of Ca(OH)<sub>2</sub> per mol. of Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>] is attained after 40 days. The heats of wetting of the kaolin in H<sub>2</sub>O and in aq. Ca(OH)<sub>2</sub> have been determined and it is shown that their difference, corresponding with the heat of adsorption of Ca(OH)<sub>2</sub>, is a max. for the most active samples. This behaviour is particularly marked when the heat of wetting per unit surface are is considered.

II. X-Ray investigations of the products of the interaction of roasted kaolin with aq. Ca(OH)<sub>2</sub>, made in comparison with the products of interaction of 3CaO,Al<sub>2</sub>O<sub>3</sub>, Ca(OH)<sub>2</sub>, and SiO<sub>3</sub> sol, indicate the presence of 3CaO,2SiO<sub>3</sub>,aq. and another solid probably 2CaO,Al<sub>2</sub>O<sub>3</sub>,SiO<sub>3</sub>,aq. (I). (I) is stable in contact with aq. Ca(OH)<sub>2</sub> but is decomposed at 250° or on hydrothermal treatment. Interaction of 3CaO,2SiO<sub>2</sub>,aq. and 3CaO,Al<sub>2</sub>O<sub>3</sub> or CaO,Al<sub>2</sub>O<sub>3</sub>,aq. in aq.

media also yields (I).  $3CaO_{2}SiO_{2}$ , and  $3CaO_{3}SiO_{2}$  are also formed during the hydration of cement clinker. J. W. S.

Basic phosphates of bivalent metals. V. Cadmium phosphates and hydroxyapatite. R. Klement and F. Zureda (Z. anorg. Chem., 1940, 245, 229—235; cf. A., 1939, I, 622).—Attempts to prepare CdHPO<sub>4</sub> have been unsuccessful. Slow addition of aq. Na<sub>3</sub>PO<sub>4</sub> to cold aq. CdCl<sub>2</sub>, with const. stirring, yields  $Cd_3(PO_4)_2, \delta H_2O$ . X-Ray examination indicates that the product obtained by heating CdF<sub>2</sub> with Cd<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> (from sintering Cd<sub>2</sub>P<sub>2</sub>O<sub>7</sub> and CdCO<sub>3</sub>) is Cd fluorapatite, Cd<sub>10</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>2</sub> (I). The compounds Ca<sub>2</sub>Cd(PO<sub>4</sub>)<sub>3</sub>F<sub>2</sub>, Ca<sub>3</sub>Cd<sub>5</sub>(PO<sub>4</sub>)<sub>4</sub>F<sub>2</sub>, and CaCd<sub>2</sub>(PO<sub>4</sub>)<sub>6</sub>F<sub>2</sub> have also been prepared. When the product of treating aq. CdCl<sub>2</sub> with hot aq. Na<sub>3</sub>PO<sub>4</sub> is heated in H<sub>3</sub>O for several days at 100°, or when (I) is heated at 100° with N-NaOH, impure Cd<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> (II) is obtained. (II) is isomorphous with the corresponding Ca and Sr compounds and has a 9-01, c 6-61 A. It is inferred that, as may be predicted from its ionic radius, Cd lies on the border between apatite- and wagnerite-forming metals.

Base exchange of mercuric ions adsorbed on wool. C. S. Narwani and G. T. Gursahani (J. Indian Chem. Soc., 1941, 18, 527—530).— Hg absorbed by wool from solutions of HgCl<sub>2</sub> in 0·025n-Hcl is only partly chemically combined; the major part is adsorbed, and is exchangeable with cations in an external solution. The amount of Hg" exchanged with Na increases with concn. up to a max. at ~0·2n-NaCl. Data for the exchange with various salt solutions are tabulated.

F. L. U.

Stereochemistry. I. Steric strains as a factor in the relative stability of co-ordination compounds of boron. H. C. Brown, H. I. Schlesinger, and S. Z. Cardon (J. Amer. Chem. Soc., 1942, 64, 325—329).—NMe<sub>3</sub> forms more stable additive compounds than  $C_5H_5N$  with HCl, HBr, BH<sub>3</sub>, and BF<sub>3</sub> but a less stable compound with BMe<sub>3</sub>. Towards HCl 2:6-lutidine acts as a stronger base than  $C_5H_5N$ , whilst towards BF<sub>3</sub>  $C_5H_5N$  is the stronger. The reactions have been explained in terms of steric strains produced by steric hindrance of the groups about the co-ordinating central atom. The significance of the results on the concept of free rotation is discussed.

W. R. A.

Normal aluminium chromate. P. C. Raychoudhury (J. Indian Chem. Soc., 1941, 18, 573—575).—By triturating AlCl<sub>3</sub> with excess of Ag<sub>2</sub>CrO<sub>4</sub> and very little ice-cold H<sub>2</sub>O a brown solution is obtained which on evaporation in a vac. at a low temp. gives a solid in which Al<sub>2</sub>O<sub>3</sub>: CrO<sub>8</sub> = 1:3. Evaporation of a solution of the solid in AcOH to const. wt. in a refrigerator yields a substance, Al<sub>2</sub>(CrO<sub>4</sub>)<sub>3</sub>,5H<sub>2</sub>O. Data for the mol. conductivity and the  $p_H$  of solutions are recorded.

Polymerisation of derivatives of aluminium trimethyl.—See A., 1942, II, 240.

