BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

DECEMBER, 1944

A I—GENERAL, PHYSICAL, AND INORGANIC CHEMISTRY

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BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

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DECEMBER, 1944.

I.—SUB-ATOMICS.

Effect of electrical field strength on the intensities of the lines of the p,p-series of the HeI and LiI spectra. R. Siksna (Naturwiss., 1943, 31, 169—170).—The effects of electrical field strength (F) on the intensities (I) of the lines of the 2p-np series of the o-HeI spectrum are summarised. I for individual lines increases at first with increasing F, reaches a max. for a definite F, and then decreases. The increase is more rapid than the decrease. Each line has a definite range of F for which it is visible. With increasing term no. the max. intensity (I_{max}) of the line is less, and the range of F over which it is visible is smaller; also, the F necessary to reach I_{max} for the mth line, that for the *n*th line is given by $F_n = F_m/2^{n-m}$. For a given F, the I ratios of different lines may be very different. Similar results are to be expected for the 2p-mp series of the Li I spectrum, with the difference that for lines characterised by the same term no. I_{max} would be reached for F approx. half that for the corresponding line in the o-He spectrum. A. J. M.

Magnetic dipole transitions in the configurations $5p^5$, $5p^4$, $6p^5$ of xenon and radon. B. Edlen (*Physical Rev.*, 1944, [ii], 65, 248).— Three unidentified lines of Xe I and Xe II correspond with transitions between the series limits of these spectra. There is exact agreement with the ground-level separations of Xe II and Xe III as obtained from the extreme ultra-violet spectrum. The lines are due to magnetic dipole transitions, the theoretical probability of which is given. N. M. B.

Stark effect in dielectrics. A. A. Vorobiev (Compt. rend. Acad. Sci. U.R.S.S., 1940, 26, 770—771).—The absorption of light by crystals (rock-salt, Iceland spar, KI, NaBr, S, mica) placed in a strong electric field has been investigated. No displacement of the absorption limit in the ultra-violet (or for irradiated crystals, in the visible) was found, even though the field strength was only 10-20%< the breakdown strength. A. J. M.

Short-wave-length limit of the continuous X-ray spectrum and determinations of h/e. P. Ohlin (Nature, 1943, 152, 329-330).—The systematic error involved in X-ray determinations of h/e is investigated, using $\lambda\lambda$ 2498.42 and 2285.03. It is shown that a precise val. is obtained only if a sufficiently narrow, well-defined spectral band is used, and the voltage varied in small steps. E. R. R.

L-Series X-ray emission "outside the diagram." Application to a first experimental determination, by means of crystal spectrography, of the states of fundamental multiple ionisation of heavy atoms. (Mlle.) Y. Cauchois (J. Phys. Radium., 1944, [viii], 5, 1-11).— Recent results on a new family of satellites lead to a tentative estimation of the energies of atoms doubly ionised in profound layers. W. R. A.

L-Spectra and characteristic levels of hafnium (72) and weak L-emission of hafnium and tantalum. (Mlle.) I. Manescu (Compt. rend., 1942, 215, 104-106).—The $\lambda\lambda$ and classification of lines are given. A. J. M.

Effect of chemical bond on X-ray absorption spectra. K Main edge. I. B. Borovski (Compt. rend. Acad. Sci. U.R.S.S., 1940, 26, 764—769).—The structure of the K edge has been investigated for clements 22 (Ti) to 25 (Mn). The multiplicity of the K main edge is particularly considered. The transition between the beginning of the edge and the first kink (the so-called white line) corresponds to a transition to a comparatively weakly excited discrete 3d level. A white line is present not only for elements of higher valency, but also for Mn^{***}, V^{***}, and Co^{***}. The behaviour of the short boundary of the edge depends essentially on the crystal structure of the compound used. The intensity of white lines in the long- λ part of the edge probably depends on the nature of the binding forces. When these are ionic the long- λ white lines will be particularly sharp. The Kunzl rule (A., 1932, 669), that the difference of terms for the main edge of cations and metallic elements is ∞ valency, needs to be supplemented. The val. of a term for a metal should be that corresponding to the middle of the interval between the beginning of the edge and the first kink. Further corrections are given for cations giving an edge with a white line, and for those without a white line. A. J. M.

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Electron affinity of bromine and its decomposition on hot tungsten. P. M. Doty and J. E. Mayer (J. Chem. Physics, 1944, 12, 323–328). —The ratio of ions to electrons leaving a hot W surface in contact with Br vapour at low pressure corresponds to an electron affinity of 80.5 ± 0.4 kg.-cal. per mol. for Br₂. The decomp. of Br₃ is a firstorder reaction between 1607° and 2276° K. and between 0.39 and 21.2μ . pressure. The accommodation coeff. is unity. L. J. J.

Phase effects with coincidence proportional counters. C. L. Meaker and A. Roberts (*Rev. Sci. Instr.*, 1944, 15, 149-151).— The fraction of true coincidences measured can be a function of counter voltages and inter-counter absorber with certain amplifier characteristics and short time const. before the mixer stage.

L. J. J. Application of bursts of X-rays for the determination of the mobility of electrons in gases. P. Herreng (Compt. rend., 1942, 215, 79-81). —An ionisation chamber with two plane, parallel metallic electrodes is arranged so that bursts of X-rays can be passed in, parallel to the electrodes. A uniform const. electric field is maintained between the electrodes. The bursts last for 10^{-6} sec., with a frequency of 50 per sec. All the ions formed are collected by the electrodes before the next burst follows. The current in the tube is amplified and passed on to a cathode-ray tube. The arrival of electrons at the anode is more rapid than discharge of positive ions, as is shown by a sudden discontinuity in the current-time curve, which, however, is usually rounded owing to diffusion. The mobility of the ions is calc. from the curve. For A at 340 mm., the mobility is 7650 cm. per sec. for a potential gradient of 1 v. per cm. This gives 91.6×10^{-3} cm. for the mean free path in A at 0° and 1 mm. pressure. The method is general and applies to ions of any mobility. A. J. M.

Photographic action of secondary electrons resulting from the action of X-rays on metals. J. J. Trillat (Compt. rend., 1943, 216, 179-181).—In the use of an X-ray method of micro- or macroradiography by reflexion (cf. A., 1943, I, 43) it is necessary to know the law of variation of photographic density as a function of at. no. of the irradiated element. This has been found for a no. of metals. The optimum range of X-ray energies is 150-200 kv. The photographic density increases rapidly with at. no. A. J. M.

Time scanning of impulse discharge spectrum. S. J. Bogdanov and K. S. Vulfson (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 30, 311—314).—A circuit for producing periodic discharges using a thyratron in series with a condenser and the discharge tube is described. Spectra of the impulse discharge in Kr at various c.d. show that lines belonging to the Kr 11 spark spectrum increase considerably in intensity with increase of c.d. The lines of the Kr 1 arc spectrum do not vary greatly in intensity with c.d. By using a rotating mirror, the variation of the spectrum during the impulse itself has been investigated. The behaviour of arc and spark lines can thus be examined. The emission of spark lines takes place during the first phase of the discharge, when the c.d. and ionisation are a max. The intensity of the arc lines attains a max. later in the discharge, when the spark lines are beginning to decrease. A. I. M.

A. J. M. Relative abundance of isotopes. L. B. Ponizovski (Compt. rend. Acad. Sci. U.R.S.S., 1943, 41, 104—108).—The max. no. of identical particles (neutrons or protons) added successively to a stable nucleus is 4. In a no. of cases the second or fourth proton is substituted by an aproton (identical with the proton except in sign). It is shown that the max. no. of stable isotopes of one element is 10, formed by addition of 1, 2, 3, or 4 neutrons, 1 or 2 protons, and an aproton on the main line or on branches. There is a periodicity of mass defect from the last particle added which is reflected in isotope abundance, in the main line of nuclear building. Nuclei on the branches of the main line are less abundant than the main nuclei of the same type, and nuclei due to addition of two protons or two neutrons at once are very rare. These rules are shown to hold true for 100 cases out of 116 where relative abundance is known. L. J. J.

Isotopic composition of snow. R. V. Teis and K. P. Florenski (Compt. rend. Acad. Sci. U.R.S.S., 1940, 28, 70-74).—Density measurements on H_2O from freshly fallen snow give negative deviations in the majority of cases. The mean deviation from ordinary H_2O is -2γ . Fractional electrolysis and interferometric and densimetric measurements show a deficit of D (-6 to -8.5γ) and an 262

excess of ¹⁶O. Thawing is associated with accumulation of D and of ¹⁶O in the solid phase. L. J. J.

Szilard isomerism effect. R. Daudel (Compt. rend., 1943, 216, 46-48).—The recoil of atoms containing active nuclei at the moment of emission of electrons of internal conversion does not necessarily give rise to the breakdown of the mol. Although the energy required for rupture is < that of the recoil, its probability is not 1. The probability of rupture of a Na₂SeO₃ mol. through emission of one of its electrons by internal conversion is considered. The coeff. of conversion is calc. The process of deactivation by emission of photons is very rare. The Szilard effect is due essentially to the ejection of electrons. A. J. M.

Disintegration schemes of radioactive substances. VII. ⁵⁴Mn and ⁵⁹Co. M. Deutsch and L. G. Elliott (*Physical Rev.*, 1944, [ii], **65**, 211-215; cf. A., 1944, I, 76).—Investigations by magnetic lens spectrometer and coincidence techniques show that ⁶⁴Mn decays by orbital electron capture to an excited state of ⁵⁴Cr, followed by emission of a 0.835-Me.v. γ -ray. A large fraction of the captured electrons are *K* electrons. Few, if any, capture transitions lead directly to the ground state. ⁵⁸Co decays to a state of ⁵⁸Fe 0.805 Me.v. above the ground state, which in turn decays by the emission of a single γ -ray. About 90% of the disintegrations of ⁵⁸Co occur by *K*-electron capture, and in the remaining 10% positrons of max. energy 0.47 Me.v. are emitted. This ratio of the two modes of decay is consistent with the idea that the transition takes place with a change of angular momentum 1 or 0, whether the parity changes in the transition or not, if the tensor theory of β -decay is correct. The lowest known excited states of ⁵⁸Co and ⁵⁸Fe have excitation energies differing by <5%. The difference between the masses of the neutral atoms of ⁵⁸Co and ⁵⁸Fe should be 2.46 $\pm 0.03 \times 10^{-3}$ a.m.u. N. M. B.

