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BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

JULY, 1944



A I—GENERAL, PHYSICAL, AND INORGANIC CHEMISTRY

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JULY, 1944.

I.—SUB-ATOMICS.

Structure of λ 5461 of mercury (^{198}Hg). J. H. Wiens (*Physical Rev.*, 1944, [ii], 65, 58).—Spectrograms show no structure for the ^{198}Hg line, but structure is clearly visible in the spectrogram for mixed Hg.

Temperature classification of gadolinium lines. A. S. King (*Astro-phys. J.*, 1943, 97, 323—380).— $\lambda\lambda$ and temp. classifications for 5775 lines of Gd from λ 2135 to λ 10677 Å. are given. The temp. classification, including segregation of the lines of Gd I and Gd II, was obtained by comparing the spectra of the C-tube furnace at three temp. with those of the arc and spark. The spectra in successive λ regions are described. In the solar spectrum ~60 lines of Gd II are present, about half of them arising from low at. levels.

Values of the energy of the electronic configuration $3d^2 4p$. M. T. Antunes (*Portugaliae Physica*, 1944, 1, 1—13; cf. A., 1943, I, 45).—Mathematical. The matrix of electrostatic interactions and orbit spin of the $d^2 p$ state is calc. Calc. and empirical vals. of the energy of the $3d^2 4p$ configuration of Ti II are given. The calc. vals. agree well with those assigned by Russell (cf. A., 1928, 679) to the energies of the various levels.

Structure of Th II spectrum. I. T. L. de Bruin, P. Schuurmans, and P. F. A. Klinkenberg (*Z. Physik*, 1943, 121, 667—678).—More than 1900 lines are identified as transitions between two term systems in the spectrum of Th⁺, by λ and Zeeman-effect measurements. One system contains 36 odd and 94 even, the other 25 even and 77 odd, terms. The odd terms are ascribed to the $5f7s^2$, $5f6d7s$, and $5f6d^2$ configurations of Th II. The coupling of 7s electrons corresponds approx. with the $J-J$ type. Only tentative allocation of even terms is possible.

Term values of X-ray spectra. T. M. Hu (*Physical Rev.*, 1944, [ii], 65, 76—79).—The term vals. of K , L , and M levels of X-ray spectra are given by the empirical formula $v(nj) = (1/n^2)[Z - \sigma_0 - \phi(Z)]^2 + (1/n^2)a^2(Z - \sigma_2)^4\{[n/(j + \frac{1}{2}) - \frac{3}{4}] + \dots - 2\sum_i Z_i[(Z - S_i)/n^2]\}$ where σ_0 and σ_2 are consts. for a given level and $\phi(Z) = -0.098 - 1.80 \times 10^{-3}Z + 1.40 \times 10^{-4}Z^2$ for the K and L levels, and zero for the M level. Vals. for the screening consts. best suited to the formula are given.

Continuous X-ray spectrum. R. Weinstock (*Physical Rev.*, 1944, [ii], 65, 150).—Mathematical note to experimenters. It is suggested that, unless angular distribution is sought, future intensity measurements be made at $50^\circ 44'$ with the (forward or reverse) direction of electron bombardments, provided the apparatus is not thereby rendered unwieldy.

Lead equivalent of thorium with respect to X-rays and radium γ -radiation. R. Jaeger (*Physikal. Z.*, 1943, 44, 153—156).—The Pb equiv. of Th (d 11.4 and 11.7) with respect to X-rays from a tube working at 15—300 kv. has been determined for 10 different hardnesses, and various thicknesses of Pb and Th filters. In general, 1 mm. of Th corresponds to >1 mm. of Pb, but for effective $\lambda\lambda$ lying between the K and L absorption edges of Th and Pb, 1 mm. of Th corresponds to ~ 0.7 mm. of Pb. The max. val. is 1.65 mm. of Pb equiv. to 1 mm. of Th, and occurs for λ 0.25 Å. Hard γ -rays from Ra-C give 1.16 mm. of Pb equiv. to 1 mm. of Th.

Quadratic Zeeman effect of the europium sulphate lines. A. Schmillen (*Ann. Physik*, 1941, [v], 39, 502—511).—The transverse Zeeman effect has been investigated with single crystals of $\text{Eu}_2(\text{SO}_4)_3$ with various orientations and with polarised light. The lines of the blue and green absorption groups, corresponding to transitions $^1F_0-X_2$ and $^1F_0-X_1$, show a Zeeman effect \propto (field strength)². The magnitude and direction of the effect are independent of the direction of the light, and the polarisation depends only on the orientation of the field with respect to the crystal. From the intensities of the absorption lines for different directions of the light and of the polarisation, conclusions about the direction of vibration of the absorbing dipoles may be drawn. The absorption of the blue group is ascribed to electric dipoles, some of which are vibrating in a definite direction, others in a single plane, and others in unspecified directions. The absorption of the green group is due to magnetic dipoles which vibrate in one direction.

Photo-electric conductivity of zinc sulphide-copper phosphors under the influence of α -rays. F. R. Lappe (*Ann. Physik*, 1941, [v], 39, 604—618).—Photo-electric determinations, especially dealing with the secondary current, are made on untreated ZnS-Cu phosphors, and on phosphors which have been irradiated with α -rays. To obtain measurable and reproducible currents on illumination the thinnest possible layers must be used. The inertia of the decay of the illumination current decreases with potential. The extinction effect of illumination of λ 550—900 m μ . is investigated. The effect on a phosphor that has been illuminated for some time is considerable. The decrease of current caused by the extinction effect reaches a saturation val. similar to excitation. The effect of α -rays on the current is investigated. There is considerable inertia. The effect of simultaneous distortion of the centres on the current is also investigated. The effect of increasing distortion on the illumination current is approx. linear. The effect of extinction on the secondary current increases linearly with the distortion. In this case the extinction effect extends over all $\lambda\lambda$. There is a marked effect of pressure on the secondary current. The dark- and the light-current increase considerably at small pressures, owing to the effect of adsorbed gas on the transition of electrons between the micro-crystals.

Adsorption of thorium on tantalum. C. J. Gallagher (*Physical Rev.*, 1944, [ii], 65, 46—50).—Th was evaporated from thoriated W on to a well-outgassed Ta ribbon, and the thermionic emission at 1390° K. was studied as a function of the time of evaporation. The work function of the ribbon decreased from 4.07 to 2.52 v., and the emission const. decreased by a factor 30. Qual. results are analogous to those for Th on W or Mo. A study of the emission from the two sides of the ribbon at 1550° K. showed a decrease from the activated side and an increase on the clean side, to equilibrium after 24 hr., indicating that the adsorbed Th had migrated around the edges of the ribbon and distributed itself uniformly over the emitting surface.

Directional distribution of X-ray intensities from massive anticathodes. H. Hinz (*Ann. Physik*, 1941, [v], 39, 573—590).—The intensity distribution is investigated for anticathodes of Be, Al, Cu, Ag, and Pb, at 150—300 kv. For Be the potential necessary to separate the intensity max. is determined, the position of the max. being followed with increasing filtering up to 250 kv. At this potential, the observed val. is $\sim 9^\circ <$ that deduced from Sommerfeld's theory, this discrepancy being explained by cathode-ray diffusion, and the superposition of different parts of the X-ray cone. The difference in intensity (I) of radiation at directions 0° and 90° increases with increased filtering and voltage. I_0/I_{90} decreases with increasing at. no. of the anticathode material, if tube potential and filtering are the same. For Pb, I_0/I_{90} is >1 .

Currents carried by electrons of uniform initial velocity. G. Jaffé (*Physical Rev.*, 1944, [ii], 65, 91—98).—Mathematical.

Interpretation of the spinning electron with bipolar co-ordinates. (Miss) M. H. Payne (*Physical Rev.*, 1944, [ii], 65, 39—46).—Mathematical. A geometrical picture of the Pauli and Dirac spin theories is developed.

Refractive index in electron optics. I. Opatowski (*Physical Rev.*, 1944, [ii], 65, 54—55).—Mathematical.

Negative ions of atomic and molecular oxygen. D. R. Bates and H. S. W. Massey (*Phil. Trans.*, 1943, A, 239, 269—304).—The properties, and modes of formation and of destruction, of the negative ions of O and O₂ are examined in detail, with quantum theory interpretation. A detailed examination is made of the $(1s)^2(2s)^2(2p)^4(3s)$ excited configuration of O⁻, and Hartree-Fock equations are solved for the deepest terms, but conflicting results prevent a decision as to the sign and magnitude of the binding energy of the 3s electron. To examine possible reasonable effects, radiative attachment and detachment rates are calc. for various vals. of the polarisability parameter. To interpret attachments of electron swarms in O₂, the deep electronic states of O₂⁻ are examined by empirical methods. The distribution makes it unlikely that O₂⁻ ions can be formed with any probability by attachment of slow electrons to O₂ at low pressures by a pressure-independent process other than direct radiative attachment. The theory of the crossing of mol. potential energy

curves is applied to the formation of oppositely charged ions from mols. by impact of electrons or light quanta, and to determination of the magnitude of cross-section for mutual neutralisation of oppositely charged ions by electron transfer on impact. The most probable val. for O ions is 10^{-12} – 10^{-13} sq. cm. N. M. B.

Analysis of β -ray spectra. A. Gibert (*Portugaliae Physica*, 1944, 1, 15–28).—Experimental facts not readily explained by supposing that β -spectra are due entirely to an internal photo-electric effect are reviewed. The work of Stahel (A., 1933, 205) on a type of coupling between the nucleus and the extranuclear electrons in β -radioactive transformations is considered, and outstanding anomalies are discussed. Stahel's results are in good agreement with more recent determinations. A. J. M.

Einstein's photo-electric law and the phenomenon of internal conversion. M. Valadares (*Portugaliae Physica*, 1944, 1, 35–41).—Comparison of the results obtained for the determination of the $\lambda\lambda$ of γ -rays by the magnetic spectrography of β -rays arising from internal conversion, and by the diffraction of γ -rays at crystals, indicates that the Einstein photo-electric law holds for the internal conversion of β -rays. A. J. M.

Inelastic scattering of slow neutrons. R. Weinstock (*Physical Rev.*, 1944, [ii], 65, 1–20).—Mathematical. The total polycryst. elastic and inelastic scattering cross-sections are calc. by Born's approximation with use of the Fermi interaction between slow neutrons and bound nuclei. Results are applied to scattering by Fe for 0–1000° K. Comparison of results for inelastic scattering with Zachariasen's theory of the diffuse scattering of X-rays is examined. N. M. B.

Angular distribution of alphas from ${}^7\text{Li}$ (p, α). C. D. Swartz, H. H. Rossi, B. Jennings, and D. R. Inglis (*Physical Rev.*, 1944, [ii], 65, 80–82).—The tracks formed in photographic emulsions at various angles from the beam were observed for bombarding energies $E = 400$ – 900 e.v. The angular distribution was $\propto 1 + A(E) \times \cos^2 \theta$, as at lower voltages (cf. Young, A., 1940, I, 426), and there is a max. of $A(E)$ at 675 kv. N. M. B.

Interpretation of the angular distribution of alphas from ${}^7\text{Li}$ (p, α). E. Eisner (*Physical Rev.*, 1944, [ii], 65, 85–87).—Proton penetration factors are calc. under several assumptions of nuclear potential. The Critchfield-Teller theory is briefly discussed in the light of these calculations and the angular distribution (cf. preceding abstract). N. M. B.

Angular distribution of alphas from ${}^{19}\text{F}$ (p, α) ${}^{16}\text{O}$. H. H. Rossi and C. D. Swartz (*Physical Rev.*, 1944, [ii], 65, 83–85).—The angular distribution, investigated for bombarding energies $E = 500$ – 900 e.v., depends markedly on E , contrary to results at lower voltages (cf. McLean, A., 1940, I, 426). N. M. B.

Strontium and yttrium isotopes from uranium disintegration. O. Hahn and F. Strassmann (*Z. Physik*, 1943, 121, 729–745; cf. A., 1944, I, 95).—The new 20-min. Y isotope has been identified as a transformation product of a Kr isotope from highly active U preps. Its direct precursor is a Sr isotope of short life, with a half-life of 2 ± 0.5 min., so far not isolated. Half-lives of a no. of Sr and Y isotopes have been more exactly determined than heretofore. L. J. J.

Cascade showers and nuclear disintegrations at 10,000 feet. W. E. Hazen (*Physical Rev.*, 1944, [ii], 65, 67–75).—In 8500 photographs obtained with a large cloud-chamber containing 8 Pb plates and operated without counter control at 10,000 ft., 1090 cascade showers and 58 nuclear disintegrations were observed. The differential energy spectrum for the shower-producing rays is $\propto E^{-1.7}$ for $E = 2 \times 10^6$ e.v., and to $E^{-3.0}$ for $E = 10^6$ e.v. The shower-producing rays with $E > 2 \times 10^6$ e.v. constituted 6.5% of the radiation; $\frac{1}{4}$ of the shower-producing rays were photons. Nuclear disintegrations initiated by neutrons or protons contained Pb-penetrating particles which were mostly protons or mesotrons. N. M. B.

Variation of mesotron intensity with altitude and latitude, together with allied phenomena, and the bearing of these matters on the nature of the primary particles. W. F. G. Swann (*J. Franklin Inst.*, 1943, 236, 1–7, 111–139).—Results stated in condensed form in earlier publications by the author are established, and detailed proofs of some of the formulæ previously cited are given. The min. meson velocity necessary to account for the sea-level latitude ratio and the intensity-altitude data is too high to permit the symmetrical electron emission at death of proton-born mesons indicated by the observed horizontal intensities at high altitudes. To give a sufficiently low meson velocity the incoming primaries also must have a low velocity, which demands a greater mass than the proton. For these primaries charged He atoms are invoked to account for high-altitude phenomena, in addition to the protons already invoked to explain phenomena at low and medium altitudes. The slow mesons born of the charged He atoms die before they penetrate far into the atm. W. J.

Polygonal surface and periodic classification of elements. W. Finke (*Z. Physik*, 1943, 121, 586–587).—Comments on work by G. Haenzel. A representation of electronic quantum nos. of known

at. species in three dimensions, employing cartesian or mixed cartesian-polar co-ordinates, is proposed. L. J. J.

Statistical theory of the atom. P. Gombás (*Z. Physik*, 1943, 121, 523–542).—Interaction of electrons with antiparallel spins is considered. Boundary electron densities $\sim 45\% >$ those corresponding to the Thomas-Fermi-Dirac atom are calc. The equations obtained are solved for a no. of ions and atoms, the Fermi-Amaldi correction term being used. The effect considered results in an increased attraction between atoms and ions. L. J. J.

Measurement of atomic radiating sources in crystals. II. Calculation of the absorption distribution for dipole radiation and determination of transition probabilities. K. H. Hellwege (*Z. Physik*, 1943, 121, 588–603; cf. A., 1944, I, 73).—The effect of at. dipole moment previously discussed is computed quantitatively for weak absorption. Absorption is dependent only on the orientation of the electric or magnetic vector. The inverse square root of the absorption const. taken in the corresponding direction gives an ellipsoid. The transition probabilities (oscillator strengths) can be determined as magnitudes independent of orientation, by one measurement for optically isotropic bodies, two for optically uniaxial crystals, and three for biaxial crystals. Of the two angles required to define the absorbing dipole, the measurements give neither, one, and both, respectively, in these cases. Data for hexagonal Nd Zn nitrate are given. L. J. J.

Theory of spherical waves excited at a finite distance from the plane separating two media for finite refractive index. M. Krüger (*Z. Physik*, 1943, 121, 377–437).—Mathematical. A. J. M.

Nuclear field theories. H. T. Flint (*Proc. Physical Soc.*, 1944, 56, 149–160).—A lecture survey covering the work of Fermi and others leading to Yukawa's deductions and theory. N. M. B.

Proper vibrations of a liquid drop and their application to nuclear physics. S. Flügge (*Ann. Physik*, 1941, [v], 39, 373–387).—Vibrations of a liquid drop for the general case of non-axially symmetric surface vibrations are calc. The rate of dissipation of such vibrational energy by radiation is calc. on the basis of classical electrodynamics and applied to the theory of nuclear isomerism. L. J. J.

Plane diffusion problems. G. C. Wick (*Z. Physik*, 1943, 121, 702–718).—An approx. method of solving plane diffusion problems is applied to problems of neutron physics. L. J. J.