Periodates of tervalent metals. P. C. Raychoudhury (*J. Indian Chem. Soc.*, 1941, **18**, 576—578).—The following have been prepared:  $3Bi_2O_3,2I_2O_4,7H_2O$ ,  $AI_2O_3,I_2O_4,H_2O$ ,  $FeH_2IO_4,4H_2O$ ,  $2II_2O_3,I_2O_4,3H_2O$ ,  $Mn_3(IO_3)_2$  (decomp. >15°). Their properties are described. F. L. U.

Structure of hydrogen cyanide. C. R. McCrosky, F. W. Bergstrom, and G. Waitkins (J. Amer. Chem. Soc., 1942, 64, 722—724).— HCNS in PhMe at  $100-110^{\circ}$  or  $150-160^{\circ}$  gives  $C_2H_2N_2S_3$ . No reaction occurs between HCN and S, Se, or Te at room temp., or S or S-PhMe at  $100-120^{\circ}$  or  $150-160^{\circ}$ . HCN and S in  $H_2O$  at  $110-120^{\circ}$  or  $150-160^{\circ}$  give by hydrolysis  $HCO_2NH_4$  and  $NH_4CN$ , identified after further reaction as  $NH_4CNS$ . Thus  $\Rightarrow$  traces of HNC exist at  $25-160^{\circ}$ . Passage of HCN into dry  $C_5H_5N+S$  (absence of air) gives exothermally  $C_5H_5N$  thiocyanate, m.p.  $99\cdot5-101^{\circ}$ , and selenocyanate, m.p.  $76-78^{\circ}$  (decomp.), and quinoline thiocyanate, m.p.  $138-139^{\circ}$ , and selenocyanate, m.p.  $99\cdot5-100\cdot5^{\circ}$  (decomp.), are similarly prepared. Evaporation of aq. NH\_2Ph,HCNS gives  $NH_4\cdot CS\cdot NHPh$ , but  $NH_2\cdot CS\cdot NHPh$  is not obtained from  $NH_2Ph$ , HCN, and Se at  $100^{\circ}$ .  $(CH_2\cdot NH_2)_2$  reacts with S or Se to give impure products.

Evaporation of aqueous solutions of sodium cyanide. E. von Papp and J. Pogany (Angew. Chem., 1941, 54, 55).—Addition of 0.5% of Zn dust or 0.5% of NaHSO<sub>3</sub> prevented decomp. of aq. 4-5N-NaCN on evaporation. Na<sub>2</sub>CO<sub>3</sub> (>20%) had no, and EtOH and glycerol a slight, effect.

J. L. E.

Mechanism of the fission of hypophosphite; use of deuterium as indicator. W. Franke and J. Mönch (Annalen, 1941, 550, 1—31).— The action between NaH<sub>2</sub>PO<sub>2</sub> (I) and KOD in D<sub>2</sub>O is not stiable for investigating the mechanism of the fission of (I). In heterogeneous catalysis (Cu, Pd, Co, Ni) in neutral solution there is very little exchange at room temp. Evolution of gas occurs mainly in such a manner that half the H arises from (I) and the other half from the H<sub>2</sub>O or OH of (I), thus confirming Wieland's conception, O:PH<sub>2</sub>OH — 2H  $\rightarrow$  O:PH:O  $\rightarrow$  O:PH(OH)<sub>2</sub> or PH<sub>2</sub>(OH)<sub>3</sub>  $\rightarrow$  O:PH(OH)<sub>2</sub>, but not Bach's formulation, H<sub>3</sub>PO<sub>2</sub> + 2OH|H = H<sub>3</sub>PO<sub>3</sub> + H<sub>4</sub>O + H<sub>2</sub>. In addition there is a second reaction in which both H atoms attached to P are removed. The last reaction appears to be favoured by increase in the concn. of H<sub>3</sub>PO<sub>2</sub> and, probably, by the use of D<sub>2</sub>O. Evolution of gas from a solvent

containing a mixture of H isotopes is accompanied by extensive isotope separation but this effect is not appreciable with a partly heavy (I). The metal-catalysed fission of formate follows the lines of the main course of decomp. of H<sub>2</sub>PO<sub>2</sub>. NaD<sub>2</sub>PO<sub>2</sub> is most economically obtained from NaH<sub>2</sub>PO<sub>2</sub> and D<sub>2</sub>O in presence of 5-2N-D<sub>2</sub>SO<sub>4</sub> at 38°.

Behaviour of chromic bromide towards ether. F. Hein and H. Kraft (Z. anorg. Chem., 1940, 245, 334—340).—Thermal decomp. of [Cr(NH<sub>3</sub>)<sub>6</sub>]Br<sub>3</sub> at 300—415° occurs approx. according to the equation 10[Cr(NH<sub>3</sub>)<sub>6</sub>]Br<sub>3</sub>  $\rightarrow$  6NH<sub>4</sub>Br + N<sub>2</sub> + 52NH<sub>3</sub> + 4CrBr<sub>3</sub> + 6CrBr<sub>2</sub>. The residue of CrBr<sub>3</sub> and CrBr<sub>2</sub> on treatment with Et<sub>2</sub>O yields CrBr<sub>2</sub>OEt (cf. A., 1930, 1019). The residual CrBr<sub>3</sub> reacts very vigorously with H<sub>2</sub>O, MeOH, and EtOH with evolution of heat, indicating that it is the active modification (cf. Birk, Z. angew. Chem., 1928, 41, 32). With Et<sub>2</sub>O, however, it reacts no more vigorously than the ordinary modification.