Isomerism induced in ¹¹⁵In by electron impact. M. I. Korsunski, V. E. Ganenko, and S. I. Zipkin (*Compt. rend. Acad. Sci.*, U.R.S.S., 1941, **30**, 403-404).—Monochromatised electrons (~1.6 Me.v.) bombarded two foils of In (0.06 cm.) separated by an Al plate (0.055 cm.). Thus the second In foil was exposed to γ -rays only and the difference in activities excited in the two foils was measured by a counter. Electron excitation occurs, and the effective cross-section for the electron effect is ~2×10⁻³³ sq. cm. W. R. A.

Nuclear scattering cross-sections (σ) for chromium, silver, cadmium, and barium, with photoneutrons within the energy range 0.1-0.9 Me.v. T. A. Goloborodko (*Compt. rend. Acad. Sci.* U.R.S.S., 1941, **30**, 309-310).—The photoneutrons were obtained by irradiating Be and D with γ -rays from RaTh and Ra. The val. of σ varies with the energy of the scattered neutrons. Neutrons from RaTh- γ +D may be regarded as monochromatic, and of energy 0.2 Mc.v. For neutrons from RaTh- γ +Be the energy is not monochromatic, and the σ -vals. obtained with these neutrons represent mean vals. within the range 0.09-0.5 Me.v. A. J. M.

Cascade theory of cosmic showers. S. Belenki (Compt. rend. Acad. Sci. U.R.S.S., 1941, 30, 608-612).—Arleys' method (A., 1939, I, 116) for obtaining the energy spectrum of cosmic-ray showers is criticised, and a more general solution of the problem is offered. An equation is obtained from which the spectrum of electrons at any depth can be deduced. A. J. M.

Spectrum of the soft component [of cosmic radiation] in air at high energies. I. Pomerantschuk and A. Kirpitschev (Compt. rend. Acad. Sci. U.R.S.S., 1943, 41, 18–20).—The spectrum of decay electrons arising immediately from mesotron disintegration is used to calculate the spectrum of the soft component. The no. of particles of energy > the crit. energy (e) is appreciable, e.g., 12–13% of the total soft charged component due to mesotron decay comprises particles with energy >4e, at sea level. L. J. J.

High-energy particles in Auger showers. A. Rogozinski (*Physical Rev.*, 1944, [ii], **65**, 207-210).—Results are given of counter experiments at 10,618 ft. altitude on extensive atm. showers of 22 m. min. spread. A (master-group) method of investigation is described. High-energy electrons or photons, initiating a shower below a 10-cm. Pb screen, are accompanied, above the absorber, by a shower of high particle density located in the central part of, or close to, the core of the Auger shower. N. M. B.

Multiple production of penetrating secondary cosmic rays in lead. W. E. Hazen (*Physical Rev.*, 1944, [ii], **65**, 249).—An explanation is given of the absence of indications of a "cascade" process in cloudchamber photographs showing multiple production of penetrating particles by cosmic-ray neutrons and protons. N. M. B.

Method of shower anticoincidences for measuring the meson component of cosmic radiation. V. Sarabhai (*Physical Rev.*, 1944, [ii], 65, 250-251).—The use of the production of secondaries by the electronic component in cutting out the slow mesons is applied to bringing them into direct experimental observation. An arrangement of anticoincidence counters and Pb absorbers is described. Total intensity and meson intensity curves at two altitudes are given and discussed. N. M. B. Is the "self-field " of the particle a physically observable quantity? M. Markov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 41, 14-17).— A general theoretical discussion on the basis of existing theories.

Atomic wave functions for ground states of elements lithium to neon. W. E. Duncanson and C. A. Coulson (*Proc. Roy. Soc. Edin.*, 1943—1944, 62, 37—39).—Wave functions of the type proposed by Morse *et al.* (A., 1936, 133) are calc., and some errors in the latter are corr. H. J. W.

Generalised electrodynamics. II. Quantum. B. Podolsky and C. Kikuchi (*Physical Rev.*, 1944, [ii], 65, 228-235).—Mathematical. N. M. B.

New representation of types of nuclear forces. M. Bunge (*Physical Rev.*, 1944, [ii], **65**, 249—250).—The physical meaning and the spatial symmetry properties of a system of nuclear particles can be described by a representation in which spin and isotopic spin are considered to be components of one quadrivalent variable. This representation does not, however, show whether a relativistic theory of the nucleon is possible without the introduction of four more states (antiproton and antineutron). N. M. B.

II.—MOLECULAR STRUCTURE.

Theory of hysteresis of rotational transformations. H. Hartmann (Z. physikal. Chem., 1942, **B**, 52, 338—347).—The stability of the hysteresis loops observed for rotational transformations can be explained by Schäfer's theory (A., 1940, I, 11) only if the existence of forbidden transitions in the rotational term spectrum is assumed. A. J. M.

Application of new analysis of molecular spectra to interesting molecules. Simple explanation of some peculiarities of molecules. H. Deslandres (*Compt. rend.*, 1942, 215, 5—9).—A summary of rules obtained from a study of the infra-red spectra of hydrocarbons is given. A. J. M.

Excited states of the ethylene molecule. H. Hartmann (Z. physikal. Chem., 1943, **B**, **53**, 96–102).—Theoretical. Ground and first excited states of C_2H_4 are calc., and give the energy difference for the IS \rightarrow IIS transition as 6.61 e.v., in fair agreement with Scheibe and Grieneisen's experimental val. of 6.48 e.v. (A., 1934, 583).

R. C. M. Experimental verification of the theory of the continuous spectra of H_2 and D_2 . A. S. Coolidge (*Physical Rev.*, 1944, [ii], 65, 236— 246; cf. A., 1930, I, 165).—The spectra have been produced and studied under conditions permitting control of the excitation processes, the electron beam being subjected to definite accelerating potentials. Modifications to theoretical predictions show that no sharp separation of even the lowest vibrational level of the radiating electronic state can be expected at any accelerating potential. The form of functional relationship between the rate of excitation of a given level and the accelerating potential is found to be linear if the latter is somewhat > the crit, excitation potential of the given level, and exponential if it is lower. Corrections to contact potentials are hence determined. At certain $\lambda\lambda$ the observed radiation can come only from a single vibrational level; intensity-voltmeter readings give a curve in which the point where linear and exponential parts merge is taken as that at which the true accelerating potential scale is thus established, there is good agreement between calc. and observed spectral energy distribution. N. M. B.

Ultra-violet spectrum of nitrogen molecule. (Mme.) R. Herman and L. Herman (Compt. rend., 1942, 215, 83-84).—The Kaplan bands of N₂ have been photographed. The lower levels of the Kaplan and the van der Ziel systems are not identical (cf. Kaplan, A., 1934, 823, 1279; van der Ziel, A., 1934, 575). A. J. M.

Spectrum of N₂. R. E. Worley (*Physical Rev.*, 1944, [ii], 65, 249; cf. A., 1944, I, 27).—A note on the lettering of singlet states agreed on by Gaydon and the author, and a correction of an error in a table by the author (A., 1944, I, 27). An explanation of Hopfield's Rydberg series in emission is proposed. N. M. B.

Activation of nitrogen at liquid air temperature. S. S. Joshi and A. Purushotham (*Current Sci.*, 1944, **13**, 155).—At liquid-air temp. the glow of N_2 suffers Rayleigh quenching at 15 mm. but not at >40 mm. With the discharge tube under liquid air Rayleigh quenching did not occur even at ~1 mm., but when the pressure was reduced to <0.1 mm. an afterglow persisting for 15—17 min. was observed, which is possibly due to adsorption of N_2 on the Pt and Al electrodes used. W. R. A.

Spectrum of deuteroacetone in the vacuum ultra-violet. Comparison with the spectrum of acetone. (Miss) M. Lawson and A. B. F. Duncan (*J. Chem. Physics*, 1944, 12, 329-335).—The absorption spectrum of $CO(CD_3)_2$ (I) has been photographed between 2000 and 1300 A. with dispersion 4·14 A. per mm. Some new $\nu\nu$ for $COMe_2$ at \sim 51,000 cm.⁻¹ are recorded. $\nu\nu$ are assigned to transitions for both compounds, and correlated with the normal state structures. The excited state of (I) shows no vibrational ν near 1200 cm.⁻¹ This ν in COMe₂ cannot be ascribed to the C-O vibration. L. J. J. Characteristic frequencies of some cyclic hydrocarbons. M. Parodi (Compt. rend., 1942, 215, 13-15).—The fundamental $\nu\nu$ of some modes of vibration of cyclo-pentane, -hexane, and -heptane are calc. on the assumption that the mols. are planar. There is satisfactory agreement with experiment, even in the case of cycloheptane, where the angle between consecutive valencies differs considerably from the tetrahedral angle. A. J. M.

Infra-red vibrations of certain organic crystals in the range of wave-lengths about 1 mm. E. Gross, A. Raskin, and V. Volkov (Acta Physicochim. U.R.S.S., 1943, 18, 430-432).—The low-frequency scattering spectrum of crystals of NHPh₂ shows lines at frequencies 8, 39, 55, 80, and 133 cm.⁻¹ The frequency of 8 cm.⁻¹ ($\lambda = 1.25$ mm.) is probably the lowest infra-red frequency observed heretofore with the aid of scattering spectra, and its use in several fields of investigations is discussed. C. R. H.