Atomic radii from atomic and quantum numbers. S. T. Li (*J. Chinese Chem. Soc.*, 1943, 10, 169–172).—Equations, $r_s = n^2/KZ$ or $n^3/(Z + 4)$ and $r_d = n^2/hZ^{2/3}$, relating these quantities, are proposed. They give vals. in agreement with experiment. J. H. Ba.

II.—MOLECULAR STRUCTURE.

Application of the new analysis of molecular spectra to certain molecules. Simple explanation of certain molecular peculiarities. H. Deslandres (*Compt. rend.*, 1942, 215, 558–562).—A general survey and discussion of results of the author's later method of band-spectrum analysis. N. M. B.

Vibration spectrum of a crystal lattice.—See A., 1944, I, 143.

Band spectrum of silver hydride. L. Gerö and R. Schmid (*Z. Physik*, 1943, 121, 459–487).—The band spectrum of AgH is reinvestigated, and the bands of the ${}^1\Sigma$ – ${}^1\Sigma$ system are analysed. Vibrational term differences and rotation consts. of the lower state are calc. The homogeneous perturbation of the upper states is analysed. The term series of two mutually perturbing electronic states form a "network" in which the rotational terms with different vibration quantum nos. intertwine with each other. The analysis of the rotational and vibrational term differences in the upper states, the unusual intensity distribution in the bands, and the irregular isotope splitting of the band-lines can thus be explained. A. J. M.

Spectrum of nitric oxide: rotational analysis of ϵ bands and new observations on the β and δ band-systems. A. G. Gaydon (*Proc. Physical Soc.*, 1944, 56, 160–174).—Full data and a rotational analysis are tabulated for the (0, 4) and (0, 3) bands of the ϵ system of NO. Rotational consts. are evaluated; the upper electronic state is of type ${}^2\Sigma^+$. Potential-energy curves for the known electronic states of NO are shown. The excitation of the β and δ systems of NO in the N_2 afterglow is discussed. Bands of the β system with $v' = 5$ and 6 have been obtained in emission. The energy of dissociation of NO and supposed predissociation in the spectrum are considered. N. M. B.

Absorption of light in soap solutions. M. E. L. McBain (*J. Physical Chem.*, 1944, 48, 89–95).—Ultra-violet absorption by Na oleate solutions does not change regularly with concn., and duplicate measurements do not correspond. This effect is not due to light scattering but to the orientation of colloidal particles or lamellar micelles. C. R. H.

Relation of starch-iodine absorption spectra to the structure of starch and starch components.—Sec A., 1944, II, 186.

Effects of solvents on the absorption spectra of dyes. III. Temperature and organic solutions of cyanine dyes. S. E. Sheppard and H. R. Brigham (*J. Amer. Chem. Soc.*, 1944, 66, 380—384).—Absorption spectra of 8 cyanine dyes in various solvents (EtOH, MeOH, Et₂O, and C₆H₁₄) have been determined in the visible region at 90—300° K. Ionised dyes show no displacement of max. absorption. Bands are sharper at low temp., owing to suppression of rotation and low-order vibrational energies. Elimination of the auxiliary bands is not attained at 90° K. Sharpening of the bands first produces an increase in ϵ_{max} , followed by a decrease, which is less or absent in non-ionised dyes. Displacement of the spectrum of merocyanine dyes depends on the polarity of the solvent, indicating a coupling of dye and solvent mols. W. R. A.

Absorption spectra of the colouring matters of saffron. F. Poggio and M. Sanz Muñoz (*Anal. Fis. Quim.*, 1942, 38, 257—264).—Extinction curves for three fractions separated chromatographically from the Et₂O-insol. EtOH extract, and also for the total colouring matter, of Spanish saffron indicate the presence of picrocrocin. F. R. G.

Dependence of the intensity of fluorescence on the composition of a fluorescing solution. G. K. Rollefson and H. W. Dodgen (*J. Chem. Physics*, 1944, 12, 107—111).—The relation between intensity (*I*) of fluorescence of solutions of fluorescein and acridone and the concn. of the fluorescer is expressed by a function which takes into account absorption of the exciting and fluorescent light and quenching by the fluorescer. At const. fluorescer concn. and in presence of KI as quencher the relation between *I* and [KI] is better expressed by Stern and Wolmer's than by Perrin's equation. This leads to the conclusion that quenching is a bimol. reaction competing with the unimol. reaction of fluorescence. C. R. H.

Luminescence spectra and vibrations in crystal lattices. D. D. Pant (*Proc. Indian Acad. Sci.*, 1943, 18, A, 309—326).—A general survey of the luminescence spectra of crystals. Crystals giving discrete spectra are divided into seven classes, typified by diamond, Cr-activated luminescent solids, rare-earth phosphors, impurity-activated fluorescent solids, UO₂⁺⁺ compounds, solid C₆H₆, and solid N₂. Examination of the luminescence and absorption spectra of these solids suggests that vibrational ν are sharply monochromatic in all crystals. The spectra of some crystal constituents, e.g., N₂, C₆H₆, and UO₂⁺⁺, are similar to their gaseous spectra, but the observed bands are more discrete, owing to the absence of rotational lines. W. R. A.

Action of added substances on the luminescence of lucigenin. I. K. Weber (*Z. physikal. Chem.*, 1941, B, 50, 100—115).—The action of added substances, which are usually inhibitors (KCl, KBr, KI, and KCNS) or catalysts (OsO₄, C₆H₅N, piperidine, and monohydric alcohols), on the fluorescence and chemiluminescence of NN'-dimethylacridylum nitrate (lucigenin) is investigated. Fluorescence is visible in neutral aq. solutions; chemiluminescence occurs when H₂O₂ is added to a strongly alkaline aq. solution. The inhibitors quench both forms of luminescence, so that either the initial intensity or both this and the total emission are reduced, as a result of action on either the exciting reaction or the excited mol. KI acts on the latter, KCl on the former, KBr and KCNS on both. Quinol possesses both a quenching and a catalytic effect. OsO₄, C₆H₅N, piperidine, MeOH, EtOH, Pr^oOH, Pr^oOH, Bu^oOH, and Bu^oOH show purely positive catalysis. The catalytic effect of the alcohols is \propto no. of C atoms in the chain. W. R. A.

Scope and limitations of infra-red measurements in chemistry. H. W. Thompson (*J. C.S.*, 1944, 183—192).—Tilden lecture. Points connected with the experimental technique of infra-red measurements are outlined. Vibrational absorption bands and their assignment to modes of vibration of the mol. are considered. The analysis of rotational structure of infra-red absorption bands also gives a method for assigning vibration frequencies, and for the determination of moments of inertia. Difficulties in the method due to perturbation of energy levels owing to interaction of vibration and rotation, and the fact that sufficient parameters cannot always be obtained to fix the structure, are emphasised. In the case of large or non-volatile mols. which do not show rotational contour, the vibration frequencies can be used to calculate useful thermodynamic properties. The allocation of a mol. to a symmetry class by using infra-red and Raman data together is considered. The application of infra-red spectroscopy to the investigation of the course of a reaction (e.g., addition to unsaturated compounds, condensation in the formation of high polymers, etc.) and the analysis of mixtures of related mols. (such as *o*-, *m*-, and *p*-isomerides, or *cis-trans* isomerides) is discussed. A. J. M.

Structure of the second CH harmonic and determination of integral extinction equivalents in the infra-red spectra of liquid aliphatic and aromatic hydrocarbons. R. Suhrmann and P. Klein (*Z. physikal. Chem.*, 1941, B, 50, 23—72).—The absorption spectra of 53 aliphatic, aromatic, and combined hydrocarbons and their derivatives are measured from 1.0 to 1.6 μ , with particular attention to the second

CH harmonic and the CH band at 1.4 μ . In standardising the spectrometer with H₂O, 5.9M-KI solution, and C₆H₆, a new H₂O band was found at 2.565 μ , together with several new C₆H₆ bands. ρ_2^{20} , mol. vol., and the wave nos., $\lambda\lambda$, and mol. extinction coeffs. of the principal bands are tabulated. In the presence of :CH₂, Me negative substituents, O bridges, and the CO group, the second CH harmonic separates into partial bands, the increase in aliphatic compounds with negative substituents occurring in the CH bonds of the C atom carrying the substituent. In aromatic compounds, the more negative are the substituents, the greater is the increase in ν of the second CH harmonic. The presence of both aromatic and aliphatic CH bonds in the mol. produces two adjacent bands in the second CH harmonic. By measuring the area between the absorption curve and the ν axis, the internal extinction coeff. per CH bond, $E_{\text{CH}}^{\text{al}}$ or $E_{\text{CH}}^{\text{ar}}$ in aliphatic or aromatic compounds, respectively, has been determined. Absorption in the second CH harmonic is the same in saturated hydrocarbons, in the alkyl halides (except EtI, Pr^oI, and Bu^oI), in the ethers, and in NEt₃, but stronger in dioxan and cyclohexane, and weaker in nitriles, NO₂-compounds, and ketones. The aromatic CH bond absorbs more weakly in the second CH harmonic, and, although unaffected by one halogen atom, absorbs even less when several such atoms, or a CN or NO₂ group, are present. Vals. of E_{CH} in aliphatic-aromatic compounds agree well with those calc. from $E_{\text{CH}}^{\text{al}}$ and $E_{\text{CH}}^{\text{ar}}$. Intensity of the second CH harmonic increases with decreasing mol. vol. It is suggested that the frequency drift on introducing a negative substituent may be determined by subtracting from the observed second CH harmonic the total absorption of the CH₂ and Me groups in the mol., vals. for the mol. extinction coeffs. of these partial bands having been derived from the spectra of the pure hydrocarbons. W. R. A.

Infra-red absorption of solid ammonium chloride and ammonium bromide. C. Beck (*J. Chem. Physics*, 1944, 12, 71—78).—Infra-red absorption of solid NH₄Cl in the 7 μ . band shows no fine structure, but a little very fine structure is given by NH₄Br. In the 5.6 μ . band both solids show at room temp. fine structure with similar spacing of the lines. NH₄Br shows also a still finer structure which cannot be resolved. At low temp. the fine structure of NH₄Br is decreased in intensity, and between -20° and -45° there is a change in the overall shape of the band. Fine structure persists down to -60°. Calculations show that the fine structure is due to rotation of the NH₄ group in the crystal and that this rotation continues, although altered, at temp. below the transition temp. of NH₄Br (-37.9°). C. R. H.

Raman spectra of crystals and their interpretation. R. S. Krishnan (*Proc. Indian Acad. Sci.*, 1943, 18, A, 298—308).—Spectrograms of the Raman effect of NaCl crystals, obtained by Rasetti (A., 1931, 1352), are re-examined. Raman shifts, relative densities, and intensity ratios of Stokes to anti-Stokes lines are estimated for the 9 distinct lines on either side of the exciting ν . These ν are identified with harmonics of the forbidden fundamentals of the 9 normal modes of the NaCl lattice given by Raman's theory (A., 1944, I, 143). These observations cannot be explained by the Born theory of crystal dynamics. W. R. A.

Raman spectroscopy and its applications to glasses and glass-like synthetic materials. A. Simon (*Kolloid-Z.*, 1941, 96, 169—186).—The Raman spectra of simple mols., mols. exerting intermol. forces, glasses, and high polymers are discussed with reference to structure. J. H. Ba.

Raman spectrum of vitamin-C and of its oxidation products. C. Bragnolo and Z. Ollano (*Gazzetta*, 1942, 72, 571—577).—The Raman spectra of l-ascorbic acid (I) and of its first C-powder oxidation product (II) suggest that (I) is a furan derivative in which the olefinic form predominates over the "aromatic" resonance form, and that (II) has an open chain with a CO₂H group. E. W. W.

Dipole moments of friedelin, cerin, isomerides of friedelinol, and isomerides of α -chloro- γ -1-naphthyl- Δ^8 -propene. J. J. Lander and W. J. Svirbely (*J. Amer. Chem. Soc.*, 1944, 66, 235—239).—Vals. of μ , calc. from dielectric const. (ϵ) measurements on C₂₆H₄₆ solutions of friedelin (I), high- (II) and low-m.p. friedelinol (III), cerin (IV), and the solid (V) and liquid (VI) forms of 1-C₁₀H₇-CH₂-CH:CHCl, are (I) 2.80 \pm 0.03, (II) 1.81 \pm 0.05, (III) 1.78 \pm 0.07, (IV) 2.39 \pm 0.05, (V) 1.27 \pm 0.02, and (VI) 1.47 \pm 0.02 d. Vals. of P_2 and μ do not depend on the abs. vals. of ϵ and ρ of the solvent. The error in P_2 , which arises from the relative errors in ϵ of the solvent, can be eliminated by using a val. of ϵ from the plot of ϵ against N_2 , extrapolated to $N_2 = 0$. Vals. of μ for (I)—(IV) support the postulated structures, whilst those for (V) and (VI) confirm the suggested *cis*-(VI)-*trans*-(V) isomerism. W. R. A.

New contributions to interferometry. III. Differential polarisation phase change on reflexion at a thin silver film. S. Tolansky (*Phil. Mag.*, 1944, [vii], 35, 179—187).—The differential phase change for light polarised in and perpendicular to the plane of incidence on reflexion at a thin Ag film is measured for angles of incidence between 20° and 80°. To a first approximation the results confirm classical theory (MacLaurin, *Proc. Roy. Soc.*, 1906, A, 78,

296) but there is a small second-order discrepancy with a pronounced increase in the neighbourhood of 63° , which may be due to transition at the surfaces or to microcryst. structure in the film. The effect of the differential phase change in a high-resolution Fabry-Perot interferometer is discussed; it can only be important for plate separations $< \sim 1$ mm. H. J. W.

Size and form of ultramicroscopic particles. W. Hanke (*Z. Physik*, 1943, 121, 438—458).—Theoretical. Diffraction patterns formed by a double slit, the slits being narrow compared with their distance apart, are considered. A characteristic "visibility function," giving curves of equal visibility, is developed for various geometrical figures, and discussed. The function is applied to a parallelogram and a triangle. The results become particularly simple when the objects are smaller than the limit of resolution. The application of the characteristic function to diffraction at a double slit where the distance between the slits is of the same order as the slit width is also considered. A. J. M.

Relation between electronegativity and atomic number, quantum number, and valency. S. T. Li (*J. Chinese Chem. Soc.*, 1943, 10, 167—168).—The formula is given relating these quantities, $E = Z^{2/3}(z + 2.6)/kn^2$, where $k = \text{const.} = 2.1$ when the quantum no. $n = 2$ and $= 2.3$ when $n = 3-6$, Z and z being at no. and valency. The calc. electronegativities of elements from Li to Bi agree with other determinations. J. H. B.

(A) **Electronic resonance of 1-methyl-2-piperidone.** (B) **Energy of electronic resonance of 1-methyl-2-piperidone.** P. S. Ugriumov (*J. Gen. Chem. Russ.*, 1943, 13, 217—221, 222—229).—(A) The dipole moment is shown by methods of analytical geometry to be 3.09×10^{-18} , whereas the experimental val. is 4.01×10^{-18} ; the difference is ascribed to resonance.

(B) The mol. heat of combustion is 882.4 kg.-cal., whereas the "calc." val. exceeds this val. by 24.0 kg.-cal. Similarly, the heat of formation from the gaseous elements exceeds that "calc." by 26.6 kg.-cal. The differences of 24.0 or 26.6 kg.-cal. represent the resonance energy. R. T.

cis-trans-Isomerism and cis-peak effect in the α -carotene set and in other stereoisomeric sets.—See A., 1944, II, 188.

Hydrogen content of white dwarf stars. G. Chertock (*Physical Rev.*, 1944, [ii], 65, 51—53).—Calculation of a mechanically stable model of the white dwarf Sirius B, considered as a completely degenerate gas, requires that the central core containing 11% of the mass and extending to 21% of the radius shall have no H_2 , and the remainder of the star shall have 45% H_2 . N. M. B.

III.—CRYSTAL STRUCTURE.

Precision determination of lattice constants by a compensation method. II. H. van Bergen (*Ann. Physik*, 1941, [v], 39, 553—572).—The lattice const. of calcite, rock-salt, Al, and Fe are determined by a compensation method due to Kossel (A., 1936, 925). The method, formerly used only for cubic crystals, is applied to hexagonal, tetragonal, and rhombic systems, and can be used for any type. The lattice const. for the above substances agree with those obtained by other methods. A. J. M.