J. W. S. Walley Land M. Walley L. Walley L. Walley Chem.

Metal carbonyls. XXXIII. Iron carbonyl iodide. XXXIV. Sysmetal carbonyls. AXXIII. If on carbonyl toduce. XXXIV. System-ferrous iodide-carbon monoxide. Course of the interaction of a gas with a solid. XXXV. Iridium carbonyl. W. Hieber and H. Lagally (Z. anorg. Chem., 1940, 245, 295—304, 305—320, 321—333).—XXXIII. Thermal decomp. of Fe(CO)<sub>4</sub>I<sub>2</sub> (I) in an inert gas at 200—400° yields principally FeI<sub>2</sub> and CO but also gives rise to Fe(CO)<sub>2</sub>I<sub>2</sub> (II) (especially in H<sub>2</sub>) and to Fe(CO)<sub>2</sub>I and FeI (especially in CO<sub>2</sub> and N<sub>2</sub>). (II) is also formed when (I) is heated at 80°, either alone or in a solvent (C. H. or cyclobevane) and on interaction of alone or in a solvent (C8H6 or cyclohexane) and on interaction of I with Fe(CO), The existence of the compounds containing only one I atom is attributed to the non-polar character of the Fe-I linkage and analogous compounds of other halogens are not to be

expected. XXXIV. Interaction of FeI<sub>2</sub> with CO at 18—20° to yield Fe(CO)<sub>4</sub>I<sub>2</sub> reaches equilibrium in 15 hr. at 120 atm. with 80% yield. The yield obtained varies linearly with  $\log p$  (p = pressure atm. This behaviour, apparently contrary to the phase rule, is

atm. This behaviour, apparently contrary to the phase rule, is attributed to surface phenomena arising through the different mol. vols. of FeI<sub>2</sub> and Fe(CO)<sub>4</sub>I<sub>2</sub>. Tests on preps. obtained by treating FeI<sub>2</sub> in Et<sub>2</sub>O with CO under high pressure indicate that its decomp. pressure at room temp. is 6·1—6·3 atm.

XXXV. When dry IrCl<sub>3</sub>, IrBr<sub>3</sub>, or IrI<sub>3</sub> is heated with Cu or Ag in CO at 140°/350 atm. Ir tricarbonyl, Ir(CO)<sub>3</sub>, is formed as canary-yellow cubic crystals. Under similar conditions (NH<sub>4</sub>)<sub>2</sub>IrCl<sub>5</sub>, Na<sub>2</sub>IrCl<sub>5</sub>, and K<sub>2</sub>IrCl<sub>6</sub> yield a mixture of Ir(CO)<sub>3</sub> and Ir tetracarbonyl, Ir(CO)<sub>4</sub>, separable by utilising the slight solubility of Ir(CO)<sub>4</sub> in CCl<sub>4</sub>. When K<sub>2</sub>IrBr<sub>6</sub> is heated in CO at 125°/200 atm. and the product sublimed in CO, Ir tricarbonyl bromide, Ir(CO)<sub>3</sub>Br<sub>7</sub> is formed as brown scales. This suggests that the reactions all is formed as brown scales. This suggests that the reactions all proceed through the formation of carbonyl halides. Action of Cl<sub>2</sub> on Ir(CO)<sub>3</sub> at 200° yields crystals of the compound Ir<sub>3</sub>(CO)<sub>4</sub>Cl<sub>3</sub>. If moist IrCl<sub>3</sub> is heated in CO at high pressure a volatile compound is produced which when passed through a strongly heated tube deposits an Ir mirror, suggesting the presence of IrH(CO)4. The analogy between the Ir and Co compounds is discussed.

Periodic corrosion of iron in polyphase systems.—See B., 1942,

#### X.—ANALYSIS.

Spectrum analysis. Review of progress. W. Seith (Z. Elektro-C. R. H. chem., 1942, 48, 33-36).

Quantitative Raman spectral analysis. J. Goubeau and L. Thaler (Angew. Chem., 1941, 54, 26—27).—General methods of quant. analysis based on the Raman spectrum are described. In the first method, the difference in blackening of two lines is determined by a spectrophotometer. From this difference for a given pair of lines from mixtures of known composition, calibration curves are drawn, whence the composition of unknown mixtures can be determined. Investigation of the method with the system amylene hydrate-BuyOH indicates the existence of two systematic errors. The blackening difference depends not only on the concn. of substances in the mixture, but also on the time of illumination and on the continuous background. The method can, therefore, be used only when the calibration and analysis are carried out under the same conditions. The second method uses comparison of intensities; the effect of the continuous background is eliminated, and no systematic error occurs. The dependence of the intensity ratio on the concn. is discussed. The application of the method to ternary mixtures is considered.

Colorimetric analysis. O. H. Weber (Angew. Chem., 1941, 54. 56-57).—A survey of methods for the determination of dyes and inorg, compounds. J. L. E.

Action of indicators. L. G. S. Brooker (J. Chem. Educ., 1941, 18, 245—246; cf. A., 1941, I, 126).—Resonance mechanisms explaining the indicator action of Me-orange and the halochromism of 2-p-dimethylaminostyrylquinoline are suggested.

Horticultural applications of microchemical analysis.—See B., 1942, III, 147.

Chemical reactions in very dilute aqueous solutions. Z. Karaoglanov (Kolloid-Z., 1941, 95, 43—58).—Data are recorded showing the relation between sensitivity of pptn. and colour reactions of inorg. ions and quantity of reagent used, presence of foreign electrolytes, pH, solubility and physical condition of the ppt., fluorescence, opalescence, and other factors.