Analysis of infra-red absorption spectra of maleates and fumarates. (Mlle.) A. Delay, C. Duval, and J. Lecomte (*Compt. rend.*, 1943, **216**, 40-42).—The infra-red absorption spectra of 16 maleates, 1 H maleate, 17 fumarates, and 1 H fumarate have been investigated. The fumarates have about half the no. of absorption bands of the maleates. The ion COO·CH:CH·COO has 24 distinct fundamental vibrations. The model with 4 masses, (COO)·(CH):(CH)·(COO), has 6 fundamental vibrations, whilst that with 8 masses, COO·(CH):(CH)·COO, has 18. The $\nu\nu$ corresponding to these vibrations are identified. Owing to the difference of ν which exists

COO·(CH):(CH)·COO, has 18. The $\nu\nu$ corresponding to these vibrations are identified. Owing to the difference of ν which exists between the vibrations introduced by the presence of H atoms and those of the rest of the model, the model of the acids can be treated as one with 6 masses, $\binom{\text{COO}}{\text{H}}$ C:C $<\binom{\text{COO}}{\text{H}}$, and the vibrations are

identified on this basis. A. J. M.

Absorption spectra of amido- and amino-complexes of bivalent platinum. A. V. Babaeva (Compt. rend. Acad. Sci. U.R.S.S., 1943, 40, 61-65).-Absorption spectra (2200-6000 A.) of 0.001-0.05M. aq. K₂[PtBr₄], K₂[PtCl₄], K₂[Pt(NCS)₄], [Pt(CS(NH₂)₂)₄]Cl₂, K₃[Pt(NO₃)₄],2H₂O, K₂[Pt(C₂O₄)₂],2H₂O, and [Pt(NH₃)₄]Cl₂,H₂O have been examined and are discussed. The influence on the character of the spectrum of stepwise replacement of Cl by NO₃ in K₂[PtCl₄] has been studied. W. R. A.

Absorption spectra of complex compounds. cis-trans-Isomerism of complex platinum compounds of the diamine series and light absorption. A. V. Babaeva (Compt. rend. Acad. Sci. U.R.S.S., 1943, 40, 148-151).—The absorption spectra (2200—6000 A.) of 0·0001— 0·01M. solutions of cis- and trans-[Pt(NH₃)₂Cl₂] (I), -[Pt(NH₃)₂NO₂Cl] (II), and -[Pt(NH₃)₂(NO₂)₂] (III) have been examined. (I) give three absorption bands. (II) and (III) show only one broad band, corresponding with the second band given by (I); in the transisomeride this band occurs at a higher λ than in the corresponding cis-isomeride. C. R. H.

Ultra-violet absorption spectra of freshly precipitated substances and colloidal solutions by reflexion. A. Berton (*Compt. rend.*, 1943, 216, 181—183; cf. A., 1938, I, 597).—An arrangement for obtaining the ultra-violet spectra of freshly pptd. substances by reflexion is described (see C., 1944, 200). The white $Sn(OH)_4$ gel formed by pptn. of 10% SnCl, with aq. NH₃ gives a different spectrum from that of the substance which has been kept for 5 hr. in the motherliquor. The change is due to dehydration. In the case of ZnS pptd. by H₂S from 10% Zn(OAc)₂ there is a similar difference, also probably due to dehydration. The degree of dispersion of the freshly produced ppts. could also account for the change. However, the ultra-violet absorption spectra by reflexion of a sol and a gel of ZnS are the same as that of Zn blende. The spectrum of Ag sols shows the same min. of reflecting power at 3200 A. as metallic Ag. The colloidal micelles are therefore composed of cryst. particles.

Absorption spectra of pyrrole-blue A and B. F. Fromm (J. Amer. Chem. Soc., 1944, 66, 1227—1228).—The absorption spectra of pyrrole-blue A and B confirm the assumption that they possess different structures. W. R. A.

Molecular compounds of the quinhydrone type in solution.—See A., 1944, II, 373.

Structure and properties of azo- β -maphthol dyes.—See A., 1944, II, 368.

New spectral method. Hertzian spectra of alcohol molecules. P. Girard and P. Abadie (*Compt. rend.*, 1942, 215, 84-86).—Investigation of the Hertzian spectra ($\lambda 2.5$ cm.—20 m.) of alcohols gives dispersion and absorption curves. The dispersion curves are directly related to the form of the mol., and the angle of the permanent moment with the plane or axis of symmetry can be determined. Alcohols with C₃, C₈, or C₁₀ give curves of the same general type. The dispersion curve considerably higher. These have two different relaxation times, τ_1 , τ_2 , indicating two directions of oscillation is α (dielectric const.)², the angle which the permanent moment makes with the axis of symmetry of the mol. is 18° for both PrOH and

02 (A., I.)

 C_8H_{17} ·OH. The ratio τ_1/τ_2 increases with the length of the C chain. It is ~3 times as great for C_8H_{17} ·OH as for PrOH. Assuming the mols. to be ellipsoidal, the ratio of the axes can be calc. from τ_1/τ_2 , but the results do not agree with data obtained by X-ray diffraction, particularly for long-chain mols. A. J. M.

Hertzian spectra of benzyl alcohol and nitrobenzene. P. Girard and P. Abadie (Compt. rend., 1943, 216, 44-46).—The forms of the mols. of CH₂Ph-OH (I) and of PhNO₂ (II) in the liquid state at ordinary temp. are deduced from their Hertzian spectra (λ 4 cm.— 4 m.). In the case of (I) there are at least two regions of dispersion, and possibly three, ascribed to the following oscillations of the mol.: (1) oscillation of the C₆H₆ disc about a normal to the axis passing through the centre; (2) oscillation of the C₆H₆ disc about a perpendicular axis passing through the centre; (3) the probable third region indicates that the C₆H₆ ring is not quite circular owing to the presence of the side-chain. The components of the permanent moment in the ring plane are small. The mol. of (I) is therefore composed of an almost circular C₆H₆ ring, the permanent moment

CH₂·OH making an angle of ~70° with the plane of the C₆H₆. In the case of (II) there are two dispersion curves, one with a very small val. of the relaxation time, τ , corresponding to the rotation of the C₆H₆ disc about its axis, the other with a large val. of τ , corresponding to rotation about the normal to the axis. The τ of rotation of the C₆H₆ disc for (II) is 2.5 times that for (I), although the η of (I) is 3 times that of (II). In (II) the permanent moment (bisector of angle of O-N-O) and the two O atoms are all in the plane of the disc. A. J. M.

Fluorescence of polyatomic molecules. G. Kortüm and B. Finckh (Z. physikal. Chem., 1942, B, 52, 263-283).—To investigate the connexion between fluorescibility and chemical constitution, the mol. fluorescence spectrum of anthracene (I) in the solid state, in the form of vapour, and in solution in various solvents has been investigated, and compared with the corresponding absorption spectrum. The max, of the absorption spectrum are displaced ~1000 cm.⁻¹ towards longer λ in the series vapour, solution, crystal, but intensity and intensity distribution are approx. the same in all three states. The absorption and fluorescence spectra in dioxan solution are the mirror images of each other. The fluorescence bands in dioxan, MeOH, cyclohexane (II), and glycerol have the same position and intensity for solutions of the same concn. The polarity of the solvent and the concn. of the solution do not affect the position of the bands. The decrease in intensity of the mol. fluorescence with increasing concn. varies from solvent to solvent, and different bands are differently affected. The effect is least in dioxan. This is discussed in relation to various theories of polymerisation. The effect of temp. on the fluorescence is also examined. In the case of a solution in dioxan, the total intensity of the spectrum is reduced as temp. rises, but the positions of the bands and the relative intensity distribution are unchanged. Photometer curves for the fluorescence of (I) in (II) show that in very dil. solution outside the region of concn. extinction, the intensity of the fluorescence decreases very considerably with rise of temp. For medium concns. ($\sim 10^{-4}$ g.-mol. per l.) the decrease is very small, but at higher concns. the decrease is greater again. The fact that the temp. coeff. thus passes through a min. cannot be explained by increasing effective-ness of collisions of the second kind with rise of temp., but indicates that two effects occur. A. J. M.

Fluorescence of organic molecules. J. Weiss (*Nature*, 1943, 152, 176—178).—Quenching is explained on the conception of "trapping centres" by which electrons are prevented from returning to normal energy levels with fluorescence. E. R. R.

Effect of temperature on brightness of crystalline phosphors when excited by monochromatic radiation. M. Schön (Naturwiss., 1943, 31, 169).—The effect of temp. $(\not\prec -190^\circ)$ on the brightness of selfactivated ZnS, Cu-activated ZnS-CdS, and self-activated ZnS-CdS phosphors has been investigated for monochromatic incident radiation of $\lambda\lambda$ 4358, 4047, 3650, 3340, 3130, and 3025 A. In the region of the fundamental lattice absorption, the brightness at low temp. increases with decreasing λ of the incident radiation, in agreement with the theory of Möglich *et al.* (A., 1942, I, 31). The luminescence of pure ZnS, which shows the greatest increase of brightness on cooling, decreases most rapidly on warming. For incident radiation of $\lambda >$ the fundamental lattice absorption, the brightness decreases with decreasing temp. A. J. M.

Broadening of the Rayleigh scattering lines depending on pressure. V. L. Ginzburg (Compt. rend. Acad. Sci. U.R.S.S., 1941, 30, 399– 402).—Theoretical. Existing theories are reviewed and a new one is developed. W. R. A.

Depolarisation of Raman lines of aqueous solutions of molybdates. (Mlle.) M. Théodoresco (Compt. rend., 1943, 216, 56-58).—The Raman spectra of aq. solutions of Na and K molybdates have been investigated. There is only one polarised line, at 897 cm.⁻¹ for neutral Na molybdate, and at 894 cm.⁻¹ for neutral K molybdate. This is the very intense line due to symmetrical valency vibrations of hydrated MoO₄". Study of the polarisation of the Raman lines has made it possible to find the components of the wide band which accompanies the polarised line. There are only three lines characteristic of anhyd. MoO_4'' . The H₂O mols. of the hydrated ion reduce the no. of elements of symmetry of the anhyd. ion.

 $3(NH_4)_2O,7MoO_3,4H_2O$ and $3Na_2O,7MoO_3,22H_2O$ have only one polarised line at 938 cm.⁻¹, corresponding to the only polarised line in the spectrum of metamolybdic acid (950 cm.⁻¹), and thus due to symmetrical valency vibrations of MoO₃. A. J. M.

