

# BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

**JUNE, 1944**

## A I—GENERAL, PHYSICAL, AND INORGANIC CHEMISTRY



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

JUNE, 1944.



## I.—SUB-ATOMICS.

**Emissivity characteristics of hot metals, with special reference to the infra-red.** D. J. Price and H. Lowery (*Iron and Steel Inst.*, March, 1944, *Advance copy*, 24 pp.).—The theoretical and practical considerations in connexion with the study of emissivity are discussed under the headings: definition of emissivity, basic theory, emissivity and pyrometer correction, experimental technique, and previous measurements. The relevant literature is critically surveyed, with 64 references. The application of emissivity data to correction of pyrometer readings is examined. Available information does not meet this need, especially in the case of Fe. Available data apparently indicate a zero temp. coeff. of emissivity for all substances at a sp. infra-red  $\lambda$ ; hence, at a certain  $\lambda$  for each substance the emissivity to a pyrometer would be much simplified.

T. D. F.

**Determination of oscillation intensities in atomic spectra.** D. S. Roshdestvenski and N. P. Penkin (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 97—101).—A graphite furnace in which metal vapours at 3000° can be examined is described. The anomalous dispersion of Fe vapours at 5060—5330 Å. could not be measured exactly because of the reaction between Fe and graphite; better results were achieved with the Cr triplet 5204.68—5208.59 Å. The probability of oscillations causing these lines agrees with theory. From the intensity of Na and Ba lines it is suspected that thermal equilibrium was not reached in the furnace.

J. J. B.

(A) Arc spectrum with carbon electrodes of cerium, neodymium, and praseodymium between 2200 and 5000 Å. for  $2 \times 10^{-4}$ ,  $2 \times 10^{-5}$ , and  $2 \times 10^{-6}$  g. (B) Arc spectrum with carbon electrodes of dysprosium, holmium, and terbium between 2200 and 5000 Å. for  $2 \times 10^{-4}$ ,  $2 \times 10^{-5}$ , and  $2 \times 10^{-6}$  g. J. M. López de Azcona (*Anal. Fis. Quím.*, 1940, 38, 154—164, 261—275; cf. A., 1940, I, 399).—(A) 202 lines are tabulated for Ce, persisting at a concn. of  $2 \times 10^{-4}$ , 130 at  $2 \times 10^{-5}$ , and 24 at  $2 \times 10^{-6}$  g. For Nd the figures are 249, 19, and 3, and for Pr, 179, 33, and 8 lines respectively. The most persistent lines are compared with those previously recorded.

(B) The corresponding figures for Dy are 194, 57, and 15, for Ho, 300, 107, and 38 (with 3 at  $2 \times 10^{-7}$  g.), and for Tb, 374, 154, and 15. The most persistent lines are compared with those previously recorded.

F. R. G.

**Arc spectrum of tungsten.** F. Poggio Mesorana (*Anal. Fis. Quím.*, 1942, 38, 281—295; cf. A., 1936, 916).—New levels in the arc spectrum of W together with those previously calc. are grouped into terms pertaining to the configurations  $5d^4 6s^2$ ,  $5d^4 6s$ ,  $5d^4 6s 6d$ ,  $5d^4 6s 6p$ , and  $5d^4 6p$ .

F. R. G.

**Relative energy distribution in the continuum of immersed sparks between 9000 and 5000 Å.** H. Schubert (*Ann. Physik*, 1941, [v], 39, 295—307).—The intensity of spark discharges beneath the surface of  $H_2O$  and  $CCl_4$  is investigated, the relative distribution being determined photographically and, under  $H_2O$ , photoelectrically. Within fairly wide limits of error the energy distribution is independent of the material of the electrodes and the nature of the liquid, but is not const. in the long- $\lambda$  region. The half-val. width of the H $\alpha$  line is  $100 \text{ Å.} \pm 10\%$ .

A. J. M.

**Absorption spectra of rare earths.** A. N. Zaidel (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 111—113).—The spectrum of  $NdCl_3$  in aq. HCl is not basically changed by heating the solution at 160° above the crit. temp., although the absorption bands (5800 and 5200 Å.) are shifted towards red by 20 Å. for every 100° temp. rise. It is suggested that the theory of spectrum line broadening by foreign gases may be extended to account for the widths of absorption bands of rare-earth ions in solution.

J. J. B.

**True line breadth and oscillator strength of europium sulphate lines.** G. Joos and K. H. Hellwege (*Ann. Physik*, 1941, [v], 39, 25—29).—Photometric data at 15° are compared with data at —190° for the Eu sulphate lines  $^1F \rightarrow X_0$ , 5793 Å.,  $^3F \rightarrow X_1$ , 5257 Å., and  $^7F \rightarrow X_2$ , 4651 Å. Half-val. breadths in sec. $^{-1}$  at 15° are  $4.35 \times 10^{10}$ ,  $6.52 \times 10^{10}$ ,  $9.72 \times 10^{10}$ , respectively, and oscillator strengths added for the components of the lines are  $1.4 \times 10^{-10}$ ,  $9.7 \times 10^{-9}$ , and  $33.8 \times 10^{-9}$ , respectively,  $\sim 10^{-3}$  times < vals. for Pr sulphate.

L. J. J.

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H (A., I.)

**Influence of chemical binding on K X-ray absorption and emission spectra.** I. B. Borovski (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 187—194).—The structure of the main edge of K absorption bands and its relation to interat. forces are discussed for various Ti, Mn, and V compounds.

J. J. B.

**Compton effect diffusion of X-rays is less for an atom contained in a crystal than for the free atom.** J. Laval (*Compt. rend.*, 1942, 215, 278—279).—Observed Compton scattering in diamond, Al, and sylvine crystals is < that calc. for corresponding free atoms.

N. M. B.

**Possible explanation of the weakening of the Compton effect in crystals.** J. Laval (*Compt. rend.*, 1942, 215, 359—360).—The weakening is attributed to the restriction of the Compton recoil electron to "allowed" energy bands.

N. M. B.

**Photo-electric threshold of copper.** A. Blanc-Lapierre (*Compt. rend.*, 1942, 215, 321—323).—Determinations on Cu foil, sealed in a vac. tube and exposed to Hg-arc radiation, give the val. 2660 Å. Vals. deduced from available curves for powdered or volatilised Cu are 2800 and 2650 Å., respectively.

N. M. B.

**Determination of relatively short optical life-periods in an atomic jet.** H. Bruck (*Compt. rend.*, 1942, 215, 431—433).—A small region of the jet is excited by electron impact, and the displacement from this region of the "centre of gravity" of the emission zone is determined. The theory of the method is outlined.

A. J. E. W.

**Energy distribution among secondary electrons. I. Longitudinal magnetic field method.** R. Kollath (*Ann. Physik*, 1941, [v], 39, 59—80).—In the magnetic analyser described, primary electrons from a hot filament in a narrow beam impinge on a target, and secondary electrons are constrained to follow a path, predetermined by diaphragms, into a measuring chamber, by the application of a variable longitudinal magnetic field, from the magnitude of which their energy is calc. Data are given for Ta, Mo, and Be targets. The method is applicable to photoelectrons.

L. J. J.

**Effect of temperature on the secondary electron emission of metals.** (A) R. Kollath. (B) A. Becker (*Ann. Physik*, 1941, [v], 39, 19—22, 23—24).—Comments on a paper by Reichelt (*ibid.*, 1940, [v], 38, 293).

L. J. J.

**Diffusion of radiation in a gas discharge.** F. A. Butaeva, L. M. Biberman, and V. A. Fabrikant (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 95—96).—Differences between diffusion phenomena involving particles and photons are discussed, and a method of taking photon diffusion into account in the theory of radiation from gas discharges is outlined.

J. J. B.

**Electrical characteristics of the ozonator discharge.**—See B., 1944, II, 93.

**Position of the transuranic elements 93 and 94 in the natural system of the elements.** C. Bedreag (*Compt. rend.*, 1942, 215, 537—539).—From a survey of available data, the elements are assigned to a new column between W, U, and Mn, Ma, Re.

N. M. B.

**The ionisation method of measuring neutron energy.** L. H. Gray (*Proc. Camb. Phil. Soc.*, 1944, 40, 72—101).—Using an ionisation chamber filled with a gas of the same at. composition as the walls, the energy  $E_n$  absorbed per unit vol. of the solid is the product of the ionisation  $J_n$  in the cavity, the average energy  $W$  used up in producing a pair of ions in the gas, and the stopping power  $\rho$  of the solid relative to the gas. Methods of estimating  $W$  and  $\rho$  are discussed, and it is concluded that at best the abs. determination of  $E_n$  is liable to errors of  $\sim 5\%$ .

H. J. W.

**Absorption and coincidence experiments with  $^{198}\text{Au}$ .** N. Feather and J. Dainty (*Proc. Camb. Phil. Soc.*, 1944, 40, 57—71).—In addition to the radiations observed by other investigators,  $^{198}\text{Au}$  emits a fairly intense  $\gamma$ -radiation of  $\sim 65$  e.k.v. energy. This is distinguished from the K X-radiation of Hg, and it is not the K X-radiation of Pt. K-electron capture cannot take place in  $> \sim 15\%$  of the disintegrations of  $^{198}\text{Au}$ .

H. J. W.

**Spectrum of  $\beta$ -rays from  $^{131}\text{I}$ .** N. A. Perfilov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 33, 485—487).—Measurements by the cloud-chamber method indicate that the  $\beta$ -rays from  $^{131}\text{I}$ , produced by bombardment of  $\text{UO}_2(\text{NO}_3)_2$  with neutrons from  $\text{Rn} + \text{Be}$ , have a max. energy of  $\sim 1.07$  m.e.v.

J. W. S.

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**Cosmic-ray showers containing non-synchronised particles.** A. Fréon (*Compt. rend.*, 1942, 215, 323—326).—Experiments with a special arrangement of counters indicate the presence of small showers arising from a meson which disintegrates above the apparatus, which receives a disintegration electron and one or several collision electrons. N. M. B.

**Absorption of the hard component of cosmic radiation.** M. E. Rose (*J. Franklin Inst.*, 1943, 236, 9—45).—Mathematical. A phenomenological theory of absorption of mesotrons in the atm. and in dense materials at and below sea-level is given. Assuming  $2 \times 10^{-6}$  sec. for the proper lifetime, the calc. energy distribution at sea level accords well with observations. The theory leads to satisfactory agreement between observed and calc. angular distribution at sea-level and absorption in Pb. N. M. B.

**Angular distribution of shower particles.** S. Z. Belenki (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, 36, 97—100).—A formula for the mean scattering angle of shower particles in passing through matter, taking ionisation losses into account, is derived. For the scattering in air, the mean angle is reduced from  $18^\circ$  to  $12^\circ$  by the ionisation losses for particles with 100 Me.v. energy, and from  $60^\circ$  to  $27^\circ$  for an energy of 30 Me.v. The theory only applies qualitatively for scattering by substances of high at. wt. H. J. W.

**Photon in the quantum theory of radiation.** J. Yvon (*Compt. rend.*, 1942, 215, 410—412).—Consideration of the transfer of an energy quantum from an excited to an absorbing atom leads to a representation of a photon as a complex potential vector. A. J. E. W.

**Nature of the planets.** A. Dauvillier (*Compt. rend.*, 1942, 215, 222—224).—The theory of planet formation from photospheric solar matter leads to the existence of large, low-density planets of light elements, and small dense planets nearer to the sun. This view of large planets is discussed in relation to their known structure to explain their density, colour, and spectral characteristics, and results are compared with observational data. N. M. B.

**Incomplete separation of variables in calculations on poly-electron atoms.** M. G. Veselov (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 102—106).—Mathematical. A method applicable to atoms with two valency electrons is developed and applied to  $\text{Li}^+$  and  $\text{Be}^{++}$ . J. J. B.

**New periodic table of the chemical elements.** (A) J. Pinilla. (B) E. Sellés (*Anal. Fis. Quím.*, 1940, 36, 227—228, 229—232).—(A) The table of Guzmán (A., 1940, I, 311) is criticised as not making a clear representation of the periodicity of the elements.

(B) Guzmán's table is criticised on the grounds that the chemical properties of the elements cannot be expressed in precise mathematical terms. F. R. G.

**Principle of spectral resolution in wave mechanics.** J. L. Des-touches (*Compt. rend.*, 1942, 215, 523—525).—Mathematical. N. M. B.

**Vortex atoms.** F. H. Loring (*Chem. Products*, 1944, 7, 40).—The connexion between probability nos. (which enter into the at. nos. of the inert gases, and into special groupings of elements in the periodic table, as well as into a no. of properties of orbits in general) and Kelvin's theory of the vortex atom is discussed. A. J. M.

**Evaluation of the cosmical number.** (Sir) A. S. Eddington (*Proc. Camb. Phil. Soc.*, 1944, 40, 37—56).—The cosmical no.,  $N = \frac{4}{3} \times 2^{256} \times 136$ , is a fundamental const., which enters into many physical formulae, and determines the ratio of the electrical to the gravitational forces between particles, the range and magnitude of the non-Coulombian forces between particles, and the cosmical repulsion manifested in the recession of the nebulae. Its interpretation as the no. ( $\frac{1}{2}nk$ ) of protons and electrons in the universe is discussed at length. W. J.

## II.—MOLECULAR STRUCTURE.

**Band spectra and energies of dissociation of diatomic molecules.** A. G. Gaydon. R. C. Pankhurst. R. F. Barrow. W. Jevons (*Proc. Physical Soc.*, 1944, 56, 204—212).—A discussion. Gaydon reviews spectroscopic methods of evaluating energies of dissociation ( $D$ ), with special reference to  $\text{CO}$ ,  $\text{N}_2$ , and  $\text{NO}$  (see A., 1944, I, 95), and gives 9.764 e.v. as the most probable val. of  $D$  for  $\text{N}_2$ . Pankhurst points out the uncertainties of evaluations of  $D$  due to long extrapolation of vibrational energy levels and to the arbitrary representation of potential energy as a function of internuclear distance. Barrow describes the trends of mol. consts. (electronic energies, vibrational frequencies, energies of dissociation, etc.) throughout the group of diat. oxides, sulphides, selenides, and tellurides of C, Si, Ge, Sn, and Pb. Jevons discusses the spectroscopic similarity between these group-IV—VI mols. and the group of mols. each of which consists of two group-V atoms, such as  $\text{N}_2$ ,  $\text{PN}$ ,  $\text{AsN}$ ,  $\text{SbN}$ ,  $\text{P}_2$ ,  $\text{As}_2$ ,  $\text{Sb}_2$ , and  $\text{SbBi}$ . W. J.

**Presence of the Lyman band system of nitrogen in the ultra-violet radiation of the night sky.** L. Herman (*Compt. rend.*, 1942, 215, 527—529).—Frequencies calc. by the Birge-Hopfield formula are

compared with experimental data for 83 bands of the  $\text{N}_2$  system  $\alpha''\Pi_u \rightarrow \alpha'\Sigma_g$ , and with vals. calc. by an alternative formula which is proposed, and leads to better agreement. N. M. B.

**Emission band system of PbSe.** R. F. Barrow and (Miss) E. E. Vago (*Proc. Physical Soc.*, 1944, 56, 76—78).—A band system ( $\nu \rightarrow \chi$ ) of  $\sim 40$  bands in the region 3350—3850 Å., excited by a heavy-current, uncondensed, positive-column discharge through PbSe in a  $\text{SiO}_2$  tube, is photographed in dispersion  $\sim 7.4$  Å. per mm. Vibrational analysis gives for the wave nos. of the band-heads the expression  $\nu_{\text{head}} = 28,416.9 + (190.5u' - 0.6u'^2) - (277.4u'' - 0.56u''^2)$ , where  $u = v + \frac{1}{2}$ . The identity of the val. of  $\omega_0''$  with that for the ground state of PbSe (cf. Walker *et al.*, A., 1938, I, 116) shows that the lower state of the new transition is the ground state. N. M. B.

**Absorption spectrum of SnTe.** R. F. Barrow and (Miss) E. E. Vago (*Proc. Physical Soc.*, 1944, 56, 78—85).—From absorption studies in the visible in the temp. range 800—1400°, data for  $\sim 140$  bands are tabulated, and the bands are assigned to four systems, one of which has previously been observed in emission (cf. Barrow, A., 1940, I, 281). N. M. B.

**Absorption spectrum of nitrogen dioxide on films of aromatic compounds.** I. O. Gorislavetz (*J. Phys. Chem. Russ.*, 1943, 17, 97—101).—It was hoped to detect intermediate compounds by determining the absorption of films of  $\text{C}_6\text{H}_6$ ,  $\text{C}_{10}\text{H}_8$ , anthracene, and  $\text{PhOH}$  in a  $\text{NO}_2$  atm. Only a general absorption at  $\lambda < 3680$  Å. (for  $\text{C}_6\text{H}_6$ ) to  $< 5800$  Å. (for  $\text{PhOH}$ ) was observed. J. J. B.

**Comparison of the spectra of nickel and cobalt halides in the crystalline and gaseous state.** (Influence of the nature of the chemical bond on the spectra of uni- and bi-valent metal halides.) K. Butkowiak and I. Wojciechowska (*Z. physikal. Chem.*, 1941, B, 49, 131—144).—The absorption spectra of  $\text{NiBr}_2$ ,  $\text{NiI}_2$ , and  $\text{CoI}_2$  in the vapour state were determined in the range 7000—1900 Å. The absorption spectra of  $\text{NiBr}_2$  and  $\text{CoI}_2$  are obscured by those of  $\text{Br}_2$  and  $\text{I}_2$ , due to thermal dissociation. The spectrum of  $\text{NiI}_2$  is so strongly obscured that it can be observed only by the addition of Ni. The observed max. are due to fission of unexcited halogen atoms from the mols. The absorption spectra of uni- and bi-valent metal halides in the cryst. and gaseous states are compared. At 140—150° a continuous max. at 2670 Å. was found in the absorption spectrum of saturated  $\text{I}_2$  vapour; this does not appear in the band system of Pringsheim and Rosen (A., 1928, 1072). J. F. H.