Diffraction of X-rays by distorted-crystal aggregates. I. A. R. Stokes and A. J. C. Wilson (*Proc. Physical Soc.*, 1944, 56, 174—181).—Mathematical. The broadening of the Debye-Scherrer lines in X-ray photographs of cold-worked metals to be expected if due to distortion of comparatively large crystal grains is given by $\eta = \beta \cot \theta = 2/\phi_{hkl}(0)$, where β is the cor. integral breadth of the hkl reflexion, θ the Bragg angle, and $\phi_{hkl}(e)de$ the fraction of the crystal for which the tensile strain in the hkl direction is between e and $e + de$. Approx. relations of η with the internal stresses are given. N. M. B.

Definition of a crystal. G. Antonoff (*J. Physical Chem.*, 1944, 48, 95).—Objection is taken to the expression "isotropic crystals" for crystals having the same properties along the three main axes (e.g., NaCl), because the properties in other directions are not the same. Objection is also taken to referring to axes as being long or short and the term "intercepts" is proposed. C. R. H.

Crystal statistics. I. Two-dimensional model with an order-disorder transition. L. Onsager (*Physical Rev.*, 1944, [ii], 65, 117—149).—Mathematical. N. M. B.

Anisotropy of metals. H. S. Coleman and H. L. Yeagley (*Physical Rev.*, 1944, [ii], 65, 56—57).—Conclusions from available data are (1) that the anisotropy in the diffusion rate of one metal into another indicates that orientation may be the primary factor in controlling this rate, and (2) that there is an intimate relation between the crystal structure, plastic deformation, ferromagnetism, growth nucleation of metals, and intermetallic diffusion in the solid state. N. M. B.

Vibration spectrum of a crystal lattice. (Sir) C. V. Raman (*Proc. Indian Acad. Sci.*, 1943, 18, A, 237—250).—The normal modes of vibration of atoms in a crystal are derived from the most general

expression for the potential energy of displacement from the equilibrium position. In all possible modes, equiv. atoms have the same amplitude of vibration and either the same or alternately opposite phases in successive cells along each of the three axes of the lattice, thus forming a repeating space pattern, the "unit cell" of which has twice the dimensions of the lattice cell. The modes are closely analogous to those of a mol. with 8 times the no. of atoms in the lattice cell, and possessing the appropriate symmetry. The spectrum consists of a finite no. of discrete monochromatic ν , the no. of which is reduced in highly symmetric crystals. Degrees of freedom not included in this description appear as quasi-elastic vibrations of specifiable low ν . W. R. A.

Modes of atomic vibration in the fourteen Bravais lattices. G. N. Ramachandran (*Proc. Indian Acad. Sci.*, 1943, 18, A, 266—282).—Mathematical. The degeneracies and directions of the normal modes of vibration in the 14 Bravais lattices are derived by considering symmetry and using the theory of Raman (preceding abstract). Vibrations are of 8 types in the general case of no symmetry, but in partly symmetrical lattices some of the types and some directions of motion are equiv. The directions of motion and degeneracies of these types are found by selecting a group of symmetry operations, which results in coincidence of atoms in the same phase; directions of motion which satisfy the symmetry requirements of the group are then found. The no. of distinct modes for the $\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4, \Gamma_5, \Gamma_6, \Gamma_7, \Gamma_8, \Gamma_9, \Gamma_{10}, \Gamma_{11}, \Gamma_{12}, \Gamma_{13}, \Gamma_{14}$, and Γ_{15} lattices are 21, 21, 15, 21, 15, 12, 12, 12, 8, 8, 5, 4, 4. The modes are also described by considering symmetry only. W. R. A.

Normal oscillations of the diamond structure. S. Bhagavantam (*Proc. Indian Acad. Sci.*, 1943, 18, A, 251—256).—Mathematical. Group-theory methods are used to obtain the normal vibrations of the diamond structure, assuming a 16-atom cell as repeating unit. There are 8 normal vibrations, of which one is 3-fold, two are 4-fold, three are 6-fold, and two are 8-fold degenerate. The corresponding ν are derived by postulating suitable potential energy functions. W. R. A.

Frequency spectrum of the diamond lattice. E. V. Chelam (*Proc. Indian Acad. Sci.*, 1943, 18, A, 334—340).—Mathematical. Expressions for the ν of the eight normal modes of vibrations of the diamond lattice (cf. Chelam, *infra*) given by Raman's theory (*supra*) are derived, a suitable force field being used. W. R. A.

Frequency spectrum of crystalline solids. II. General theory and applications to simple cubic lattices. E. W. Montroll (*J. Chem. Physics*, 1944, 12, 111).—Errors are corr. (cf. A., 1944, I, 6). C. R. H.

Frequency spectrum of crystalline solids. III. Body-centred cubic lattices. E. W. Montroll and D. C. Peaslee (*J. Chem. Physics*, 1944, 12, 98—106).—The dynamics of a Born-Karman at. model have been developed on the assumption that the significant interactions are those between the nearest and next nearest at. neighbours, and that all internal vibrations are essentially harmonic. On the basis of this model the moments of the frequency spectrum, the relation between frequency spectrum and lattice const., and expressions for sp. heat have been deduced. C. R. H.

Normal vibrations in typical cubic crystals. E. V. Chelam (*Proc. Indian Acad. Sci.*, 1943, 18, A, 257—265).—The normal modes of vibration of simple, body-centred, and face-centred cubic lattices and of the lattices of ZnS, diamond, NaCl, CaF₂, and CsCl are derived, the theoretical methods of Raman (A., 1944, I, 143) being used. These lattices have 5, 4, 4, 9, 8, 9, 14, and 11 distinct ν . W. R. A.

Character tables for the atomic vibrations in cubic crystals. E. V. Chelam (*Proc. Indian Acad. Sci.*, 1943, 18, A, 327—333; cf. preceding abstract).—Mathematical. Character tables for groups associated with the vectors defining the normal modes are given for NaCl, diamond, ZnS, and CaF₂ lattices. The method of obtaining the normal modes from the tables is illustrated. W. R. A.

Normal vibrations of crystal lattices. Application of group theory. E. V. Chelam (*Proc. Indian Acad. Sci.*, 1943, 18, A, 283—297).—Group-theory methods, based on Raman's theory (A., 1944, I, 143), are used to derive the harmonic vibrations of a general crystal lattice. The rigorous derivation of the no. of normal modes, and their ν and degeneracies, is described. W. R. A.

Modes of vibration of the hexagonal close-packed lattice. G. N. Ramachandran (*Proc. Indian Acad. Sci.*, 1943, 18, A, 341—344).—Mathematical. The modes of vibration of the hexagonal close-packed lattice are derived by Chelam's method (cf. *supra*) based on Raman's theory of crystal vibrations (A., 1944, I, 143). Character tables are constructed. There are 13 distinct modes, of which one is non-degenerate, two are 2-fold, six are 3-fold, one is 4-fold, and three are 6-fold degenerate. The crystal planes involved, and the direction of vibration of each mode, are described. W. R. A.

State of order in felled and netted structures caused by mechanical deformation, especially in the case of polystyrene. F. H. Muller (*Kolloid-Z.*, 1941, 96, 326—332).—A review (cf. A., 1944, I, 29). J. H. B.

Molecular structure of liquids. H. A. Stuart (*Kolloid-Z.*, 1941, 96, 149—160).—The structure of liquids consisting of mols. of various shapes and charge distributions is discussed on the basis of the results of experiments with models (cf. A., 1938, I, 123). Physical properties are correlated with the structures obtained.

J. H. Ba.

Chemical morphology of liquids. III. Liquid-crystalline aliphatic monocarboxylic acids.—See A., 1944, II, 179.

Structure of water. F. I. Havlíček (*Z. Physik*, 1943, 121, 495—500).—Starting from the crystal structure of ice given by Bragg, Barnes, and Bernal and Fowler, and Debye's model of the H_2O mol., a model for the association of H_2O is drawn up, a hexagon being the fundamental structural element. The binding energy is discussed.

A. J. M.

Structure relationships between salts and amorphous hydroxides of polyvalent metals. H. W. Kohlschütter (*Kolloid-Z.*, 1941, 96, 237—244).—A review of the experiments on the formation of the hydroxides of Fe^{+++} , Cr^{+++} , and Al^{+++} from neutral and basic salts in the solid state and in solution. The structures and properties of the hydroxides formed are determined in part by those of the salts from which they are prepared.

J. H. Ba.

Electron-microscopic and X-ray investigation of the structure of soots. M. von Ardenne and U. Hofmann (*Z. physikal. Chem.*, 1941, B, 50, 1—12).—The particle sizes of three soots, (I) from a C_2H_2 flame, (II) from the explosive decomp. of C_2H_2 , and (III) from the action of finely-divided Fe on CO at 700° , are determined by X-ray analysis and with the electron microscope. Surface area per g. was determined by colorimetric estimation of the adsorption of methylene-blue. The soot was prepared for electron-microscopic examination by evaporation of a xylene suspension on a vibrating slide. Particle diameters are (I) 25, —; (II) 200, 200—300; (III) 400, 100—500 Å., the first val. being that from X-ray analysis. Surface area, calc. from particle size, differs markedly in (I), but less in (II) and (III), from that determined by adsorption. These deviations are explained by the fact that electron-micrographs show that (I) consists of dense aggregate particles, and that in (II) and (III) aggregation is much less compact.

W. R. A.

Structure of micro-crystalline carbon. U. Hofmann, A. Ragoss, and F. Sinkel (*Kolloid-Z.*, 1941, 96, 231—236).—Differences in activity between various types of C are attributed to various crystal sizes and their packing. X-Ray comparison of C_2H_2 soot (I), retort-scale C, and coke show that graphitisation occurs the more readily the more dense is the original structure. The structures of (I), gas (II), and flame soots (III) are examined by methylene-blue adsorption, X-rays, and electron microscope, before and after graphitisation. The ratio of the surface area, as determined by X-rays and adsorption, gives a measure of the close packing of the crystals, and is found to increase in the order (III) > (II) > (I). Electron micrographs confirm that on graphitisation the tendency to recrystallise to bigger crystals is also in this order.

J. H. Ba.

Crystal structure of potassium silver carbonate, $KAgCO_3$. J. Donohue and L. Helmholz (*J. Amer. Chem. Soc.*, 1944, 66, 295—298).—The crystal of $KAgCO_3$ is orthorhombic holohedral, a_0 20.23, b_0 5.75, c_0 5.95 Å., space-group D_{2h}^{17} —*Ibca*. The Ag—O distance, 2.42 Å., is discussed in relation to other Ag salts, including Ag_2CO_3 , for which preliminary data are: a_0 4.83, b_0 9.52, c_0 3.23 Å., β 92.7° , z 2, probable space-group C_{2h}^2 — $P2_1$. The application of the rule of Pitzer *et al.* (A., 1941, I, 451) to the probable nature of the Ag—O bond is discussed.

W. R. A.

Constitution of the aluminium-vanadium compound. VAI_3 . G. Brauer (*Z. Elektrochem.*, 1943, 49, 208—210).—Interaction of V_2O_5 , pure Al, and Na_3AlF_6 in an atm. of A, followed by slow cooling of the product from 1200° to 500° , yields the compound VAI_3 , which can be separated from the excess of Al by utilising its less rapid dissolution in HCl or aqua regia and finally by centrifuging in MeI + Et_2O mixture (d 3.2). Like $TiAl_3$ it crystallises in a tetragonal quadratic form, space-group D_{4h}^{17} , with a 5.334 and c 8.305 Å.; d 3.68 from X-ray data, and 3.34 pyknometrically.

J. W. S.

Active substances. XLIX. X-Ray and electron-microscopic investigation of the thermal transformation $\gamma\text{-FeOOH} \rightarrow \gamma\text{-Fe}_2O_3 \rightarrow \alpha\text{-Fe}_2O_3$. R. Fricke, T. Schoon, and W. Schröder (*Z. physikal. Chem.*, 1941, B, 50, 13—22).—Changes in particle and crystal structure in the series $\gamma\text{-FeOOH} \rightarrow \gamma\text{-Fe}_2O_3 \rightarrow \alpha\text{-Fe}_2O_3$ are investigated by X-ray diffraction and with the electron microscope. The large differences in dimensions of the crystals, calc. from the X-ray diffraction diagrams, and of the particles visible in the electron microscope, show that the latter are secondary aggregates. The shape and size of these secondary aggregates remain almost unchanged up to the transformation into $\alpha\text{-Fe}_2O_3$ at 500° , whereas the size of the primary particles of FeOOH increases on heating, but decreases considerably in the transformation into $\gamma\text{-Fe}_2O_3$, finally increasing, with the formation of plate-shaped crystals. In the transformation into $\alpha\text{-Fe}_2O_3$, heating to 750° is necessary before the needles, visible in the electron microscope, are replaced by dense secondary aggregates.

W. R. A.

Crystal structure of copper *NN*-di-*n*-propyldithiocarbamate. I. G. Peyronel (*Gazzetta*, 1943, 73, 89—94).—The crystal structure of this compound (cf. Malatesta, A., 1938, I, 128) is studied goniometrically and by X-ray (rotating crystal and Weissenberg) methods. It belongs to the $2_1 \times 2/m$ prismatic class of the monoclinic system, with lattice consts. a 13.25, b 18.60, c 8.27 Å.; β $99^\circ 48'$; 4 mols. per unit cell. The symmetry group is C_{2h}^2 or C_{2h}^1 . Cu occupies a centre of symmetry with planar co-ordination.

E. W. W.

Structure of the "B" modification of starch from film and fibre diffraction diagrams. R. E. Rundle, L. Daasch, and D. French (*J. Amer. Chem. Soc.*, 1944, 66, 130—134; cf. A., 1941, I, 451).—Films were prepared from solutions of amylose (I) and used, after stretching, for X-ray examination. The specimens, in contrast with whole starch, contain no branched chains, the mols. being linear aggregates of ~ 200 glucose residues. The unit cell has a_0 16.0, b_0 10.6, c_0 9.2 Å., and is probably orthorhombic. Calc. d of crystal. portion 1.6. The structure proposed is based on the space-group D_2^1 , although D_2^2 is equally likely. Fibres were also prepared, but are difficult to stretch sufficiently to produce good orientation. The configuration of (I), unlike that of cellulose, depends on its treatment. In "B" the chains are fully extended, in "V" and in the I-complex they are helical, and when treated with certain plasticisers they assume an intermediate crumpled form.

F. L. U.

Micellar structure of cellulose. O. Kratky (*Kolloid-Z.*, 1941, 96, 301—310).—The state of dispersion of cellulose in xanthate solutions is considered, and X-ray pictures of cellulose pptd. from such solutions and in various degrees of extension and swelling are shown to agree quantitatively with a structure consisting of plate micelles joined by thread mols.

J. H. Ba.

Microscopic and electron-microscopic investigations on macromolecular substances. (Frl.) M. Staudinger (*Chem.-Zig.*, 1943, 67, 316—320).—The study of synthetic polymers of known structure, e.g., polyoxymethylenes and polyethylene oxides, as a preliminary to investigation of natural polymers, e.g., cellulose, is discussed. With linear macromol. substances the capacity for fibre formation runs parallel with the chain length. Photomicrographs are shown of polyoxymethylene crystals degraded by acids and alkalis. Cellulose fibrils are more stable towards chemical degradation, but its effect becomes apparent after swelling or mechanical treatment. Bacterially degraded fibres are attacked only locally, and the average degree of polymerisation is not much reduced. The possible arrangements of macromols. in the cell-wall are considered.

R. H. F.

The ultrasonic diffraction grating. R. A. Houstoun (*Phil. Mag.*, 1944, [vii], 35, 192—202).—Stationary ultrasonic waves produced by a quartz plate in a periodic electric field are accompanied by a harmonic variation in n ; the plate can then act as a diffraction grating. Experiments with various quartzes and oscillators are described. The quartz grating can be used for measuring the velocity of light by reflecting the diffracted beam back through the quartz after traversing a path of known length (~ 4 m. in H_2O). The quartz can also be used as a wave-meter since the grating effect depends on resonance between the applied field and the natural frequencies of the quartz. An arrangement for determining the persistence of luminosity in an electrodeless discharge in a gas at low pressure is also suggested; no positive results have so far been obtained.

H. J. W.

Loss of colour of alkali halide crystals. H. Kurzke and J. Rottgardt (*Ann. Physik*, 1941, [v], 39, 619—632).—Moisture may cause bleaching of a coloured alkali halide crystal. The mechanism of the process is discussed.