Depolarisation of Raman lines of simple and complex tungstates. (Mile.) M. Théodoresco (*Compt. rend.*, 1943, 216, 117-118).— Neutral tungstates have only one polarised Raman line, characterised by its intensity. For Na tungstate it is at 931 cm.⁻¹ The four components accompanying the polarised line, and together with it constituting the characteristic band, have frequencies 819, 833, 858, and 878 cm.⁻¹. They all have different depolarisations. The so-called acid tungstates have a double polarised line constituting the most intense doublet of the characteristic band. The WO₂ group may have a pyramidal structure with W at the apex, symmetry group C_{3v} , or it could be planar, symmetry group D_{3a} .

A. J. M.

Depolarisation of Raman lines. G. Glockler, J. F. Haskin, and (Miss) C. C. Patterson (*J. Chem. Physics*, 1944, **12**, 349).—The use of a mica plate to rotate one of the components when using Polaroid in the measurement of depolarisation factors of Raman lines (Glockler and Baker, A., 1944, I, 3) is unnecessary if the two Polaroid films are positioned in front of the spectrograph so that their line of contact is at 45° to the vertical axis of the spectrograph. L. J. J.

Theory of intensities and polarisation in Raman spectra of halogensubstituted methanes. M. V. Volkenschtein and M. A. Eliaschevitsch (*Compt. rend. Acad. Sci. U.R.S.S.*, 1944, **43**, 51—53).—The theory previously developed (A., 1943, I, 116) is applied to CCl₄, CHCl₃, CH₂Cl₃, MeCl, MeBr, CH₂Br₃, CHBr₃, and CBr₄. The original theory depends on the additivity of effects due to valency bonds, but this approximation is not always valid. The polarisability of a bond is not only a function of its length, but it also varies with the length of neighbouring bonds and with valency angle. However, the theory gives satisfactory agreement between observed and calc. vals. of intensity and polarisation, the agreement being better in the case of intensity. The calc. degree of depolarisation of deformational vibrations is > observed vals. The polarisability (a) of the C-H bond is small, but the variation of a with bond-length (r) is considerable. da/dr is the smaller the more ionic is the nature of the bond.

A. J. M. A. J. M. A. J. M. Bioperformation of the strain theory. K. Dicyclohexadienes, a further contribution to the strain theory. K. W. F. Kohlrausch, R. Seka, and O. Tramposch (Ber., 1942, 75, [B], 1385— 1398).—Raman spectra of dicyclo-[2:2:2:]-octane, 3:6-endoethyl= enehexahydrodimethylaniline, Et 2:5-endoethylenehexahydrobenzoate, Me, 3:6-endoethylenehexahydro-o-phthalate, tetrahydrodicyclohexadiene, dihydrodicyclohexadiene (mixture of isomerides), dicyclohexadiene, Me, 3:6-endoethylene- Δ^4 -tetrahydroo-phthalate, Et 3:5-endoethylene- Δ^3 -tetrahydrobenzoate, 2:5endoethylene- Δ^3 -tetrahydrobenzaldehyde, dicyclo-[2:2:2:]-octene, dihydrodicyclohexadiene (possibly a mixture of isomerides), dihydrodicyclohexadiene (possibly mixed with tetrahydrodicyclohexadiene), and trans- Δ^4 -octahydronaphthalene are recorded and discussed.

H. W.

Raman effect. CXXXVIII. Nitrogen compounds. XXV. Aromatic nitro-compounds. H. Wittek (Z. physikal. Chem., 1942, B, 52, 315—337).—The Raman spectra of PhNO₂ and p-C₉H₄F·NO₂ have been reinvestigated and polarisation determinations have been carried out with PhNO₂. The Raman spectra of cryst. o_- , m_- , and p_- X·C₆H₄·NO₂ (X = OH, OMe, Cl, Br, CN, CO·NH₂, CO₂H, CO₂Me, CHO, NO₂) (except o-OH·C₆H₄·NO₂), and of three liquid nitroxylenes, have been investigated. The lines due to PhNO₂ and p_- X·C₆H₄·NO₂ have been analysed, and the behaviour of the NO₂ valency frequency ω_{\bullet} and the valency frequencies ω (C:O) and ω (C:N) is considered. By oo'-dimethylation of PhNO₂ ω_{\bullet} is raised, owing to steric hindrance, to a val. corresponding with that for CH₂Ph·NO₃, in which lowering of ω_{\bullet} by mesomerism is not possible. An attempt is made to account for the change of ω_{\bullet} when PhNO₂ is mono-substituted, on the basis of the mesomeric effect, but a complete explanation is not achieved. A. J. M.

Raman effect. CXXXIX. Structure of diborane. J. Wagner (Z. physikal Chem., 1943, B, 53, 85–95).—Infra-red and Raman spectra of B_2H_6 are in better agreement with the ethylenic structure $H_2BH_2BH_2$ (symmetry group D_{2h}) than with the "ethane" formula, H_3B ·BH₃, suggested by Bauer (A., 1937, I, 397), Anderson and Burg (A., 1938, I, 600), and Stitt (A., 1942, I, 83). R. C. M.

Formation and structure of some organic molecular compounds. III. Dielectric polarisation of some solid crystalline molecular compounds. H. Kronberger and J. Weiss (J.C.S., 1944, 464-469).— The mean dielectric consts. and mol. polarisations of the following mol. compounds and of the parent substances have been determined: anthracene (I)-picric acid; (I)-, benzidine-, 3:4-benzpyrene-, chrysene-, coronene-, 20-methylcholanthrene-, phenanthrene-, p-C₆H₄(NH₂)₂-, and pyrene-s-C₈H₃(NO₃)₃; quinhydrone. The deviations from additivity of mol. polarisations in the case of the compounds, which in some cases are considerable, are both positive and negative. The effects can be interpreted on the view that compound formation is accompanied by transfer of electrons. Coronene-s-C₆H₃(NO₂)₃, which was cryst. from boiling C₆H₆, decomposes below its m.p. Pyrene-s-C₆H₃(NO₂)₃, m.p. 248°, was cryst. from C₆H₆. C. R. H.

Measurement of the velocity of light in water. R. A. Houstoun (Proc. Roy. Soc. Edin., 1943—1944, 62, 58—63).—The quartz ultrasonic diffraction grating (A., 1944, I, 146) was used, and the formula for the group velocity was verified with an accuracy of 0.1% for red, green, and blue light. H. J. W.

Havelock's formula and a new formula for the dispersion of electric and magnetic birefringence. R. Servant (*Compt. rend.*, 1943, 216, 177—178).—The formula previously proposed (*ibid.*, 1940, 211, 780) is compared with Havelock's formula. If it is supposed that the optical anisotropy is const. the theory of orientation agrees with Servant's formula but not with that of Havelock. A. J. M.

Light-scattering in solutions [and its applicability to optical analysis of solutions of polymers.] P. Debye (J. Appl: Physics, 1944, 15, 338-342).—A theoretical consideration of some of the conclusions derivable from measurement of light-scattering by turbid solutions; the possibility of mol. wt. determination by this principle is indicated. D. F. T.

Developments of valency theory. E. J. Bowen (*Chem. and Ind.*, 1944, 338—341).—A review dealing with the application of wavemechanics to valency problems. The formation of a single link by the merging of electron clouds is described, and the wave-mechanical interpretation of the double bond is considered. Conjugation and the $C_{6}H_{6}$ formula are also discussed. Pauling's treatment is outlined. The association of liquids, and the nature of van der Waals forces, are considered. A. J. M.

Developments of valency theory. A. A. New (Chem. and Ind., 1944, 367).—It is suggested that a dipole might be regarded as two atoms which have merged their electron clouds to give a pear-shaped form. This would give a method of representing a dipole on paper, the magnitude of the dipole moment being roughly represented by the sharpness of the pointed end. An error in a formula given by Bowen (preceding abstract) is reported.

A. J. M.

Developments of valency theory. M. W. Travers (*Chem. and Ind.*, 1944, 367).—It is pointed out that "borohydrates" and B hydrides cannot be satisfactorily explained on the modern theory of valency (cf. Bowen, *supra*). A. J. M.

Co-ordination numbers of elements. P. Pfeiffer (J. pr. Chem., 1943, [ii], 162, 279-306).—A review and classification. W. R. A.

Model for hydrogen bond (chain association of hydrogen fluoride). G. Briegleb (Z. physikal. Chem., 1942, B, 52, 368).—Corrections to data used in a previous paper (A., 1942, I, 318) are reported.

A. J. M. Quantum mechanics of compounds. II. Bond system and stereochemistry of cumulenes. F. Seel (Z. physikal. Chem., 1943, B, 53, 103-116).—Theoretical. Hund and Milliken's simplified theory (A., 1032, 10, 215, 562, 902, 1191) applied to allenes etc. gives structures in harmony with stereochemical behaviour. R. C. M.

Empirical correlation and method of calculation of barriers hindering internal rotation. J. G. Aston, S. Isserow, G. J. Szasz, and R. M. Kennedy (*J. Chem. Physics*, 1944, 12, 336-344).—The barriers hindering internal rotation of Me groups can be calc. by assuming that they are solely due to repulsion between H atoms according to the potential relation $V = 4.99 \times 10^5 r^{-5}$ between a H atom of a rotating group and a H atom of the remainder of the mol., assumed stationary and at a distance r. The vals. calc. are too low for Me₂O, Me₂S, and CHMe²CH₂. Vals. are calc. for EtOH and Pr^βOH and some *n*-paraffins, and entropy, heat capacity, and equilibrium const. vals. are calc. L. J. J.

Variation of thermal conductivity with pressure and the formation of double molecules in ethyl chloride. K. Schäfer and O. R. F. Gazulla (Z. physikal. Chem., 1942, B, 52, 299-314).—It is possible to determine the no. of double mols. in a gas by finding the variation of thermal conductivity with pressure. This variation is due to dissociation of the double mols., and it is possible to obtain from it the heat of dissociation and the equilibrium const. of the dissociation. The method is applied to EtCl. A method of obtaining the second virial coeff. is described; this makes it possible to separate the part due to swarm formation from that due to double mols. A. J. M.