**Spectral investigation of high-frequency discharge in acetylene-air flame.** V. S. Rossichin and V. P. Timkovski (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 219—221).—The combustion of a mixture of  $\text{C}_2\text{H}_2$  25 and air 75% is accelerated by electric vibrations of frequency  $> 3.4 \times 10^7$  cycles per sec. The emission spectrum of the flame in a field of  $2.5 \times 10^7$  cycles contains, in addition to the usual bands,  $\text{N}_2$  bands, more CN bands, and Zn lines (from brass electrodes). In a field of  $3.7 \times 10^7$  cycles  $\text{N}_2$  and  $\text{N}_2^+$  bands appear, and the intensity of CH bands (3900 Å.) and CN bands (3883 and 3871 Å.) rises; this is associated with the acceleration of combustion. J. J. B.

**Relations between chemical activity and absorption in the ultra-violet of certain organic molecules. VII. Absorption spectra of the amides of acetoacetic acid.** K. G. Naik, R. K. Trivedi, and B. N. Mankad (*J. Indian Chem. Soc.*, 1943, 20, 389—391; cf. A., 1944, II, 157).—Curves are plotted and discussed for aq. solutions of acetoacetanilide, -o- and -p-tolylamide, -m-4-xylylamide, -a- and -β-naphthylamide. N. M. B.

**Absorption curve of perline.** F. B. Shorland (*New Zealand J. Sci. Tech.*, 1943, 24, B, 159—160; cf. A., 1944, II, 113).—Absorption for the free base in  $\text{CHCl}_3$  and the hydrochloride in 0.1N-HCl begins at 515 and 435 mμ. and exhibits max. at 470 and 398 mμ. and min. at 375 and 325 mμ. respectively. S. A. M.

**Colour and constitution of azo-dyes.**—See B., 1944, II, 102.

**Absorption spectra of pyrethrum extracts.**—See B., 1944, III, 76.

**Pigments of cottonseed.**—See A., 1944, III, 444.

**Luminescence spectra of rare-earth ions.** J. I. Larionov (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 107—110).—The discrete luminescence spectrum of  $\text{Tb}^{IV}$  in its salts and solutions is due not only to the presence of an unfilled 4f shell, but also to  $\text{Tb}^{IV}$  ion in salts and solutions being identical with the theoretical  $\text{Tb}^{IV}$  ion. The same identity holds for  $\text{Cr}^{IV}$  in a  $\text{Cr}_2\text{O}_3$  phosphor and, perhaps, for  $\text{Mn}^{III}$  in a  $\text{Mn-MgO.TiO}_2$  phosphor. The effect of the environment of the ion is discussed. J. J. B.

**Luminescence spectra of electrolyte solutions.** A. A. Schischlovski (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 126—129).—A review (cf. A., 1940, I, 66). J. J. B.

**Spectral study of a luminescent reaction.** P. Groh and A. Kirrmann (*Compt. rend.*, 1942, 215, 275—276).—The reaction  $2\text{KOH} + \text{Cl}_2 + \text{H}_2\text{O}_2 \rightarrow 2\text{KCl} + \text{O}_2 + 2\text{H}_2\text{O}$  is accompanied by a red luminescence showing an unresolved band at  $\sim 610$ — $650$  mμ. with a max. at  $\sim 632$  mμ., and a weaker, narrower band with a max. at  $\sim 578$  mμ. Explanations are discussed. N. M. B.



**Dielectric after-effect phenomena in phosphors.** H. Ruffler (*Ann. Physik*, 1941, [v], 39, 203—208).—The after-effect in CdS-Cu phosphors, of varying [Cu] is investigated at different temp. (20—100°) in both the unexcited and the excited states. At const. temp. the after-effect diminishes with decreasing [Cu]. Exposure to light causes a considerable increase in the after-charge current, the increase being greater for lower than higher [Cu]. Increase of temp. accentuates the after-effect; in the case of unexcited phosphors this is independent of [Cu]. Irradiation increases the effect of temp. on the after-charge current considerably, and the higher is the [Cu] the greater is the increase. The results can be explained by assuming the presence of dipoles which determine both the dielectric and optical properties of the phosphor. A. J. M.

**Characteristic frequencies.** L. S. Mayantz (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 158—161).—Conditions are discussed for a definite frequency of the Raman spectrum to be a function of one linking only. The difference between the force consts. of similar mols., e.g.,  $(\text{CCl}_2)_2$  and  $(\text{CBr}_2)_2$ , cannot be immediately deduced from the shift of the characteristic frequency. J. J. B.

**Calculation of the frequencies of polyatomic molecules.** M. A. Eliashkevitch and B. I. Stepanov (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 155—157).—A method is indicated for calculating the vibration frequencies of polyat. mols. Application of the method to  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ , and  $\text{C}_3\text{H}_8$  is successful. J. J. B.

**Infra-red absorption spectrum of phosphorus trimethyl.** F. J. Wagstaffe and H. W. Thompson (*Trans. Faraday Soc.*, 1944, 40, 41—42).—Measurements are recorded for the range 3—20  $\mu$ . F. L. U.

**Infra-red absorption spectra and structure of metallic carbonates, bicarbonates, and thiocarbonates.** (Mme.) R. Duval, C. Duval, and J. Lecomte (*Compt. rend.*, 1942, 215, 525—528).—Approx. general data and their interpretation are given and discussed for 12 carbonates, 5 bicarbonates, and 5 thiocarbonates, all of unspecified metals. N. M. B.

**Raman spectra of complex mercury halides.**—See A., 1944, I, 85.

**Raman spectra of liquid and solid chlorine, bromine, and iodine compounds of aluminium.** H. Gerding and E. Smit (*Z. physikal. Chem.*, 1941, B, 50, 171—193).—Raman spectra of liquid and solid  $\text{AlCl}_3$  have been examined at 215°, 180°, 170°, and 20°,  $\text{AlBr}_3$  at 115° and room temp., and  $\text{AlI}_3$  at 215° and room temp. For liquid  $\text{AlCl}_3$  three polarised and four or five depolarised lines are found, agreeing with an  $\text{Al}_2\text{Cl}_6$  mol. with  $D_{2h}$  symmetry. A model with tetrahedral distribution of Cl about two Al, the two tetrahedra having a common side, is postulated in preference to a planar distribution. This correlates the Raman lines found with nine Raman-active normal vibrations.  $\text{AlBr}_3$  and  $\text{AlI}_3$  give spectra agreeing with double mols. in both solid and liquid phases.  $\text{AlCl}_3$  frequencies are lower for the solid than the liquid phase, whilst their intensities are unchanged. The 340  $\text{cm}^{-1}$  line of the liquid appears as a double line in the solid. This decrease in  $\Delta\nu$  is attributed to denser packing and consequent electrostatic interaction. No change is observed between 170° and 180°. L. J. I.

**Raman spectra and structure of sulphuric acid.** V. M. Kudrjavtzeva (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 131—143).—The  $\nu$  of the Raman lines of  $\text{H}_2\text{SO}_4$  at 0°, 35°, and 50°, and of aq.  $\text{H}_2\text{SO}_4$ ,  $\text{Me}_2\text{SO}_4$ , and a mixture of  $\text{H}_2\text{SO}_4$  and  $\text{Me}_2\text{SO}_4$  (1:1) at 16° are determined; contrary to literature indications there are no lines between 2500 and 3000  $\text{cm}^{-1}$  in pure  $\text{H}_2\text{SO}_4$ . For the lines 382—1350  $\text{cm}^{-1}$  in  $\text{H}_2\text{SO}_4$  the probable vibrations in the mol. are suggested. The frequencies 160 and 275  $\text{cm}^{-1}$  are attributed to H bonds between  $\text{H}_2\text{SO}_4$  mols.; they persist in the  $\text{H}_2\text{SO}_4$ - $\text{Me}_2\text{SO}_4$  mixture. The OH vibrations (3340—3650  $\text{cm}^{-1}$ ) of this mixture are similar to those in  $\text{H}_2\text{SO}_4$  at higher temp. (60°), as both heating and dissolution destroy multimol.  $\text{H}_2\text{SO}_4$  chains. J. J. B.

**Ionisation, Raman spectrum and vibrations of perchloric acid.**—See A., 1944, I, 127.

**Raman spectra and structure of the orthophosphates, phosphites, and hypophosphites.** J. P. Mathieu and J. Jacques (*Compt. rend.*, 1942, 215, 346—347).—Tabulated data on the frequencies, state of polarisation, and intensity of Raman lines for the Na and K salts lead to classifications of the corresponding modes of vibration and information on structure. N. M. B.

**Depolarisation of the Raman lines of metamolybdic acid in aqueous solution.** (Mlle.) M. Murgier and (Mlle.) M. Théodoresco (*Compt. rend.*, 1942, 215, 530—531).—A single polarised line, 950  $\text{cm}^{-1}$ , has been obtained. The depolarised line is 853  $\text{cm}^{-1}$ . Significance and interpretation are discussed. N. M. B.

**Raman spectra of hydrocarbons. IV.  $\beta$ -Dimethyl- $\Delta^{\alpha\omega}$ -hexadiene and  $\beta$ -dimethyl- $\Delta^{\beta\delta}$ -hexadiene.** F. F. Cleveland (*J. Chem. Physics*, 1944, 12, 53—55).—The olefinic lines of  $(\text{CH}_2\text{CMeCH}_2)_2$  (I) and  $(\text{CMe}_2\text{CH})_2$  (II) have the following Raman frequencies, relative intensities, and depolarisation factors: (I) 1297 (50), 1414 (430) 0.74, 1651 (1000) 0.21, 2977 (580) 0.28, 3074 (220) 0.78, (II) 1227 (75) 0.46, 1663 (1000) 0.18, 3012 (very weak), 3040 (very weak). Vals. for (I) agree with earlier data for  $\text{CXY:CH}_2$  olefines, H 2 (A., I).

and vals. for (II) show conjugation decreases in frequency of 19, 19, 0, 10  $\text{cm}^{-1}$  relative to  $\text{CXY:CH}_2$  in dipentene. L. J. J.

**Raman spectra of two forms of alloocimene.** J. J. Hopfield, S. A. Hall, and L. A. Goldblatt (*J. Amer. Chem. Soc.*, 1944, 66, 115—118).—Two forms of alloocimene (I), A and B, have been isolated in the pyrolysis products of  $\alpha$ -pinene at  $\sim 375^\circ$ , and, whilst both yield the same additive product with  $(\text{CH}_3\text{CO})_2\text{O}$ , they have different b.p., f.p.,  $\rho$ , and Raman spectra. A exhibits a strong Raman displacement of 1365  $\text{cm}^{-1}$  and B one of 1272  $\text{cm}^{-1}$ , thus enabling identification of each in a mixture. The Raman spectra support the interpretation that A and B are two of the four possible geometrical stereoisomerides of (I). W. R. A.

**Spectra of scattered light and viscosity of liquids.** E. F. Gross and A. A. Siromiatnikov (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 144—147).—The intensity of light depolarised and scattered without frequency change is high in PhOH and *p*-cresol at 19°. At 140—174° this intensity is less, but a diffuse depolarised background appears on both sides of the unchanged frequency. The background is due to mol. movement and becomes noticeable when the relaxation time of a mol. is comparable with the period of light vibrations. J. J. B.

**Relaxation and light scattering in liquids.** M. A. Leontovitsch (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 148—149).—The  $\lambda$  distribution and degree of depolarisation in the Rayleigh line and its background are determined by application of the relaxation theory of viscosity. A connexion exists between double refraction in a flowing liquid, relaxation time, and depolarisation of scattered light. J. J. B.

**Study of the structure of Rayleigh lines by means of resonance absorption.** M. F. Vuks (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 150—154).—The light of a Na lamp is separated into a beam which passes through a wedge, and another which is scattered by liquid  $\text{CCl}_4$  or  $\text{C}_6\text{H}_6$ , and the scattered part of which passes through Na vapour. If the intensities of the beams are made equal by adjusting the wedge at room temp., a temp. increase of the Na vapour reduces the intensity of the second beam. This reduction is different for unscattered light, for light scattered by  $\text{C}_6\text{H}_6$ , and for light scattered by  $\text{CCl}_4$ ; this shows that the fine structure of the scattered line is not identical with that of the original line and depends on the scattering liquid. Similar results are obtained with a modification of the above method. The Na vapour temp. is changed between 100° and 350°. The results permit calculation of the intensity distribution in the Rayleigh line. J. J. B.

**Production of a photo-voltage in phosphor cells.** F. Goos (*Ann. Physik*, 1941, [v], 39, 281—294).—Phosphors with transparent, metal-sputtered electrodes behave like Se or  $\text{Cu}_2\text{O}$  photo-elements when exposed to light, giving a photo-e.m.f. In addition to a pure photo-effect there are disturbing secondary phenomena, including a crystal photo-effect. The effect is particularly marked with CdS-Cu phosphors, which are as good as Se. The effect is widely independent of phosphorescence properties. The photo-e.m.f. has been measured for CdS-Cu, CdS-Ni, and ZnS-Cu, and also for a non-luminous but photosensitive NaS crystal, and for mixed phosphors ZnS-CdS-Cu. A rectifier action occurs at the boundary layer. Like Se, the max. in the spectrum of photo-e.m.f. in the case of CdS-Cu is displaced towards shorter  $\lambda$ . This is not so with the secondary current and dielectric const., which depend on the material of the base, and are connected with the phosphorescence. The e.m.f. is almost independent of temp. over the range —180° to 50°. The widening of the spectrum is due to secondary effects of the base. There is a change in the spectrum if the CdS-Cu cell is sputtered with Au instead of Pt. The spectral distribution is dependent on the conditions of prep. of the phosphor base and the nature of the photo-sensitive centres, but is independent of the luminescence. A. J. M.

**Electrical conductivity of thorium oxide at high temperatures.** M. Foëx (*Compt. rend.*, 1942, 215, 534—536).—Measurements on the compressed oxide in air,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CO}_2$ , vac.,  $\text{H}_2$ , and CO in the range 600—2100° are given and discussed. The variation of resistance with temp. is more rapid than for most refractory oxides and its insulating power is inferior. The conductivity depends markedly on the nature of the gaseous medium. N. M. B.

**Electrostatic contribution to hindered rotation in certain ions and dipolar ions in solution. III.** T. L. Hill (*J. Chem. Physics*, 1944, 12, 56—61).—Effective dielectric consts. are calc. for glutamic acid and its ions, and an empirical relation between them valid for a no. of substances is indicated. (Cf. A., 1944, I, 78.) L. J. J.

**Use of refractive index measurements in fatty acid ester analyses.** K. F. Mattil and H. E. Longenecker (*Oil and Soap*, 1944, 21, 16—19).—The  $n$  (Abbé refractometer) of highly purified Me deoate, laurate, myristate, palmitate, and oleate and their mixtures have been determined at temp. from 20° to 45°. It is shown that for each ester the relation  $n_D/\theta$  is linear and given by  $n_D^\theta = x + a\theta$ , where  $\theta$  is the temp.  $x = 1.4334, 1.4395, 1.4446, 1.4486$ , or  $1.4595$ , and  $a = -0.00040, -0.00039, -0.00039, -0.00039$ , or  $-0.00038$ .



for the respective esters, in the above order. The vals. 1.42515<sup>20.4°</sup>; 1.43136<sup>20.8°</sup>; 1.43667<sup>20.4°</sup>; —; and 1.45157<sup>21.0°</sup>, respectively, were determined by the more accurate Pulfrich refractometer. Me stearate had  $n_D^{20}$  1.4365 and  $n_D^{45}$  1.4345, Me linoleate  $n_D^{25}$  1.4597, and Me linolenate  $n_D^{25}$  1.4692. Examination of binary mixtures of the esters at 30° and 45° showed that a linear relation exists between  $n_D$  and the % composition by wt. (but not with molar composition); a similar relationship holds for three- and four-component mixtures. (See also C., 1944, Part 3.) E. L.

**Dispersion of magnetic birefringence.** R. Servant (*Compt. rend.*, 1942, 215, 574—576).—The expression  $C = c\lambda/(\lambda^2 - \lambda_0^2)$  for the Kerr const.  $C$  is applied to various substances, and its significance in the case of gases and liquids is discussed. N. M. B.

**Hydrogen bond.** L. Hunter (*Chem. and Ind.*, 1944, 155—157).—A review. The effect of the existence of the H bond in determining the properties of H<sub>2</sub>O is discussed. Types of H bond involving the atoms F, O, N, and C are listed and discussed. A. J. M.

**Hyperconjugation in paraffin hydrocarbons.** G. W. Wheland and J. T. Pinkston, jun. (*J. Chem. Physics*, 1944, 12, 69).—Resonance energy due to hyperconjugation in paraffin hydrocarbons is shown to increase the energy of each C—C single bond without appreciably affecting its constancy from substance to substance. L. J. J.

**Intermolecular correlation.** A. Tschintschin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 33, 482—484).—Mathematical. J. W. S.

**Identity of the properties of covalencies and co-ordinations.** J. P. Mathieu (*Compt. rend.*, 1942, 215, 325—327).—A review of various evidence shows that there are, at present, no experimental facts which establish, between covalencies and co-ordinations, a difference already abolished by electronic theory. N. M. B.