A. J. M.

Flow of polycrystalline metals. U. Dehlinger and A. Kochendorfer (*Z. Elektrochem.*, 1943, 49, 228—233).—The plastic deformation of single crystals is discussed and compared with flow in fluids. For a crystal deranged by rapidly varied stress, as with a crystal containing occluded foreign atoms, the crit. deformation resistance is greatly increased. With metals containing crystals of varying orientation the elastic limit is reached when the stress equals the mean val. of the elastic limits of the individual crystals. The special stresses arising near the crystal interfaces are discussed. The theory developed leads to the inference that the elastic limits of soft Al and Cu should vary little with varying temp., whereas that of Fe should be very temp.-dependent. This has been confirmed experimentally.

J. W. S.

Cross-section contraction number [Poisson's ratio] in the periodic system. W. Koster (*Z. Elektrochem.*, 1943, 49, 233—237).—Poisson's ratio (μ) for metals, calc. from the ratio of the moduli of compression and elasticity, is a periodic function of the at. no., metals of the same group having closely similar vals. The μ vals. calc. from the c_{12} and c_{44} elasticity consts. of single crystals are in closer accord with the vals. obtained from polycryst. samples the lower is the elastic anisotropy of the metal.

J. W. S.

Structure of fritted powders. G. F. Hüttig (*Kolloid-Z.*, 1941, 96, 227—230).—The process of fritting is defined as the joining of powder particles without the formation of a liquid phase. The vol. occupied by capillaries ($1.5\text{--}5.5 \times 10^{-7}$ cm. diameter) in powdered Cu on raising the temp. to 600° shows two max. at $\alpha = 0.35$ and

$\alpha = 0.48$, where $\alpha = (\text{abs. temp.})/(\text{abs. m.p.})$. Similar max. at approx. the same vals. of α are observed for Fe, Fe_2O_3 , $\alpha\text{-Al}_2\text{O}_3$, and BeO. The first max. is concerned with the surfaces only, but the second involves the crystal lattice. J. H. Ba.

IV.—PHYSICAL PROPERTIES OF SUBSTANCES.

Physical data of Δ^{α} -olefines and n -paraffins.—See A., 1944, II, 177.

Physical data of $\alpha\alpha$ -diphenyl-alkenes and -alkanes and $\alpha\omega\omega$ -tetraphenylalkenes.—See A., 1944, II, 189.

Approximate method for the calculation of magnetic susceptibility. H. Koppe (*Z. Physik*, 1943, 121, 614—628).—Susceptibility calculations are based on the eigenfunctions of H in a magnetic field, taking into account perturbations due to coulombian interaction of electrons. L. J. J.

Magnetic properties of non-homogeneous systems. L. F. Bates and E. M. Somekh (*Proc. Physical Soc.*, 1944, 56, 182—194).—The magnetic susceptibilities of dil. amalgams of 12 metals were measured by a new method using cylindrical pole surfaces shaped in accordance with recent theoretical work. Results tabulated and discussed show that all these metals are paramagnetic in dil. solution in Hg to an extent which is usually compatible with an increase in the no. of free electrons in the amalgam. N. M. B.

Absolute diamagnetism of superconductors. K. M. Koch (*Z. Physik*, 1943, 121, 488—494).—A reply to criticism by Neugebauer (A., 1943, I, 222). A. J. M.

Damping of mechanical oscillations by magnetic hysteresis. M. Kornetzki (*Z. Physik*, 1943, 121, 560—573).—Changes in magnetisation caused by uniform mechanical strain in the Weiss regions show a residual effect after removal of the applied stress. Hence there is a dissipation of energy during mechanical oscillation. The resulting damping increases with amplitude of vibration, and \propto the Rayleigh hysteresis const. and \propto the third power of the ratio of saturation magnetostriction to saturation magnetisation. L. J. J.

Collision excitation of intramolecular vibration in gases and gaseous mixtures. VIII. Ease of excitation of various normal vibrations from measurements of the dispersion of sound. K. F. Buschmann and K. Schäfer (*Z. physikal. Chem.*, 1941, B, 50, 73—99).—The dispersion of sound in CO_2 , NH_3 , N_2O , and Me_2O is measured at normal temp., and relaxation times are calc. A dependence of relaxation time on the pressure of the gas and ν of the sound could be recognised. This dependence shows that vibrations requiring a collision from a direction perpendicular to the mol. axis for their excitation are less easily excited than those requiring a collision in the direction of the mol. axis, in agreement with results obtained from exchange reactions. Deviations, observed only in N_2O , appear to arise from the tendency of this gas to thermal decomp., although a rigid explanation cannot be advanced. W. R. A.

Refractive indices of the normal saturated aliphatic nitriles. A. Dorinson and A. W. Ralston (*J. Amer. Chem. Soc.*, 1944, 66, 361—362).—Vals. of n_D^{20} ($\theta = 20\text{--}75^\circ$) are given for normal aliphatic nitriles from butyrol to stearyl-nitrile; for each compound, an abrupt change in slope in n - θ curves is exhibited at $\sim 40\text{--}45^\circ$. W. R. A.

Specific heats at low temperatures of calcium sulphite, sodium sulphite, and manganese dithionate dihydrate. K. K. Kelley and G. E. Moore (*J. Amer. Chem. Soc.*, 1944, 66, 293—295).—Vals. of C_p from 53° to 295°K . have been determined for CaSO_3 , Na_2SO_3 , and $\text{MnS}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$, giving vals. of entropy at 298.16°K . of 24.2 ± 0.3 , 34.9 ± 0.4 , and 66.7 ± 1.0 g.-cal. per degree per g.-mol. There appears to be a difference in entropy between a sulphate and a sulphite group in a solid of ~ 1 g.-cal. per degree per g.-mol. at 298.16°K . W. R. A.

Heat capacity, heats of transition and vaporisation, vapour pressure, and entropy of $\alpha\alpha\alpha$ -trichloroethane. T. R. Rubin, B. H. Levedahl, and D. M. Yost (*J. Amer. Chem. Soc.*, 1944, 66, 279—282).— C_p for CCl_3 has been measured at $14\text{--}300^\circ\text{K}$. At 224.20° there is a transition point with heat of transition 1786 ± 2 g.-cal. per g.-mol. M.p. $\sim 240.2 \pm 0.5^\circ\text{K}$, heat of fusion $\sim 450 \pm 300$ g.-cal. per g.-mol. From 268° to 290°K . the v.p. equation is $\log p = -(1729/T) + 6.92013$. Heat of vaporisation at 286.53°K . is 7962 ± 12 g.-cal. per g.-mol. Entropy vals. are: gas at 286.53°K , 76.22 ± 0.16 , and at 298.16°K , 76.97 ± 0.16 ; liquid at 298.16°K , 54.37 ± 0.12 g.-cal. per degree per g.-mol. From spectroscopic data, on the assumption of free rotation, $S_{286.53}^\circ$ (1 atm.) is 77.47 ± 0.10 g.-cal. per degree per g.-mol., corresponding with a barrier of 2700 ± 350 g.-cal. per g.-mol. W. R. A.

Densities of liquids and their temperature changes. G. Antonoff (*J. Physical Chem.*, 1944, 48, 80—85).—The thermal history of a liquid influences its d ; bringing the liquid to a given temp. does not necessarily give the same val. of d . Accurate d data for Pr°OH , obtained over the range $25\text{--}85^\circ$, show that there is a kink in the d curve at $\sim 60^\circ$, and that the d of freshly purified Pr°OH is $< d$ of

aged specimens. Intramol. tautomerism, intermol. reaction, and polymerisation are suggested as reasons for the observed effects. C. R. H.

Densities and transition points of normal paraffin hydrocarbons. W. F. Seyer, R. F. Patterson, and J. L. Keays (*J. Amer. Chem. Soc.*, 1944, 66, 179—182).—Measurements of ρ for even-numbered paraffin hydrocarbons (C_{18} to C_{34}) show that, for each, the structure in the liquid and solid states is identical. The C_{28} homologue has a solid phase much less dense than even-numbered neighbours. The transition points of hydrocarbons C_{24} to C_{34} can be observed with either heating or cooling, whilst for C_{18} to C_{20} the transition point is observed only on cooling. W. R. A.

Vapour pressure of beryllium at $1170\text{--}1340^\circ\text{K}$. R. Schuman and A. B. Garrett (*J. Amer. Chem. Soc.*, 1944, 66, 442—444).—Vals. of the v.p. of Be between 1170° and 1340°K , determined by the Langmuir method, are given. The mean val. of ΔH_0° is $122,000 \pm 2500$ g.-cal. per g.-mol. The calc. heat of vaporisation at 1250°K . is 78,800 g.-cal. per g.-mol. The accommodation coeff. appears to be 1. W. R. A.

Regularity of vapour pressures of organic substances belonging to homologous series. A. Giacalone (*Gazzetta*, 1942, 72, 370—377).—In aliphatic series, the ratio (R) of the v.p., at const. temp., of any member to that of the one next above is approx. const. (at 20° , $\sim 2.5\text{--}3.5$), and differs little from series to series; it decreases with temp. The decrease in molar free energy, calc. from R , for each additional CH_2 group in the hydrocarbon series ~ 710 g.-cal. (cf. Parks *et al.*, A., 1930, 877). There is an approx. const. difference in the temp. at which two successive homologous members have the same v.p. E. W. W.

Vapour pressure and heat of vaporisation of trichloroethylene. H. J. McDonald (*J. Physical Chem.*, 1944, 48, 47—50).—Over the range $18\text{--}86^\circ$ the v.p. of C_2HCl_3 is represented by $\log p = 30.482609 - 2936.227/T - 7.999975 \log T$, where $T = \text{abs. temp.}$. At the b.p. and at 1 atm. the heat of vaporisation is 7679 ± 100 g.-cal. per g.-mol. Over the range $0\text{--}60^\circ\text{C}$, C_2HCl_3 has $d_4^{20} = -0.001618\theta + 1.4980$, and over the range $17\text{--}27^\circ$ $n_D = -0.0005765\theta + 1.4890$, where $\theta = \text{temp. in } ^\circ\text{C}$. C. R. H.

Thermal expansivity and density of indium. P. Hidnert and (Miss) M. G. Blair (*J. Res. Nat. Bur. Stand.*, 1943, 30, 427—433).—The linear thermal expansion of high-purity cast In is investigated at $20\text{--}100^\circ$ by the precision micrometric thermal expansion apparatus of Souder and Hidnert (B., 1926, 789) and at -190° to 0° by the fused-quartz tube thermal expansion apparatus of Hidnert and Sweeney (B., 1928, 930). Within the range -190° to 100° , the linear expansion of In is expressed by the equation: $L_\theta = L_0[1 + (28.9\theta + 0.013\theta^2) \times 10^{-6}]$, where L_0 and L_θ are the lengths of the metal at 0° and θ° . The average coeffs. of cubical expansion of In are 77×10^{-6} ($0\text{--}25^\circ$) and 101×10^{-6} ($25\text{--}50^\circ$). These are not three times the corresponding coeffs. of linear expansion because of the anisotropy of In. The d of cast In, calc. from the best data on at. wt. and lattice consts., is 7.40, within 2% of the observed val. of 7.281 for $d^{22.6}$. J. F. H.

Supplementary postulates and the gas law. R. W. Pohl (*Z. Physik*, 1943, 121, 543—545).—Examples of confusion arising from neglect of certain assumptions in the formulation of fundamental laws are given. L. J. J.

Equation of state for saturated fluids. J. E. Haggengrader (*J. Amer. Chem. Soc.*, 1944, 66, 313).—The expression, $p = CT/(v_s + v_l + 2B)$, where $C = R/M$, $B = (CT_c/2P_c) - v_c$ (p = saturation pressure; T = saturation temp. in $^\circ\text{K}$; v_s , v_l = sp. vols. of saturated vapour and saturated liquid; M = mol. wt.; T_c , P_c , v_c = crit. temp., pressure, and vol.), has been derived from a more general, three-const. quadratic equation of state for saturated fluids. Of the 59 substances tested with this expression, only AcOH shows anomalous behaviour, which may be explained by association. Agreement with observation is best for the simple gases, e.g., He, H_2 , Ne, N_2 . W. R. A.

Relation between liquid and gaseous states of metals. L. Landau and J. Zeldovitch (*Acta Physicochim. U.R.S.S.*, 1943, 18, 194—196).—The existence of a continuous spectrum of electron energy levels is necessary but not sufficient for the metallic state; to ensure conductivity it must be possible for charge to be transferred between the fundamental state and adjacent excited levels. In dielectrics there is a finite gap at all temp. between such levels, continuous transition to metallic conduction being impossible except at $\sim 10^4^\circ\text{K}$. Three cases are distinguished for metal-gas transition: (i) a single crit. point at very high temp., (ii) a liquid-gas crit. point at a temp. \ll that of the crit. metal-dielectric point (e.g., Hg), with the co-existence of two metallic and one dielectric phases, or (iii) one metallic and two dielectric (liquid and gaseous) phases. For Hg there are predicted a non-conducting liquid phase and a phase transition above the normal crit. point with a discontinuous change of electrical conductivity, sp. vol., and other properties. L. J. J.

Determination of critical temperature from b.p. M. C. Chen and D. B. Hu (*J. Chinese Chem. Soc.*, 1943, 10, 212—215).—The expres-

sion $T_c = 101.59/\sqrt{M} \cdot T_B$ gives good agreement with observed vals. of T_c for a large no. of compounds. J. H. BA.

Additive function of mol. wt. and critical temperature. D. B. Hu and M. C. Chen (*J. Chinese Chem. Soc.*, 1943, 10, 208—211).—The expression $M \log_{10} T_c + 6.41/\sqrt{M}$ is shown to be additive for a large no. of compounds (cf. Burnop, A., 1938, I, 393).

Viscosity of compressed gases. O. Leipunski (*Acta Physicochim. U.R.S.S.*, 1943, 18, 172—182).—According to available published data, Enskog's formula describes accurately the viscosity of pure gases up to ~1000 atm. for N_2 , H_2 , CO_2 at 100°, and CO , and up to 300 atm. for H_2O at 370°, 600 atm. for CH_4 at 25°, 30 atm. for NH_3 at 80°, and 150 atm. for O_2 at 50°. The formula describes the change of η of gas mixtures with pressure with fair accuracy if the const. b is taken as the mean of vals. for the components.

Hydrogen bond. J. N. Friend (*Chem. and Ind.*, 1944, 179).—Investigation of η of a no. of org. compounds from room temp. to the b.p. agrees with the view that there is a close connexion between η and the H bond. Replacement of OH in PhOH by OMe markedly reduces η in spite of the increase of mol. wt. Replacement of Me by heavier alkyl groups causes increase of η . Similarly the η of NH_2Ph is progressively reduced by successive replacement of the H of NH_2 by Me, but the η of $NPhMe_2$ is increased by substituting Me by heavier alkyl groups. Extrapolation indicates that the η of $NPhBu_2$ will probably be approx. the same as that of NH_2Ph .

Viscosities of di- and tri-methylamine at 15°, 25°, and 35°. E. Swift, jun., and D. L. Wolfe (*J. Amer. Chem. Soc.*, 1944, 66, 498—499).—Experimentally determined vals. of η at 15°, 25°, and 35° (reliable to only 1%) are: for $NHMe_2$ 2.07, 1.86, and 1.67, and for NMe_3 1.94, 1.77, and 1.61 m-poise.

Kinetic theory of thermo-diffusion in liquids. K. Wirtz and J. W. Hiby (*Physikal. Z.*, 1943, 44, 369—382).—Thermal diffusion in liquids is considered, using a quasi-cryst. model for the place-exchange process. Isothermal migrational processes (diffusion and ionic mobility) are discussed on the basis of the model. The activation energy for place exchange is divided arbitrarily into two parts, one the energy necessary to bring the particle into the position of rest before the change, and the other the energy the particle has in the new position of rest; the latter depends on the size of the particle. These two portions of the energy influence the Soret effect in opposite directions. The movement of a stream of particles in a temp. gradient is considered on this basis, and an expression for the Soret coeffs. is obtained. The work is extended to dil. solutions of electrolytes, giving diffusion potentials. The laws obtained agree with those deduced by Wagner on thermodynamic grounds. The anomalous behaviour of the Soret effect in alkalis is related to anomalies of mobility. The theory explains why the heavier mols. of a liquid mixture migrate towards the warm wall in thermo-diffusion. The isotope effect of the Soret coeffs. is discussed, and it is shown that it is the size of the isotope mol. which is responsible for separation.

Thermodynamics of thermal diffusion. J. Meixner (*Ann. Physik.*, 1941, [v], 39, 333—356).—Irreversible processes, e.g., diffusion, can be approached by "thermodynamic-phenomenological" methods, taking into account (i) material, energy, and impulse conservation principles and a spatial distribution of entropy sources, but no entropy sinks, (ii) experimental laws relating rates of irreversible processes with the appropriate potential factors, and the Onsager reciprocity law. These methods are applied to thermal conduction in anisotropic crystals, thermo-diffusion with convection in a binary ideal gas mixture, and thermo-diffusion in paramagnetic gases. The theory is in harmony with Eastman and Wagner's transfer-heat concept.

calc. from the observed temp.-time integral. An application of the effect to gas analysis is suggested. L. J. J.