Theory of the liquid state. I. Prigogine (J. Phys. Radium, 1944, [viii], 5, 16—22).—An approx. method is developed which permits the use of the Lennard-Jones and Devonshire model in the case where the van der Waals consts., but not the intermol. consts., are known. This theory is in good accord with experimental data. B.p. of ~40 substances have been calc. A quant. theory of the liquid state is given. The first five energy levels of H_2 for different vals. of ν/ν^* have been computed. A val. of the sp. heat of liquid $H_{2\nu}$ in agreement with the experimental val., has also been calc. W. R. A.

Surface tension and van der Waals' equation.—See A., 1944, I, 222.

Surface tensions of glasses.—See B., 1944, I, 334.

Rupture of water drops falling on liquid surfaces. B. N. Singh and S. P. Sinha (*Current Sci.*, 1944, 13, 157).—For drops of H_2O falling on an oil surface rupture takes place only when the drops fall from a height > a crit. val. depending on the size of the drop and on the oil. W. R. A.

Free energy of diffuse double layer. A. Frumkin (J. Phys. Chem. Russ., 1943, 17, 310—312).—An explanation is offered for the difference between the energies of a condenser and an electric double layer. J. J. B.

III.—CRYSTAL STRUCTURE.

X-Rays, crystals, and molecules. J. M. Robertson (Proc. Roy. Phil. Soc. Glasgow, 1943-1944, 58, 81-90).—A lecture.

Intensity measurements with focussing cameras of the Seemann-Bohlin type. G. Hagg and G. Regnström (Arkiv Kemi, Min., Geol., 1944, **18**, **A**, No. 5, 9 pp.).—A formula is derived for the calculation of X-ray reflexion intensities in powder photographs taken with Seemann-Bohlin type cameras, from photographic density data. Calc. and observed intensities agree within $\pm 20\%$ for NaCl powder samples with Cu K radiation. L. J. J.

X-Ray topographs of diamond. G. N. Ramachandran (Current Sci., 1944, 13, 156-157).-Description of a modification in technique of work already noted (A., 1944, I, 215). W. R. A.

Abnormal diffusion of X-rays by diamond. A. Guinier (Compt. rend., 1942, 215, 114—115).—A group of four very weak spots appears when a diamond crystal is turned a little from the position for reflexion from (111). One of these (diffuse) is due to thermal agitation. The other three are not affected by temp. and are sharp. For other positions of the crystal the spots are less intense and are less sharp. The explanation is discussed. A. J. M.

Imperfect crystal. J. S. Anderson (J. Proc. Roy. Soc. New South Wales, 1943, 76, 345—358).—A lecture. The lattice imperfections displayed by heteropolar binary compounds and their influence on electrolytic conduction and on diffusion and reactions in the solid state are discussed in the light of recent advances in the knowledge of crystal structure. C. R. H.

Lattice energy of ionic crystals. A. Kapustinski (Acta Physicochim. U.R.S.S., 1943, 18, 370-377).—From the Born-Mayer quantum-mechanical equation for the energy of the lattice and the author's relation between structure coeffs. and ionic distances, the universal expression $U = 287 \cdot 22n \times v_1 v_s/R \times (1-0.345/R)$ has been derived, where U is the lattice energy, v_1 and v_s are valencies of cation and anion, R is the sum of the ionic radii (Goldschmidt's), and 2n is the no. of ions in the mol. The formula gives vals. within 2% of the observed vals. for numerous inorg. halides, oxides, sulphides, and selenides. C. R. H.

Crystal chemistry of the Laves phases. G. B. Boki and E. E. Vainschtein (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 40, 232-233, and *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1943, 241-247).— The intermetallic compounds which do not fit into the scope of the classical ideas of valency (Laves phases) have the formula AB_g or $AB_zB'_{2-z}$. The structures of Laves phases are characterised by co-ordination nos. (12, 6), but each *B* atom has six *B* atoms as its closest neighbours; this accounts for the fact that similar structures are not observed in ionic compounds. These structures permit no variation in the ratio between the radii of the components; contact of uninomial spheres occurs with $R_A: R_B = 1.225$ and the A-B distance $(a/8)\sqrt{11}$. The experimental vals. for $R_A: R_B$ lie between 1'11 and 1.33 (calc. vals. 1.09-1.34). Contrary to the views of Schulze, polarisation plays an important role, although mutual polarisation are classed as (a) elements acting as *A* component only (Na, K, Ca, Ti, Ag, Pb, V, Cr, Mo, Re), (b) elements acting as *B* components only (Zn, Be, Co, Ni, Al), and (c) those capable of acting as either *A* or *B* (Mn, Fe, Cu, Au, Bi, Mg). Laves phases should not be regarded as an independent group of intermetallic compounds, and the term should be applied only to a definite type of cryst.

X-Ray investigation of the structure of boron carbide. G. Shdanov and N. Sevastianov (J. Phys. Chem. Russ., 1943, 17, 326-335).— B₄C forms a deformed NaCl lattice in which groups of 12 B and 3 C atoms play the part of Na' and Cl'. The distances between various B atoms are 1.77, 1.78, and 1.80 A., and between B and C 1.63 A.

J. J. B. Structure of nickel oxide. H. P. Rooksby (*Nature*, 1943, 152, 304).—X-Ray powder photographs taken on a 19 cm. diameter camera show that some a-doublets are doubled or tripled. These observations are accounted for by a very slight distortion of the crystal from the face-centred cubic towards the rhombohedral; at $20^{\circ}, a_0 = 2.9459 k X, a = 60^{\circ} 4.2'$. The effect is common to NiO from many sources, but absent in FeO and CoO. E. R. R.

Measurement of X-ray wave-lengths by the powder method: $\operatorname{Gr} K\beta_1$ and $\operatorname{Mn} K\beta_1$. H. Lipson and (Mrs.) L. E. R. Rogers (*Phil.* Mag, 1944, [vii], 35, 544---549).---Using Cu Ka and Co Ka radiations as standards, the lattice parameter of powdered Si is found to be $5 \cdot 41964 \pm 0 \cdot 00005kX$ at 25°. From photographs taken with mixed radiations (Cu + Cr and Co + Cr) $\lambda = 2080 \cdot 61 \pm 0 \cdot 04kX$ for Cr $K\beta_1$. For Mn $K\beta_1$ different results were obtained according to whether the Mn was plated on Cu or Co in the target. For Mn on Cu, $\lambda = 1906 \cdot 34 \pm 0 \cdot 06kX$, and for Mn on Co, $\lambda = 1906 \cdot 21 \pm 0 \cdot 05kX$, the former val. being the one most likely to occur in practice. H. J. W.

Unit cell and space-group of colemanite, 2CaO,3B₂O₃,5H₂O. V. A. Nikolski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 28, 59).—Unit cell dimensions are: a 8.72 ± 0.02 , b $11\cdot29\pm0.02$; c 6.06 ± 0.04 A.; a:b:c=0.7728:1:0.5367. Assuming $\rho = 2.42$ and $\beta = 110^{\circ}$ 09', the unit cell contains 2 mols. The most probable space-group is $C_{2k}^1 - P2/m$. L. J. J.

X-Ray investigation of the structure of ammonium chloroiridate. G. B. Boki and P. I. Usikov (Compt. rend. Acad. Sci. U.R.S.S., 1940, 26, 782—784).—The crystals belong to the cubic system. Etched figures show that they belong to the hexaoctahedral class $(3L_44L_36L_29pc)$. X-Ray analysis gives a 9.87 A.; 4 mols. in unit cell; $\rho_{calo.}$ 3.06; space-group O_A^5 . The structure is similar to that of K₂PtCl₆. A. J. M.

Crystal structure of ammonium pentachlorozincate. H. P. Klug and L. Alexander (J. Amer. Chem. Soc., 1944, **66**, 1056–1064).— The crystal structure of $(NH_4)_3ZnCl_5$, determined from Laue and rotating and oscillating crystal photographs by the Patterson-Harker and Bragg-Fourier methods, is orthorhombic bipyramidal, $a_0 \, 8.74, \, b_0 \, 9.84, \, c_0 \, 12.61 \, \text{A.}$, space-group D_{20}^{16} —Puma, four $(NH_4)_3ZnCl_5$ mols. per unit cell. The positions of the atoms are fixed by 16 parameters. Zn atoms are surrounded by Cl atoms at 2.25 A. and one extra Cl not co-ordinated with Zn. These extra Cl atoms are surrounded by NH_4^{-1} ions at an average distance of 3.41 A. One kind of NH_4^{-1} ion is surrounded by a trigonal prism of Cl atoms at an average distance of 3.44 A., whilst the other NH_4 groups are surrounded by an irregular polygon of 8 Cl at an average distance of $3.32 \, \text{A.}$ The Zn-Cl linkings in the ZnCl'' tetrahedra are essentially covalent whilst all other bonds (N-H excepted) are essentially ionic. The structure consists of NH_4^{-1} , Zn'', and Cl' ions and the formula is $(NH_4)_2ZnCl_4, NH_4Cl.$ W: R. A.

X-Ray study of the copper-manganese binary alloy system.—See A., 1944, I, 276.

X-Ray examination of crystals of triphenylmethyl chloride and bromide. S. N. Wang and C. S. Lu (J. Amer. Chem. Soc., 1944, 66, 1113—1114).—From X-ray examination of crystals of CPh₃Cl and CPh₃Br the hexagonal units of structure have a_0 13.97 \pm 0.02 and 13.86 \pm 0.02, c_0 13.17 \pm 0.02 and 13.36 \pm 0.03 A., six mols. per unit cell, space group C_{34}^{-} —H3 or C_{3}^{-} —H3. The halogen atoms have been approx. located. W. R. A.

Fine structure of polyamide fibres. K. Hess and H. Kiessig (Naturwiss., 1943, 31, 171).—The condensation products of $NH_{s}\cdot[CH_{s}]_{e}\cdot NH_{2}$ with adipic acid (polyamide HA) and with e-aminohexoic acid (polyamide eA) have been investigated. Very intense reflexions on the meridian were observed. They appear to be characteristic of this class of substance. The lattice-plane distance of the length period is ~74 A. for HA and eA; for fibres from poly- ω -hydroxyudecoic acid it is 79 A., and for those from poly- ω -hydroxyudecoic acid, 65.5 A. For fibres from OH-acids the reflexions are weaker than from polyamide fibres. The identity periods, I_{p} , are 16.5 A. for HA, and 16.8 A. for eA, in good agreement with the calc. length of the fundamental group. If the stretched polyamide threads are heated the lattice plane distance is irreversibly increased to 95 A. for HA and 120 A. for eA, at 210°. A. J. M.