**Connexion between decrease of refraction and reduction of susceptibility in crystal lattices and in molecules.** T. Neugebauer (*Ann. Physik*, 1941, [v], 39, 241—260).—In the case of both decrease of refraction and reduction of susceptibility the wave equation of a double perturbation problem is involved, one perturbation arising from the field of the neighbouring ions, and the other from the field of the light wave or the external magnetic field. In the case of the decrease of refraction the second approximation of the characteristic function is used, whereas only the first is required for reduction of susceptibility. The quantum-mechanical basis of this is discussed. A simple method is described for the direct application of the formulae deduced to multi-electron problems. The refraction of the HCl mol. is calc. with the aid of the new Hartree tables. A. J. M.

**Symmetry of certain thermodynamic relations.** J. W. Creely, G. C. Le Compte, and W. W. Lucase (*J. Franklin Inst.*, 1943, 235, 617—622).—The underlying similarity of thermodynamic relations between the variables which determine the state of a system, viz., heat content, intrinsic energy, work content, free energy, temp., pressure, entropy, vol. heat, and work, is emphasised. A. J. M.

**Molecular structures of silicon dimethyl dichloride, silicon methyl trichloride, and trifluorosilicon chloride.** R. L. Livingston and L. O. Brockway (*J. Amer. Chem. Soc.*, 1944, 66, 94—98).—From electron diffraction data for the vapours of SiMe<sub>2</sub>Cl<sub>2</sub>, SiMeCl<sub>3</sub>, and SiF<sub>3</sub>Cl the Si—C distances are < in SiMe<sub>2</sub>, whilst the Si—Cl distances are approx. those in Si chlorides. The SiF<sub>3</sub> group in SiF<sub>3</sub>Cl does not bind the Cl more tightly than in SiCl<sub>4</sub>, in contrast to the behaviour of CF<sub>3</sub> in CF<sub>3</sub>Cl. W. R. A.

**Nature of static friction.** W. Claypoole and D. B. Cook (*J. Franklin Inst.*, 1942, 233, 453—463).—From a brief crit. survey of factors concerned and the limitations of various approaches a more satisfactory view of the basic cause is developed in relation to modern experimental knowledge. N. M. B.

**Molecular surface energy of sulphur dioxide additive compounds.** III. J. J. Jasper and J. R. Bright (*J. Amer. Chem. Soc.*, 1944, 66, 105—106).—The influence of temp. on the mol. surface energy of the compound NPr<sub>3</sub>SO<sub>2</sub> and the equimol. mixture of NPr<sub>3</sub> and SO<sub>2</sub> has been determined. Vals. of  $\rho$ ,  $\gamma$ , and  $\eta$  are given for temp. between 0° and 45°. Eotvos consts. have been calc. and are < those for additive compounds of lower mol. wt., indicating that the temp. coeff. decreases with increasing mol. wt., whilst the tendency to associate increases. Parachor data suggest the presence of a N—O—S linking. W. R. A.

**Parachor of chromium trioxide in water.**—See A., 1944, I, 122.

### III.—CRYSTAL STRUCTURE.

**Improvements in practical Fourier analysis and their application to X-ray scattering from liquids.** G. C. Danielson and C. Lanczos (*J. Franklin Inst.*, 1942, 233, 365—380, 435—452).—Mathematical. Results are applied to the X-ray analysis of molten LiCl. N. M. B.

**Resetting a triclinic unit-cell in the conventional orientation.** J. D. H. Donnay (*Amer. Min.*, 1943, 28, 507—511).—Procedure is described, and examples are given. L. S. T.

**Ordered and disordered structures of titanates and ferrites and ordered transformations of the TiO<sub>2</sub> modifications.** F. Barblan, E. Brandenberger, and P. Niggli (*Helv. Chim. Acta*, 1944, 27, 88—96).—Disordered forms of heteropolar substances such as Li<sub>2</sub>TiO<sub>3</sub> and Li<sub>2</sub>Fe<sub>2</sub>O<sub>4</sub> are obtained by reactions in the solid state, quenching from the melt, or continuous tempering below the stability temp. of the disordered modification. Tempering of quenched Li<sub>2</sub>Fe<sub>2</sub>O<sub>4</sub> at 570° produces a tetragonal form in which the Fe and O are related as Ti and O in the ideal anatase structure. Li<sub>2</sub>Ti<sub>2</sub>O<sub>6</sub>, obtained by reaction in the solid state and tempered for 40 hr. at 1200°, gives the same system of interference lines as Li<sub>2</sub>TiO<sub>3</sub>.  $\rho$  measurements show that some metal atom positions are empty. Li<sub>2</sub>Fe<sub>10</sub>O<sub>18</sub> gives an interference diagram similar to that of magnetite, for which a quarter of the positions occupied in FeO are empty. Magnetite has a regular distribution of Fe<sup>II</sup> with co-ordination no. 4 referred to O, the AB<sub>2</sub> structure of the NaCl type thus being stabilised. When there are more O atoms than Fe, the latter structure is at first maintained, and then part of the Fe is transformed from an octahedral into a tetrahedral structure. Structures with unoccupied positions then permit entry of alkali metal atoms, as Li, which compensate electrostatically for the valency change, thereby stabilising the valency. Thus Li<sub>2</sub>Fe<sub>2</sub>O<sub>4</sub>, ordered and disordered, possesses the FeO structure, and Li<sub>2</sub>Fe<sub>10</sub>O<sub>18</sub>, the Fe<sub>2</sub>O<sub>3</sub> structure, although in both cases the Fe is tervalent. The cell consts. of certain compounds containing Fe, Li, and O are given; they show the effect of replacement of Fe by Li to be small. Brookite, but not anatase, can be transformed into rutile. The flat (100) plane of brookite and the (100) plane of rutile remain parallel on transformation. Inside the flat plane the rutile needles lie in different directions, the  $c$  axes being either parallel to the  $c$  and  $b$  axes of brookite or in the directions of the zones (027) and (023) of brookite. J. O'M.-B.

**Crystallography of acanthite, Ag<sub>2</sub>S.**—See A., 1944, I, 92.

**Crystal structure of gillespite, BaFeSi<sub>3</sub>O<sub>10</sub>.**—See A., 1944, I, 92.

**Crystal structure of parkerite, Ni<sub>3</sub>Bi<sub>2</sub>S<sub>2</sub>.**—See A., 1944, I, 92.

**Four known crystalline forms of soap.** R. H. Ferguson (*Oil and Soap*, 1944, 21, 6—9).—A crit. survey. The existence of four cryst. polymorphic forms of pure Na soaps, viz.,  $\alpha$ ,  $\beta$  (cf. Thiessen and Stauff, A., 1936, 1186),  $\delta$  (cf. Ferguson *et al.*, A., 1943, 1, 306), and  $\omega$  (probably identical with the " $\gamma$  soap" of De Bretteville and McBain; A., 1943, I, 300), has been established by X-ray diffraction studies, the short (or side) spacing being especially valuable for phase identification. The cryst. phase composition of commercial soaps depends on the soap, moisture, and electrolyte composition of the system, and on the conditions of processing, e.g., rapid cooling of neat soap induces the formation of  $\omega$ -soap, whilst slow cooling increases the amount of  $\beta$ ; working and extrusion of plastic soap also induce changes; thus extrusion of soap assists in producing phase equilibrium, and under appropriate conditions may induce change from  $\beta$  to  $\omega$ , or the reverse. Each crystal form has its own field of stability, its composition, temp. range, and possible equilibria with other phases constituting the phase diagram for the particular soap-H<sub>2</sub>O system involved. Whilst soap crystallising from solution in H<sub>2</sub>O may form a crystal phase containing H<sub>2</sub>O, it is very doubtful if this constitutes a definite hydrate; the X-ray diffraction patterns do not indicate any definite hydrates over the range 2.5—95% of H<sub>2</sub>O, and the existing evidence suggests that the solid modifications of soap are of the nature of solid solutions, being cryst. phases of variable composition. It appears that no sol. gel, or mother-liquor exists in many types of bar soap, so that the old conception of commercial bar soaps as "fibres of insol. soap enmeshing a gel or sol of the more sol. soaps" must be modified. Also, in most commercial soaps, the "fractionation" of the fatty acids suggested by this old definition does not appear to occur, though a certain degree of fractionation between two different solid solutions may take place. E. L.

**Variation of the magnetic anisotropy of stretched rubber as a function of tension.** (Mme.) E. Cotton-Feytis (*Compt. rend.*, 1942, 215, 299—301).—On analogy with a uniaxial crystal, the anisotropy is measured by the Krishnan oscillation method as used for crystals. Data are tabulated and discussed. The anisotropy appears to increase to a max. when the mol. chains are oriented parallel under the effect of stretching. The anisotropy-tension curve is similar to the curve of intensity variation of the diffraction spots with tension in X-ray diagrams. N. M. B.

**Magnetostriction of iron in intense magnetic fields.** O. Rüdiger and H. Schlechtweg (*Ann. Physik*, 1941, [v], 39, 1—18).—Change in length due to magnetostriction in the direction of the field is calc., especially its asymptotic behaviour in intense fields, for all field-crystal lattice orientations. Comparison with experimental data for single crystals and quasi-isotropic polycrystals shows that any departure from calc. results can be expected only at higher field strengths. L. J. J.

**Colour and constitution of glasses.**—See B., 1944, I, 136.

**Deformation of solids.** C. de Carbon (*Compt. rend.*, 1942, 215, 241—244).—Deformations which give rise to departures from



Hooke's law can be considered as the sum of two terms, one independent of, and the other increasing with, time. Theorems of these two terms are postulated and examined mathematically.

N. M. B.

#### IV.—PHYSICAL PROPERTIES OF SUBSTANCES.

Physical properties of butadiene and styrene.—See B., 1944, II, 120.

Mol. wt., gram-molecule, and Avogadro's number. W. E. Duncan (Phil. Mag., 1944, [vii], 35, 73—80).—Difficulties may arise in dimensional theory if the distinction between mol. wt. (a ratio) and g.-mol. (a mass) is overlooked. Temp., the gas const., mol. heats, and latent heats are discussed as examples.

H. J. W.

Elementary processes in magnetisation in the region of initial susceptibility. G. Thiesse (Ann. Physik, 1941, [v], 39, 30; cf. *ibid.*, 1940, [v], 38, 153).—A correction.

L. J. J.

Temperature-dependence of the magnetic susceptibility of europium sulphate. H. Fritsch (Ann. Physik, 1941, [v], 39, 31—32).—Vals. for the magnetic susceptibility of  $\text{Eu}^{III}$  sulphate at 20°, 80°, 196°, and 356° K. are 1.29, 1.29, 1.16, and 0.83 times the val. at 0°.

L. J. J.

Gray and Cruickshank's method and the diamagnetic susceptibilities of dicyanodiamide, acetamide, and cyanuric acid. S. K. Siddhanta and P. Ray (J. Indian Chem. Soc., 1943, 20, 359—364).—Measurements on carefully purified specimens give results showing only moderate agreement with vals. calc. by Gray and Cruickshank (A., 1936, 19) from magnetic analysis of resonating mol. structures, but the latter are a marked improvement on vals. from Pascal's earlier procedure.

N. M. B.

Absorption of sound in mixtures of monatomic gases. M. Kohler (Ann. Physik, 1941, [v], 39, 209—225).—The effect of ordinary and thermal diffusion on the absorption of sound in mixtures of monatomic gases is investigated using the Enskog equations; the equations of motion are derived from the kinetic theory, and the propagation of waves of infinitely small amplitude is considered. A sound wave in the mixture produces periodic variations not only of  $\rho$  and temp., but also of the mean mol. wt. The equations of motion reduce to three linear homogeneous equations for  $\rho$ , temp., and mean mol. wt. In addition to the Kirchhoff terms arising from friction and thermal conduction, three new terms enter, due to diffusion; they depend on frequency and pressure. The first of these terms is due to the effect of ordinary diffusion, and is  $\propto$  diffusion coeff., to  $(M_2 - M_1)^2/M_0^2$  ( $M$  = mol. wt.), to  $C_p/C_v$ , and to  $C_1C_2$ , the product of the mol. conns. The second term is due to thermal diffusion and is  $\propto (C_p/C_v) - 1$ , to  $C_1C_2$ , to  $(M_2 - M_1)/M_0$ , and to a coeff. which accounts for the thermal diffusion. The third term is due to increased thermal conductivity due to thermal diffusion. The possibility of deriving thermal diffusion coeffs. from determinations of sound absorption in gaseous mixtures is mentioned.

A. J. M.

Absorption of sound, specific heat, and period of adjustment of electron spin in nitric oxide. H. O. Kneser (Ann. Physik, 1941, [v], 39, 261—272).—The half-val. widths and frequencies of the resonance points of a cylindrical resonator are measured in NO by means of a condenser-microphone; the absorption and velocity (relative to air) of sound in the gas are obtained. Between 300 and 3000 cycles per sec. the absorption is too weak to be measured. The sp. heat is calc. from the velocity of sound, the val. obtained agreeing closely with that calc. from spectroscopic data. At these frequencies there is no delay in establishing thermal equilibrium, and the distribution of the mols. on the two levels of the split ground state occurs in  $<10^{-8}$  sec. The probability of reversal of the electron spin in a gas-kinetic collision at 289° K. is  $\leq 1:6500$ .

A. J. M.

Heat capacity, heats of transition, fusion, and vaporisation, vapour pressure, and entropy of *aaa*-trifluoroethane. H. Russell, jun., D. R. V. Golding, and D. M. Yost (J. Amer. Chem. Soc., 1944, 66, 16—20).—Vals. of  $C_p$  for  $\text{CMeF}_3$  are measured calorimetrically from 12° to 220° K. The following vals. are found: m.p.  $161.82 \pm 0.04^\circ$  K.; heats of transition, fusion, and vaporisation  $\sim 71$ ,  $1480 \pm 75$ , and  $4582 \pm 5$  g.-cal.; v.p.,  $\log p = 48.37340 - 2015.675/T - 16.81950 \log T + 0.0133816T$ ;  $S_{298.16} = 60.87 \pm 0.15$ ;  $S_{224.40} = 62.48 \pm 0.10$  (calorimetric) and  $63.95 \pm 0.10$  (spectroscopic) g.-cal. per degree per g.-mol. at 0.9330 atm. There is thus a barrier of  $3450 \pm 400$  g.-cal. per g.-mol. hindering internal rotation of the mol.

W. R. A.

Molecular heat of organic vapours. I. Method of measurement and preliminary results. A. Eucken and B. Sarstedt (Z. physikal. Chem., 1941, B, 50, 143—170).—The flow method of Blackett *et al.* (A., 1930, 282) is employed, with improvements which increase its accuracy for the measurement of mol. heats of org. vapours to  $\sim 1\%$  at 200° and  $\sim 2\%$  at 300°.  $C_p$  for  $\text{C}_6\text{H}_6$  shows the temp. variation predicted from Kohlrausch's normal vibrations.  $C_p$  vals. for  $\text{CCl}_4$  are  $>$  those calc. from Planck's formula by  $\sim 1$  g.-cal. per g.-mol., as a result of vibrational anharmonicity. For  $\text{C}_6\text{H}_{12}$ — $\text{C}_7\text{H}_{16}$  the mol. heats are  $3.5$ — $7.0$  g.-cal.  $>$  existing published vals.

at 180°, but  $<$  vals. predicted from Pitzer's theory by  $\sim 1$  g.-cal. for *n*-paraffins and  $\sim 2$  g.-cal. for isoparaffins.

L. J. J.

Transition temperatures and heats of transition of alkali hydrosulphides and hydroselenides.—See A., 1944, I, 38.

Thermal expansion of titanium. P. Hidnert (J. Res. Nat. Bur. Stand., 1943, 30, 101—105).—The coeff. of linear expansion of Ti (97.2%) increases from  $\sim 5 \times 10^{-6}$  per °C. at  $-150^\circ$  to  $\sim 12 \times 10^{-6}$  per °C. at 650°. The data on thermal expansion do not indicate the existence of polymorphic transformations of Ti between  $-190^\circ$  and 700°.

A. J. M.

Table of thermodynamic properties of air. J. H. Keenan and J. Kaye (J. Appl. Mechanics, 1943, 10, A123—130).—Over the range of conditions for which  $p v = RT$  satisfactorily represents the  $p$ - $v$ - $T$  relation, a table having a single argument, *i.e.*, temp., serves all the purposes given by vapour (steam,  $\text{NH}_3$ , etc.) tables having two arguments. A table of this type with intervals small enough for linear interpolation is presented for dry air. Data from the table are compared with the vals. of Gerhart *et al.* (A., 1942, I, 262).

R. B. C.

A steady-state problem in heat conduction. A. N. Lowan (Phil. Mag., 1943, [vii], 34, 502—504).—Mathematical.

W. J.

Problem in heat conduction. C. J. Tranter (Phil. Mag., 1944, [vii], 35, 102—105).—The temp. variation in a semi-infinite annulus bounded by the plane  $z = 0$  and the cylinders  $r = a$  and  $r = b$ , the surfaces  $z = 0$  and  $r = a$  being maintained at zero temp. and  $r = b$  at  $f(z)$ , is solved in the case where the initial temp. of the annulus is zero (cf. Lowan, preceding abstract, for a steady-temp. solution).

H. J. W.

Viscosity of sulphuric acid.—See B., 1944, I, 133.

Viscosities of unsaturated six-membered isocyclic compounds. J. N. Friend and W. D. Hargreaves (Phil. Mag., 1944, [vii], 35, 136—142).—In the series  $\text{C}_6\text{H}_{12}$ ,  $\text{C}_6\text{H}_{10}$ ,  $\text{C}_6\text{H}_8$ , the  $\eta$  decreases as the degree of unsaturation increases, but rises again in  $\text{C}_6\text{H}_6$ . The rheochor ( $R$ ) of the Ph group attached to alkyl groups is 100.7 (mean), but if the attached group is electronegative  $R$  is raised by up to 4.5 units above this.  $R$  increases with the mass of the substituent group in the Ph ethers.