Thermodynamics of thermal diffusion.—See A., 1944, I, 149.

Determination of mol. wt. of organic substances by dialysis. (A) H. Brintzinger. (B) H. Spandau (*Ber.*, 1941, 74, [B], 1025—1028, 1028—1030).—(A) The method of Spandau and Gross (A., 1943, I, 304) is invalid because of variation of K for different org. substances, even for isomerides; mol. shape is an over-riding factor. A difficulty of technique is noted.

(B) K vals. are const. (23 examples) if wide-pored membranes are used. The difficulty of technique is overcome. R. S. C.

Mixture law for viscosity. F. Kottler (*J. Physical Chem.*, 1944, 48, 76—80).—Derivations are given for the fluidity equations for ideal and non-ideal mixtures previously reported (cf. A., 1943, I, 224). The conditions which must be fulfilled in obtaining the data so as to test the equations are laid down. The use of mol. fractions and not wt. or vol. fractions is imperative. C. R. H.

Pyrazine-water azeotrope. H. F. Pfann (*J. Amer. Chem. Soc.*, 1944, 66, 155).—Pyrazine and H_2O form a min.-boiling 60:40 azeotrope, b.p. 95.5°.

Influence of electrolytes on the rotatory power of *d*-tartaric acid. L. Yang and P. F. Hu (*J. Chinese Chem. Soc.*, 1943, 10, 184—189).—HCl causes an initial sharp fall in the rotation followed by a gradual decrease at higher concns. Addition of NaOH shows a max. and NaCl is similar to HCl at the higher concns. The observations are accounted for in terms of the effect of the additions on the ionisation of tartaric acid and an electrolyte effect. J. H. BA.

Entropy change during alloy formation.—See A., 1944, I, 155.

Diffusion of copper, magnesium, manganese, and silicon in aluminium. H. Buckle (*Z. Elektrochem.*, 1943, 49, 238—242).—The diffusion consts. (D) of Cu, Mg, Mn, and Si in Al have been determined at 400—600°. In each case D decreases with increasing concn. of alloying element. The energies of dissolution are evaluated.

Solubility in aluminium of Mg, Si, Mg, Ge, Mg, Sn, and Mg, Pb. H. Westlinning and W. Klemm (*Z. Elektrochem.*, 1943, 49, 198—200).—At 500° the solubilities in Al of Mg_2Si , Mg_2Ge , Mg_2Sn , and Mg_2Pb , as determined by X-ray and microscopic examination of quenched samples, are ~0.4, 0.2, 1.8, and 0.2 mol.-%, respectively. These vals. show a decrease with increasing polarisability of the anion. The solubilities of Mg_2Sn and Mg_2Ge decrease with decreasing temp. much more rapidly than that of Mg_2Si .

Surface treatment of metallic surfaces by diffusion. H. Vosskuhler (*Z. Elektrochem.*, 1943, 49, 204—208).—Heating of Al—Li alloy (6.69% Li) in air or in a $Na_2Cr_2O_7$ — $K_2Cr_2O_7$ bath at 590°, Mg—Ca alloy (1.98% Ca) in air at 500°, or Al—Mg alloy (~8.5% Mg) in a $NaNO_3$ — KNO_3 bath at ~400° decreases the surface concn. of Li, Ca, and Mg, respectively. In each case a homogeneous layer is formed over the heterogeneous material and the metal becomes less corrodible.

Solubility of $MgZn_2$ in aluminium. G. Siebel (*Z. Elektrochem.*, 1943, 49, 218—220).—X-Ray and microscopic investigations indicate that the solubility of $MgZn_2$ in Al increases from 1.4 wt.-% at 150° to ~17 wt.-% at 475°. The results are in accord with previous data for temp. >325° but are < previous vals. for higher temp.

Magnetic investigation of a nickel-carbon alloy. W. Gerlach and J. von Rennenkampff (*Z. Elektrochem.*, 1943, 49, 200—203).—The anomalous temp.-variation of the magnetisation of Ni saturated with C by fusion in a C crucible is explained by assuming that the cooled sample is a mixture of alloys of varying C content in which that with Curie point ~50° predominates. Reheating causes pptn. of C and hardening of the metal.

Structures of metalloid alloys and ferromagnetism. H. Nowotny (*Z. Elektrochem.*, 1943, 49, 254—260).—The binary systems of Cr, Mn, Fe, Co, and Ni with N, P, As, Sb, and Bi are closely analogous in that several compounds of the types MX , M_2X , M_3X , and M_4X are formed. These are regarded as interstitial compounds. Such compounds of Cr and Mn are often ferromagnetic, this behaviour being discussed theoretically.

Magnetic properties [of dilute amalgams].—See A., 1944, I, 147.

Line co-ordinate representation of solubility curves. F. E. E. Germann and R. P. Germann (*Ind. Eng. Chem.*, 1944, 36, 93—96).—On the basis of Mortimer's solubility equation, $-\log X = 0.05223a/T + b$, where X = mol. fraction of solute in solution at temp. T and a and b are consts., a chart, which enables the solubility of a solute in a given solvent over a range of T to be obtained, has been constructed. The chart is applicable to 17 org. solutes with several org. solvents for each solute, 131 two-component systems being represented.

Thermochemistry of chlorine monoxide [solubility in water].—See A., 1944, I, 155.

Solubility of sodium iodide in aqueous sodium hydroxide at 20°. R. Pomeroy and H. D. Kirschman (*J. Amer. Chem. Soc.*, 1944, 66,

V.—SOLUTIONS, DISPERSIONS, AND MIXTURES.

Demonstration experiment on emanation diffusion. A. Krebs (*Ann. Physik.*, 1941, [v], 39, 330—332).—The diffusion of radioactive emanation through different gases is followed by observations of the progress and intensity of fluorescence on a phosphor film supported on a glass strip or tube in a glass tube to one end of which the emanation is admitted.

Diffusion of inert gases through metals. W. Lumpe and R. Seeliger (*Z. Physik.*, 1943, 121, 546—559).—Inert gas occluded in metals becomes appreciably mobile at ~100° and its mobility increases markedly with temp.

Diffusion thermo-effect. L. Waldmann (*Z. Physik.*, 1943, 121, 501—522).—The kinetics of thermo-diffusion are derived from the Boltzmann equation. The material and thermal flux of diffusion are proportional to the same coeff., the "thermodiffusion factor" (α). Temp. distribution in diffusion chambers with adiabatic walls is calc. Diffusion of N_2 into H_2 can give temp. differences up to 7°, and diffusion of ^{22}Ne into ^{20}Ne can give 0.8°. The coeff. α can be

178—179).—The solubility and ρ of NaI in aq. NaOH (0—15.2N.) have been determined. A discontinuity, representing the transition $\text{NaI} \cdot 2\text{H}_2\text{O} \rightarrow \text{NaI}$, has been found with a solution 8.20N. in NaOH and 6.92N. in NaI. W. R. A.

Acetone-, ethyl alcohol-, dioxan-, and glycerol-water-lead chloride systems.—See A., 1944, I, 164.

Decrease of free surface energy as a basis for the development of equations for adsorption isotherms, and the existence of two condensed phases in films on solids. W. D. Harkins and G. Jura (*J. Chem. Physics*, 1944, 12, 112—113).—The adsorption of vapours on solid surfaces is part of the general behaviour of insol. adsorbed films on liquids and solids. The free energy of the surface is the fundamental basis for the treatment of this subject. Equations giving the pressure-area relations of insol. oil films on H_2O should and do apply to adsorbed films on solids or on other liquids. Two such equations (linear) are formulated. When applied to films on solids the plot exhibits two straight lines, thereby indicating the existence in the film of two condensed phases with a second-order transition. Examples of this are films of PrOH on BaSO_4 or anatase and films of N_2 on certain catalysts used in the petroleum industry and on certain charcoals. C. R. H.

Condensation and supersaturation of adsorbed phases. H. M. Cassel (*J. Chem. Physics*, 1944, 12, 115—116).—The validity of Langmuir's adsorption isotherm is discussed in view of the interaction of neighbouring adatoms not having been taken into account. Starting with the Emmett-Brunauer-Teller adsorption isotherm and eliminating surface density, it can be shown that the surface tension of adsorbed, built-up film (presumably liquid) is negative. This conclusion is due to disregarding lateral cohesion in the design of the film model. If mutual attraction of adatoms is taken into account, cluster formations and phase transitions leading to metastable mono- or multi-layers are to be expected. Existence of the latter is possibly indicated in the observed hysteresis in capillary condensation. C. R. H.

Van der Waals adsorption of H_2 , D_2 , CH_4 , N_2 , and Ne on nickel plates. A. van Itterbeek and J. Borghs (*Z. physikal. Chem.*, 1941, B, 60, 128—142).—The van der Waals adsorption has been measured for H_2 , D_2 , CH_4 , and N_2 at the temp. of liquid N_2 , and for Ne, H_2 , and D_2 at the temp. of liquid H_2 , on Ni platelets of known macroscopic surface area. The results for N_2 , Ne, and CH_4 agree with the Polanyi potential theory, and satisfy the equations $q_A(v)/q_B(v) = (a_A/a_B)^{1/2}$, $Q = q + q_i$ [$q_A(v)$ = the adsorption potential function of gas A, at adsorption vol. v , a = van der Waals const., Q = experimental ΔH of adsorption, q = the Polanyi potential energy, and $q_i = \Delta H$ of vaporisation]. H_2 and D_2 at the temp. of liquid H_2 possess a potential function which differs from the Polanyi function, is dependent on T , and is such that the potential of $\text{H}_2 > \text{D}_2$. $q_{\text{D}_2}(0)/q_{\text{H}_2}(0) \approx 1$, as for H_2O and D_2O on glass plates at room temp., and for H_2 and D_2 on charcoal at liquid H_2 temp. The microscopic surface area of the Ni plates, calc. from the vals. of the const. v_m of the multilayer theory of Brunauer, Emmett, and Teller (A., 1938, I, 190), was ~ 5 times the macroscopic surface area. W. R. A.

Adsorption of gases on smooth surfaces of steel. M. H. Armbruster and J. B. Austin (*J. Amer. Chem. Soc.*, 1944, 66, 169—171).—The adsorption of A, Ne, H_2 , N_2 , CO, and CO_2 on three samples of cold-rolled steel has been determined at 20°, —78°, —183°, and —195° and at pressures up to 0.12 cm. The measurements were made first on the grease-free, outgassed surface, and then on the same surface after reduction in H_2 . Numerous preliminary adsorptions and desorptions were necessary before the results were reproducible. H_2 and Ne are not measurably adsorbed on either surface under these conditions. A monolayer of physically adsorbed N_2 , A, or CO is formed on the unreduced surface at —183°, but $\sim 15\%$ of each gas cannot be desorbed by reducing the pressure. On the reduced surface, N_2 and A form physically adsorbed monolayers, which can be completely removed by reducing the pressure; sorption of a similar monolayer of CO is partly chemisorption. CO_2 is measurably adsorbed on both surfaces at —78°. The isotherms, although similar to the saturation type, probably represent the low-pressure sections of sigmoid isotherms. ΔH of adsorption, calc. by the equation of Brunauer *et al.* (A., 1938, I, 190), is ~ 3 kg.-cal. per mol. for all physical adsorption, and depends more on the nature of the surface than on the chemical nature of the adsorbate. $v = v_s(p/(1 + ap))^{1/n}$ (v = vol. adsorbed at pressure p , v_s = vol. adsorbed at saturation, a , n are consts.), a combination of the Freundlich (low-pressure) and Langmuir (higher-pressure) equations, represents the isotherms over the complete range of pressures. n , which decreases with T , is a measure of the deviation of the adsorbed film from an ideal two-dimensional gas. When some of the gas is strongly adsorbed, the force/area curves exhibit phase transformations similar to those of monolayers on H_2O . The sp. surface of the samples was 4 times the geometrical surface. W. R. A.

Effect of neutral salts on the adsorption of alkalis by silica. Y. Fu (*J. Chinese Chem. Soc.*, 1943, 10, 103—112).—Neutral salts cause increase in the adsorption of NaOH and KOH by SiO_2 as measured by titration with acid, but the adsorption of the cation is

decreased. The adsorption from the mixtures follows the Freundlich law. An explanation based on hydrolytic adsorption of the neutral salts is proposed and applied to other cases. J. H. BA.

Antonoff's so-called rule. H. L. Cupples (*J. Physical Chem.*, 1944, 48, 75—76).—It is impossible to predict from the considerations advanced by Yoffe and Heymann (cf. A., 1943, I, 276) whether the work of adhesion for org. liquid- H_2O is $>$ or $<$ the work of cohesion of org. liquid saturated with H_2O , or whether, therefore, the equilibrium spreading coeff. is zero (as required by Antonoff), negative, or positive. C. R. H.

Equations for the pressure-area relations (isotherms) of liquid-expanded and intermediate monolayers on water. G. Jura and W. D. Harkins (*J. Chem. Physics*, 1944, 12, 113—114).—The linear equations referred to earlier (cf. A., 1944, I, 151) are not applicable to liquid-expanded or to liquid intermediate phases on an aq. subphase. Empirical logarithmic equations are proposed for such cases. C. R. H.

Existence of expanded and intermediate phases in films on solids. G. Jura and W. D. Harkins (*J. Chem. Physics*, 1944, 12, 114).—The logarithmic equations developed for insol. monolayers on H_2O in the liquid-expanded and intermediate phases (cf. preceding abstract) are valid for adsorbed $\text{C}_{18}\text{H}_{38}$ on porous catalysts at 0°. C. R. H.

Permeability of built-up fatty acid films towards molecules and ions. D. Beischer and G. Oechel (*Z. Elektrochem.*, 1943, 49, 310—315).—Stearic acid-Ba stearate and arachidic acid-Ca arachidate multilayers on Cu, built up by the method of Blodgett (A., 1935, 931), hinder but do not stop completely the tarnish of the metal in H_2S . Similar films on Ag cause a more rapid and more intense attack on the metal in I vapour, max. attack being observed when the layer is 3 mols. thick. This is attributed to the high solubility of I in the film. Coating of Cd with a single film greatly reduces attack in aq. CuSO_4 whilst a film 5 layers thick prevents attack completely, showing it to be impermeable to Cu^{++} ions. On using a Cu sheet partly covered by a single film as cathode in aq. CuSO_4 , no Cu deposits on the area covered by the film, whilst if the whole surface is covered by a film deposition occurs only where the film breaks down on the irregularities of the surface. "Skeleton" films produced by dissolving the arachidic acid from the films are much more permeable. The built-up films are not very strong mechanically and are easily damaged by rubbing. J. W. S.

Modified diffusion in membranes. R. E. Liesegang (*Ann. Physik*, 1941, [v], 39, 326—329).—The rate of diffusion of methylene-blue solution through a paper membrane floating on its surface is modified by air currents incident on its surface, by access of moisture through its cut edges, and by damage to the membrane surface. L. J. J.

Atomic arrangement in aluminium hydroxide gel. S. Geiling and R. Glocker (*Z. Elektrochem.*, 1943, 49, 269—273).—Using monochromatic Cu X-radiation interference rings have been obtained with α - and β -hydrated Al_2O_3 gels, but Fourier analysis indicates that the α -gel has no space-lattice structure. J. W. S.

Silicic acid gels. XV. Effect of temperature on the time of setting of alkaline gel mixtures. C. B. Hurd, R. C. Pomati, J. H. Spittle, and F. J. Alois. XVI. Effect of radiant energy on time of set. C. B. Hurd and W. U. Day (*J. Amer. Chem. Soc.*, 1944, 66, 388—390, 391—392).—XV. The time of setting of silicic acid gels, prepared from Na silicate and AcOH , has been determined at 0°, 25.1°, and 38.5° and at pH 6.8—10.73. At pH > 10.5 rise in temp. increases time of set, but at pH < 10 the effect is reversed. Owing to curvature in the plot of log (time of set) against T , ΔE of activation could not be calc. The temp./time of set relation at pH > 10 is ascribed to a temp.-acceleration of dissolution of the gel being $>$ acceleration of its formation. At pH > 11 , acceleration of dissolution is predominant, and gels do not form. pH increases during setting of gels at pH > 10 , possibly because of a decrease in ionisation with increase in the complexity of the polysilicic acid. No thermally reversible gels were found. Alkaline gels are softer and less elastic than acid gels, as condensation and cross-linking are probably not so extensive.