Relation between structure of polyamides and that of silk fibroin. R. Brill (Z. physikal. Chem., 1943, **B**, 53, 61—74).—The val. of 2:3 A., calc. by Nowotny and Zahn (A., 1942, I, 354), from their experimental data, for the O-N distance (H-bond) in polypeptides is corr. by unpublished data of Brill, Hermann, and Peters to 2:85 A. X-Ray examination of polyamides gives for the unit cell a 9.66, b 8:32, c 17:2 A., γ 65° (a = distance between alternate zigzag chains). Comparison with data for silk fibroin (Kratky and Kurikama, A., 1931, 415) suggests that the structure of the latter is similar, with an extension of the *b* distance to accommodate side-chains, and lateral connexion of the zigzag chains in the *ac* plane by H-bonds between amide-N and carbonyl-O atoms, as in the polyamides and polypeptides. R. C. M.

X-Ray studies of chain polymers. I. Fankuchen and H. Mark (J. Appl. Physics, 1944, 15, 364-370).—Consideration is given to the small-angle scattering of high polymers and to their X-ray micro-examination. Study of the former for oriented chain polymers

appears capable of indicating the existence of (quasi-)periodic heterogeneities perpendicular and (sometimes) parallel to the axis of stretch. The X-ray micro-technique permits the study of local heterogeneities, e.g., of weak spots in rayon yarns or the alteration in the structure of a polyamide fibre in the "necking down" area during drawing. D. F. T.

X-Ray structure of rubber and size and shape of rubber crystallites. S. D. Gehman and J. E. Field (*J. Appl. Physics*, 1944, **15**, 371– 379).—The cross-linked net-work of chain mols. in vulcanised rubber includes segments which locally are sufficiently free to form a crystal lattice on stretching. The crystallites so formed provide automatic reinforcement analogous in effect to that of a reinforcing filler. X-Ray investigation indicates that the size distribution of the crystallites is heterogeneous and includes small crystallites which broaden the base of the diffraction peaks and that a high degree of crystallinity is associated with small crystallite size. Increase in the proportion of combined S appears to limit crystallite growth but the widening of the diffraction. D. F. T.

Electron-microscopy of rubber latex and fibres.—Scc B., 1944, II, 296.

Lipins of tubercle bacilli. LXVI. Structure of tuberculostearic acid.—See A., 1944, II, 319.

Electronographic investigation of the structure of lead iodide. Z-Pinsker, L. Tatarinova, and V. Novikova (Acta Physicochim. U.R.S.S., 1943, 18, 378—386).—The investigation has established the existence of two modifications. PbI₂ obtained by crystallisation from aq. solutions belongs to the space-group D_{3d}^{s} with one mol. per unit cell, and cell dimensions $a \ 4.54$, $c \ 6.90$ A. PbI₂ obtained by sublimation belongs to the space-group D_{3d}^{s} with 3 mols. per unit cell and $a \ 4.54$, $c \ 20.7$ A. At. parameters are given. C. R. H.

Electron-microscopic study of dextran molecules. B. Ingelman and K. Siegbahn (*Arkiv Kemi, Min., Geol.,* 1944, **18**, **B**, No. 1, 6 pp.). —A dil. lextran solution dried on zapon lac foil shows a branched thread-like structure with magnification 65,000 diameters. The threads have a min. thickness 30—100 A., with swellings at intervals of ~800 A. The observed thickness is of the order expected for the polysaccharide chains. L. J. J.

Magnetisation of polycrystalline iron and iron-silicon alloys. G. C. Richer (*Iron and Steel Inst.*, Sept., 1944, *Advance copy*, 50 pp.).—A survey has been made of the competency of the domain theory of ferromagnetism to account for the observed characteristics of such material. This theory is described and its relations to the virgin magnetisation curve of single crystals, the magnetisation curve of polycryst. aggregates, and the cyclic magnetisation and the hysteresis effect are discussed. It is concluded that the basic theory can provide reliable guidance for industrial effort, though unexplained discrepancies between theory and observations exist. A new method has been evolved for analysis of the technical magnetisation curve. T. D. F.

Hysteresis of polycrystalline ferromagnetics in weak magnetic fields. E. Kondorski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 30, 603—607).—In extension of previous work (A., 1940, I, 200) an approx. theory of hysteresis of polycryst. ferromagnetic substances is developed, account being taken of the magnetic interaction between the separate parts. Equations obtained for hysteresis work agree with those of Rayleigh. A. J. M.

Magnetostriction of polycrystals. K. V. Vladimirski (Compt. rend. Acad. Sci. U.R.S.S., 1943, 41, 10–13).—It is shown that the microscopical magnetostriction of polycrystals can be expressed in terms of the free strains as the vol. average with a weighting factor representing the stress at a given point of the body when extended by the forces applied at the external surface. As an example the longitudinal magnetostriction of polycryst. Fe between its demagnetised state and saturation is calc. L. J. J.

Discharges in rock-salt crystals. A. A. Vorobiev (Compt. rend. Acad. Sci. U.R.S.S., 1940, 26, 772—774).—The spreading of an electric discharge through crystals owing to the presence of mechanical strains has been investigated. Spreading of the discharge does not occur within parts of the crystal subject to pressures approaching those causing fracture. The discharge proceeds along the boundary between the strained and unstrained parts in the direction of the greatest gradient of strain. Discharges in crystals with regions of different concn. of free electrons were also studied. The length of the discharge in the part of the crystal which has an increased concn. of free electrons is about twice as great as that in the original crystal. The path of the discharge is more branched, and the discharge is stronger. The breaking up of the crystal along the path of the discharge is also more marked. When the point electrode is positively charged the path of the discharge follows the crystallographic axes, and is unaffected by an applied electric field. When the point is negative, the direction of the discharge is less definite, and is more easily affected by the application of an electric field.

A. J. M.

Form of the first Brillouin zone in the case of hexagonal structure of nickel arsenide type. E. S. Makarov (Compt. rend. Acad. Sci. U.R.S.S., 1943, 40, 191—193).—The low or negative temp. coeff. of electrical conductivity in Fe-Ni-Sb alloys with Ni arsenide structure implies nearly complete filling up of the Brillouin zone, which should include ~2.5 electronic states per atom. Data from powder photographs show that the shape of the Brillouin zone is a combination of 3 types of plane, (022-112), (200-130), and (002), with vol. in the K-space $(32a^2 - 2c^2)/3\sqrt{(3a^4c)}$ and $(16a^2 - c^3)/6a^2$ states per atom. Vals. for Fe-Sb (47.1 at.-% Sb), Co-Sb (48.2 at.-% Sb), and Ni-Sb (49.46 at.-% Sb) are 2.402, 2.372, and 2.386 states per atom. Overlapping into the second zone occurs across the (002) plane, and accounts for electrical properties and metallic character. L. J. J.

Inversion of direction of dispersion of anisotropy in some opaque orthorhombic crystals. L. Capdecomme (Compt. rend., 1942, 215, 88-90).—The anisotropy of reflexion of a unicryst. section is the ratio of the two principal reflecting powers. There is an inversion in the direction of the dispersion in the case of some orthorhombic crystals, including enargite, manganite, and stibine. A. J. M.

Debye's transverse heat waves and the scattering of light in crystals. E. Gross (Compt. rend. Acad. Sci. U.R.S.S., 1940, 26, 757-759).— The existence of six components of the Rayleigh line in crystals (cf. A., 1938, I, 175) is discussed. Their origin may be explained by supposing that the two displaced components are due to Debye's longitudinal heat waves, and the four additional components are due to light scattered from two transverse heat waves of the acoustic spectrum of the crystal. This view is confirmed by the determination of the shifts of λ in the displaced components in quartz. The velocities of propagation of the longitudinal and transverse heat waves can be obtained from these displacements, the results being 6400 m. per sec. for the longitudinal, and 3500 and 2800 m. per sec. for the two transverse, waves. These vals are in good agreement with those obtained from the known velocities of propagation of longitudinal and transverse waves along the direction of the crystal which would be taken by the elastic waves scattering the light, calc. from the torsion moduli. The results are also in agreement with the amount of light scattered by crystals, and are confirmed by the work of Michailov on the diffraction of light at high-frequency transverse elastic waves in cubic crystals (see following abstract). A. J. M.

Diffraction of light from high-frequency transverse elastic waves in cubic crystals. I. G. Michailov (Compt. rend. Acad. Sci. U.R.S.S., 1940, 26, 760—763).—The propagation of ultrasonic waves through crystals is accompanied by the formation of longitudinal and transverse waves. Like the longitudinal waves, the transverse waves can also act as a diffraction grating. This effect with transverse waves has been investigated for NaCl and KCl crystals. The torsion moduli of NaCl and KCl cale. from the diffraction agree with the vals. obtained by Voigt (1888) by the static method. Under different conditions of excitation it is possible to observe the diffraction of light from the first and second transverse waves are at right angles to each other. In order to obtain diffraction with both waves simultaneously the crystal must be oriented in such a way that the directions of vibration of the waves make an angle of 45° with the direction of the light. The diffraction phenomena could be observed with comparatively low ultrasonic-wave energies. A. J. M.

Morphology of liquids. IV. Stable, individual liquid crystal structures. G. Weygand (Z. physikal. Chem., 1943, B, 53, 75-84; cf. A., 1944, II, 179).—In p-C₈H₁₇·O·C₆H₄·CH:N·C₆H₄Pr^a-p the following liquid crystal transitions are observed : liquid (85°) \rightleftharpoons nematic I (83°) \rightleftharpoons smectic I (70°) \rightleftharpoons smectic III (54°) \rightleftharpoons smectic III \rightarrow solid (m.p. 54·5°). The smectic III phase is a supercooled liquid. Doubly refracting structures, for which the name "crystalloid" is proposed, separate from a 7% alcoholic solution on cooling. The observations are discussed. R. C. M.