H. J. W.

#### V.—SOLUTIONS, DISPERSIONS, AND MIXTURES.

Viscosity of sulphuric acid [solutions].—See B., 1944, I, 133.

Chemical and biological studies of aqueous solutions of boric acid and of calcium, sodium, and potassium metaborates.—See A., 1944, III, 378.

Nucleus formation in aqueous solutions. U. Dehlinger and E. Wertz (Ann. Physik, 1941, [v], 39, 226—240).—The spontaneous formation of nuclei in supersaturated solutions of  $\text{KAl}(\text{SO}_4)_2$  has been investigated at 0°, 20°, and 40°, by determining the time at which crystallisation begins. Below a concn.  $\sim 4$  mol.-%, which is to some extent dependent on temp., no spontaneous nucleus formation sets in after a year. There is a sharp boundary between metastable and stable supersaturated solutions. An attempt to apply the theory of Volmer *et al.* on the formation of nuclei from the vapour state to this boundary curve shows that the sharpness of the experimental boundary and the effect of temp. on it do not agree with the theory. Nucleus formation by negative diffusion, however, gives a satisfactory explanation. It is assumed that each dissolved ion tends to surround itself with 6  $\text{H}_2\text{O}$  mols. Thus above 4 mol.-% only a part of the ions is separated by a layer of  $\text{H}_2\text{O}$  mols. The Coulomb forces between the ions produce at lower temp. a max. in the variation of thermodynamic potential with concn. at  $\sim 4$  mol.-% and thus a negative diffusion coeff. above this concn.

A. J. M.

Parachor of chromium trioxide in water. P. M. Toshniwal, V. A. Moghe, and W. V. Bhagwat (J. Indian Chem. Soc., 1943, 20, 341—342).—The parachor of  $\text{CrO}_3$  ( $\sim 103$ ) indicates that in solution it exists in ionic form and by combining with  $\text{H}_2\text{O}$  forms  $\text{H}_2\text{CrO}_4$  or  $\text{H}_2\text{Cr}_2\text{O}_7$ . The calc. val. is 134 and the difference suggests that ionic parachors are  $<$  at. parachors for the same element.

C. R. H.

Pyrazine-water azeotrope. H. F. Pfann (J. Amer. Chem. Soc., 1944, 66, 155).—The azeotrope distils at  $95.5^\circ$  (uncorr.)/760 mm. and has  $n_D^{25} 1.4510$ ,  $d_4^{25} 1.06$ , 60% pyrazine—40%  $\text{H}_2\text{O}$ . No azeotrope is formed with MeOH or EtOH.

W. R. A.

Iron-rich iron-nickel alloys.—See B., 1944, I, 171.

Solubilities of normal aliphatic nitriles of high mol. wt. C. W. Hoerr, E. F. Binkerd, W. O. Pool, and A. W. Ralston (J. Org. Chem., 1944, 9, 68—80).—The solubilities of deco-, dodeco- (I), myristo-, palmito-, and stearo-nitrile have been determined in  $\text{C}_6\text{H}_6$ , cyclohexane (II),  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{Et}_2\text{O}$ ,  $\text{AcOH}$ ,  $\text{EtOAc}$ ,  $\text{BuOAc}$ ,  $\text{COMe}_2$ ,  $\text{COMeEt}$ ,  $\text{MeOH}$ , 95%  $\text{EtOH}$ ,  $\text{Pr}^i\text{OH}$ ,  $\text{Bu}^i\text{OH}$ ,  $\text{EtNO}_2$ , and  $\text{MeCN}$ . In general the solubilities decrease with increasing polarity of the solvent. In any given solvent, the solubilities decrease regularly as the mol. wt. of the nitrile increases. The aliphatic nitriles form simple eutectics with the non-polar solvents,  $\text{C}_6\text{H}_6$  (II), and  $\text{CCl}_4$ ;



the compositions and f.p. are recorded. Of the three non-polar solvents used the nitriles are most sol. in  $C_6H_6$  and least sol. in  $CCl_4$ . As the mols. are symmetrical and of practically identical dielectric const. it appears that the resonance of the  $C_6H_6$  mol. is an important factor affecting the solubility of the nitriles. In general, the nitriles are less freely sol. in the slightly polar solvents, ( $CHCl_3$ ,  $Et_2O$ ,  $AcOH$ ,  $EtOAc$ ,  $BuOAc$ ) than in the non-polar solvents but considerably more sol. in  $CHCl_3$  than in  $CCl_4$  at any given temp. They are less sol. in  $COMe_2$  than in  $COMeEt$ ; they are, however, more sol. in both of these solvents than in any of the less polar solvents except in the lower concn. ranges. They are less sol. in  $MeOH$ , 95%  $EtOH$ ,  $PrOH$ , and  $BrOH$  than in any of the preceding solvents. (II) is much less sol. in  $BuOH$  than in  $EtOAc$ , the polarity of which is of the same order of magnitude as that of  $BuOH$ . The solubilities of the nitriles in the alcohols differ relatively little at corresponding temp. in spite of the wide range of polarity of the alcohols. The nitriles are less sol. in the highly polar  $EtNO_2$  and  $MeCN$  than in any of the other solvents investigated with the exception of the alcohols and less sol. in  $MeCN$  than in  $EtNO_2$ . The shape of the solubility curves of the nitriles is characteristic of a wide variety of aliphatic compounds of high mol. wt. Mol. association is probably one of the factors influencing the slope of the temp.-concn. curve of long-chain compounds. No conclusions, however, regarding the nature or the extent of this association should be drawn until further investigations of the behaviour of long-chain compounds are available. H. W.

**Solubilities of normal aliphatic primary amines of high mol. wt.** A. W. Ralston, C. W. Hoerr, W. O. Pool, and H. J. Harwood (*J. Org. Chem.*, 1944, 9, 102—112).—The solubilities of decyl-, dodecyl-, tetradecyl-, hexadecyl-, and octadecyl-amine (I) have been observed in a no. of solvents. Their solubility graphs are similar to those of the fatty acids, ketones, and nitriles but they do not exhibit the marked correlation between solubility and polarity of the solvent which is so striking with the other compounds. They form simple eutectics with the non-polar solvents  $C_6H_6$ , cyclohexane, and  $CCl_4$ , the compositions and f.p. of which are determined. In these solvents they are most sol. in  $C_6H_6$  and least in  $CCl_4$ . Among the slightly polar solvents  $CHCl_3$ ,  $Et_2O$ ,  $EtOAc$ , and  $BuOAc$  the highest solvent power is shown by  $CHCl_3$ . The solubilities in  $EtOAc$  and  $BuOAc$  are practically identical. The amines are somewhat more sol. in  $COMeEt$  than in  $COMe_2$ . The solubility of (I) in  $COMe_2$  becomes so limited that a considerable region consisting of two immiscible solutions appears. Of the fatty acid derivatives thus far investigated (I) is unique in forming conjugate solutions with a solvent of polarity as low as that of  $COMe_2$ . With  $MeOH$ , 95%  $EtOH$ ,  $PrOH$ , and  $BuOH$  the amines differ from other fatty acid derivatives in being more sol. in the lower members of the series than in any of the other solvents used except  $CHCl_3$ . The amines differ widely in their solubilities in the various alcohols whilst the solubilities of other long-chain compounds do not differ greatly in these solvents. In the highly polar  $MeCN$  the amines are less sol. than in any other solvent studied and (I) shows a region of immiscibility similar to that found in the system, (I)— $COMe_2$ . In this system the entire immiscible region exists below the b.p. of the solvent, and the upper limit of the region of conjugate solutions can, therefore, be located. The solubilities of the amines in  $EtNO_2$  are not determinable owing to their reaction with this solvent. H. W.

**Solutions of lead in its fused chloride.** S. Karpatshev, A. Stromberg, and E. Jordan (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, 36, 101—104).—From measurements of the potential of a C electrode in a solution of Pb in fused  $PbCl_2$  at  $700^\circ$  as a function of the concn. of the metal, it is concluded that the Pb goes into solution as a univalent positive ion. The solubility of Pb in  $PbCl_2$  at  $700^\circ$  is 0.0417%.

**Factors affecting precipitation of insoluble quinaldates.** J. F. Flagg and F. T. McClure (*J. Amer. Chem. Soc.*, 1943, 65, 2346—2349).—Solubility products of insol. quinaldates have been found by a method involving fractional pptn. Applications of solubility data to problems of pptn. and separation with quinaldic acid are given. W. R. A.

**Hysteresis and capillary theory of adsorption of vapours.** L. H. Cohan (*J. Amer. Chem. Soc.*, 1944, 66, 98—105).—Several predictions based on the capillary theory of adsorption and the open pore theory of hysteresis show reasonable agreement with experimental data. This agreement indicates that the capillary theory, which postulates the formation of a unimol. layer followed by capillary condensation, is a fairly good first approximation for the adsorption mechanism in the systems discussed. Vals. of  $\gamma$  and mol. vol. of a liquid confined in a capillary of radius only twice the diameter of the liquid mol. appear to be approx. those for the liquid in bulk. W. R. A.

**Water-adsorption isotherm of wool.**—See B., 1944, II, 104.

**Adsorption in relation to constitution. II. Adsorption of organic acids on activated silica gel.** B. P. Gyani and P. B. Ganguly (*J. Indian Chem. Soc.*, 1943, 20, 331—337).—The adsorption on activated  $SiO_2$  gel of a large no. of org. acids from  $EtOH$  solution has been investigated. With the exception of  $HCOH$ , adsorption of which

is high, the adsorption of fatty acids appears to be almost independent of chain length. The % adsorption of dibasic acids decreases with increase in the no. of C in the chain. The product of adsorption coeff. and the no. of C in the mol. is const. ( $\sim 242$ ) with the exception of  $H_2C_2O_4$ , for which the product is 167. This suggests that the mols. lie flat on the adsorbent surface. Substitution of OH and halogen increases adsorption, ( $CHBrCO_2H$ ), being the one exception observed. Positional and optical isomerides differ little in adsorbability. C. R. H.

**Adsorption of  $NN'$ -diethyl- $\psi$ -isocyanine chloride on mica.** T. Škerlak (*Kolloid-Z.*, 1941, 95, 265—286).—Polymerisation of  $NN'$ -diethyl- $\psi$ -isocyanine chloride (I) is induced by adsorption on certain ionic lattices such as mica. Adsorption was examined by measurement of light absorption by the dyed mica plates. The difficulties in preparing satisfactory mica surfaces and in the light-intensity measurements are indicated. With increasing concn. of solutions of (I) the extinction rises rapidly to a max., indicating saturation of the surface. The amount of (I) adsorbed corresponds with a unimol. layer, the mols. being adsorbed on their long edge. Polymerisation occurs on adsorption as a consequence of this orientation. The distance between positively charged N atoms of (I) is approx. equal to that between points of negative charge in the cleavage surface of mica. Adsorption is reversible, and decreases with rising temp. The adsorption on Ag halides is of technical importance, and is in general similar, but is irreversible, indicating stronger forces. R. H. F.

**Surface area of porous materials calculated from capillary radii.** E. N. Harvey, jun. (*J. Amer. Chem. Soc.*, 1943, 65, 2343—2346).—Equations, based on the Kelvin formula, have been derived, by which the surface area of a porous adsorbent can be calc. from the high-pressure region of its adsorption isotherms. After correction for monolayer adsorption, and by using the desorption isotherm, surface areas are in good agreement with those obtained by the "point B" method. W. R. A.

**Effect of electrolytes on the surface activity of solutions of paraffin chain salts.** R. G. Aickin and R. C. Palmer (*Trans. Faraday Soc.*, 1944, 40, 116—120).—The treatment used by Cassie and Palmer (*A.*, 1941, I, 207) to calculate the change in potential energy in a surface film caused by increasing the concn. of counter-ions in the aq. solution is extended by taking into account the size of the ions. An expression is derived for the dependence of the lowering of interfacial tension on ion size, in satisfactory agreement with experimental data for the effects of  $Na^+$  and  $K^+$  on the tension of aq. Na alkyl sulphate-oil interfaces. F. L. U.

**Minima in surface tension-concentration curves of solutions of sodium alcohol sulphates.** G. D. Miles and L. Shedlovsky (*J. Physical Chem.*, 1944, 48, 57—62).—As dodecanol is added to solutions of Na dodecyl sulphate (I) the min. in the surface tension-concn. curves become more pronounced. The addition of a higher homologue of the corresponding sulphate to solutions of (I) or of Na tridecyl  $\beta$ -sulphate also causes pronounced min. Thus min. are due to the presence in the solution of more than one type of surface-active material; in the former case the presence of a slightly sol. surface-active substance and in the latter an admixture of two anionic surface-active electrolytes results in min. C. R. H.

**Spreading of liquids on mercury surface.** B. Ghosh (*J. Indian Chem. Soc.*, 1943, 20, 349—354).—For liquids to spread on Hg the presence of a promoter, the function of which is to spread a unimol. layer of some ion on the Hg, is necessary. For  $H_2O$  to spread,  $\sim 10^{-8}$  g. of acid or salt per g. of  $H_2O$  is necessary. Alkaline salts are less effective.  $H_2O$  containing traces of colloidal Au or graphite spreads after irradiation with X-rays. For acid promoters  $\sim 10^{14}$  H<sup>+</sup> per 1 sq. cm. of Hg surface are necessary before spreading takes place. For the alkali halides the no. of cations necessary increases as the size of the cation increases. C. R. H.

**Structure of an ovalbumin-detergent complex.** K. J. Palmer (*J. Physical Chem.*, 1944, 48, 12—21).—A structure for a denatured ovalbumin-detergent (Nacconol NRSF) complex, which is in agreement with the results of Lundgren *et al.* (*cf. A.*, 1943, III, 838), consists of a polar protein monolayer with the detergent mols. adsorbed on one side only and with their long axes perpendicular to the protein layer. It is possible that the polar  $NH_2$ -acids alternate along the peptide chain in ovalbumin. The structure of native ovalbumin is discussed and a schematic drawing, in which the mol. possesses one polar and two non-polar interfaces, is presented. With this structure it is possible to explain two facts with respect to native ovalbumin-detergent complexes, viz., the occurrence of free native ovalbumin in equilibrium with a complex containing 25% of detergent, and the presence in the complex of  $<25\%$  of the detergent. C. R. H.

**Theoretical considerations on emulsions and their separation.** A. Dobrowsky (*Kolloid-Z.*, 1941, 95, 286—296).—The energy content of the emulsified phase is represented as a function of the degree of dispersity. Applying the Boltzmann-Einstein statistical energy distribution theorem, the distribution of particle sizes is derived.



Assuming no disturbing factors, Stokes' law is applied to the falling particles, and a function obtained relating the vol. of the separated phase to the time. This is in satisfactory agreement with available data.

R. H. F.

**Effect of sand on the viscosity, yield value, and thixotropic gelation of mud suspensions.** J. N. Mukherjee and B. R. Majumdar (*Proc. Indian Assoc. Cult. Sci.*, 1943, 28, 3—6).— $\eta$ , and the cumulative vol. of  $H_2O$ , of suspensions of Powai clay with two samples of sand, (i) 48—100- and (ii) >100-mesh, have been determined. With (i) there is no marked variation of  $\eta$  with sand concn., but addition of 5% of (ii) greatly increases  $\eta$ . Up to 3%, addition of both (i) and (ii) reduces the thixotropic gel strength, but above 3% it again increases. Relative yield vals. also vary with sand concn. The cumulative vol. of  $H_2O$  after 1 hr. increases up to 3% of sand, and then decreases.

W. R. A.

**Bredig platinum sols.** J. Mindel and C. V. King (*J. Amer. Chem. Soc.*, 1943, 65, 2112—2115).—Pt sols were prepared by arcing between 2-mm. Pt wires with d.c. of 220 v. and 4 amp., using  $H_2O$ ,  $HCl$  (0.0001—0.0007N.), and  $HNO_3$  (0.0001—0.0004N.) as dispersion media and air,  $O_2$ , and  $N_2$  as stirring gases. Composition and stability are only slightly affected by variation of dispersion medium and gaseous atm. The Pt content of the micelle is unaffected by coagulation with acids. Sols prepared by arcing in the gas phases are similar in all respects to normal Bredig sols. Formation of Bredig sols appears to follow the mechanism of formation of gas-phase sols which are stabilised by oxidation products of Pt formed when the Pt particles come in contact with  $H_2O$ .

W. R. A.

**Osmotic activity of colloidal electrolytes.** J. W. McBain and A. P. Brady (*J. Amer. Chem. Soc.*, 1943, 65, 2072—2077).—All osmotic coeffs. of colloidal electrolytes fall on three curves, one for straight-chain, one for branched, and one for polycyclic colloidal electrolytes and, consequently, activity coeffs. can be obtained with fair accuracy from one f.p. measurement. Both osmotic and conductivity data support the evidence of previous migration data that very dil. solutions contain a small proportion of highly conducting micelles. Addition of  $KCl$  or  $K_2SO_4$  to very dil. solutions of K laurate promotes the formation of colloid and f.p. lowering is  $\ll$  additive, whereas at higher concns., where the colloid is already formed, the f.p. lowering is slightly  $>$  additive.

W. R. A.

**Solubilisation and colloidal micelles in soap solution.** J. W. McBain and K. E. Johnson (*J. Amer. Chem. Soc.*, 1944, 66, 9—13).—The solubilisation of  $H_2O$ -insol. dye by four K soaps has been measured for equilibrium conditions at various concns.; it increases so rapidly with the higher soaps as to suggest its incorporation between the lamellar micelles rather than dissolution in the hydrocarbon fraction of the micelle.  $KCl$  greatly increases the solubilising power of fully-formed micelles and produces micelles of still higher solubilising power in dil. solution.