XVI. The effect of radiation on the time of set of Na silicate- AcOH gels has been investigated. Illumination by an incandescent lamp, a capillary Hg arc, and an Fe spark produced no observable effects. Determination of the absorption of radiation at 4000—7000 Å. by the sol before setting indicates an absorption increasing with age, the greater increase taking place at the lower λ . W. R. A.

Thermodynamics of heterogeneous polymer solutions. P. J. Flory (*J. Chem. Physics*, 1944, 12, 114—115).—Thermodynamic equations for polymer solutions, where the polymers are composed of numerous species differing in mol. size, have been deduced. Their applicability to solubility and fractional pptn. and dissolution is forecast. C. R. H.

Study of the flexibility of macro-molecules with ultrasonic waves. G. Schmid and E. Beuttenmüller (*Z. Elektrochem.*, 1943, 49, 325—334).—Solutions of polystyrene (I) (mean mol. wt. 150,000—200,000) in various binary mixtures of PhMe, CCl_4 , COMe_2 , cyclohexane, and MeOH of differing d have been treated with ultrasonic waves for

various times and the mol. wt. of the solute has been determined viscometrically. The relative d of solvent and solute has no essential effect on the depolymerisation, and especially when they have equal d the solvent does not decrease the degree of depolymerisation. It is inferred that the depolymerisation is due to a difference in the case of deformation of (I) and solvent mols., the gel framework being very rigid at least during the period of one ultrasonic wave and being capable of an independent conduction of the vibration over a considerable distance.

J. W. S.

Sedimentation and diffusion measurements on cellulose and cellulose derivatives. N. Gralén (*Thesis, Uppsala*, 1944, 115 pp.).—The principles of sedimentation using the ultracentrifuge are described, and an empirical relation between rate of sedimentation and concn. is given. Taking this into account the shape of the sedimentation curve for polydisperse systems is analysed mathematically. The width of the curve is regarded as a measure of the polydispersity. Sedimentation experiments are performed on cellulose (I) in cuprammonium solution, cellulose nitrate (II) in COMe, Na cellulose xanthate (III) in aq. alkali, and Na cellulose glycolate (IV) in H₂O. Apparatus and precautions for preparing and transferring cuprammonium solutions in a N₂ atm. are described. Data are given for native fibre celluloses (unbleached and bleached) and for several wood celluloses. The effects of different chemical treatments in reducing the sedimentation consts. are evident; in general a reduction in sedimentation const. is accompanied by an increase in polydispersity. (II) of N content ~13.8% are prepared by nitration of several (I) in HNO₃—H₂PO₄—P₂O₅ mixtures. The sedimentation curves are similar in shape to those of (I). Only a few measurements on (III) and (IV) are recorded. Apparatus for diffusion measurements, based on change of n , is described, and measurements are made on the same materials as above. The skewness of diffusion curves arises from the dependence of the diffusion const. on concn. Diffusion of a polydisperse substance is treated mathematically, and a method for determining the polydispersity suggested. For (I) the diffusion process reaches its true velocity only after the lapse of some time. The derivatives of (I) behave normally. A formula is derived for determining mol. wts. from sedimentation equilibrium (equilibrium between sedimentation and diffusion). Equilibrium is reached in a reasonable time only for (I) of fairly low mol. wt. The partial sp. vol. of (I) was found to be 0.664. Mol. wts. of (I) and its derivatives determined by sedimentation and diffusion are reviewed, and shown to differ from those obtained from η measurements, using Staudinger's relation. The relation between intrinsic η and mol. wt. is not linear. Comparison of mol. wts. of (I) and (II) shows that some depolymerisation takes place in nitration (~3 bonds per 10,000 ruptured). (III) and (IV) have relatively low mol. wts. Approx. data for the shape of mols. are given; (I) mols. are less fully extended than (II) mols. The polydispersity of each substance tends to increase with decreasing mol. wt., but (II) has rather lower polydispersity than corresponding (I), indicating that the larger mols. are preferentially degraded during nitration. Results from sedimentation and diffusion are not usually in good agreement, but the experimental errors and approximations involved are considerable. Full references are given.

R. H. F.

Interpretation of the cellulose-water adsorption isotherm and data concerning the effect of swelling and drying on the colloidal surface of cellulose. A. G. Assaf, R. H. Haas, and C. B. Purves (*J. Amer. Chem. Soc.*, 1944, 66, 66—73).—Three highly swollen celluloses were subjected to TIOEt and then MeI and finally analysed for OMe. The results, extrapolated to solvents having mol. vol. 18 and 35, give % theoretically accessible to H₂O vapour and N₂, respectively. H₂O-adsorption at 20° and 25° is determined; the final change in direction of the isotherm (at R.H. ~50%) occurs at ~1 H₂O per accessible OH in the cellulose, which is interpreted as being equiv. to a unimol. layer of H₂O over the accessible surface; the first change in direction of the isotherm (at R.H. ~10%) corresponds to adsorption of 1 H₂O per primary OH. The latter portion of the isotherm corresponds to adsorption by sec. OH and cannot occur at >80%. 98% of the surface of moist, swollen cellulose is destroyed by drying, but >25% is lost by solvent-exchange. Adsorption of 6—9% of H₂O increases the colloidal surface of highly swollen cellulose by ~20% but that of unswollen samples 30-fold.

R. S. C.

VI.—KINETIC THEORY. THERMODYNAMICS.

Determination of order of reaction. Dissociation constant of hypochlorous acid. J. M. González Barredo (*Anal. Fts. Quím.*, 1940, 36, 328—331).—Experimental errors are greatly magnified in the calculation of dissociation consts. as shown by the wide variation of the vals. for the decomp. of HOCl. The order of this reaction cannot be determined by the author's method (cf. A., 1936, 1074).

F. R. G.

Potentiometric measurements of hydrogen-ion concentration in solutions of low dielectric constant. A. Gemant (*J. Chem. Physics*, 1944, 12, 79—88).—E.m.f. (glass electrode) and conductivity

measurements have been made on dioxan solutions of *p*-C₆H₄Me-SO₃H (I), CCl₃-CO₂H, and HCl and on xylene solutions of (I) and picric acid. The acids behave essentially as weak electrolytes, deviations from the mass law being explainable on the basis of varying dielectric const. with varying acid concn. H transference nos. and the ionic radii of the acids in the solvents have been calc. from the data. The use of a cell consisting of two half-cells in which the solutions have slightly different dielectric const. is described.

C. R. H.

Solution theory and pH measurements. P. G. Nutting (*J. Franklin Inst.*, 1943, 236, 573—580).—A general theory of electrolytic solutions is outlined. Exact buffer equations indicate that when very dil. alkali is titrated with very dil. acid the pH at first increases and then decreases; the converse happens in titrating very dil. acid with alkali. It is shown that a linear relation between pH and log concn. is consistent with exact solution theory. An extension of the theory to conditions where ion adsorption may take place is discussed with special reference to the operation of the glass electrode where the presence of different anions, each with its own adsorption coeff., none of which is able to overpower the others, may result in multiple pH readings or buffer points.

C. R. H.

Thermodynamic study of lead chloride in dioxan-water by means of electromotive force and solubility data at 25°. The acetone-ethyl alcohol-, dioxan-, glycerol-water-lead chloride systems. M. V. Noble and A. B. Garrett (*J. Amer. Chem. Soc.*, 1944, 66, 231—235).—The e.m.f. of the cell Pb(Hg)[PbCl₂][AgCl]Cl has been measured at 25° in 20, 40, and 60% dioxan-H₂O mixtures, [PbCl₂] varying from 4.24 × 10⁻⁴M. to saturation. The solubility of PbCl₂ has been determined in dioxan-H₂O mixtures containing various concns. of added KCl or KNO₃, and in EtOH-H₂O, glycerol-H₂O, and COMe-H₂O mixtures. Activity coeffs. and solubility products have been computed for dioxan-H₂O. Divergences in the slopes of the plot of -log γ against $\mu^{\frac{1}{2}}$ are attributed to association.

W. R. A.

Thermal analysis of binary systems. (A) A. Stock. (B) L. Kofler and A. Kofler (*Ber.*, 1941, 74, [B], 1049, 1050).—(A) Priority is claimed for Stock (A., 1909, ii, 543) (cf. Rheinboldt, A., 1943, I, 308). (B) The original priority is much antecedent.

R. S. C.

Phase equilibria in hydrocarbon systems. Methane-carbon dioxide in the gaseous region. H. H. Reamer, R. H. Olds, B. H. Sage, and W. N. Lacey (*Ind. Eng. Chem.*, 1944, 36, 88—90).—Pressure-vol. relations over the ranges 38—238° and 100—10,000 lb. per sq. in. for CO₂ and for four CO₂-CH₄ mixtures have been determined. Compressibility factors are tabulated. The simple behaviour of CH₄-rich mixtures at all pressures investigated suggests that the effect of small concns. of CO₂ on the behaviour of gaseous hydrocarbons can be satisfactorily predicted.

C. R. H.

Solid-liquid phase equilibria of the system *p*-toluidine-acetic acid. W. W. Lucase, R. P. Koob, and J. G. Miller (*J. Physical Chem.*, 1944, 48, 85—89).—Determination of the m.p. curve of the system confirms the existence of *p*-C₆H₄Me-NH₂·2AcOH (m.p. 49.1°). The m.p. of the eutectics at 30.2 and 89.7 mol.-% of AcOH are 28.6° and 6.4° respectively.

C. R. H.

Normal mixed crystal formation with some so-called group-isomorphous substances. (Frl.) A. Kofler (*Z. physikal. Chem.*, 1942, A, 191, 241—247).—A short discussion. Contrary to previous reports, the systems C₁₀H₈- β -C₁₀H₇-OH (I) and - β -C₁₀H₇-NH₂ (II) exhibit normal isomorphism and isodimorphism respectively. An equimol. compound is formed in the system (I)-(II), which is completely miscible with (I) and partly miscible with (II). The appearance of a mol. compound does not exclude the possibility of mixed crystal formation; indeed this may be favoured when the crystal units of the components are double mols.

J. F. H.

System ammonium nitrate-sodium nitrate. E. O. Holmes, jun., and D. Revinson (*J. Amer. Chem. Soc.*, 1944, 66, 453—457).—The system NH₄NO₃-NaNO₃ has been re-examined over the range 0—35 wt.-% NaNO₃. Solubility curves for the two forms of NH₄NO₃ are linear whilst that for NaNO₃ is parabolic. The eutectic temp. is 121.2 ± 0.2° and the transition temp. 126.2 ± 0.2°; the eutectic composition is 21.0 ± 0.1 and the transition composition is 18.0 ± 0.1 wt.-% NaNO₃. The method of purification of NaNO₃, the length of time of drying, and the size of the sample appear to have no effect on the temp. of disappearance of the last crystal on heating the melt.

W. R. A.

Phase relations in the system calcium orthosilicate-orthophosphate. M. A. Bredig (*Amer. Min.*, 1943, 28, 594—601).—A discussion. Two different crystal structures, isotypic with hexagonal α - and orthorhombic β -K₂SO₄, occur in Ca₂SiO₄ containing small amounts of various additions. This, and the fact that γ -Ca₂SiO₄ is isotypic with β -Na₂BeF₄, the high-temp. α form of which is also isotypic with α -K₂SO₄, indicates that above 1420° Ca₂SiO₄ is isodimorphous with K₂SO₄. A schematic equilibrium diagram of the system Ca₂SiO₄-Ca₃(PO₄)₂ is given.

L. S. T.

Ternary system dioxan-benzene-water. R. J. Berndt and C. C. Lynch (*J. Amer. Chem. Soc.*, 1944, 66, 282—284).—The isotherm of the dioxan-C₆H₆-H₂O system at 25° has been determined. An analysis diagram for the miscible region of the system and vals. of

$n_2^{\text{H}_2\text{O}}$ and ρ_4^2 for dioxan- C_6H_6 mixtures and for the ternary system are given. Phase equilibria in the ternary system satisfy the relation employed by Bancroft *et al.* (A., 1942, I, 240) for several ternary liquid systems. W. R. A.

System potassium carbonate-sodium carbonate-water at 100° and 150°. G. Ervin, jun., A. L. Giorgi, and C. E. McCarthy (*J. Amer. Chem. Soc.*, 1944, 66, 384—387).—The system $\text{K}_2\text{CO}_3\text{--Na}_2\text{CO}_3\text{--H}_2\text{O}$ at 100°, studied by the usual chemical methods and by microscopic and X-ray examination, gives an isotherm with branches corresponding with $\text{K}_2\text{CO}_3\cdot 1.5\text{H}_2\text{O}$, $\text{K}_2\text{CO}_3\cdot \text{Na}_2\text{CO}_3$, and $\text{Na}_2\text{CO}_3\cdot \text{H}_2\text{O}$, whilst the three branches of the 150° isotherm correspond with $\text{K}_2\text{CO}_3\cdot 1.5\text{H}_2\text{O}$, $\text{K}_2\text{CO}_3\cdot \text{Na}_2\text{CO}_3$, and Na_2CO_3 . The double salt, which exists to a slightly greater extent at 150°, is incongruently sol. at 100° and 150° and, in contact with H_2O , decomposes to give solid $\text{Na}_2\text{CO}_3\cdot \text{H}_2\text{O}$ or Na_2CO_3 and a solution relatively richer in K_2CO_3 . W. R. A.

The lines in quaternary liquid systems. J. C. Smith (*Ind. Eng. Chem.*, 1944, 36, 68—71).—A graphical method of representing equilibria in quaternary liquid systems, which is based on data for the system $\text{CHCl}_3\text{--COMe}_2\text{--AcOH--H}_2\text{O}$, is described. The application of the method to the solution of problems in mixed solvent extraction is described. C. R. H.

Graphical representation of the thermodynamic potential in multi-component systems. G. Masing (*Z. Elektrochem.*, 1943, 49, 216—218).—Although for a binary mixture $d\xi/dc = \pm\infty$ and $d^2\xi/dc^2 = +\infty$ for $c = 0$ or 100% ($c = \text{concn. of one component}$), the radius of curvature of the $\xi\text{--}c$ curve is zero at $c = 0$ or 100% and hence this curve does not meet the pure component axes tangentially. It is derived graphically that for a binary system in which a compound of congruent m.p. is formed, the liquidus curve at the temp. max. is continuous and has a horizontal tangent, whilst at the eutectic point the primary crystallisation curve forms a finite angle to the concn. axis. J. W. S.

Principles of thermodynamics. B. Leaf (*J. Chem. Physics*, 1944, 12, 89—98).—A formulation of thermodynamics which has been developed demonstrates the limitations of the classical treatment and leads to an equation for entropy (S) produced and heat dissipated in irreversible processes. A generalised form of the second law of thermodynamics has been deduced. The new concepts have been applied to discussions on the phase rule, the derived functions $H (=E + PV)$, $A (=E - TS)$, $F (=H - TS)$ where $E = \text{energy}$ and P , V , and T have their usual significance, and to generalisations of Kelvin's postulate and the Carnot cycle. The principles of Brønsted's system of energetics have also been derived. C. R. H.

Thermochemistry of chlorine monoxide. W. A. Roth (*Z. physikal. Chem.*, 1942, A, 191, 248—250).—The results of Secoy and Cady (A., 1942, I, 19) on the partial pressures (p) of Cl_2O over aq. solutions of Cl_2O and HOCl are combined with the author's earlier determination of the hydrolysis const. of Cl_2O aq. (A., 1930, 163), to obtain Henry's coeff. (K) for the system. With p expressed in mm., $K = 0.0093 \pm 0.00005$ at 3.46° . The true solubility of Cl_2O is five times that of Cl_2 . J. F. H.

Heats of dilution of sodium chloride in ethylene glycol at 25°. W. E. Wallace, L. S. Mason, and A. L. Robinson (*J. Amer. Chem. Soc.*, 1944, 66, 362—365).—Heats of dilution of NaCl in $(\text{CH}_2\text{OH})_2$ have been measured from 0.0001 to 0.17M. at 25°, and equations for the relative apparent molal heat content of the solute and for the relative partial molal heat contents of the solute and solvent have been derived. The experimental data agree with the calc. vals. W. R. A.

Calculation of heat of mixing from the phase diagram. E. Scheil (*Z. Elektrochem.*, 1943, 49, 242—254).—The method of calculating the heat of mixing from the phase diagram of a binary mixture is described. The theory developed is applied to the systems Zn--Pb , Zn--Bi , Ni--Au , Zn--Cd , and Cu--Ag . The heat of mixing of mixed phases is also discussed. J. W. S.