IV.—PHYSICAL PROPERTIES OF SUBSTANCES.

Mol. wt. in high polymers.—See A., 1944, I, 201, 202.

Ferromagnetism of thin layers of nickel. A. Colombani (Compt. rend., 1943, 216, 115-117).—An oscillograph method (cf. A., 1940, I, 176) has been used to study the ferromagnetism of thin layers of Ni. Unannealed layers have a very weak ferromagnetism, with very slight hysteresis. X-Ray analysis indicates that these layers are composed of groups of atoms. Layers of thickness <220 mµ., after being heated to 410°, show little change in magnetic properties or in X-ray structure. Between 220 and 360 mµ., the hexagonal structure appears, but there is still only weak ferromagnetism. For thickness >360 mµ., a very strong ferromagnetism is observed, and the structure becomes face-centred cubic. The magnetic properties are related to the electrical conductivities of the layers. A. J. M.

Magnetic studies of chromium oxide catalysts. J. Turkevich (J. Chem. Physics, 1944, 12, 345-346).—No difference in magnetic susceptibility between active Cr oxide gel and "glowed" inactive

Cr oxide is found from -183° to 444° . Activated adsorption of H causes no magnetic change. The active oxide, obtained by interaction of $Cr(NO_3)_2$ with NH₃, is intermediate in composition between Cr₂O₃ and CrO₃. L. J. J.

Magnetic behaviour of potassium cyanonickelite. D. P. Mcllor and D. P. Craig (J. Proc. Roy. Soc. New South Wales, 1943, 76, 281-282).—A new examination of $K_2Ni(CN)_3$ shows that it is diamagnetic with a susceptibility approx. the same as that of $K_2Ni(CN)_4$. The structure of $K_2Ni(CN)_3$ probably involves the ion \subseteq CN CN \neg ¹¹¹ diamagno... The str K₂Ni(CN).. The str ion CN CN -CN·Ni-Ni·CN CN CN -

C. R. H.

Magnetic properties of porous substances. C. Courty (Compt. rend., 1942, 215, 18-20).—The variation of susceptibility of porcelain and activated C in passing gradually from an atm. of dry air to one saturated with H_2O vapour, and then when completely immersed in H_2O , has been investigated. The additive rule applies to porce-lain and H_2O . With coconut C in bulk the rule does not apply, but when the substance is powdered it holds well. Non-activated C is diamagnetic, but after activation with H₂O or CO₂ it is paramagnetic. It is shown that the physical consts. of air adsorbed by C are different from those of free air, and that there is a difference between the nature of the porosity of porcelain and that of C.

A. J. M.

Diamagnetic anisotropy of crystalline liquids. V. Zvetkov an A. Sosnovski (Acta Physicochim. U.R.S.S., 1943, 18, 358-369). V. Zvetkov and Measurements of the diamagnetic anisotropy of *p*-methoxycinnamic acid, *p*-azoxy-anisole and -phenetole, di-*p*-acetoxybenzylideneazine, anisylidene-azine and -p-aminoazobenzene, and dibenzylidene- and dianisylidene-benzidine are recorded. The data support the view that magnetic anisotropy is essentially determined by the no. of $C_{0}H_{0}$ rings in the mol., observed discrepancies being due possibly to anisotropy of non-aromatic groups. C. R. H.

Propagation of sinusoidal thermal waves in a heterogeneous medium. M. Parodi (*J. Phys. Radium*, 1944, [viii], 5, 23-24).— Mathematical. W. R. A.

Optical properties of very thin layers of chromium obtained by thermal projection. M. Perrot (*Compt. rend.*, 1943, 216, 38-40).--Reflexion and transmission coeffs. of thin films of Cr obtained by cathodic sputtering on to glass surfaces indicate that the film is an oxide layer. By thermal projection in vac., films of pure Cr were obtained, and the coeffs. of reflexion from air-metal and glassmetal interfaces, and the coeff. of transmission, were obtained. The min. coeff. of reflexion from glass-metal occurs for a thickness of metal varying with λ . The coeff. of reflexion for air-metal shows a max. followed by a min. as thickness increases, at all $\lambda\lambda$. The vals. obtained are quite different from those for the oxide film.

A. I. M.

Variations of phase on normal reflexion from very thin layers of chromium obtained by thermal vaporisation. M. Perrot (*Compt.* rend., 1943, 216, 150—152).—There is a change of phase on reflexion from very thin layers of Cr deposited on quartz. In addition to the variation of phase difference with thickness of the film, there is a jump in phase of 2π for films of thickness 15-20 m μ . A. J. M.

Optical constants of tungsten and antimony determined by reflected polarised light. L. M. Chatterjee and K. N. Prasad (*Current Sci.*, 1944, **13**, 177-178).—Optical consts. of Sb and W in the range 4600-6600 A. have been measured. By using specimens hand-polished to different extents, the effect of polishing has been in-vestigated. vestigated. W. R. A.

Small-angle interference of myosin.—See A., 1944, III, 746.

Specific heats of hydrocarbon gases.-See B., 1944, I, 356.

Heat capacity of carbon tetrachloride from 15° to 300° K. Heats of transition and fusion. Entropy from thermal measurements compared with the entropy from molecular data. J. F. G. Hicks, J. G. Hooley, and C. C. Stephenson (J. Amer. Chem. Soc., 1944, 66, 1064–1067).— C_p vals have been determined calorimetrically for CCl₄ from 17.09° to 298.49° K. The m.p. is $250.3 \pm 0.1°$ K. and there is a transition point at $225.35 \pm 0.03°$ K. Heats of transition and fusion are 1095 ± 3 and 601 ± 2 g.-cal. per mol. Vals. of entropy from calorimetric data are: liquid $51\cdot25\pm0\cdot15$; gas $73\cdot7\pm0\cdot3$ g.-cal. per degree per mol. at $298\cdot19^{\circ}$ K. The vals. are compared with those derived from mol. data (74·0—74·3 g.-cal. per degree per mol.). W. R. A.

Heat capacity and entropy, heats of fusion and vaporisation, and vapour pressure of trimethylamine. Entropy from spectroscopic and molecular data. J. G. Aston, M. L. Sagenkahn, G. J. Szasz, G. W. Moessen, and H. F. Zuhr (J. Amer. Chem. Soc., 1944, 66, G. W. Moessen, and H. F. Zuhr (*J. Amer. Chem. Soc.*, 1944, 00, 1171–1177).—C_p has been measured calorimetrically from 11.88° to 275.90° k. for NMe₃ (m.p. 156.08±0.05° k.; b.p. 276.03±0.05° k.). The v.p. determined from 190° k. to the b.p. can be represented by $\log_{10} P$ (mm.) = -2141.7743/T -11.400327 $\log T$ +0.006349001T +36.715267. The heats of fusion and vaporisation (at b.p. and at 250.00° k./250.01 mm.) are 1564.0±1.0, 5482.4±7, and 5822.6±7 g.-cal. per mol. Vals. of vapour density fit the equation

 $\rho/P = 0.000079051P + 0.00241364$. The following entropy (S)vals. were derived from calorimetric data: liquid at m.p. 30.867 ± 0.09 ; liquid at normal b.p. 47.28 ± 0.14 ; superheated liquid at 298.16° x. 49.82; ideal gas at 200.00°, 250.00°, and the b.p. 61.60 ± 0.14 , 65.39 ± 0.16 , 67.31 ± 0.19 g.-cal. per degree per mol. An assignment of the Raman spectrum has been made and the vals. of S from spectroscopic data are: 200° K., 61.60; 250° K., 65.39; b.p., 67.31 g.-cal. per degree per mol. W. R. A. b.p., 67.31 g.-cal. per degree per mol.

Apparent second-order transition point of polystyrene. T. Alfrey, G. Goldfinger, and H. Mark (J. Appl. Physics, 1943, 14, 700-705). -At > 80° the sp. vol. (dV/dT) of polystyrene (I) is 0.00043, whilst at <40° it depends on the past thermal history and is 0.00024. When (I) is could at a const task it contracts to the bickness. (I) is cooled at a const. rate it contracts to the higher expansion coeff. until some crit. region of temp. and then contracts to the smaller coeff., but the position of the crit. temp. depends on the rate of cooling, being higher at faster rates. Between 40° and 80° complex time effects are observed. Results accord with a "second-order transition point" of (I) as the temp. at which rate of vol. change becomes comparable with the experimental time scale. W. R. A

Specific and latent heats of fusion of vegetable fats and oils .-- See B., 1944, II, 287.

Thermal expansion of concrete aggregate materials.-See B., 1944, I, 368.

Van der Waals' equation of state and the compressibility of molecules. D. B. Macleod (*Trans. Faraday Soc.*, 1944, 40, 439-447; cf. A., 1937, I, 355).—If van der Waals' equation is written P(v - b') = RT, where $P = p + a/v^2$ and $b' = b_0(1 - BP + CP^2)$, satisfactory consts. can be found for a no. of typical org. fluids when $b'_c \sim v_c/2$. Substituting this val. of b'_0 in the equation for the arit with a core baseds directly from ord data and $(P + a/v^2)$ the crit. point a can be calc. directly from crit. data, and $(P + a/v^2)$ can thus be obtained from experimental vals. of p and the corresponding mol. vols. If the consts. B and C are now used to calculate b', the resulting vals. of RT/(v-b') are found to agree closely, for CO₂ at the crit. temp., with those of $(p + a/v^3)$ obtained as described. Hence b' can be expressed very accurately as a function of P when b'_o = $v_c/2$, but not if $b'_o = v_c/3$ as required by the simple form of the equation. Corresponding vals. of P and RT/(v-b') are tabulated for CCl₄, n-C₅H₁₂, and C₆H₆, for both liquid and vapour phases, and good agreement is shown over a wide range of temp. Vals. of the consts. a, b_0, B , and C are given for these substances and for CO₂ and Et₂O. It is claimed that b_0 represents the mole value of the moles in the extreme gaseous conthese substances and for 60°_{2} and 12°_{20} . It is channel in the optimized in the extreme gaseous condition; the val. of b' undergoes changes of 30-40% in passing from the vaporous to the liquid state. These changes may represent an actual compressibility of the mols. For elementary substances and those for which the val. of $RT_o/p_{0}v_{0}$ lies between the theoretical 2.67 and the more usual 3.8, $b'_{0} = v_{0}/2$ no longer gives satisfactory results, and a suitable val. must be found by trial. Thus for H_2 , $b'_e = 0.36v_e$. F. L. U.