Mordant dyes and organic reagents for metals. G. N. Copley (Ind. Chem., 1941, 17, 307—309).—In both cases the substance must have an acidic H atom, usually present as OH, replaceable by a metal; this H must be capable of taking part in a 5- or 6-membered chelate ring, and if the ring contains double bonds these must be conjugated and resonance should be possible in the chelate rings.

Determination of bromides in presence of other halides. P. L. Kapur, M. R. Verma, and B. D. Khosla (Ind. Eng. Chem. [Anal.], 1942, 14, 157—158).—Br, liberated by aq. H<sub>2</sub>CrO<sub>4</sub> + HNO<sub>3</sub>, is extracted with CCl<sub>4</sub> and I liberated therewith from KI is titrated with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. I' is oxidised to IO<sub>3</sub>', and only excessive amounts of Cl' interfere. L. S. T.

Determination of bromides in presence of chlorides. M. Lane (Ind. Eng. Chem. [Anal.], 1942, 14, 149).—Free Br is liberated by addition of aq. Cl<sub>2</sub>, and the colour of the aq. solution measured photo-electrically.

Determination of iodine in periodates. R. K. Bahl, S. Singh, and N. K. Bali (J. Indian Chem. Soc., 1941, 18, 587—588).—I evolved by heating is titrated with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. Theoretical results are obtained for Ce, Y, and Cu periodates. F. L. U.

Determination of iodine in desiccated thyroid.—See B., 1942, III, 156.

Phosphate separation in qualitative analysis. J. Reilly and M. O'Brien (Sci. Proc. Roy. Dublin Soc., 1942, 22, 447—458).—The procedures recommended by Curtman (A., 1936, 951) and Pittmann (A., 1940, I, 444) have been tested critically and their disadvantages are enumerated. An amended technique is based on pptn. with NH<sub>4</sub>Cl and ZrOCl<sub>2</sub>. The slight excess of Zr is pptd, in group III and is separated with Fe but does not interfere with the detection of Fe. This procedure causes practically no loss of cations. I. W. S

Determination of hypophosphites by potassium permanganate, J. R. Pound (J.C.S., 1942, 307).—Hypophosphites are oxidised by KMnO<sub>4</sub> in dil. H<sub>2</sub>SO<sub>4</sub>, with a little KBr (catalytic action) at room temp.; after 2-3 hr., FeSO<sub>4</sub> is added and the excess titrated.

Colorimetric determination of phosphorus in soils.—See B., 1942, III, 145.

Determination of argon in oxygen-nitrogen mixtures. K. G. Zimmer (Angew. Chem., 1941, 54, 33-35).—A review of physical

Colorimetric determination of silver with 2-thio-5-keto-4-carbethoxy-1: 3-dihydropyrimidine. J. H. Yoe and L. G. Overholser (Ind. Eng. Chem. [Anal.], 1942, 14, 148—149).—This compound (I) (Ind. Eng. Chem. [Anal.], 1942, 14, 148—149).—This compound (I) gives the following reactions in addition to those reported previously (A., 1936, 1000): in neutral solutions, Co", Mn", Ni", pink colours; Hg", pink ppt.; and Tl', blue ppt.; in aq. HNO<sub>3</sub>, Au" and Hg', pink ppts.; and Pd", a slight, red ppt.; in HNO<sub>3</sub>—NaOAc buffer, Ag', purple colour and ppt.; Au" and Pd", orange colour and ppt.; Hg and Hg", pink colour and ppt. The purple compound with Ag' and (I) can be used for the colorimetric determination of Ag' (procedure described). Hg' and Hg' must be absent, and limiting concns. of other interfering ions are Co", 3-5 mg.; Cu", 1 mg.; Fe", 2 mg.; and Ni", 1-5 mg. SO<sub>4</sub>" and NH<sub>4</sub>" increase the intensity of colour. On the spot plate, the sensitivity is 0-25 µg. per 0-05 ml., and in aq. solution, 0-15 µg.

L. S. T. is  $0.25 \,\mu\text{g}$ . per  $0.05 \,\text{ml}$ ., and in aq. solution,  $0.15 \,\mu\text{g}$ .

Analysis of calcium carbonate.—See B., 1942, I, 262.

Analysis of solutions containing zinc hydroxide and sodium hydroxide. S. M. Mehta and M. B. Kabadi (J. Univ. Bombay, hydroxide. S. M. Menta and M. D. Asabada. 1941, 10, Part 3, 69—71).—The solution is treated with a known vol. of standard H<sub>2</sub>SO<sub>4</sub> and made up to a definite vol., Zn and excess of H<sub>2</sub>SO<sub>4</sub> being determined volumetrically [K<sub>4</sub>Fe(CN)<sub>6</sub>; aq. NH<sub>4</sub> + Me-red]. F. J. G.

Spectrochemical determination of lead, calcium, and zinc in dusts, fumes, and ores.—See B., 1942, I, 272.

Determination of copper in presence of iron. P. L. Kapur and Badar-ud-Din (*J. Indian Chem. Soc.*, 1941, **18**, 585—586).—The Cu is determined iodometrically after reduction of Fe<sup>III</sup> to Fe<sup>II</sup>. Since the oxidation of Fe<sup>III</sup> by I is reversible, any of the liberated I lost in this way is recovered towards the end of the final Na2S2O3

Photographic emulsions as specific reagents for traces of mercury and copper. A. Steigmann (J.S.C.I., 61, 51-52).-The fading of latent images on exposed emulsions in presence of traces of Hg" ions is used to detect 0.0015 µg. Hg as Hg". Aq. Na<sub>2</sub>SO<sub>3</sub> is added to prevent interference by Fe", Cu", and Ce". Traces of Cu in spots in photographic paper bases are detected by adding small amounts of SH·CH<sub>2</sub>·CO<sub>2</sub>H to the coating emulsion. After drying, exposure, and development the Cu spots appear white and may be verified as Cu by the use of rubeanic acid.