W. R. A.

**Comparative osmotic and viscosity measurements with polystyrene fractions.** T. Alfrey, A. Bartovics, and H. Mark (*J. Amer. Chem. Soc.*, 1943, 65, 2319—2323).— $\eta$  and  $\pi$  have been measured for PhMe solutions of polystyrene fractions, prepared by polymerising styrene at 60°, 120°, and 180° and fractionated by pptn. with MeOH from PhMe solution. The consts.  $k'$  and  $\mu$ , of the viscosity and osmotic laws, and the mol. wt. have been calc. for each fraction.  $k'$  and  $\mu$  differ for samples prepared at different temp.; the consts. of  $[\eta] = KM^a$  also differ for different samples. It is suggested that, for fractions of equal mol. wt., ease of pptn. is related to  $[\eta]$ .

W. R. A.

**Dependence of viscosity on concentration in [solutions of] organic high polymers.** M. Takei and H. Erbring (*Kolloid-Z.*, 1941, 95, 322—326).—The Philippoff-Hess eighth-power formula is modified by introduction of a term depending on particle shape. The modified formula is shown to reproduce the experimental data in three cases where the original formula failed, viz., "Cellite" in  $AcOH$ , polymerised  $\omega$ -hydroxydecoic acid in  $(CHCl_3)_2$ , and polystyrene in  $C_6H_6$ .

R. H. F.

**Analysis of thermodynamic measurements on highly elastic fibrous materials.** E. Wöhlisch (*Kolloid-Z.*, 1941, 95, 296—302).—Highly elastic materials are characterised by their anomalous thermoelastic behaviour, which is described by a thermal extension coeff. and a thermal stress coeff. Materials are classified according to the magnitude of these coeffs., and data are given for some biological materials. Relations between measurable properties of stretched materials and thermodynamic magnitudes are indicated. Swelling and irreversible heat effects have in some cases to be taken into account.

R. H. F.

**Molecular orientation and some properties determined by it in macro-molecular substances with chain and network structures.** II. F. H. Müller (*Kolloid-Z.*, 1941, 95, 306—322; cf. A., 1944, I, 29).—The nature of the orientation distribution function is discussed for chain and network structures, and the change in directional distribution of bonds on deformation is examined. The return of stretched materials to the undeformed state requires time, which is shorter at higher temp. Below a certain temp. contraction no longer occurs and the material freezes up. The relaxation time,

which is obtained from the contraction-time curve, is related to the place-exchange frequency of monomer residues or small units. High viscosity and plasticity are consequences of low place-exchange frequency. It is necessary to assume a series of relaxation times in many cases. With polystyrene the relaxation spectrum shows two time groups, corresponding with movement of monomer residues and of whole mols. The variation of each with temp. accounts for freezing and flow phenomena.

R. H. F.

**Statistical length of rubber molecules.** L. R. G. Treloar (*Trans. Faraday Soc.*, 1944, 40, 109—116).—The length distribution for mols. containing up to 256 isoprene units is worked out by the methods previously used (A., 1943, I, 299) for paraffin chains.

F. L. U.

**Isoelectric point of asclepain.** D. C. Carpenter and F. E. Lovelace (*J. Amer. Chem. Soc.*, 1943, 65, 2364—2365).—Measurements have been made in the pH range 1.8—8.0 of the electrophoretic velocity of asclepain in citrate, acetate, and phosphate buffers. The electrical charge on the particle has been calc. The isoelectric point is at pH 3.11.

W. R. A.

**Electrokinetics. XXVI. Electroviscous effect. III.  $\beta$ -Lactoglobulin systems. Interpretation of the meaning of  $K\phi$  values obtained from electroviscosity data.** D. R. Briggs and M. Hanig (*J. Physical Chem.*, 1944, 48, 1—12).—A modified form of the Krasny-Ergen electroviscosity equation, which gives better agreement with experimental data for colloid electrolytes, is proposed. The electroviscous properties of cryst.  $\beta$ -lactoglobulin (I) have been investigated at pH 6.60 and 4.22 with and without addition of  $NaCl$ . With increase of  $[NaCl]$  the entire change in  $\eta$  is due to a change in the extent of the electroviscosity effect. The degree of hydration, calc. vals. for which agree closely with those previously reported, is small, and little change occurs in its val. or in the asymmetry of the mols. as pH changes. It can be concluded that the mols. of (I) are rigid particles which are not subject to osmotic expansion or contraction when the nature or the no. of the gegenions is changed. Gum arabic is unlike (I) since it is subject to swelling and contraction under similar conditions. The system Na gum arabic- $NaCl$  has been examined and compared with the (I)- $NaCl$  system. The  $K\phi/C$  vals. ( $K = \text{const.}$  dependent on the shape of the micelle,  $\phi = \text{viscometrically effective percentage vol. occupied by the colloid, } C = \text{concn.}$ ) for the former system decrease at high ionic strengths, whereas for the latter system the vals. are const.

C. R. H.

## VI.—KINETIC THEORY. THERMODYNAMICS.

**Equilibrium measurements by infra-red absorption for the formation of nitric acid from oxygen, water vapour, and nitrogen dioxide.** E. J. Jones (*J. Amer. Chem. Soc.*, 1943, 65, 2274—2276).—By using the infra-red absorption at 1.4  $\mu$  of  $HNO_3$  vapour a direct determination was made of the equilibrium const. for the reaction  $H_2O(g) + NO_2(g) + \frac{1}{2}O_2(g) \rightarrow 2HNO_3(g)$  and the val. agrees with that of Forsyth *et al.* (A., 1942, I, 146). Transmission vals. of  $HNO_3$  and  $HNO_2$  in the 1.4  $\mu$  region are given.

W. R. A.

**Microscopic equilibria in ampholytes.** T. L. Hill (*J. Amer. Chem. Soc.*, 1943, 65, 2119—2121).—Mathematical. Microscopic and macroscopic equilibrium consts. are related by general expressions which have been derived. The concn. of a microscopic ion is given in terms of microscopic equilibrium const.,  $[H^+]$ , and total concn. of ampholyte.

W. R. A.

**Dissociation of dimethyl ether-boron trifluoride at low temperatures.** H. C. Brown and R. M. Adams (*J. Amer. Chem. Soc.*, 1943, 65, 2253—2254).—Criticism of Laubengayer *et al.* (A., 1943, I, 193).

W. R. A.

**Dielectric constant, ionic equilibrium, and ionic force in solutions.** L. Ebert (*Naturwiss.*, 1943, 31, 263—265).—A review, dealing particularly with the work of Nernst.

A. J. M.

**Basic ionisation constant of m-cresolsulphonaphthalein; pH values and salt effects.** E. E. Sager, H. J. Keegan, and S. F. Acree (*J. Res. Nat. Bur. Stand.*, 1943, 31, 323—343).—The ionisation const. ( $K$ ) of m-cresol-purple (I), calc. from spectrophotometric data for solutions of (I) in  $H_2O$  and  $HCl$ , is  $1.98 \times 10^{-2}$ , from which  $pK = 1.703 \pm 0.005$ . Activity coeffs. ( $f$ ) of (I) determined in presence of  $KCl$ ,  $BaCl_2$ , and  $SrCl_2$  show that  $f$  passes through a min. at 0.2—0.5M-chloride, the  $f$  vals. being somewhat  $>$  vals. calc. from electro-metric data. The significance of this difference is discussed with reference to  $f$  vals. for the various ions involved.

C. R. H.

**Lewis and Brønsted-Lowry definitions of acids and bases.** I. M. Kolthoff (*J. Physical Chem.*, 1944, 48, 51—57).—The conflict between the two definitions is discussed. The term protoacids is proposed for acids conforming to the Lewis definition, whilst the Brønsted-Lowry definition should be left unchanged. The two concepts are complementary rather than contradictory.

C. R. H.

**The Kirkwood-Westheimer theory of acid strength in the light of existing experimental data for dissociation constants of dibasic acids.** W. F. K. Wynne-Jones and G. S. Rushbrooke (*Trans. Faraday Soc.*, 1944, 40, 99—109).—The Kirkwood-Westheimer theory (cf. A.,



1938, I, 574) is in only qual. agreement with data for the influence of solvent or temp. on the dissociation consts. of dibasic acids. Reasons are given for attributing the lack of better agreement to failure to take sufficient account of sp. interactions between solvent and solute mols. or ions. F. L. U.

**Acid strengths of mono- and di-esters of phosphoric acid.** *n*-Alkyl esters from methyl to butyl, the esters of biological importance, and the natural guanidinephosphoric acids. W. D. Kumler and J. J. Eiler (*J. Amer. Chem. Soc.*, 1943, 65, 2355–2361).—*K* of alkylphosphoric acids (alkyl = Me, Et, Pr<sup>a</sup>, Bu<sup>a</sup>, Me<sub>2</sub>, Et<sub>2</sub>, Pr<sub>2</sub>, and Bu<sub>2</sub>) have been measured. That the acid strengths of dialkyl > monoalkyl > unsubstituted H<sub>3</sub>PO<sub>4</sub> is explained by solvation. Steric effects also exist and, to a smaller extent, statistical and inductive effects. Glycerol and sugar esters of H<sub>3</sub>PO<sub>4</sub> are discussed with relation to these effects. The groups responsible for the dissociation of natural guanidinephosphoric acids have been assigned by analogy. Chelation through H-bonding and the inductive effect of the PO<sub>4</sub> group are discussed in relation to reactions of biological importance. W. R. A.

**Ionisation of strong electrolytes. II. Ionisation, Raman spectrum, and vibrations of perchloric acid.** O. Redlich, E. K. Holt, and J. Bigeleisen (*J. Amer. Chem. Soc.*, 1944, 66, 13–16).—A refined photographic method has been developed for comparing the intensities of spectral lines of unequal width. The degrees of ionisation of HClO<sub>4</sub> have been determined. It is ionised to a greater extent than HNO<sub>3</sub>. The ionisation const. could not be calc. because the activity coeffs. are not known at high concns. Raman spectra of anhyd. HClO<sub>4</sub> and of conc. solutions of HClO<sub>4</sub> and NaClO<sub>4</sub> have been measured and are discussed. W. R. A.

**pH values of certain phosphate-chloride mixtures, and the second dissociation constant of phosphoric acid from 0° to 60°.** R. G. Bates and S. F. Acree (*J. Res. Nat. Bur. Stand.*, 1943, 30, 129–155).—The e.m.f. of cells of the type Pt|H<sub>2</sub>|NaH<sub>2</sub>PO<sub>4</sub> or KH<sub>2</sub>PO<sub>4</sub> (*m*<sub>1</sub>), Na<sub>2</sub>HPO<sub>4</sub> (*m*<sub>2</sub>), NaCl (*m*<sub>3</sub>)|AgCl|Ag was determined at 5° intervals between 0° and 60°. Three vals. of *m*<sub>1</sub>/*m*<sub>2</sub> were used, and a wide range of concn. was covered. The second dissociation const. (*K*<sub>2</sub>) of H<sub>3</sub>PO<sub>4</sub> was calc. The effect of temp. on  $-\log K_2$  is given by  $pK_2 = (1970.5/T) - 5.3541 + 0.019840T$ , where *T* = abs. temp. For each temp. the heat and entropy of dissociation, the change of heat capacity and the free energy change accompanying the dissociation of 1 mol. of H<sub>2</sub>PO<sub>4</sub><sup>−</sup> were calc. The pH vals. of phosphate-chloride mixtures over the above temp. range are given by (pH)<sub>1</sub> =  $(pK_2)_1 - \log (m_{Na_2HPO_4}/m_{NaH_2PO_4}) - 3A\sqrt{\mu}(1 + Ba_1\sqrt{\mu})$ , where  $\mu$  = ionic strength, *a*<sub>1</sub> is a parameter representing average ion size, and *A* and *B* are const. at a particular temp. This equation holds when  $m_{Na_2HPO_4} = m_{NaCl}$ , and the ratio  $m_{Na_2HPO_4}/m_{NaH_2PO_4}$  is 0.2–5.0. It is suggested that such solutions could be used as pH standards over the range 6.4–7.4. A. J. M.

**pH values of acid-salt mixtures of some aromatic sulphonic acids at various temperatures and a criterion of completeness of dissociation.** W. J. Hamer, G. D. Pinching, and S. F. Acree (*J. Res. Nat. Bur. Stand.*, 1943, 31, 291–304).—E.m.f. measurements show that aq. solutions of *p*-phenol- and 4-chlorophenol-2-sulphonic acids (>0.3*M*.) are completely dissociated between 10° and 60°. The method used was to determine the activity coeff. (*f*) of HCl in the sulphonate solutions and to plot  $-\log f$  against  $\sqrt{c}$ , where *c* = ionic strength. Since the vals. of  $-\log f$  are > those predicted by Debye and Hückel's limiting law, it can be shown that the SO<sub>3</sub>H groups must be completely dissociated. Solutions of the sulphonic acids, the corresponding Na or K sulphonates, and NaCl or KCl are suitable as pH standards over the pH range 1.2–2.5. C. R. H.

**Complex ions. VIII. Pyridine-silver ions.** W. C. Vosburgh and S. A. Cogswell (*J. Amer. Chem. Soc.*, 1943, 65, 2412–2413).—The results of the solubilities of AgIO<sub>3</sub>, Ag<sub>2</sub>SO<sub>4</sub>, and AgBrO<sub>3</sub> in dil. C<sub>5</sub>H<sub>5</sub>N have been interpreted in terms of two complex ions, Ag<sup>+</sup>C<sub>5</sub>H<sub>5</sub>N<sup>+</sup> and Ag(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub><sup>+</sup>, having dissociation consts.  $1.0 \times 10^{-2}$  and  $7.8 \times 10^{-8}$ . W. R. A.

**Complex ions. VII. A solubility method for the determination of instability constants in solutions and the amines of nickel, cadmium, and magnesium.** P. F. Derr and W. C. Vosburgh (*J. Amer. Chem. Soc.*, 1943, 65, 2408–2411).—The solubility of AgIO<sub>3</sub> in aq. NH<sub>3</sub> containing Ni, Cd, and Mg complexes of the form [M(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup> has been determined. The instability consts. of [Ni(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup>, [Ni(NH<sub>3</sub>)<sub>5</sub>]<sup>2+</sup>, [Ni(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>, [Cd(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup>, and [Mg(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup> have been calc. The solubility of Ba(IO<sub>3</sub>)<sub>2</sub> and Ca(IO<sub>3</sub>)<sub>2</sub> in aq. NH<sub>3</sub> has also been determined. W. R. A.

**Thermodynamics of the nitrogen-hydrogen mixture.** V. Fischer (*Ann. Physik*, 1941, [v], 39, 273–280).—A graphic method is described for the determination of the equilibrium concns. in a binary mixture when temp. and pressures occur which are above the crit. temp. and crit. pressure of the component of lower b.p. The method is used to calculate the equilibrium isotherms of a N<sub>2</sub>-H<sub>2</sub> mixture. A. J. M.

**System trimethyl phosphate-acetic acid.** H. A. Pagel and W. V. Ryle (*J. Amer. Chem. Soc.*, 1943, 65, 2186).—F.p. data for α-Me<sub>3</sub>PO<sub>4</sub>-AcOH mixtures give a eutectic at 52.9 mol.-% Me<sub>3</sub>PO<sub>4</sub>

with f.p.  $-89.9 \pm 1^\circ$ . F.p. of β-Me<sub>3</sub>PO<sub>4</sub>-AcOH mixtures could not be successfully determined at <75 mol.-% Me<sub>3</sub>PO<sub>4</sub>. W. R. A.

**Systems with boron trifluoride. III.** H. S. Booth and J. H. Walkup (*J. Amer. Chem. Soc.*, 1943, 65, 2334–2339).—Binary systems of BF<sub>3</sub> with the following F compounds have been investigated by thermal analysis: CF<sub>2</sub>Cl<sub>2</sub>, completely immiscible; CF<sub>3</sub>Cl (m.p.  $-181.6 \pm 0.5^\circ$ ) sol. in BF<sub>3</sub> up to 10 mol.-% and BF<sub>3</sub> sol. in CF<sub>3</sub>Cl up to 20 mol.-% at  $-130.5^\circ$ , whilst at higher temp. they are completely miscible; CF<sub>4</sub> (m.p.  $-180.1 \pm 0.5^\circ$ ) sol. in BF<sub>3</sub> up to 15 mol.-% and BF<sub>3</sub> sol. in CF<sub>4</sub> up to 25 mol.-% at  $-131.4 \pm 0.5^\circ$ ; PF<sub>3</sub> gives a eutectic at  $-163.5 \pm 0.5^\circ$  and 21.5 mol.-% BF<sub>3</sub>; POF<sub>3</sub> gives a eutectic at  $-47.5 \pm 0.5^\circ$  and 16.5 mol.-% BF<sub>3</sub>; and it is suggested that a 1:1 compound (f.p.  $\sim -20^\circ$ ) is formed; PSF<sub>3</sub> (f.p.  $-148.8 \pm 0.5^\circ$ ) gives a eutectic at  $-152.1 \pm 0.5^\circ$  and 16.00 mol.-% BF<sub>3</sub>, but the curve shows no max., although there is a change in slope at  $-130.8^\circ$  and 82.5 mol.-% BF<sub>3</sub> probably owing to transition at this temp. of β-BF<sub>3</sub> to α-BF<sub>3</sub>; SOF<sub>2</sub> (f.p.  $-129.0 \pm 0.5^\circ$ ) forms a 1:1 compound (f.p.  $-140.8 \pm 0.5^\circ$ ) and two eutectics at  $-145.9^\circ$  (34 mol.-% BF<sub>3</sub>) and  $-145.4^\circ$  (68.5 mol.-% BF<sub>3</sub>). W. R. A.