Entropy of argon. K. Clusius and A. Frank (*Z. Elektrochem.*, 1943, 49, 308—309).—The b.p. of A has been redetermined as $87.29 \pm 0.02^\circ \text{K}$. From calorimetric data the entropy of A at the b.p. is 30.850 ± 0.10 entropy units, compared with the statistical val. of 30.869 entropy units. From these vals. the v.p. and entropy const. are 0.808 ± 0.020 and 0.810 , respectively. J. W. S.

Thermochemistry of alloys. X. Entropy change during alloy formation. O. Kubaschewski and A. Schneider (*Z. Elektrochem.*, 1943, 49, 261—269).—The entropy of formation of alloys is discussed theoretically. Entropy-composition curves for several alloys, deduced from thermochemical and e.m.f. measurements, are given. J. W. S.

VII.—ELECTROCHEMISTRY.

Temperature coefficients of electrical conductance of solutions containing sodium chloride, potassium chloride, magnesium sulphate, or their mixtures. R. W. Bremner (*J. Amer. Chem. Soc.*, 1944, 66,

444—446).—The coeffs. of the equation $\Lambda = a + b\theta + c\theta^2 + d\theta^3$ have been calc. from previous data on aq. KCl , NaCl , MgSO_4 , NaCl--KCl , and NaCl--MgSO_4 (Bremner *et al.*, A., 1939, I, 15, 373), the average deviation from experimental vals. being 0.006%. Temp. coeffs., $d\Lambda/dt$, at 5° intervals between 0 and 25° , have been calc. from this equation. Temp. coeffs. of sp. conductance have been calc. for the conductivity H_2O used, and for 0.01 and 0.1 demal standard KCl solutions, at 5° intervals from 0 to 25° , and at 18° . The relations between temp. coeffs. and changes in concn. or temp., or the addition of a second salt, are discussed. W. R. A.

Mobility of the hydrogen ion in water-dioxan mixtures. H. Hartmann (*Z. physikal. Chem.*, 1942, A, 191, 197—212).—An equation is deduced for the mobility of H^+ ions in mixed solvents on the assumption of an exchange mechanism between H_3O^+ and H_2O , using the postulates of the Hückel theory. Vals. of d , η , and ϵ for H_2O -dioxan mixtures were determined over the entire solubility range and at $20\text{--}70^\circ$. The conductivity of various dil. solutions of HCl in H_2O -dioxan mixtures (0—60 mol.-% dioxan) was determined at $20\text{--}60^\circ$, and hence the corresponding equiv. conductivity at infinite dilution. The results are in qual. agreement with the deduced equation. J. F. H.

Mechanism of migration of the hydrogen ion in aqueous solution and its behaviour in diffusion processes. H. Hartmann (*Z. physikal. Chem.*, 1942, A, 191, 213—226).—Theoretical. From the postulates of the Hückel theory of the anomalous mobility of the H^+ ion in aq. solution, the Nernst equation for the mobility of the H^+ ion is derived. Comparison of this equation with diffusion data gives discrepancies \gg experimental error. The migration mechanism suggested by Wulff and Hartmann (A., 1944, I, 87) expresses the results better than that of Hückel. J. F. H.

Concentration distribution in two-salt moving boundaries. L. G. Longworth (*J. Amer. Chem. Soc.*, 1944, 66, 449—453).—The movement of $\text{KIO}_3\text{--KCl}$ and LiCl--KCl concn. boundaries under an applied potential has been studied by the schlieren scanning method. With const. current the concn. distribution is independent of time, and is accurately given by Weber's theory. The adjusted concn., and, hence, the transference no., of the indicator electrolyte (KIO_3 , LiCl) may be determined from the schlieren photographs. W. R. A.

Cu-Cu" potential in concentrated copper sulphate solutions at various temperatures. III. Temperature coefficient of the normal potential of copper. F. Müller and H. Reuther (*Z. Elektrochem.*, 1943, 49, 277—280).—From e.m.f. measurements on cells of the type $\text{Cu}|\text{CuSO}_4, \text{H}_2\text{SO}_4, \text{Hg}_2\text{SO}_4|\text{Hg}$ the temp. coeff. of the normal electrode potential at $20\text{--}50^\circ$ has been determined as 0.01 mv. per degree. This low val. is accounted for by the temp. coeff. of the potential of this electrode being almost equal to that of the H_2 electrode. The calculation of an isothermal temp. coeff. from two non-isothermal vals. for half-cells is discussed. J. W. S.

Polarographic behaviour of aniline oxidation products. D. Lester and L. A. Greenberg (*J. Amer. Chem. Soc.*, 1944, 66, 496).—The oxidation of NHPH-OH (I), $p\text{-NH}_2\text{-C}_6\text{H}_4\text{-OH}$, and azoxybenzene (II) at the dropping Hg cathode has been studied. In 0.07M-phosphate buffer (pH 6.3), (I) does not give a cathodic wave, but does give an anodic oxidation wave with a half-wave potential, against the saturated Hg_2Cl_2 electrode, of -0.02 v. in contrast to the results of Levitan *et al.* (A., 1944, I, 130), who find a cathodic wave in 0.1M- NaOH , but no anodic wave. In the presence of alkali, (I) is converted completely into (II), which gives a cathodic wave. Two electrons are involved in the oxidation of the buffered solution of (I), whereas the reduction of (II) in the same buffer containing 20% of EtOH involves four electrons. W. R. A.

Electrolytic reduction of aqueous chromic acid solutions. E. Müller (*Z. Elektrochem.*, 1943, 49, 280—282).—The $E\text{--}c$ curves ($E = \text{cathode potential}$, $c = \text{cathode c.d.}$) for the electrolysis of $2\text{M--H}_2\text{CrO}_4$ using Pt or Ir cathodes are almost identical with the curves obtained for these electrodes in $2\text{M--H}_2\text{SO}_4$, whereas the $E\text{--}c$ curves for Cu and Au cathodes are displaced towards more negative vals. of E . After use the Cu and Au electrodes are covered with a dirty brown deposit of Cr , and hence the displacement of the $E\text{--}c$ curve is attributed to the higher overpotential of H_2 at a Cr surface although the $E\text{--}c$ curve for a massive Cr electrode lies towards even higher vals. of E . The mechanism of the deposition of the Cr is discussed. J. W. S.

Uses and limitations of membrane electrodes. C. E. Marshall (*J. Physical Chem.*, 1944, 48, 67—75).—The difficulties which arise in the measurement by means of membrane electrodes of ionic activities in true solutions are discussed. The probable uncertainty of measurement is $>4\%$ at ionic strengths $\sim 0.1\text{M}$, and $\sim 2\%$ at ionic strengths $< 0.01\text{M}$. The properties of montmorillonite and beddellite membranes and the effect of thermal pretreatment are reviewed, and a method of analysing mixtures by determining the mobility ratio of two cations within a given membrane is outlined. C. R. H.

VIII.—REACTIONS.

The rate-determining reaction in chain reactions, particularly polymerisation reactions. G. V. Schulz (*Z. physikal. Chem.*, 1941, B, 50, 116—123).—The concept of the rate-determining reaction in chain reactions is discussed with reference to the polymerisation of styrene (I) and $\text{CH}_2=\text{CMe}-\text{CO}_2\text{Me}$ (II). It is shown that, in polymerisation reactions, where no stoichiometric relation exists between the various steps, there can be no rate-determining reaction. The concept can be replaced by a consideration of which process in the chain is directly influenced by a particular change in conditions. Special cases exist, in which a rate-determining reaction can be defined, e.g., the Bz_2O_2 -catalysed polymerisation of (I) or the atm. O_2 -catalysed polymerisation of (II), where the primary process consists of two or more steps, stoichiometrically related.

W. R. A.

Mathematics of polymerisation.—See B., 1944, II, 125.

Reaction of acetaldehyde with ethyl bromide at 400°. J. G. Roof (*J. Amer. Chem. Soc.*, 1944, 66, 358—360).—The dark reaction of mixtures of MeCHO and EtBr at 400°, studied by pressure measurements and analysis of the products, shows a pronounced induction period of an autocatalytic type in the early stages of the reaction. A sharp decrease in the rate of pressure rise occurs after an increase of ~ 1.1 times the original partial pressure of MeCHO . On the average ~ 10 mols. of MeCHO are decomposed per mol. of EtBr .

W. R. A.

Allylic rearrangements. XIV. Hydrolysis of butenyl chlorides. W. G. Young and W. J. Andrews (*J. Amer. Chem. Soc.*, 1944, 66, 421—425).—The hydrolyses of crotyl (I) and methylvinylcarbinyl (II) chlorides have been studied under conditions designed to produce different S_N1 to S_N2 ratios, and the composition of the resulting butenols has been determined. (II) reacts by the S_N1 process to give a mixture of allylic isomers, whereas (I), which is very sensitive to changes in conditions, reacts by both processes, giving more of the normal reaction products when a bimol. reaction is favoured. Kinetic studies of the hydrolysis of (I) and (II) by NaOH in $\text{EtOH}-\text{H}_2\text{O}$ show that the reaction rate with (II) is independent of $[\text{OH}^-]$, whereas (I) undergoes both first- and second-order reactions. The first-order reaction of (I) is partly a bimol. reaction with the solvent.

W. R. A.

Semi-polar bond. Its effect on chemical reactivity. Hydrolysis of phosphorus trichloride and oxychloride. J. Rodríguez de Velasco and R. Castro Ramos (*Anal. Fis. Quím.*, 1942, 38, 171—178).— k for the hydrolysis of PCl_3 and POCl_3 in PhMe is respectively 9.3×10^{-2} and 1.8×10^{-2} at 20°, and 13.0×10^{-2} and 3.7×10^{-2} at 35°. It is concluded that the semi-polar bond in POCl_3 causes a reduction in k .

F. R. G.

Kinetics of transformation of 2-ketopolyhydroxy-acids. P. P. Regna and B. P. Caldwell (*J. Amer. Chem. Soc.*, 1944, 66, 246—250).—The kinetics of the consecutive reactions of 2-keto- d -gluconic, l -gulonic, d -galactonic, d -glucoheptonic, d -galactoheptonic, and of l -, d -, d -arabo- d -gluco-, and d -galacto-ascorbic acid in 5M- HCl at 59.9° and 69.9° have been investigated. Rates of rearrangement of the 2-ketopolyhydroxy-acids to their ascorbic acid analogues are influenced by groups on the C atoms outside the lactone ring. Rate coeffs. of the decomp. of ascorbic acids are higher for a *cis*- than for a *trans*-arrangement of the H atoms on $\text{C}_{(4)}$ and $\text{C}_{(5)}$. A method is described for determining the rate coeffs. of the reaction system $A \rightarrow B \rightarrow C$, where only B can be determined experimentally.

W. R. A.

Hydrolysis of pantothenate; a first-order reaction. Relation to thiamin stability. D. V. Frost and F. C. McIntire (*J. Amer. Chem. Soc.*, 1944, 66, 425—427).—The hydrolysis of Ca pantothenate (I) has been studied in aq. solution of pH 3.7—4.0 at temp. of 10—100°. The hydrolysis is a first-order reaction, with a rate independent of the type of buffer used. ΔE of activation is 19 ± 1 kg.-cal. per mol. The effect of pH on the rate of decomp. of (I) and of thiamin hydrochloride (II) has been determined at pH 3—7. Decomp. of (I) is reduced and decomp. of (II) increased by increasing pH.

W. R. A.

Kinetics of the antioxygenic synergism of quinones with ascorbic acid in fat systems. V. P. Calkins and H. A. Mattill (*J. Amer. Chem. Soc.*, 1944, 66, 239—242).—The abs. reaction rate of oxidation of ascorbic acid (I) in the Et esters of lard fatty acids has been determined in presence and absence of benzoquinone (II). The synergism of (II) with (I), in the stabilisation of the esters, is due to the catalytic action of (II), which is reduced to a semiquinone, capable of reducing the fat peroxides. (II) reduces the ΔG of formation of the activated complex in the fat-(I) system, so that the no. of (I) mols. possessing the necessary energy of reaction is doubled. A mechanism for the synergism, based on the views of Michaelis (*Chem. Rev.*, 1935, 16, 243), is developed.

W. R. A.

Decomposition of chloral hydrate by piperidine.—See A., 1944, II.

Active materials. LXII. Catalytic behaviour of preparations of $\gamma\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3 + \text{BeO}$ made in different ways. R. Fricke and G. Wessing (*Z. Elektrochem.*, 1943, 49, 274—277).—At 177.2° the

catalytic dehydrogenation of Pr^2OH on an activated Al_2O_3 surface is of zero order. The velocity of reaction v increases initially with time but finally becomes const. with any particular specimen of catalyst. The energy of activation (E) of the reaction increases with increasing temp. of preheating of the catalyst. Max. v was obtained with carefully purified pptd. Al_2O_3 preheated for $5\frac{1}{2}$ hr. at 600°. Less pure material similarly heated showed similar E but gave much lower v owing to a decrease in the action const. C of the Arrhenius equation $k = Ce^{-E/RT}$. Addition of 2—4% of BeO to the Al_2O_3 has practically no effect on E but decreases v . With mixtures containing 50 mol.-% of BeO and with pure BeO v is much decreased and the reaction is no longer of zero order.

J. W. S.

Hydrocarbon synthesis by Friedel and Crafts' reactions. H. Ulich, A. Keutmann, and A. Geirhaas (*Z. Elektrochem.*, 1943, 49, 292—296; cf. A., 1935, 1207).—Study of the kinetics of the reactions with and without the introduction of dry HCl indicates that the addition of C_2H_4 to C_6H_6 with AlCl_3 as catalyst occurs both through the intermediate formation of EtCl and also directly as a surface reaction on the AlCl_3 , whereas with GaCl_3 as catalyst it is exclusively a surface reaction on the catalyst. InCl_3 does not catalyse the reaction. GaCl_3 is a more efficient catalyst than AlCl_3 , the max. efficiency being attained at 55°; the main product is PhEt , with smaller amounts of homologues than are obtained with AlCl_3 .

J. W. S.

Catalytic effect of acetate and phosphate buffers on the iodination of tyrosine. C. H. Li (*J. Amer. Chem. Soc.*, 1944, 66, 228—230).—The catalytic effect of $\text{PO}_4^{''}$ and OAc^{\prime} buffers on the I-tyrosine reaction at 25° has been studied. In $\text{PO}_4^{''}$ buffer, the sp. rate, $k_2 = 10^5[\text{OH}^-] + 150[\text{HPO}_4^{''}] + 12[\text{H}_2\text{PO}_4^{\prime}]$. In OAc^{\prime} buffer, $k_2 \propto [\text{OAc}^{\prime}]/[\text{H}^+]$. The complex anion $\text{OH}^-\text{CMeO}_2^{\prime}$ is suggested as the catalytic agent in OAc^{\prime} buffer.

W. R. A.

Kinetics of reactions between iodine and histidine. C. H. Li (*J. Amer. Chem. Soc.*, 1944, 66, 225—227).—From investigations of the kinetics of the I-histidine reaction, in citrate and $\text{PO}_4^{''}$ buffers at 25°, the formation of di-iodohistidine, similar to di-iodo-tyrosine formation, is indicated. In citrate buffer at 25°, the rate law is $-d[\text{histidine}]/dt = 2.5[\text{histidine}][\text{I}] + 1.2 \times 10^5[\text{histidine}][\text{HOI}]$. HPO_4^{\prime} has a sp. catalytic effect on the rate.

W. R. A.

Electrolytic catalysis in the ammonolysis of 9-chloro-9-phenylfluorene by liquid ammonia. P. M. Williamson, R. C. Anderson, and G. W. Watt (*J. Amer. Chem. Soc.*, 1944, 66, 376—379).—The catalysis of the ammonolysis of 9-chloro-9-phenylfluorene by liquid NH_3 by NaCl , NaNO_3 , and NH_4NO_3 has been studied, and vals. for velocity coeffs. and ΔE of activation determined. The reaction is subject to electrolyte catalysis by NH_3 and non-onium salts. The relation to the theory of acid catalysis is discussed.

W. R. A.

Esterification under the catalytic influence of acid chlorides.—See A., 1944, II, 179.