S. B.

Spectrochemical analysis of duralumin-type alloys.—See B., 1942,

Ceric sulphate in the determination of iron using the molybdisilicic (silicomolybdic) acid method. A. C. Titus and C. W. Sill (Ind. Eng. Chem. [Anal.], 1942, 14, 121).—Ce( $SO_4$ )<sub>2</sub> and o-phenanthroline—Fe<sup>H</sup> are substituted for  $K_2Cr_2O_7$  and o-NHPh· $C_8H_4$ · $CO_2H$ , respectively, in the method described previously (A., 1941, I, 388).

Reaction of ferric ion with orthophosphate in acid solution with thiocyanate as an indicator for ferric ions. O. E. Lanford and S. J. Kiehl (J. Amer. Chem. Soc., 1942, 64, 291—296).—The reaction between Fe'' and HPO4'' ions has been studied using CNS' ions as indicator for Fe''. The reversible reaction is Fe''' + HPO4''  $\rightleftharpoons$  FeHPO4'. FeHPO4' has a dissociation const. of 4.44  $\times$  10-10 at an ionic strength of 0.665 and 30°. The relationship between the extinction coeff. and the molar concn. of FeCNS'' ions at 5500 A. has been established. W. R. A.

#### XI.—APPARATUS ETC.

Determination of critical temperatures by the rotating bomb. V. N. Ipatieff and G. S. Monroe (Ind. Eng. Chem. [Anal.], 1942, 14, 171—174).—A method for determining crit. temp. to within  $\pm 2^{\circ}$  by means of the rotating bomb is described. Data for  $C_3H_8$ ,  $C_3H_8$  and  $H_2$ ,  $C_6H_{14}$ ,  $C_6H_{14}$  and  $H_2$ , cyclohexane (I), (I) and  $H_2$ ,  $C_6H_6$ ,  $C_6H_6$  and  $H_2$ ,  $CH_4+C_6H_6$ , and  $C_6H_{14}+C_6H_6$ , are recorded. The pressure-temp. curves of two-component systems show points of discontinuity similar to those shown by single substances, and the crit. temp. of the systems lie probably within the break on the curves. L. S. T.

Determination of the humidity of the air by means of the evaporation temperature of water. K. Oswatitsch (*Physikal. Z.*, 1941, 42, 343—347).—Theory and technique are given. A. J. M.

Two bridge-controlled thyratron thermostats. D. Bancroft (Rev. Sci. Instr., 1942, 13, 114).—Errors in diagrams (A., 1942, I, 155) are pointed out.

A. A. E.

Effect of [variations in] colour vision on temperature measurement with the Bioptix pyrometer. S. Fornander (Jernkont. Ann., 1941, 125, 67—80).—Four normal and one green-colour-blind observers measured temp, with four Bioptix pyrometers (Öhman, ibid., 1935, 119, 343). All obtained similar vals, with the same instrument, but different instruments gave widely varying results. A very green-colour-blind observer obtained vals, 200—300° apart with the same instrument.

M. H. M. A.

Phase-contrast microscopy. C. R. Burch and J. P. P. Stock  $(J.Sci.\ Instr., 1942, 19, 71-75)$ .—A method for adapting an ordinary microscope for the use of Zernike's phase-contrast illumination is described. It involves the provision of a slit source and the preparant mounting of a phase-accelerating strip etched  $\lambda/2$  deep in a glass plate.

A. A. E.

X-Ray microscope. (Sir) W. L. Bragg (Nature, 1942, 149, 470—471),—Simplifications and improvements in the optical method previously reported (A., 1939, I, 389) for summing a double Fourier series and so producing an image of a crystal structure are described and illustrated by reference to diopside and hæmoglobin.

Simple recording spectrophotometer. G. A. Boutry and J. Gillod (Compt. rend., 1941, 213, 235—238).—The difficulties of the const. deviation method or differential methods with two cells are avoided by a simple arrangement using a new photo-emissive cell (cf. A., 1939, I, 538) and single-stage amplification in conjunction with a double monochromator. Amplified photo-electric currents are recorded directly as a function of  $\lambda$  and are measured by means of a galvanometer. Curves obtained are given and discussed.

Blank and background effect on photographed spectral lines. L. W. Strock (J. Opt. Soc. Amer., 1942, 32, 103—111).—A detailed discussion of the establishment of calibration curves for the determination of Sr in powdered lepidolite, using Li as internal standard.

Application of a calculating board to quantitative spectroanalysis. C. King (J. Opt. Soc. Amer., 1942, 32, 112—115).—A graphical method, of converting densitometer readings into concn. ratios, applicable to the internal standard method of spectrochemical analysis, is described.

O. D. S.

Photo-electric fluorimeters and their uses. G. F. Lothian (J.S.C.I., 1942, 61, 58—60).—A description is given of the Spekker photo-electric fluorimeter. The use of this and similar instruments is considered and the effects of concn. of solution and of impurities on accuracy of estimation are considered.

Spectrographic analysis. Relationship between photographic contrast and wave-length for the Ilford ordinary plate in the ultra-violet.