**System Li<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O.** A. N. Campbell (*J. Amer. Chem. Soc.*, 1943, 65, 2268–2271).—The following data are presented for the system Li<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O: (i) the transition point of the change Li<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O ⇌ Li<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O, determined dilatometrically, thermometrically, and by v.p. measurements, lies at 232.8° and 26.7 atm.; (ii) the solubility between 110° and 214°; (iii) the ice line. The existence of a higher hydrate of Li<sub>2</sub>SO<sub>4</sub>, possibly Li<sub>2</sub>SO<sub>4</sub>·2H<sub>2</sub>O, is considered to be doubtful, but is not entirely disproved by dilatometric methods or by a study of the equilibrium diagram of Li<sub>2</sub>SO<sub>4</sub>-LiCl-H<sub>2</sub>O at  $-12.25^\circ$ . W. R. A.

**Reciprocal salt pair NaClO<sub>3</sub> + KCl ⇌ NaCl + KClO<sub>3</sub> in water at 0° and 40°.** P. A. Munter and R. L. Brown (*J. Amer. Chem. Soc.*, 1943, 65, 2456–2457).—The isothermally invariant points for the system NaClO<sub>3</sub> + KCl ⇌ NaCl + KClO<sub>3</sub> in H<sub>2</sub>O have been determined at 0° and 40°. The stable salt pair is KClO<sub>3</sub> + NaCl and appears to remain stable up to <100°. The isothermally invariant point of the system NaClO<sub>3</sub>-KClO<sub>3</sub>-H<sub>2</sub>O at 0° is at 44.21-0.44–55.35%; those for NaClO<sub>3</sub>-KClO<sub>3</sub>-H<sub>2</sub>O at 40° and for KClO<sub>3</sub>-KCl-H<sub>2</sub>O at 0° have been redetermined and agree closely with recorded vals. W. R. A.

**Relations between daltonide and berthollide phases in metallic systems.** N. V. Ageev and E. S. Makarov (*J. Gen. Chem. Russ.*, 1943, 13, 242–248).—The two phases are fundamentally of the same nature, and can pass continuously one into the other. Both owe their existence to formation of definite chemical compounds. R. T.

**Dicalcium silicate solid solutions.** K. T. Greene (*J. Res. Nat. Bur. Stand.*, 1944, 32, 1–10).—X-Ray diffraction, optical, and thermal data show that at  $\sim 1450^\circ$  2CaO·SiO<sub>2</sub> forms, with Na<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub> (or Fe<sub>2</sub>O<sub>3</sub>), solid solutions with hexagonal crystal structures, this structure being the fundamental one for α-2CaO·SiO<sub>2</sub> since it reverts to the β-form on cooling. When cooled below 1175° the material becomes inhomogeneous and Na<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub> (or Fe<sub>2</sub>O<sub>3</sub>) are thrown out of solid solution at the same time as the α-form is transformed into the β-form. The α-β inversion temp. lies within the range 1175–1420°, approaching the upper temp. as the purity of the 2CaO·SiO<sub>2</sub> becomes greater. The conditions of cooling Portland cement clinker are unfavourable to the preservation of the α-solid solution; to retain the α-form the % of Na<sub>2</sub>O must be >> that normally present in commercial clinker. C. R. H.

**Phase equilibrium in the system Li<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>.** R. A. Hatch (*Amer. Min.*, 1943, 28, 471–496).—Liquidus and solidus temp. for preps. in the range 22–85% SiO<sub>2</sub> of the system Li<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> are recorded, and represented graphically. Three-component compounds in the system are (i) β-spodumene (I), Li<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·4SiO<sub>2</sub>, a high-temp. form melting congruently at 1423°, and (ii) β-eucryptite (II), Li<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>, melting, with dissociation, at 1397°. No compounds with the compositions of petalite (III), Li<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·8SiO<sub>2</sub>, or Li orthoclase are stable above the solidus. (III) dissociates at >950°. The system includes (i) the SiO<sub>2</sub> field, (ii) the (I)-SiO<sub>2</sub> solid solution field, (iii) the field of (I) solid solution, (iv) the (II) solid solution field, (V) the γ-Al<sub>2</sub>O<sub>3</sub> field, and possibly the Li aluminate field. Attempts to synthesise α-spodumene hydrothermally at pressures <100 atm. and at temp. from 400° to 500° failed; (I) always crystallised from the spodumene glass. Vals. of *n* for glasses in this system are given. L. S. T.

**System CaSiO<sub>3</sub>-CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>-NaAlSiO<sub>4</sub>.** W. K. Gummer (*J. Geol.*, 1943, 51, 503–530).—Thermal data obtained at high temp. and normal pressures are recorded. Phase equilibrium diagrams are reproduced, and the course of crystallisation in typical mixtures of the above compounds is discussed. L. S. T.

**Systems lead oxide-alumina and lead oxide-alumina-silica.** R. F. Celler and E. N. Bunting (*J. Res. Nat. Bur. Stand.*, 1943, 31, 255–270).—In the system PbO-Al<sub>2</sub>O<sub>3</sub> evidence has been obtained for the existence of a compound PbO·Al<sub>2</sub>O<sub>3</sub>, unstable at >970° and forming a eutectic with PbO (94% PbO) of m.p. 865°. In the



system  $\text{PbO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ , the compounds  $8\text{PbO} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ ,  $4\text{PbO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , and  $6\text{PbO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$  have been identified, with incongruent m.p.  $735^\circ$  and  $837^\circ$  and congruent m.p.  $811^\circ$ , respectively. Evidence has also been obtained for the existence of four other compounds of undetermined composition.  $\text{Al}_2\text{O}_3$  (purity  $>99.9\%$ ) has m.p.  $2035 \pm 10^\circ$ . J. W. S.

**Thermodynamics of the reduction of magnesium oxide with carbon and calcium carbide.** B. Mauderli, E. Moser, and W. D. Treadwell (*Helv. Chim. Acta*, 1944, 27, 105–116).—Reduction of  $\text{MgO}$  by C and  $\text{CaC}_2$  is examined by calculations of the free energies of reduction from known thermal data. A distinctive feature of the method is the use of the entropy-log mol. wt. graph to calculate the entropy of  $\text{CaC}_2$ . The reduction is easier with  $\text{CaC}_2$ , but at low temp. a part is obtained as carbides, which dissociate to Mg and C again in the range  $800\text{--}1000^\circ$  (A., 1937, I, 320). In experiments on the thermal dissociation of  $\text{CaC}_2$  in a vac. between  $1800^\circ$  and  $1800^\circ$  94% of the C was recovered as graphite, and no  $\text{C}_2\text{H}_2$  was found when the products were treated with  $\text{H}_2\text{O}$ . J. O'M.B.

## VII.—ELECTROCHEMISTRY.

**Conductance of salts in ethylenediamine.** W. H. Bromley, jun., and W. F. Luder (*J. Amer. Chem. Soc.*, 1944, 66, 107–109).—Conductances of KI, AgI, and  $\text{AgNO}_3$  in  $(\text{CH}_2\text{NH}_2)_2$  ( $9 \times 10^{-8}$  mho) have been measured at  $25^\circ$  using concns. sufficiently low to permit calculation of  $\Lambda_0$  and  $K$ . A suggested explanation for the very low val. of  $K$  for AgI is based on the electronic theory of acids and bases. W. R. A.

**Mechanism of electrical conduction in the Nernst pencil.** C. Wagner (*Naturwiss.*, 1943, 31, 265–268).—A review dealing particularly with electrolytic conduction of heated oxide filaments, the nature of the ions carrying the current, and the reasons for the higher conductivity of mixed oxides compared with single oxides. A. J. M.

**Discussion and interpretation of the migration data of laurylsulphonic acid in aqueous solution.** P. Van Rysselberghe (*J. Physical Chem.*, 1944, 48, 62–65).—Comparison of the author's calc. vals. for the transference no. of the laurylsulphonate radical with experimental vals. obtained by McBain (cf. A., 1943, I, 226) for solutions of laurylsulphonic acid indicates the probable presence of large amounts of nearly neutral micelles with compensating migrations at concns. above the max. in the transference curve, i.e., at acid concns.  $>0.055\text{M}$ . At concns.  $<0.055\text{M}$ , the agreement between calc. and observed vals. is excellent. Errors in one of McBain's data tables are corr. C. R. H.

**Potentials of electrochemical phase systems.** E. Lange (*Naturwiss.*, 1943, 31, 260–263).—A review. A. J. M.

**Diffusion potential in solutions of electrolytes.** J. J. Hermans (*Naturwiss.*, 1943, 31, 257–260).—A review, dealing particularly with the work of Nernst. A. J. M.

**Geo-electric effect in membranes.** L. Brauner (*Rev. Fac. Sci. Istanbul*, 1942, 7, 46–102).—From measurements using  $\text{NH}_3$  and KCl solutions it is inferred that the change in potential across a membrane separating solutions of different concns. on bringing it from a vertical to a horizontal position (geo-electric effect of the first order  $\Delta E$ ) is due not to gravitational stratification of the diffusing solution, but to a direct influence of gravity on the relative mobilities of the ions. Investigations with various salts diffusing through a vertical parchment paper (anionic) membrane show that the rate of loss of p.d. is the more rapid the greater is the mobility of the cations and the more inert are the anions, whereas when the more conc. solution is above the membrane and the more dil. below it the reverse is the case. Both the membrane potential and the  $\Delta E$  are reduced by a decrease in pH, and with protein (cationic) membranes  $\Delta E$  changes in sign at pH vals.  $<$  the isoelectric potential. When two electrodes filled with the same solution ( $<10^{-2}\text{N}$ .) are separated by a horizontal membrane an e.m.f. is established when the solutions are one above the other, the lower layer being positive with an anionic and negative with a cationic membrane. This effect ("geo-electric effect of the second order") is attributed to the shifting of the mobile part of an electrical double layer under the action of gravity. The adsorption potential, ionic mobilities,  $d$  of the ions, and the conductivity of the solution all affect its magnitude. From the results obtained it is inferred that the actual  $d$  of all ions in aq. media is  $>1$ . J. W. S.

**Development of polarography.** K. Bennewitz (*Naturwiss.*, 1943, 31, 268–270).—A review, tracing the development of polarography from Nernst. A. J. M.

**Polarographic investigation of hydrogen bonding.** II. Nitroresols. M. J. Astle and W. P. Cropper. III. Nitrodi-hydroxybenzenes. M. J. Astle and S. P. Stephenson (*J. Amer. Chem. Soc.*, 1943, 65, 2395–2399, 2399–2402; cf. A., 1943, I, 155).—II. The reduction at various pH of 3:1:2-, 4:1:2-, 5:1:2-, 4:1:3-, 6:1:3-, 2:1:4-, and 3:1:4- $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{OH}$  at the dropping Hg cathode has been studied. Half-wave potentials are most negative when  $\text{NO}_2$  is  $p$  and least negative when  $o$  to OH.  $p\text{-NO}_2$

is reduced to  $\text{NH}_2$  at all pH:  $o\text{-NO}_2$  is reduced to  $\text{NH} \cdot \text{OH}$  at pH  $<7$  and to  $\text{NH}_2$  at pH  $>7$ ;  $m\text{-NO}_2$  is reduced at pH  $<7$  to  $\text{NH} \cdot \text{OH}$  and  $\text{NH}_2$  in two distinct steps, whilst at pH  $>7$  reduction stops at  $\text{NH} \cdot \text{OH}$ . These results indicate a stabilisation of  $o\text{-NO}_2$  by H-bonding, absent in  $p\text{-NO}_2$ , and that reduction to  $\text{NH}_2$  at pH  $>7$  can occur only through the quinonoid form of the nitroresol.

III. The reduction at various pH of 2:1:3- (I), 4:1:3- (II), 3:1:2- (III), 4:1:2- (IV), and 2:1:3- $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{OH})_2$  (V) has been studied with the dropping Hg cathode. When H-bonding is sterically possible [(I), (III), and (IV)] ease of reduction of  $\text{NO}_2$  is  $>$  in (IV), where a H-bond is not possible. Similarity to (III) and (V) shows that (I) must have only one H-bond. A weak H-bond seems to exist in (II) at pH  $<5$ . At pH  $>9$ , (IV) is reduced in two separate steps to 4-nitroso- and 4-amino-pyrocatechol, but at pH  $<9$ , as for all the other compounds, direct reduction to  $\text{NH}_2$  occurs. Introduction of a second OH weakens the H-bond between  $o\text{-NO}_2$  and  $-\text{OH}$ , and the ease of reduction of  $\text{NO}_2$  depends on the relative position of the two OH. W. R. A.

**Polarographic studies of sulphonamides.** I. Oxidation products of sulphanilamides. N. I. Levitan, I. M. Kolthoff, W. G. Clark, and D. J. Tenenberg (*J. Amer. Chem. Soc.*, 1943, 65, 2265–2268).— $p$ -Hydroxylamino- (I), 4:4'-azoxy-, and  $p$ -nitro-benzenesulphonamide have been investigated polarographically, and are capable of electrolytic reduction at the dropping Hg cathode. The mol. compound of 2 mols. of (I) and one mol. of sulphanilamide (II) has also been investigated polarographically. Bacteriostatic activity of (I) against *Escherichia coli* in vitro is  $\gg$  that of (II). W. R. A.

**Neutralisation reactions in selenium oxychloride.** Potentiometric titration. W. S. Peterson, C. J. Heimerzheim, and G. B. L. Smith (*J. Amer. Chem. Soc.*, 1943, 65, 2403–2406).—Potentiometric titration for several acid-base reactions in  $\text{SeOCl}_2$  has been investigated. The Müller "retarded electrode" has been adapted and a KCl reference electrode developed for the potentiometric titration of non-protonic neutralisations in  $\text{SeOCl}_2$ . The relative strengths of the acids and bases have been determined, and are in the order  $\text{SO}_3 > \text{FeCl}_3 > \text{SnCl}_4$ ; isoquinoline  $>$  quinoline  $>$   $\text{C}_6\text{H}_5\text{N} >$  KCl. W. R. A.

**Compounds of iron deposited on both poles simultaneously.** G. Antonoff (*J. Physical Chem.*, 1944, 48, 21–23).— $\text{Fe}(\text{OH})_2$  (30 g.) was suspended in 2 l. of  $\text{H}_2\text{O}$  containing 2 c.c. of conc.  $\text{H}_2\text{SO}_4$  and the suspension electrolysed at  $60^\circ$  with Pt electrodes ( $2 \times 2$  in.), keeping the liquid stirred; the current was  $\sim 2$  amp. and the voltage varied over a wide range. If the cathode was inserted in a porous cup deposits were obtained which were similar to those obtained at the anode. The deposits appeared to be complex peroxides of Fe. X-Ray analysis did not offer any explanation of their composition or structure. C. R. H.

## VIII.—REACTIONS.

**Pyrolysis of digermane.** H. J. Emeléus and H. H. G. Jellinek (*Trans. Faraday Soc.*, 1944, 40, 93–99).—The thermal decomp. of  $\text{Ge}_2\text{H}_6$  in the range  $195\text{--}220^\circ$  resembles kinetically that of  $\text{C}_2\text{H}_6$  and  $\text{Si}_2\text{H}_6$ . It has an induction period, is of the first order and homogeneous in the middle stages, and is retarded later. The activation energy, 33.7 kg.-cal., is assumed to be associated with a disruption of the Ge-Ge bond. The data are discussed and a chain mechanism is proposed. F. L. U.

**Kinetics of the decomposition of sodium hypochlorite.** A. Rius Miró and J. M. González Barredo (*Anal. Fis. Quím.*, 1940, 38, 332–334).—A study of previous work on the decomp. of  $\text{NaOCl}$  leads to the conclusion that the reaction is autocatalytic. F. R. G.

**Autoxidation of inorganic reducing agents.** II. Stannous chloride (experimental). III. Stannous chloride (theoretical). S. J. Lachman and F. C. Tompkins (*Trans. Faraday Soc.*, 1944, 40, 130–136, 136–141).—II. Results are given for the rate of oxidation of aq.  $\text{SnCl}_2$  at  $30^\circ$  by  $\text{O}_2$ . The effect of varying the concn. of  $\text{SnCl}_2$ , of added chlorides, and of various impurities was examined.

III. Analysis of the experimental curves indicates that the rate is  $\propto [\text{HSnCl}_3]^{\frac{1}{2}}$ . Other species may be oxidised much more slowly. The increase in the rate of oxidation caused by adding Fe salts is  $> \propto [\text{Fe}^{+++}]$ , in contrast to its effect on the oxidation of  $\text{TiCl}_3$  (cf. A., 1943, I, 38). F. L. U.

**Elimination of bromide ion from aqueous solutions of phenylbromoacetic acid.** H. M. Dawson, W. R. Bulcraig, and G. F. Smith (*J.C.S.*, 1944, 90–94).—A general equation and three simpler equations valid under restricted conditions have been derived and satisfactorily applied to kinetic data for the elimination of Br $^-$  from  $\text{HNO}_3$  solutions of  $\text{CHPhBr} \cdot \text{CO}_2\text{H}$  (I) in presence of  $\text{NaNO}_3$ . The increase in reaction coeff. with increase in  $[\text{HNO}_3]$  is due either to hydrolysis of (I) or to the primary salt effect of  $\text{HNO}_3$  on the sp. reaction rate of the ion brought about by increase in  $[\text{HNO}_3]$ . The latter alternative is preferred and it is shown that the reactivity of undissociated (I) cannot be  $> 0.002$  of that of  $\text{CH}_2\text{PhBr} \cdot \text{CO}_2^-$ . The dissociation const. of (I), calc. from kinetic data, is  $6.1 \times 10^{-3}$  at  $25^\circ$ . C. R. H.