Photolysis of hydroxylamine. R. N. Smith and P. A. Leighton (*J. Amer. Chem. Soc.*, 1944, 66, 172—177).—The photolysis of NH_2OH vapour at 1—4 mm. Hg pressure by ultra-violet radiation from a Zn arc has been studied. The ultra-violet absorption spectrum is continuous at λ of 2350 to ~ 2000 Å. Absorption in this region causes photolysis to H_2 , N_2 , and H_2O , together with small amounts of N_2H_4 , N_2O , and NH_3 . Thermal decomp. at room temp. produces chiefly N_2 , NO , N_2O , H_2O , and NH_3 . At const. light absorption, the rate of formation of H_2 decreases with increasing NH_2OH pressure, and \propto (incident intensity) $^{3/2}$. The data support a photolysis mechanism involving NH_2 and OH radicals.

W. R. A.

IX.—PREPARATION OF INORGANIC SUBSTANCES.

Reaction of potassium chromate with an indium salt. M. F. Stubbs (*J. Amer. Chem. Soc.*, 1944, 66, 498).—Addition, with stirring, of 0.2222M- K_2CrO_4 to 0.02M- $\text{In}_2(\text{SO}_4)_3$ at room temp. was followed by pH measurement. A yellow turbidity appeared at pH 3.3, complete flocculation of the yellow ppt. occurred at 3.36—3.42, and pH rose steadily with further addition of K_2CrO_4 . Analysis data for the yellow ppt. suggest that it is formed either as $\text{In}_2(\text{CrO}_4)_3$ which is extensively hydrolysed or as a mixture of $\text{In}_2(\text{CrO}_4)_3$ and $\text{In}(\text{OH})_3$.

W. R. A.

Cuprous isothiocyanate. D. Krüger and E. Tschirch (*Ber.*, 1941, 74, [B], 1378—1386; cf. A., 1936, 1078).—The appearance of violet CuSCN with its characteristic c -lines in the X-ray spectrum is barely affected by the temp. at which it is prepared (0—70°). Heating this form at 150° changes the colour to pale yellow and at $\sim 275^\circ$ to grey but does not remove the c -lines or cause loss of wt. Differentiation of the forms crystallographically is shown to be erroneous. The occasional brown colour of the b -form, particularly the parts crystallising later, is due to adsorbed I. Formation of the violet form is favoured by presence in solution of large amounts of certain neutral salts which, however, are not absorbed into the ppt. Differences between the forms are due to arrangement of Cu^+ , S, C, and N in the crystal lattice.

R. S. C.

Formation, reducibility, and extractability of zinc ferrites and ferrite-rich products of roasting of zinc blende. II. A. Simon and H. Höppner (*Z. Elektrochem.*, 1943, 49, 296—305; cf. *ibid.*, 1940, 46, 458; B., 1944, I, 109; C., 1944, Part 3).—The products of roasting christophite ($4\text{ZnS} \cdot 2\text{FeS}$) at various temps. until no further SO_2 is evolved have been examined by microscopical, analytical, and X-ray methods. At low temp. $\text{Fe}_2(\text{SO}_4)_3$, FeSO_4 , and ZnSO_4 are formed, the optimum temp. for production of the two first being 400° whilst max. yield of ZnSO_4 is obtained at 650° . At 700 — 1100° oxidation to $\text{ZnO} \cdot \text{Fe}_2\text{O}_3 + 3\text{ZnO}$ occurs. The max. content of material extractable with "Muspratt's solution" (71%) is attained after roasting at 600° , but this contains a considerable amount of SO_4^{2-} . At $>800^\circ$ most of the material extracted is free ZnO . After roasting at 1300° the ratio $\text{ZnO} : \text{Fe}_2\text{O}_3$ in the residue not extractable by this solution is 2.67 and suggests the existence of other Zn ferrites, but heating of a synthetic mixture of ZnO and Fe_2O_3 gave no evidence of the existence of such compounds.

J. W. S.

Removal of mercury from solutions of mercuric nitrate by mercuric sulphide. G. H. Spaulding and W. M. McNabb (*J. Franklin Inst.*, 1944, 237, 207—212).—The removal of Hg⁺⁺ from dil. solutions of $\text{Hg}(\text{NO}_3)_2$ by freshly pptd. HgS follows the Freundlich adsorption isotherm. At higher concns. the isotherm is not followed, and there is a gradual change in the colour of the HgS from black to varying shades of grey until at $[\text{Hg}^{++}] > 4.7 \times 10^{-2} \text{M}$, a pure white ppt. remains. The formation of a substance with the possible formula $2\text{HgS} \cdot \text{Hg}(\text{NO}_3)_2$ is indicated.

C. R. H.

Mechanism of mercuri-chloro-oxalate complex formation in Eder's solution. M. C. Chen and C. J. Hsiao (*J. Chinese Chem. Soc.*, 1943, 10, 154—166).—Assuming an equilibrium between Hg_2Cl_4 , HgCl_3^+ , $\text{Hg}_2\text{Cl}_6^{2-}$, HgCl_4^{2-} , and HgCl_4^{2-} with HgCl_2 and $\text{C}_2\text{O}_4^{2-}$ in Eder's solution (cf. A., 1933, 1118), the concn. of the complex $\text{Hg}_2\text{Cl}_4(\text{C}_2\text{O}_4)_2^{2-}$ (I) has been determined by a partition method. The results of Roseveare (A., 1930, 1135) are found to agree with a first-order decomp. of (I) and not of $\text{HgCl}_2(\text{C}_2\text{O}_4)_2^{2-}$.

J. H. BA.

Interaction of boron fluoride with aluminium, silicon, and titanium oxides, and with silicates. Possible use of this reaction for opening up aluminosilicates for preparation of materials for the manufacture of aluminium. P. Baumgarten and W. Bruns (*Ber.*, 1941, 74, [B], 1232—1236).—The reaction, $\text{Al}_2\text{O}_3 + 3\text{BF}_3 \rightarrow (\text{BOF})_3 + 2\text{AlF}_3$, is quant. at 450° . The reverse reaction, $2\text{AlF}_3 + \text{B}_2\text{O}_3 \rightarrow \text{Al}_2\text{O}_3 + 2\text{BF}_3$, occurs at $\sim 800^\circ$ if an excess of AlF_3 is used but is not quant. owing to removal of B_2O_3 as $(\text{BOF})_3$. At 450° (not 350°), the reaction, $3\text{SiO}_2 + 6\text{BF}_3 \rightarrow 3\text{SiF}_4 + 2(\text{BOF})_3$, occurs, both products volatilising. TiO_2 reacts similarly but more slowly. Silicates are also attacked by BF_3 at 450 — 700° ; the Si is removed as SiF_4 , the Al becomes AlF_3 , the BF_3 is removed as $(\text{BOF})_3$, alkaline earths and Mg become fluorides, alkalis become fluoroborates (which at $>500^\circ$ yield fluorides and BF_3), and Fe remains as Fe_2O_3 ; after treatment with H_2O and conc. HCl , the AlF_3 can be used in the cryolite process for prep. of Al. By suitable recovery processes, a cyclic system can be set up.

R. S. C.

Rare earths. L. Separation of erbium from yttrium by fractional precipitation of the ferrocyanides. T. Moeller and H. E. Kremers (*J. Amer. Chem. Soc.*, 1944, 66, 307).—Details of the ferrocyanide procedure are given. Its success depends on complete removal of Fe.

W. R. A.

Metal carbonyls. XLVI. Osmium carbonyls. W. Hieber and H. Stallmann (*Z. Elektrochem.*, 1943, 49, 288—292).—The action of CO under pressure on Os halides in presence of Cu or Ag yields Os carbonyls. Max. yield is obtained with the oxyiodide (from OsO_4 and conc. HI) which when heated at 150° and 200 atm. CO pressure yields a mixture of carbonyls and $[\text{Os}(\text{CO})_4\text{I}_2]$. Carbonyls are also produced on heating OsO_4 at 150 — 200° in CO at >50 atm. and can be separated by fractional distillation. The main product is the yellow pseudo-hexagonal *diosmium nonacarbonyl*, $\text{Os}_2(\text{CO})_9$. The more volatile fraction contains the colourless liquid *Os pentacarbonyl*, $\text{Os}(\text{CO})_5$, m.p. -15° . The most volatile material contains traces of *Os carbonyl hydride*, $\text{OsH}_2(\text{CO})_4$, but no $\text{Os}(\text{CO})_4$ could be detected.

J. W. S.

XI.—GEOCHEMISTRY.

Cause of the increase in salinity of Barcelona's water supply. C. Chorower (*Anal. Fis. Quim.*, 1942, 38, 43—70).—Coincident with the exploitation of the Suria potash beds and the flow thence of saline effluent into the River Cardener over the period 1926—36, the H_2O supply of Barcelona contained excessive amounts of K^+ , Br^- , and Cl^- . This salinity could not be due to sea- H_2O as the SO_4^{2-} content of the supply remained normal.

F. R. G.

Limnological studies in Connecticut. VII. Critical examination of the supposed relationship between phytoplankton periodicity and chemical changes in lake water. G. E. Hutchinson (*Ecology*, 1944, 25, 3—26).—The spring appearance of *Dinobryon divergens* is correlated with a rise in the $\text{NO}_3^- : \text{PO}_4^{3-}$ ratio but is independent of

the concn. of sol. silicate. The appearance of *Asterionella formosa* does not appear to depend on the content of inorg. nutrients whilst *Anabaena circinalis* and *Fragilaria crotonensis* appear late when inorg. nutrients are at a low level, the former being favoured when NO_3^- is especially low. N fixation by *Anabaena* results in a more favourable habitat for *Fragilaria* as the *Anabaena* declines.

L. G. G. W.

Limnological observations on three lakes in eastern Vilas Co., Wisconsin. T. H. Flanigan (*Trans. Wisconsin Acad. Sci.*, 1942, 34, 167—174).—Temp., transparency, pH, free and combined CO_2 , and dissolved O_2 are recorded for the Crampton, Merrill, and Wood lakes. Benthos and plankton contents are high in Crampton and Wood lakes.

L. S. T.

Generation of magma by frictional heat. J. S. DeLury (*Amer. J. Sci.*, 1944, 242, 113—129).—An hypothesis to explain the origin of magmas within the earth's crust by reference to mechanical sources of heat is advanced.

L. S. T.

Paragenesis of the ore of the Normetal mine, Abitibi Co., Quebec. H. M. Putman (*Econ. Geol.*, 1943, 38, 313—322).

L. S. T.

Layered or banded chromite at Campo Formoso, Baía, Brazil. W. D. Johnston, jun., and H. C. A. de Souza (*Econ. Geol.*, 1943, 38, 287—297).—Chromite (I) at Campo Formoso occurs in layers alternating with layers of serpentine derived from olivine (II). The layered rocks may have been formed by the settling of alternate showers of (I) and (II) crystals on the floor of a magma chamber. Chemical analyses [R. E. Stevens] of (I) concentrates are given.

L. S. T.

Manganese oxide minerals: preliminary report. M. Fleischer and W. E. Richmond (*Econ. Geol.*, 1943, 38, 269—286).—X-Ray powder photographs, supplemented by chemical tests, provide the best means for identifying these minerals. X-Ray photographs, X-ray data, and physical properties are given for the commoner minerals and for those for which new data have been obtained. Formulae, and rules of nomenclature, are suggested.

L. S. T.

Gold ores of the Little Long Lac Area, Ontario. H. S. Armstrong (*Econ. Geol.*, 1943, 38, 204—252).—General geology, the nature of the ore bodies, and the mineral paragenesis of the various mines are described. The ore deposits of this area belong to Lindgren's upper hypothermal, or lower mesothermal, zone. Possible sources of the ore-depositing solutions are discussed.

L. S. T.

Chemical limestone in Central Pennsylvania. G. M. Kay (*Econ. Geol.*, 1943, 38, 188—203).—Deposits of high-grade limestone, particularly that of the Valentine member of the Curtin formation, are described. Chemical analyses of Valentine limestones are given.

L. S. T.

Post-mine leaching of galena and marmatite at Broken Hill. F. L. Stillwell and A. B. Edwards (*Econ. Geol.*, 1943, 38, 253—254).— Cl^- may be present in the underground waters of the North Broken Hill mine in sufficient concn. to cause reversal in the relative solubility of PbS and ZnS .

L. S. T.

Rare element prospecting in pegmatites. T. T. Quirke and H. E. Kremers (*Econ. Geol.*, 1943, 38, 173—186).—Certain chemical and mineralogical associations of the elements are proposed as a guide to the location of deposits of rare minerals in pegmatites. Lepidolite is a test mineral for the rare alkalis in pegmatites, ilmenite is a test mineral for V in magnetite, high-temp. epidotes are test minerals for the rare earths, titanite is probably a test mineral for Nb and Ta and apatite for the rare earths. Titaniferous magnetites should be examined for V as coulsonite.

L. S. T.

Effect of heat-treatment on magnetic properties of iron- and manganese-bearing minerals. G. G. Bring (*Jernkont. Ann.*, 1943, 127, 447—490; *Bull. Iron Steel Inst.*, 1944, No. 96, 37A).—The minerals studied were knebelite (I) from Tuna Hästberg, Bastkärn, and Stollberg, grünerite (II) from Bastkärn, granite (III), "gröna mineral" (IV) (a green, partly converted pyroxene) from Tuna Hästberg, and dolomite (V) from Tuna Hästberg and Klackberg. (I) and (II) became more magnetic and had increased remanence after being heated for 2 hr. at 800 — 900° . (I) from all localities and (II) are relatively strongly ferromagnetic. (III) and (IV) are paramagnetic after heating and no coercive force could be detected even after heating up to 900° with C. The only change in (V) from Tuna Hästberg was that the Mn content was increased by heating to 900° owing to expulsion of CO_2 . When Klackberg (V), which is higher in Fe, was heated at $\sim 700^\circ$ its magnetic susceptibility was increased 3—5 times; after roasting at higher temp. the val. decreased almost to that at room temp., whilst after roasting with C it rose steadily over the whole temp. range, probably because of formation of magnetite. (I) and (II) are sufficiently magnetic to be easily attracted in powerful magnetic separators, or to be separated in an a.c. field. (III) and (V) could be treated in a.c. fields of the strength used in these tests. After heat-treatment (III) responded somewhat better in powerful magnetic separators. Untreated specular Fe ore from different districts responded only slightly in powerful d.c. magnetic separators but quite well in a.c. separators.

R. B. C.

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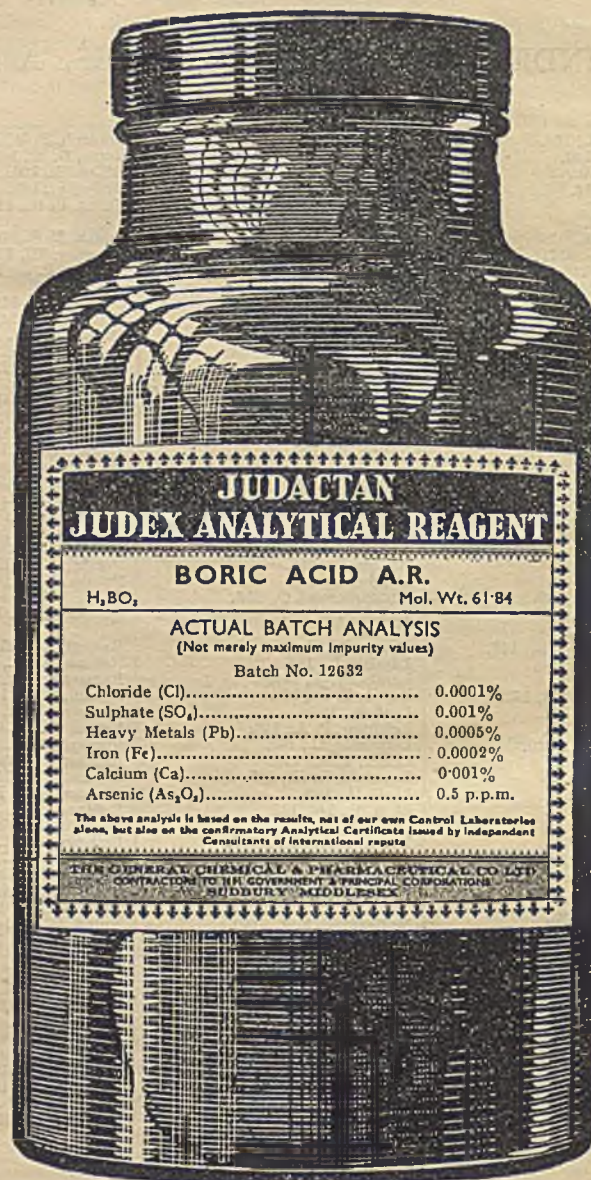
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