A. C. Coates and E. H. Amstein (J.S.C.I., 1942, **61**, 65—66).—A curve between photographic contrast,  $\gamma$ , and wave-length,  $\lambda$ , is given for the Ilford Ordinary plate. The contrast is obtained from density/log relative intensity plots, using a stepped sector to give known relative intensities. The  $\gamma/\lambda$  curve shows that  $\gamma$  is const. between 2500 and 3100 A. (cf. A., 1942, I, 156). By the use of the stepped sector the formula given for calculating the error incurred in comparing two spectrum lines in  $\lambda$  regions of differing contrast (loc. cit.) is shown to hold satisfactorily.

Photometry. H. Buckley (Physical Soc. Rep. Progr. Physics, 1941, 8, 318—337).—A progress report. W. J.

Photo-electric colorimeter for rapid reactions. B. Chance (Rev. Sci. Instr., 1942, 13, 158—161).—With the differential photo-electric colorimeter described small absorption changes in enzyme—substrate reactions can be measured with an accuracy of 3% and a time resolution of 0.01 sec.

A. A. E.

Colorimetry in metallurgical analysis.—See B., 1942, I, 271.

Specimen holder for powder diffraction samples. A. A. Burr (Rev. Sci. Instr., 1942, 13, 127—128).—Background fog from Pyrex is avoided by using Cellophane specimen tubes. A. A. E.

Instrumental technique in astrophysics. A. Hunter (Physical Soc. Rep. Progr. Physics, 1941, 8, 186—199).—A progress report. W. J.

Electron microscope for accelerating potentials of 220 kilovolts, H. O. Müller and E. Ruska (Kolloid-Z., 1941, 95, 21—25).—Electron-micrographs are reproduced to illustrate the improvement in detail obtained by the use of higher electron velocities up to 220 kv. The construction and use of the instrument are described.

F. L. U.

Thermostable and durable support film for electron diffraction and electron-microscopic investigations. G. Hass and H. Kehler (Kolloid-Z., 1941, 95, 26—29).—The use of  $Al_2O_3$  films removed from the oxidised surface of Al is described. These films give very weak interference patterns which do not seriously compete with those of the material under examination and are unaffected by temp.  $\Rightarrow 500^\circ$ .

Alternating-current apparatus for measuring dielectric constants.

B. E. Hudson and M. E. Hobbs (Rev. Sci. Instr., 1942, 13, 140—143).—A heterodyne beat apparatus is described.

A. A. E.

Research with the polarograph. O. H. Müller (Ind. Eng. Chem. [Anal.], 1942, 14, 99—105).—A summary of uses. L. S. T.

Polarographic reading directly in percentage. Analysis of lead arsenate. B. P. Caldwell and S. Reznek (Ind. Eng. Chem. [Anal.], 1942, 14, 187—189).—A manually-operated polarograph to give direct % readings is described. Application to the analysis of commercial Pb arsenate is given.

L. S. T.

Micro-burette. P. F. Scholander (Science, 1942, 95, 177—178).— Hg is replaced by the spindle of a micrometer. An accuracy in delivery of 0·1 cu. mm. is claimed. E. R. R.

Dumas micro-method for nitrogen. Automatic apparatus for combustion micro-methods.—See A., 1942, II, 183.

Adjustable resistor for flowmeters. E. L. Gooden (Science, 1941, 94, 309—310).—The resistance to flow in a capillary is adjusted by means of a movable, exchangeable wire.

E. R. R.

Test-tube spiral absorption vessel. R. E. Girton (Science, 1942, 95, 25—26).—A simple efficient CO<sub>2</sub>-absorption vessel, suitable for plant respiration measurements, is described in detail. E. R. R.

Molecular still heads. A. J. Bailey (Ind. Eng. Chem. [Anal.], 1942, 14, 177—178).—A mol. still made from two standard Pyrex micro-bell jars, and a larger still made in a standard Pyrex vac.-distilling dome, are described and illustrated. L. S. T.

Theory of open-tube distillation columns.—See B., 1942, I, 249.

Plate yield and determination of dimensions of elements of distilling and rectifying columns.—See B., 1942, I, 249.

Progress in microchemistry. III. Preparative micro-technique. E. Pfeil (Angew. Chem., 1941, 54, 161—167).—A review. C. R. H.

Determination of solubilities of gases at high temperatures and high pressures by the rotating bomb. V. N. Ipatieff and G. S. Monroe (Ind. Eng. Chem. [Anal.], 1942, 14, 166—171).—A rotating bomb for determining solubilities and crit. temp., and sampling apparatus for determining solubilities, are described. The results obtained show that the bomb can be used for determining solubilities of gases at high pressures and at temp. approaching the crit. temp. Pressure is the chief factor affecting the solubility of CH4 in C4H6; the effect of temp. is of minor importance. Both temp. and pressure exert a marked effect on the solubility of C2H4 in C4H6. Results with SO2 in C6H3 are also recorded.

L. S. T.

Continuous washing apparatus for solutions in organic solvents. A. L. LeRosen (Ind. Eng. Chem. [Anal.], 1942, 14, 165).—A const, air space is maintained in a separating funnel while a stream of H<sub>2</sub>O is passed through the solvent. L. S. T.

Pressure-regulating and indicating apparatus for vacuum systems. B. Ferguson, jun. (Ind. Eng. Chem. [Anal.], 1942, 14, 164—165).— Apparatus incorporating an automatically-controlled air leak, and accurate to  $\pm 0.2$  mm, for pressures of 5—760 mm, is described. A closed-end manometer also is illustrated. L. S. T.

Adjustable safety shield. A. Furst (Ind. Eng. Chem. [Anal.], 1942, 14, 158). L. S. T.