**Transformation of diazocyanides.** M. A. Saboor (*Indian J. Physics*, 1943, 17, 223—228).—The rate of spontaneous transformation of *cis*- to *trans*-*p*-chlorobenzenediazocyanide in  $C_6H_6$  and  $CCl_4$  solutions has been followed by dielectric const. measurements. The half-life period is independent of initial concn., indicating a first-order reaction. Measurements of velocity coeffs. at various temp. give  $\Delta E$  of activation of  $\sim 23$  kg.-cal. W. R. A.

**Inflammability and explosibility of metal powders.**—See B., 1944, I, 144.

**Catalytic action of ozone in the slow combustion of paraffins. Ozonisation of the terminal groups of the saturated hydrocarbons of the aliphatic series.** J. Carceller Fernández (*Anal. Fis. Quím.*, 1940, 36, 235—240; cf. A., 1935, 1103, 1466).— $O_3$  accelerates the oxidation of  $C_2H_6$ ,  $C_3H_8$ ,  $C_4H_{10}$ , and  $C_5H_{12}$  to  $RCHO$  and  $RCO_2H$  ( $R$  = alkyl),  $CO$ ,  $H_2O$ , and peroxides. The ease of oxidation  $\propto$  mol. wt. of the paraffin. Fission of the C chain represented by  $CO$  and  $H_2O$  is for *iso*- > for *n*- $C_4H_{10}$ , and increases with the higher members of the series. The chain mechanism is favoured to explain the reaction. F. R. G.

**Hydrocarbon polymerisation and method of determining catalyst activity.** R. F. Cane (*J. Proc. Austral. Chem. Inst.*, 1943, 10, 279—286).—A review of existing theories of the action of  $H_3PO_4$  as catalyst for the polymerisation of unsaturated hydrocarbons shows these to be untenable. The suggested procedure for determining the activity of polymerisation catalysts involves mixing 50 g. of  $\alpha$ -phellandrene with 20 g. of catalyst at  $20^\circ$  in a Dewar vessel of known  $H_2O$ -equiv. and cooling correction, the temp. being observed at 1-min. intervals for 5 min. and thence at 5-min. intervals for 30 min. The time required for the evolution of 10 g.-cal. per g. of catalyst is called the "activity no."  $H_2O$  on the catalyst decreases its activity whilst adsorbed  $O_2$  causes initial acceleration of the polymerisation followed by a retardation. Basic N compounds ( $NH_3$ , amines, nitriles, or  $C_3H_5N$ ) depress the activity of the catalyst whilst  $NO_2$ -compounds have little or no effect. Traces of mercaptans decrease the activity considerably. J. W. S.

**Properties of chromic oxide gel and its catalytic activity for the aromatisation of *n*-heptane.** E. J. Dickinson (*Trans. Faraday Soc.*, 1944, 40, 70—79).— $Cr_2O_3$  gel is reduced by dry  $H_2$  at  $450^\circ$  to an extent corresponding with  $\sim 8\%$  conversion into Cr and some  $H_2$  is irreversibly absorbed, whereas at  $800^\circ$  the irreversible absorption is negligible but the reduction is greater (10–5% conversion) than at  $450^\circ$ . There is evidence that in this reduction no new phase is formed, and that the product is  $Cr_2O_3$  from which some O atoms have been removed without collapse of the lattice structure. The reduced gel is completely oxidised by  $O_2$  at  $450^\circ$ , all combined H being removed as  $H_2O$ .  $H_2O$  oxidises only a small fraction of the reduced gel at  $450^\circ$ , and some  $H_2O$  is reversibly adsorbed. It is thought that the part of the gel attacked by  $H_2O$  is identical with the part catalytically active in the dehydrogenation of hydrocarbons. The poisoning action of  $O_2$ ,  $H_2O$ , and oxidation products of hydrocarbons is probably due to "saturation" of the active parts of the gel, the effect of  $H_2O$  being temporary owing to its adsorption being reversible. Restoration of the activity of the poisoned gel includes the removal of carbonaceous material and re-forming of the active part of the surface, and is best effected by treatment at  $600^\circ$  first with  $O_2$  and then with  $H_2$ . The pressures employed in these experiments were  $\sim 3$ –4 mm. F. L. U.

**Ethylation of benzene. Course of the reaction.**—See A., 1944, II, 155.

**Interaction of carbon monoxide with [Fischer-Tropsch] cobalt catalyst used in synthesis of gasoline from water-gas.**—See B., 1944, I, 158.

**Catalytic cracking of oils.**—See B., 1944, I, 126, 127.

**[Catalytic] hydrogenation and liquefaction of coal.**—See B., 1944, I, 156.

**Behaviour of metals in nitric acid.** U. R. Evans (*Trans. Faraday Soc.*, 1944, 40, 120—130).—By considering the attack of  $HNO_3$  on metals to be composed of an anodic reaction, e.g.,  $M + 2e = M^{2+}$ , and a cathodic reaction, the principal facts regarding their behaviour can be explained without special assumptions other than that those reactions are most probable that involve fewest mols. Two such reactions are (1)  $NO_2 + e = NO_2^-$  and (2)  $HNO_2 + HNO_3 = 2NO_2 + H_2O$ , according to which the attack on metals such as Cu, Ag, or Hg will be autocatalytic and will start when a trace of  $NO_2$  is present. The influence of vol. of liquid, stirring, and production of NO is discussed. The behaviour of Fe depends on the formation of a coherent film of  $Fe_2O_3$  which is not attacked by  $HNO_3$ , but can be reduced to  $Fe^{2+}$  when the acid is sufficiently dil. to produce H. If a high enough % of Cr is alloyed with the Fe a protective film of  $Cr_2O_3$  is formed, which remains unattacked in dil.  $HNO_3$  since  $Cr^{III}$  compounds are not stable. F. L. U.

**Effect of salts of mercury, tin, and lead on the cathodic process in zincate electrolytes.**—See B., 1944, I, 172.

**Electrochemical deposition of tin from solutions of tin compounds.**—See B., 1944, I, 172.

**Strip steel electroplating with tin, using a sodium stannate bath.**—See B., 1944, I, 172.

**Current efficiency in a series of electrolytic cells.**—See B., 1944, I, 164.

**Electrodeposition of manganese from a sulphate bath.**—See B., 1944, I, 172.

**Mercury-sensitised reaction between hydrogen and nitric oxide.** H. A. Taylor and C. Tanford (*J. Chem. Physics*, 1944, 12, 47—52).—The rate of reaction of at. H, produced by Hg sensitisation, with NO is  $\propto [H_2]$  at low  $[H_2]$ , and  $<$  proportional at higher  $[H_2]$ . [NO] is without influence except when NO is in excess, when it retards the reaction. At const. total pressure there is a max. rate with a particular excess of  $H_2$ . HNO radicals are probably formed and decompose on the wall to  $N_2O$ , which is rapidly reduced to  $N_2$ . L. J. J.

**Photochemical studies in gels. I. Reduction of ferric chloride by mandelic acid in light of different frequencies in thorium phosphate gel as a solvent medium.** J. C. Ghosh and S. K. Bhattacharyya (*J. Indian Chem. Soc.*, 1943, 20, 377—381).—The reaction, studied for frequencies 366 and 436  $m\mu$ , is zero-mol., and the velocity coeff. increases with rise in concn. of  $FeCl_3$  or of mandelic acid (I) and  $\propto$  intensity of absorbed radiation; the quantum efficiency is very low. The reaction rate is the same in both sol and gel states of Th phosphate but in  $H_2O$  it is much greater. Extinction coeffs. of  $FeCl_3$  in excess of (I) measured in all three media are tabulated. A mechanism is suggested. N. M. B.

**Photochemical chlorination and photochemical oxidation of tetra-chloroethylene sensitised by chlorine.** C. Schott and H. J. Schumacher (*Z. physikal. Chem.*, 1941, B, 49, 107—125).—The photochemical chlorination of  $C_2Cl_4$  to  $C_2Cl_6$  proceeds according to  $d[C_2Cl_6]/dt = k[I_{abs.}]^{1/2}[Cl_2]$ . At  $80^\circ$  with 100 mm. of  $Cl_2$  and  $I_{abs.} = 1.6 \times 10^{12}$   $hv/sec. cm.^2$  the quantum yield is 340 mols. per  $hv$ . Increase of the total pressure and addition of  $SO_2$  do not affect the reaction. The temp. coeff. is 1.33 per  $10^\circ$  rise in temp., which leads to an activation energy for the total reaction of 7.35 kg.-cal. per g.-mol. The reaction proceeds via the free radical  $C_2Cl_5$ . The oxidation of  $C_2Cl_4$  sensitised by  $Cl_2$ , in which  $\sim 80\%$  and  $20\%$  of the  $C_2Cl_4$ , respectively, are converted into  $CCl_3COCl$  and  $COCl_2$ , proceeds according to  $dp/dt = [I_{abs.}][O_2]/(k' + k''[O_2])$ . At  $60^\circ$  with 100 mm. of  $Cl_2$ , 200 mm. of  $O_2$ , and  $I_{abs.} = 1.6 \times 10^{12}$   $hv/sec. cm.^2$  the quantum yield is 230 mols. per  $hv$ . The temp. coeff. of the reaction is  $\sim 1.0$ . The total pressure has little effect on the reaction. Addition of EtOH causes strong inhibition. Mechanisms for the two reactions are proposed. The results are compared with the corresponding reactions of  $C_2HCl_3$ . J. F. H.

**Application of probability considerations to the mechanism of the photochemical polymerisation of acetylene.** B. L. Dunicz (*J. Chem. Physics*, 1944, 12, 37—45).—Quantum yields and heats of reaction in fair agreement with the author's experimental results (A., 1941, I, 480) are obtained by assuming equal probabilities for the formation of products of addition and breaking down of single C-C linkings in the unstable intermediate products. L. J. J.

**Photolysis of methylamine.** O. C. Wetmore and H. A. Taylor (*J. Chem. Physics*, 1944, 12, 61—68).—Photolysis of  $NH_2Me$  at  $100^\circ$  irradiated with a low-pressure Hg arc proceeds by two consecutive reactions:  $H_2$ ,  $NH_3$ , and  $CH_3NMe$  are first formed, and the latter is dehydrogenated. Both reactions are first order, the rate coeff. of the second being approx. double that of the first. The final product has the approx. composition  $C_2H_3N$ . H atoms react with  $NH_2Me$  and are involved in the reaction. L. J. J.

**Relations between chemical activity and absorption in the ultra-violet of certain organic molecules. III. Velocity of replacement of the chlorine atoms in the chloro-derivatives of the substituted amides of malonic acid.** K. G. Naik, R. K. Trivedi, and C. M. Mehta (*J. Indian Chem. Soc.*, 1943, 20, 365—368).—Investigations show that the velocity curves are in general agreement with those of absorption in the ultra-violet, the velocity is augmented by the presence of Me in the  $C_6H_5$  nucleus, the Cl atoms of the  $Cl_2$ -derivatives are replaced in succession, and the aliphatic straight chain attached to the CO groups increases the rate of replacement. N. M. B.

**Photolysis of the *d*-glycosides:  $\alpha$ -benzylfructofuranoside,  $\beta$ -benzylfructopyranoside, and  $\alpha$ - and  $\beta$ -phenyl-, -benzyl-, and  $\beta$ -phenyl-ethyl-glycosides; and the bearing of the data on the transfer of energy within molecules.** L. J. Heidt (*J. Franklin Inst.*, 1942, 234, 473—485; cf. A., 1939, I, 620).—The absorption spectrum of freshly prepared fructose has a deeper min. at  $\lambda$  240  $m\mu$ . than previously reported vals. The latter were approached with old samples, although no change in sp. rotation or m.p. had taken place. The absorption spectra of  $\alpha$ -benzylfructofuranoside and  $\beta$ -benzylfructopyranoside are almost identical, in the near ultra-violet, with those of benzyl-glycosides and  $CH_3Ph\cdot OH$ . Aq. buffered solutions of the glycosides were photolysed with monochromatic light of  $\lambda$  254  $m\mu$ . The products were examined for reducing material with the alkaline  $Cu^{II}$  reagent of Shaffer, Hartmann, and Somogyi, and for optical activity with a polarimeter. The products of photolysis are, in general, identical with those obtained by thermal hydrolysis; the  $\beta$ -glucos-



ides and  $\alpha$ -fructosides, however, yield optically inactive photolytic products. <5% of the light absorbed produces reaction. The above results lead to the hypothesis that the photochemical reaction is produced by an intermol. transfer of the absorbed energy from the aglycone to the hemiacetal O-bridge, which is the reactive centre. J. F. H.

**Radiochemistry.** A review of recent progress. C. B. Allsopp (*Trans. Faraday Soc.*, 1944, 40, 79—87). F. L. U.

## IX.—PREPARATION OF INORGANIC SUBSTANCES.

**Method of obtaining fresh water from salt [by distillation].** T. Jefferson (*J. Chem. Educ.*, 1943, 20, 575—576). L. S. T.

**Enrichment of chlorine isotopes by irradiation of chlorine dioxide at low pressure.** W. Kuhn, H. Martin, and K. H. Eldau (*Z. physikal. Chem.*, 1941, B, 50, 213—254).—Pure  $\text{ClO}_2$  at  $\sim 0.2$  mm. pressure, when irradiated with  $\lambda\lambda$  3650.15, 3654.83, and 3663.27  $\text{\AA}$ , is decomposed without reaction chain formation and with quantum yield  $\sim 1$  to  $\text{Cl}_2$  and  $\text{O}_2$ . The  $\text{Cl}_2$  liberated has at. wt. 0.016 < that of normal  $\text{Cl}$ . The small degree of isotope separation is due to the coincidence of only the last-named of the above lines with a  $^{35}\text{ClO}_2$  absorption band. The other two lines have intensities  $\sim 4$  times greater. L. J. J.

**Separation of radiothorium and radium-D and the purification of radium-mesothorium salts.** B. A. Nikitin and A. E. Polesitzki (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 33, 494—497).—Distillation in  $\text{HCl}$  at  $800^\circ$  effects complete separation of Ra-Th and Th-B or Ra-D from Ba salts. Further heating at  $500^\circ$  in  $\text{HCl}$  causes volatilisation of Th-B and Ra-D, whilst Ra-Th remains. The method can be used for the purification of Ra and for the regeneration of Ra from metallic hydroxides containing adsorbed Ra, since  $\text{FeCl}_3$ ,  $\text{AlCl}_3$ , and  $\text{ThCl}_4$  are all volatile in  $\text{HCl}$  whilst  $\text{RaCl}_2$  is non-volatile. J. W. S.

**Constitution of "pernitrous acid."** I. A. Rius and O. R. Foz (*Anal. Fis. Quim.*, 1940, 36, 308—321).—Potentiometric measurements that [active O] =  $[\text{NO}_2]$  in pernitrous acid. Decomp. by alkali yields nitrites and is accelerated by  $\text{H}_2\text{O}_2$  and light. F. R. G.

**Chemistry of polonium. II. Preparation of hexavalent polonium.** A. G. Samartzeva (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 33, 498—501).—By observations on the distribution of Po between crystals of  $\text{K}_2\text{TeO}_4 \cdot 3\text{H}_2\text{O}$  (I) and its saturated solution, both in presence and in absence of  $\text{K}_3\text{PO}_4$ , it has been shown that Po crystallises isomorphously with the Te compound and enters the crystal lattice of (I). Hence Po can yield hexavalent compounds derived from  $\text{H}_2\text{PoO}_4$ . J. W. S.

**New sources of bromine.**—See B., 1944, I, 133.

**Reaction between ferrous sulphide and cupric sulphide in the solid state, at room temperature.** H. Forestier and (Mlle.) J. Longuet (*Compt. rend.*, 1942, 215, 439—440).—By addition of aq.  $\text{Na}_2\text{S}$  to a solution of equimol. proportions of  $\text{FeCl}_2$  and  $\text{CuCl}_2$ , at room temp., a ppt. is obtained which, after drying in vac. over  $\text{P}_2\text{O}_5$ , gives the Debye-Scherrer X-radiogram of chalcopyrite (I); sharper and stronger X-ray lines are obtained if the aq. suspension is boiled for 15 hr. prior to filtration. (I) is also obtained after mixing suspensions of FeS and CuS, showing that copptn. of the sulphides is not essential to their combination. FeS and CuS combine more readily than FeO and CuO (cf. A., 1939, I, 482; 1942, I, 276, 336). A. J. E. W.

**Hydrogen dihydroxotetrachloroplatinate as a reagent for tin.** I. G. Fesenko (*Zavod. Lab.*, 1939, 8, 1323—1324).—The compound  $\text{Sn}[\text{PtCl}_4(\text{OH})_2]$  (cf. Chotulev, A., 1939, I, 41) does not exist. J. J. B.

## X.—LECTURE EXPERIMENTS AND HISTORICAL.

**Wetting and spreading.** Laboratory experiment [with lauric acid]. L. J. Bircher (*J. Chem. Educ.*, 1943, 20, 428—430). L. S. T.

**Autocatalytic experiment to illustrate virus growth.** P. Hersch (*J. Chem. Educ.*, 1943, 20, 376).—Conditions under which the reduction of  $\text{Ni}(\text{OH})_2$  to Ni by  $\text{H}_2\text{PO}_4^-$  can be made to resemble the growth of bacterial colonies on a culture medium are described. L. S. T.

**Thomas Jefferson's relation to chemistry.** C. A. Browne (*J. Chem. Educ.*, 1943, 20, 574). L. S. T.

**Benjamin Chew Tilghman, and the origin of the sulphite process for delignification of wood.** M. Phillips (*J. Chem. Educ.*, 1943, 20, 444—447). L. S. T.