Sublimation apparatus. O. A. Nelson (Ind. Eng. Chem. [Anal.], 1942, 14, 153).—The concave inner tube is fitted with a Germansilver mesh screen to catch falling particles of the sublimate.

Determining liquid and vapour densities in closed systems. G. H. Wagner, G. C. Bailey, and W. G. Eversole (Ind. Eng. Chem. [Anal.], 1942, 14, 129—131).—The method uses a quartz bob suspended from a quartz helix. V.d. of SO<sub>2</sub> in equilibrium with its solutions at 15°, 20°, and 25° determined by this method agreed with v.d. calc. from v.p. data to 0.00001 g. per c.c. L. S. T.

Continuous liquid extractor for large volumes of solution. R. Hossfeld (Ind. Eng. Chem. [Anal.], 1942, 14, 118).—Vigorous agitation and continuously recirculated dispersion of the solvent through the layer being extracted are achieved. L. S. T.

Electrically driven high-speed laboratory centrifuge. E. G. Pickels (Rev. Sci. Instr., 1942, 13, 93—100).—The instrument utilises a direct universal motor drive capable of spinning an 8-in. rotor at 18,000 r.p.m. for 180 v. and at 12,500 r.p.m. for 115 v. Specifications and operational data are given for rotors of diameter 7—10-25 in. and capacities 112—610 c.c. of fluid.

A. A. E.

Stress analysis and design of high-speed angle centrifuges. E. G. Pickels (Rev. Sci. Instr., 1942, 13, 101—114).—A graphical method for determining mechanical stresses is explained and equations leading to approx, vals, are given. Design is discussed. A properly designed rotor of diameter 20 cm. and accommodating several hundred c.c. of fluid can operate at speeds >50,000 r.p.m. for thousands of runs.

A. A. E.

High-speed centrifuging. J. W. Beams (Physical Soc. Rep. Progr. Physics, 1941, 8, 31—49).—A progress report. W. J.

Analytical cell for the ultracentrifuge, M. Rosenfeld (Rev. Sci. Instr., 1942, 13, 154—157).—The cell is divided into 2 or 3 compartments by sieve-like partitions covered with filter-paper and is used with the angle type quantity rotor of the air-driven ultracentrifuge.

A. A. E.

Apparatus for supersonic velocity and absorption measurements. D. Telfair and W. H. Pielemeier (Rev. Sci. Instr., 1942, 13, 122—126).—Apparatus and technique are described. The velocity of low-frequency sound in dry air (0.03% CO<sub>2</sub>) at 0° and 1 atm. is  $331.45\pm0.05$  m. per sec. Experimental results for  $C_2H_4$  and  $CH_4$  are briefly reviewed. A. A. E.

#### XII.—LECTURE EXPERIMENTS AND HISTORICAL.

Demonstration of cis-trans isomerism [using dimethyl maleate and bromine in light]. O. Grummitt (J. Chem. Educ., 1941, 18, 477).

Dynamos and electrochemistry. G. Eger (Z. Elektrochem., 1942, 48, 1—6).—Commemorative. G. R. H.

Samuel Higley, an early American metallurgist. F. H. Getman (J. Chem. Educ., 1941, 18, 453—457).

L. S. T.

#### XIII.—GEOCHEMISTRY.

Limnological studies of Lake Eric. II. Light penetration with relation to turbidity. D. C. Chandler (Ecology, 1942, 23, 41—51).

Salesite (CuIO<sub>3</sub>OH) and olivine (Mg<sub>2</sub>SiO<sub>4</sub>). H. Strunz (Z. Krist., 1941, 103, 359—360).—The structures of salesite (cf. Palache and Jarrell, A., 1939, I, 542) and olivine are isotypical; true isomorphism is unlikely.

A. J. E. W.

Celestite in Cis-Indus Salt Range [near Jaba]. B. S. Lamba (Current Sci., 1942, 11, 54—55). W. R. A.

Yorkshire Dogger. H. Lower Eskdale. R. H. Rastall and J. E. Hemingway (Geol. Mag., 1941, 78, 351-370). L. S. T.

Origin of strontianite deposits in the Münster district. F. Micklinghoff (Glückauf, 1942, 78, 217—220, 229—235).—Analyses.

R. B. C.

Pyroxenes of common mafic magmas. I, II. H. H. Hess [Amer. Min., 1941, 26, 515—535, 573—594].—The pyroxenes of fine- and coarse-grained mafic intrusives and of mafic extrusives are described. Hypotheses concerning the trend of crystallisation of pyroxenes from basalts are reviewed. Augite (I) probably does not grade into pigeonite (II), which is probably a definite and distinct mineral

variety. (I) and (II) crystallise together and in equilibrium with each other. On slow cooling, (II) inverts to hypersthene (III), and this inversion can be used as a point on the geological thermometer. (III) inverted from (II) can be distinguished from (III) of primary crystallisation. The temp, of basaltic intrusions is \$\text{\scale=1}140^\circ\$, and normally is near to \$1120^\circ\$. L.S.T.

Validity of paragonite as a mineral species. W. T. Schaller and R. E. Stevens (Amer. Min., 1941, 26, 541—545).—Alkali determinations on mica from Fenestrella, Italy, and from Monte Campione, Switzerland, and on euphyllite from Corundum Hill, Pa., show that paragonite (I) is a definite species. Optical differentiation between (I) and muscovite is not possible.

L. S. T.

Nepheline. A. N. Winchell (Amer. Min., 1941, 26, 536—540).— The composition of nephelines in mol.-% of NaAlSiO<sub>4</sub>, KAlSiO<sub>4</sub>, CaAlAlO<sub>4</sub>, SiSiO<sub>4</sub>, AlSiO<sub>3</sub>(OH), and CaCaSiO<sub>4</sub>, as calc. from recent chemical analyses, is tabulated and discussed. L. S. T.

Valentinite crystals from California. J. Murdoch (Amer. Min., 1941, 26, 613—616).—Valentinite crystals from Lone Tree Canyon, Kern Co., California, show an unusual lath-like habit. New crystallographic forms are described.

L. S. T.

Sedimentary analoite. C. S. Ross (Amer. Min., 1941, 26, 627—629).—Analoite from Wikieup, Arizona, is described. It is derived from glassy volcanic ash. L. S. T.

Shortite. Correction of space-group. W. E. Richmond (Amer. Min., 1941, 26, 629—630).—The space-group is  $C_{2v}^{14}$ —Amm2 (cf. A., 1941, I, 490).

L. S. T.

Structural control and form of oreshoots in the southern Appalachian gold deposits. C. F. Park, jun. (*Econ. Geol.*, 1939, 34, 470).—Descriptive. L. S. T.

Geology of the Ropes Gold mine, Marquette Co., Michigan. T. M. Broderick (*Econ. Geol.*, 1939, 34, 939—940).—The ore occurs in nearly vertical quartz (I) lenses cutting Keewatin lavas and volcanic fragments separating two bodies of peridotite. The mineralisation is probably post-middle Huronian. The (I) veins carry tetrahedrite, pyrite, chalcopyrite, and minor amounts of other sulphides. Another type of richer ore occurs as a pyritic dissemination in schist adjacent to the (I) veins.

Peridotite and sagvandite from south Madagascar. A. Lacroix (Compt. rend., 1941, 213, 261—265).—Occurrence is described, and chemical analyses are recorded.

L. S. T.

Trachyandesite with kaersutite and cristobalite among the lavas of the Puy chain. Y. Bentor (Compt. rend., 1941, 213, 211—214).—Chemical and mineral analyses are given.

L. S. T.

Fluorescent sodalite and hackmanite from Magnet Cove, Arkansas. H. D. Miser and J. J. Glass (Amer. Min., 1941, 26, 437—445).—
Two varieties of fluorescent sodalite (I) occur in the tinguaite rocks of Magnet Cove, a blue (I) that fluoresces purplish-red to violet-red, and a white variety, hackmanite (II), that fluoresces a reddishorange, and shows a change of colour from rose to colourless and back again with alternate exposure to light and darkness. Reappearance of the rose colour is induced by exposure to ultra-violet radiation; the colour disappears in daylight. Chemical analyses of (I) and (II) are compared with those of specimens from other localities. (I) and (II) from Magnet Cove have approx. the same composition; (II) contains a trace of sulphide, and (I), a small amount of Mn.

Metasomatism of a coaly sediment into an igneous-appearing rock. G. E. Goodspeed, R. E. Fuller, and H. A. Coombs (J. Geol., 1941, 49, 190—198; cf. A., 1940, I, 239).—In Mount Rainer National Park, seams of lignitic material occur locally in a thick series of arkosic sandstones and shales. Some members of this series have been altered by low-temp, metasomatic replacement to resemble portions of an andesitic series of the Miocene. The carbonaceous material is replaced by an igneous-appearing dacitic groundmass containing quartz and plagioclase.

L. S. T.

Petrified tree-trunks (dolomitised sphaerolite-wood) in the coal formation of the Ruhr district. P. Kukuk and W. Hartung (Glück-auf, 1941, 77, 698—703).—The dolomitic remains of trunks are so-called sphaerolite-wood similar to that from the brown coal of Ville. They differ in their allochthonous occurrence. Analyses are given.

R. B. C.

Petrified coal. W. Petrascheck (Berg-u. Hüttenm. Monatsh., 1941, 89, 148—150; Glückauf, 1942, 78, 71).—Coal seams can be so saturated by mineral matter percolating from without as to be converted in effect into rock.

R. B. C.

Coal district of Nürschan near Pilsen. W. May (Glückauf, 1942, 78, 29—31).—Geological. R. B. C.

Geology of British oilfields. III. Oilfields of Burma. P. Evans and C. A. Sansom (Geol. Mag., 1941, 78, 321—350).—History, geology, and the various fields are described.

L. S. T.

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# JUDACTAN

#### ANALYTICAL REAGENTS WITH ACTUAL BATCH ANALYSIS

AMMONIUM MOLYBDATE A.R. (NH<sub>4</sub>)<sub>4</sub>Mo<sub>7</sub>O<sub>14</sub>·4H<sub>2</sub>O Mol. Wt. 1236·3 **ACTUAL BATCH ANALYSIS** Batch No. 11050 Molybdenum Oxide (MoO3)...... 81.0% Chloride (CI)...... 0.0004% Sulphate (SO<sub>4</sub>)..... Phosphate (PO<sub>4</sub>)..... Heavy Metals (Pb & Fe).....

Each Batch

subjected

to

INDEPENDENT

**ANALYSIS** 

before

label is printed

You are invited to compare the above actual batch analysis with the purities

ACTUAL

BATCH

ANALYSIS

guaranteed by the specifications of any competing maker in this Country or abroad

THE GENERAL CHEMICAL & PHARMACEUTICAL CO. LTD.

Chemical Manufacturers, Judex Works, Sudbury, Middlesex