**M. Carey Lea, chemist, 1823—1897.** E. F. Smith (*J. Chem. Educ.*, 1943, 20, 577—579). L. S. T.

**Jacob Green, chemist, 1790—1841.** E. F. Smith (*J. Chem. Educ.*, 1943, 20, 418—427). L. S. T.

**Franklin Bache, chemist, 1792—1864.** E. F. Smith (*J. Chem. Educ.*, 1943, 20, 367—368). L. S. T.

**Scientific and technical work of A. G. Green.** K. H. Saunders (*J. Soc. Dyers and Col.*, 1944, 60, 81—93).

## XI.—GEOCHEMISTRY.

**Presence of phosphorus in the solar atmosphere.** K. N. Rao (*Indian J. Physics*, 1943, 17, 197—203).—The presence of  $\text{P}_2$  in the solar atm. is inferred from coincidences of the lines of two of its strong bands (8,27) and (9,28) with the Fraunhofer lines. W. R. A.

**New method of measuring the mean height of the ozone in the atmosphere.** K. Watanabe (*J. Franklin Inst.*, 1943, 236, 461—471).—Measurements made and results obtained by Strong's method (cf. A., 1940, I, 310) are reported and discussed. N. M. B.

**Isotopic composition of oxygen of different origin.** A. P. Vinogradov and R. V. Teis (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 33, 490—493).—Determinations of the  $d$  of  $\text{H}_2\text{O}$  synthesised from  $\text{H}_2$  (produced by the action of  $\text{HCl}$  on  $\text{Zn}$ ) and  $\text{O}_2$  from various sources indicate that O from the atm. is heavier than that from  $\text{H}_2\text{O}$  whilst that evolved under [the action of light by *Helodea canadensis* growing in tap- $\text{H}_2\text{O}$  containing 0.1% of  $\text{NaHCO}_3$  is intermediate. The O in  $\text{CO}_2$  produced by the action of  $\text{HCl}$  on  $\text{NaHCO}_3$  is heavier than atm. O. J. W. S.

**Pentathionic acid in water from Copahue.** H. Corti and R. J. Manuele (*Rev. Fac. Cienc. Quim., La Plata*, 1942, 17, 7—14).—A sample of  $\text{H}_2\text{O}$  collected from the volcano of Copahue (Chile) 22 years earlier contained 0.688% of  $\text{H}_2\text{S}_5\text{O}_8$  and 0.07% of  $\text{As}_2\text{O}_3$ .  $\text{S}_2\text{O}_6^{2-}$  is attributed to atm. oxidation of suspended S. F. R. G.

**Chlorophyll content and productivity in lakes in N.E. Wisconsin.**—See A., 1944, III, 380.

**Sediments of four woodland lakes, Vilas Co., Wisconsin. II.** W. H. Twenhofel, V. E. McKelvey, S. A. Carter, and H. Nelson (*Amer. J. Sci.*, 1944, 242, 85—104).—The dominant and most abundant form of org. sediment is a pale greenish-yellow gel of small globules. The composition of the various sediments is described. L. S. T.

**Recent deposits of vesiculated mud along south-western Ohio streams.** R. H. Griffin and R. E. Shanklin (*J. Geol.*, 1943, 51, 488—494).—Calcareous silts deposited along these streams contain a high proportion of finely-divided, partly-digested org. matter, mainly sewage. Desiccation is accompanied by vesiculation as gases are generated by decomp. of org. matter, and by reaction of org. acids formed during decomp. with carbonate in the mud. L. S. T.

**Factors influencing the distribution of the elements.** J. H. Pannell (*Amer. Min.*, 1943, 28, 605—613).—A discussion. L. S. T.

**New type of stichtite found in the serpentine massif of Bou-Oufroh, Morocco.** (Mlle.) S. Caillère (*Compt. rend.*, 1942, 215, 420—422).—Analyses [by R. Frey and J. Burghelle] of the mineral (cf. A., 1934, 386) are:  $\text{CO}_2$  7.86, 8.50;  $\text{FeO}$  0.31, 0.16;  $\text{Fe}_2\text{O}_3$  13.90, 14.18;  $\text{Al}_2\text{O}_3$  2.08, 2.06;  $\text{Cr}_2\text{O}_3$  6.19, 4.92;  $\text{MgO}$  37.34, 38.26;  $\text{H}_2\text{O} + 32.52$ , 31.92%. These give the composition  $9\text{MgO} \cdot (\text{Fe}, \text{Cr})_2\text{O}_3 \cdot 2\text{CO}_2 \cdot 18\text{H}_2\text{O}$ . Optical properties (including  $n_g$  1.562,  $n_p$  1.543) are summarised. Identity with stichtites from Tasmania and Transvaal is confirmed by thermal and X-ray analysis, the Fe content indicating a passage from stichtite to brugnatellite and pyroaurite. A. J. E. W.

**Associations of heavy minerals in certain post-Cretaceous formations in the Paris basin (region south of the Seine).** B. Bräjniov (*Compt. rend.*, 1942, 215, 491—493).—The occurrence of characteristic groups of associated minerals is discussed, and the petrological significance of the appearance of augite is noted. A. J. E. W.

**Spectroscopic study of the mineral deposits of Kazakhstan with regard to the content of rare and scattered elements.** S. K. Kalinin (*Bull. Acad. Sci. U.R.S.S., Sér. phys.*, 1941, 5, 253—255).—A short review of work on the minerals of Kazakhstan to determine the distribution of rare and scattered elements. Deposits enriched in Ga, In, Tl, Ge, and other elements have been discovered. R. C. P.

**Brucitic limestones and hastingsite syenite near Wakefield, Quebec.** I. J. W. Ambrose (*Trans. Roy. Soc. Canada*, 1943, [iii], 37, IV, 9—22).—Occurrence is described, and chemical analyses are recorded and discussed. The amount of brucite (I) in the purer varieties of brucitic limestone ranges between 20 and 30%. The syenite has played an essential rôle in producing (I) and the history of these limestones is sedimentary limestone, dolomitisation, intrusion of syenite, dedolomitisation with formation of periclase (II), and hydration of (II) to (I). L. S. T.

**Morphology of carborundum.** J. D. H. Donnay (*Trans. Roy. Soc. Canada*, 1943, [iii], 37, IV, 43—47).—The theoretical significance of the morphology of carborundum is discussed. The dependence of the external forms on the internal structure is illustrated, and is considered to be the final indictment of Goldschmidt's views on normal form-series. L. S. T.



**Gold-silver ratios in certain Ontario gold mines.** E. L. Bruce (*Trans. Roy. Soc. Canada*, 1943, [iii], 37, IV, 23–31).—The Au : Ag ratios of the bullion from 7 mines are recorded graphically and are discussed. In some deposits the Au : Ag ratio appears to decrease with depth. The ratio differs for different kinds of wall rocks even on the same level. Ag shows less variation than Au.

L. S. T.

**Yorkshire Dogger. III. Upper Eskdale.** R. H. Rastall and J. E. Hemingway (*Geol. Mag.*, 1943, 80, 209–230; cf. A., 1942, I, 251).

L. S. T.

**Self-diffusion in minerals, particularly copper sulphides.** A. M. Gaudin and K. C. Vincent (*Amer. Inst. Min. Met. Eng.*, 1944, *Tech. Publ.* 1663, 6 pp.; *Min. Tech.*, 8, No. 1: cf. A., 1936, 424).—It has previously been found that chalcocite (I) abstracts Cu<sup>+</sup> xanthate from C<sub>6</sub>H<sub>6</sub> solution, and that the xanthate cannot be removed by leaching. Experiments have been made by the method of radioactive indicators to determine whether Cu diffuses into (I) from the xanthate. Radioactive solutions of Cu, Zn, and S were agitated with powders of natural (I), azurite (II), tetrahedrite (III), and sphalerite (IV), and synthetic (I) and covellite (V). The radioactivity of the solution and mineral, before and after contact with one another, was determined. The minerals acquired no radioactivity from the Zn or S solutions, but (I), and to a smaller degree (II), (III), and (V), became radioactive in the Cu solution. (IV) did not show this effect. Apparently in (I) the solid consists of two entities—S which is immobile, and Cu which is wandering freely.

C. E. H.

**Chemical relationship of cryptomelane (psilomelane), hollandite, and coronadite.** J. W. Gruner (*Amer. Min.*, 1943, 28, 497–506).—These minerals are isostructural and form isomorphous mixtures. The unit cell of the group contains 16 O ions, and has the formula  $Mn^{IV}_{8-(x/2+y/4+z/2)}(Mn^{II}, R^{II})_x(K, Na)_y(Ba, Pb)_{16O}(H_2O)_{2-(y+z)}$ . K, Ba, and Pb occupy identical positions, and the ratio  $x : y : z$  depends on the state of oxidation of Mn, which, in turn, depends on the conditions under which the mineral is formed. H<sub>2</sub>O occupies positions that could be filled by K, Ba, or Pb. The mineral originally named romanechite by Lacroix consists of minute crystals of cryptomelane. X-Ray powder spectra are compared.

L. S. T.

**South-Western end of the Newry igneous complex. Petrogenesis of the granodiorites.** D. L. Reynolds (*Quart. J. Geol. Soc.*, 1943, 99, 205–246).—Chemical analyses are recorded, and chemical changes involved in the petrogenesis of hornblende-, biotite-, and porphyritic granodiorite discussed.

L. S. T.

**Portencorkie complex of Wigtownshire.** N. Holgate (*Geol. Mag.*, 1943, 80, 171–195).—Chemical analyses of adamellite and a pyroxene-mica-diorite are given.

L. S. T.

**Intrusive rocks of the Shelve area, South Shropshire.** F. G. H. Blyth (*Quart. J. Geol. Soc.*, 1943, 99, 169–204).—The intrusions range from picrite to alkali-rich andesite; their structure and petrology are described. Chemical analyses are recorded.

L. S. T.

**Migmatite area around Bettyhill, Sutherland.** Y.-C. Cheng (*Quart. J. Geol. Soc.*, 1943, 99, 107–154).—The migmatization of pelitic, semi-pelitic, siliceous, and hornblende rocks of the Moine Series is a record of a lengthy series of metasomatic changes brought about by the activity of alkaline solutions. Variation diagrams and chemical analyses are recorded and discussed.

L. S. T.

**Fibrous sepiolite from Yavapai Co., Arizona.** A. J. Kauffman, jun. (*Amer. Min.*, 1943, 28, 512–520).—Chemical analyses, optical and X-ray data identify a hydrous Mg silicate from this locality as fibrous sepiolite (I). Well-cryst. specimens of (I), free from impurities, have lower  $v$ als. of  $n$  and better defined X-ray patterns than those containing amorphous material. The continued use of the term "parasepiolite" when referring to the highly cryst. variety of this mineral is recommended.

L. S. T.

**Phase equilibrium in the system  $Li_2O-Al_2O_3-SiO_2$ .**—See A., 1944, I, 128.

**Unidentified mineral in the quartz basalt [at Cinder Cone], Lassen Volcanic National Park, California.** R. Merriam and T. G. Kennard (*Amer. Min.*, 1943, 28, 602–604).—Occurrence of a light-blue glass and a blue-green mineral,  $\alpha$  1.545,  $\beta$  1.565,  $\gamma$  1.575 ( $\pm 0.002$ ),  $\rho$  2.60  $\pm 0.02$ , hardness 3, is described. Spectrographic analyses of glass and mineral show the presence of Al, Si, small amounts of Ca, Mg, Fe, Cu, and traces of Li, Na, B, Ba, Mn, Pb, and Ti.

L. S. T.

**Calculation of molecular formulæ for glauconite.** C. O. Harvey (*Amer. Min.*, 1943, 28, 541–543).—The procedure described by Hendricks and Ross (*ibid.*, 1941, 26, 683) is unnecessarily elaborate. A shorter method is given. A chemical analysis of glauconite obtained from a sand at Chobham, Surrey, is recorded.

L. S. T.

**New data on agricolite, bismoclite, koechlinite, and the bismuth arsenates.** C. Frondel (*Amer. Min.*, 1943, 28, 536–540).—Agricolite is identical with eulytite, and rhagite with atlestite (I). Arseno-

bismite (II) from Tintic, Utah, is a valid species; a new locality for it is at Tazna, Bolivia. A new, unnamed Bi arsenate, which alters to (II), occurs abundantly in association with (II) at the Mammoth mine in the Tintic district, Utah. X-Ray powder data for (I), (II), koechlinite, and the new Bi arsenate are tabulated.

L. S. T.

**Two andalusite pegmatites from Riverside Co., California.** R. W. Webb (*Amer. Min.*, 1943, 28, 581–593).—Reported occurrences of andalusite (I) in pegmatite are reviewed, and two new occurrences in which (I), corundum, microcline, and quartz are found in giant intergrowths, in metamorphic terrains, are described. Geological setting and genesis are discussed.

L. S. T.

**Pegmatite crystallisation.** T. T. Quirke and H. E. Kremers (*Amer. Min.*, 1943, 28, 571–580).—The geological, physical, and chemical conditions that control the pptn. and growth of pegmatite minerals are discussed.

L. S. T.

**Internal structure of silicate minerals that gelatinise with acid.** K. J. Murata (*Amer. Min.*, 1943, 28, 545–562).—A list of silicate minerals reported to gelatinise on being treated with acid is arranged according to a classification based on the internal structures of the minerals. Examination of the data indicates that the following classes of minerals, if vulnerable to acid attack, will gelatinise: (1) minerals containing silicate radicals of small mol. wt., viz., orthosilicates, pyrosilicates, and possibly silicates containing ring structures of three Si atoms, (2) minerals with large continuous Si-O networks that will disintegrate into units of low mol. wt., (a) disilicates containing much Fe<sup>III</sup> in the Si-O sheets, (b) minerals of the SiO<sub>2</sub> type with 3-dimensional networks that contain  $<2Al$  to 3Si. Minerals that separate insol. SiO<sub>2</sub> instead of gelatinising on treatment with acid are characterised by Si-O structures of large dimensions that do not disintegrate into small units under acid attack. These are SiO<sub>2</sub> chains, Si<sub>4</sub>O<sub>11</sub> double chains, Si<sub>2</sub>O<sub>6</sub> sheets not containing large amounts of Fe<sup>III</sup> replacing Si, and 3-dimensional networks with  $<2Al$  to 3Si. Exceptions to these rules are discussed.

L. S. T.

**Mineralogy of the oxides and carbonates of bismuth.** C. Frondel (*Amer. Min.*, 1943, 28, 521–535).—Bismutite, (I),  $\rho$  6.61–7.33, Bi<sub>2</sub>CO<sub>3</sub>, supposedly a hydrate, contains only non-essential H<sub>2</sub>O. On heating, (I) and artificial Bi<sub>2</sub>CO<sub>3</sub>· $n$ H<sub>2</sub>O lose H<sub>2</sub>O gradually to ~290°, when CO<sub>2</sub> is lost, and  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> remains. Artificial hydrates of Bi<sub>2</sub>CO<sub>3</sub> are unknown. 46 proven localities for (I) are given. Bismutospherite and basobismutite, and probably hydrobismutite and normannite, are identical with (I). Walthelite (II), a Bi carbonate of unknown formula, is a distinct species, monoclinic with  $c_0$  5.42  $\pm$  0.05 Å.;  $\rho$  5.32. Beyerite (III) is the name given to a new Bi Ca carbonate of unknown formula. (III),  $a_0$  3.78  $\pm$  0.01,  $c_0$  21.77  $\pm$  0.05 Å.,  $\rho$  6.56, hardness  $>3$ , space-group type, primitive, occurs at the Stewart mine, Pala, California, as compact greenish-grey masses embedded in quartz. The crystals are small, thin yellow plates. (III) contains traces of Si, Al, Mn, Pb, Mg, Cd, and Cu. The name bismite (IV) should be restricted to the  $\alpha$ -polymorph of Bi<sub>2</sub>O<sub>3</sub>. Sillenite (V) is the name given to a body-centred isometric polymorph of Bi<sub>2</sub>O<sub>3</sub> found as a secondary product at Durango, Mexico. Evidence for the existence of a definite hydrate of Bi<sub>2</sub>O<sub>3</sub> in nature is reviewed, and a probable occurrence of Bi<sub>2</sub>O<sub>3</sub>·3H<sub>2</sub>O is described. X-Ray powder spacing data and photographs for (I), (II), (III), (IV), and (V) are given. (See also C., 1944, Part 3.)

L. S. T.

**Crystal chemistry and geochemistry. Applications for recovery of rare elements in science and industry.** V. M. Goldschmidt (*Chem. Products*, 1944, 7, 29–34).—A lecture dealing with the distribution of elements in nature. The size of atoms and ions as the controlling factor in distribution is emphasised, and it is shown how a knowledge of these magnitudes makes it possible to predict the occurrence of elements. The "camouflage" of elements, i.e., the fact that a rare element with approx. the same at. radius as a more common one may exist with the latter and remain undetected (e.g., Ga and Al; Hf and Zr), is discussed. The effect of bond strength on sequence of crystallisation is dealt with.

A. J. M.

**Thermal analysis of clay minerals.**—See B., 1944, I, 133.

**Nevis oil-shale deposit, Nevis Survey District, Otago Central.** R. W. Willett (*New Zealand J. Sci. Tech.*, 1943, 24, B, 239–254).—The geology of the deposits, their extent, physical properties, chemical composition, and exploitation are described.

L. S. T.

**Oil shales at Cambrian, Freshford, and Waitati, Otago and Southland.** R. W. Willett (*New Zealand J. Sci. Tech.*, 1943, 24, B, 255–271).—Previous work on these deposits is reviewed, available chemical analyses are recorded, and geology of the deposits is described. Estimates of probable quantities are given.

L. S. T.

**Mode of preservation of plant fossils and its bearing on the problem of coal formation.** A. Kryštofovich (*Amer. J. Sci.*, 1944, 242, 57–73).—Some of the special types of plant preservation that throw light on the alteration of plant tissues into coal are discussed.

L. S. T.



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