Thermal and electrical conductivity of graphite and carbon at low temperatures. R. A. Buerschaper (J. Appl. Physics, 1944, 15, 452-454).—The transverse and longitudinal thermal conductivities of graphite are measured in the range 191-100°; they show an increase with decrease in temp., the latter being about half the val. of the former. The electrical conductivities show a decrease with decreasing temp., the former having again the larger val. For C both thermal and electrical conductivities show a decrease with J. H. BA. decreasing temp.

decreasing temp. **Viscosity of hydrogen fluoride.** J. H. Simons and R. D. Dresdner (J. Amer. Chem. Soc., 1944, 66, 1070-1072).—Details are given of a viscometer suitable for determining η of HF between -70° and 10° (see C., 1944, 204). η has low vals. (approx. the same as Et_2O in the same temp. range) which are raised greatly by small amounts of EtOH. W. R. A.

Applicability of the principle of similitude of H. Kamerlingh Onnes to prediction of the magnitude of viscosity. M. Trautz (J. pr. Chem., 1943, [ii], 162, 218-223).—Mathematical. W. R. A.

Reynolds number and liquid helium II. D. V. Gogate (Current Sci., 1944, 13, 177).—Since the flow of liquid He II is independent W. R. A. of pressure, the Reynolds no. should be const.

Viscosity of mercury under the action of a magnetic field. G. Destriau and G. Massieu (*Compt. rend.*, 1942, 215, 64-65).—In a method in which the effect of Foucault currents was reduced to a min., η of Hg in very fine tubes was found to increase with increasing magnetic field strength, up to a max. at 13,500 gauss. Under these conditions η is 7% > normal. A. J. M.

V.—SOLUTIONS, DISPERSIONS, AND MIXTURES.

Thermal diffusion of gases. Method of Clusius and Dickel. A. Fournier (J. Phys. Radium, 1944, [viii], 5, 11-16; cf. A., 1938, I, 539).—Theoretical. An elementary theory of the thermal diffusion of gases, which takes into account only the mass of the mols., is given. The influences of factors other than mol. mass predominate in thermal diffusion of mixtures of gases of equal mol. mass. W. R. A.

Thermal diffusion in liquids. H. Carr (J. Chem. Physics, 1944, 12, 349).—A thermal diffusion tube $1.59 \times 0.057 \times 100$ cm., with temp. difference 49° between upper and lower sides, shows concn. differences increasing with time between samples from top and bottom. $ZnSO_4$ (0.6M.) showed concns. differing by a factor of 17.1 after 12 hr. when the tube was inclined at 45°. The max. effect after 2 hr. was given with 45° inclination and concn. 0.6M.

Viscosity of aqueous solutions of calcium chloride at 35°. T. Patnaik and B. Prasad (J. Indian Chem. Soc., 1944, 21, 125—126). $-\eta$ and d data for 0.001—0.05M-CaCl₂ are recorded. The η data obey the Jones-Dole equation.

Viscosity and vapour pressure of dilute solutions. II. Relation between viscosity and vapour pressure. H. G. de Carvalho (Anais Assoc. Quim. Brasil, 1944, 3, 88-94).—It is deduced that the re-Assoc. Quim. Brasil, 1944, 3, 88–94).—It is deduced that the re-lationship between viscosity (η) and v.p. (p) is $p\eta^{\alpha} = k$, where a is a const. for each substance and varies with temp. This relation combined with Raoult's law gives $\eta = \eta_0(1 + n/N)^{1/\alpha}$ (η_0 applies to the solvent, n and N are g.-mols. of solute and solvent), which is applicable to glycerol up to 7% concn. Osmotic pressure is thence $(aRT \log \eta/\eta_0)/V_0$ and mol. wt. of the solute is $M_0 w \eta_0^a / W(\eta^a - \eta_0^a)$, where V_0 is the partial mol well of solvent in the solution and W where \mathcal{V}_0 is the partial mol. vol. of solvent in the solution, and \mathcal{W} is the no. of g. of solvent of mol. wt. M_0 containing w g. of solute. F. R. G.

Molar friction coefficients in solutions of associated and solvated substances with special reference to diffusion theory. O. Lamm (Arkiv Kemi, Min. Geol., 1944, 18, A, No. 10, 11 pp.).—The friction coeffs. (mean friction per g.-mol.) are considered in the case of a two-component system where one component diffuses into more dil. solution. Under ideal conditions the mean friction coeff. in the case of diffusion agrees with that calc. from sedimentation velocity. There is also agreement between diffusion and ionic mobility, as required by the Nernst theory of diffusion. A. J. M.

Theory of diffusion with special reference to characteristic diffusion. O. Lamm (Arkiv Kemi, Min., Geol., 1944, 18, B, No. 5, 8 pp.).-The characteristic diffusion of two- and three-component systems should be independent of the proportions of the mixture, although this is not directly established by the author's theory. Elementary statistical considerations are now shown to lead to the expected results. A. J. M.

Charge effect in sedimentation and diffusion determinations and determination of mol. wt. of high-molecular metaphosphates. O. Lamm (Arkiv Kemi, Min., Geol., 1944, 18, A, No. 8, 7 pp.) .- The charge on the high-mol. metaphosphate ion when completely dissociated is very high, and can give rise to anomalies in vals. of the sociated is very high, and can give rise to anomalies in vals, of the mol. wt. calc. from sedimentation and diffusion observations. The conductivities of 0.4M-NaCNS (I), (I) + 0.547% of K meta-phosphate (corresponding to 0.0463M-KPO₃), and (I) + 0.0463M-NaCNS were determined. The increase in conductivity for the KPO₃ was 0.12×10^{-2} , whilst that for the equiv. addition of NaCNS was 0.25×10^{-2} . The KPO₃ has mol. wt. ~160,000 and is 0.33dissociated. The effect of charge is considered, and the correcting factor is calc. Although it cannot be neglected it does not greatly affect the calc. val. of the mol. wt. A. J. M.

Theory of diffusion of ternary solutions. O. Lamm (Arkiv Kemi, Min., Geol., 1944, 18, A, No. 2, 10 pp.).—Complete differential equations for diffusion in a three-component system are derived.

L. J. J. K. Light absorption of nickel acetate and nickel perchlorate. K. Veeraiah and M. Qureshi (J. Indian Chem. Soc., 1944, 21, 127–130).—Ni(OAc)₂ solutions show continuous absorption in the violet region with a max. in the red at \sim 715 m μ . Dilution increases the mol. extinction coeff. especially in the region of max. absorption, although the position of the max. is unchanged. Ni(ClO₄)₂ solutions show similar characteristics but the max. in the red shifts to lower wave lengths on dilution. C. R. H.

Interferometric studies of light scattering in binary liquid mixtures. II. K. S. Bai (*Proc. Indian Acad. Sci.*, 1944, **20**, **A**, 18–23).—The scattering of light by 7 PhOH-H₀O mixtures has been examined spectro-interferometrically. For mixtures containing 15, 28, 34, and 60 with 90 PhOH Phillouin components are there the distinguishing the second spectro second and 60 wt.-% PhOH Brillouin components are absent, indicating the presence of mol. clusters of size comparable with the λ of light, whilst in mixtures containing 10, 70, and 80 wt.-% PhOH Brillouin components are present, weakly at 80° and more pronounced at higher temp., indicating the breaking up of large clusters to smaller groups. The tendency to form mol. clusters was greatest at the crit. composition, in agreement with other optical data. W. R. A.

Dielectric polarisation of solid organic molecular compounds.—See A., 1944, I, 267.

Analysis data for ternary system acetone-benzene-water. E. Honold and H. Wakcham (Ind. Eng. Chem. [Anal.], 1944, 16, 499-E. 501).—n and d of mixtures in the homogeneous region of the system

have been determined at 25°. Lines of equal n and of equal d are plotted on a triangular diagram against composition of the mixture. The graph enables the composition of a homogeneous mixture to be read off if the n and d at 25° are known. Cloud point compositions at 25° may also be derived. F. Hu.

Supersaturation limits of solutions. II. R. Gopal. III. R. Gopal and A. C. Chatterji (*J. Indian Chem. Soc.*, 1944, 21, 103–108, 145–147).—II. The investigation reported previously (cf. A., 1943, I, 302) has been extended to K_2SO_4 , $K_2Cr_2O_7$, $K_3Fe(CN)_8$, $K_4Fe(CN)_8$, K_2CrO_4 , and $HgCl_2$. The vals. of $\lambda(T_s - T)$, where λ = heat of dissolution, T_s = saturation temp., and T = temp. of first spontaneous crystallisation, vary considerably from the val. 80,000 g.-cal. found for univalent K and Na salts. On the other hand $\lambda(T_s - T)gV_s$, where g = sp. surface energy and V_s = mol so,000 g.-cal. found for univalent K and Na saits. On the other hand, $\lambda(T_s - T)\sigma V_m$, where $\sigma = \text{sp. surface energy and } V_m = \text{mol.}$ vol., is reasonably const. (~13.0), *i.e.*, for substances with V_m vals. approx. equal, the limit of supersaturation $(T_s - T) \propto 1/\lambda$. From the relation $\lambda(T_s - T)/\sigma V_m = 13.0$ the radius (r) of the stable crystal nucleus has been calc. Its val. increases from 1.0×10^{-6} to 1.13×10^{-6} cm. as T_s increases from 10° to 40° . If T_s for a given relate is large const. $\tau(T_s - T) = \text{corect}$ solute is kept const., $r(T_s - T) = \text{const.}$

III. From a consideration of the Jones-Partington equation it has been shown that vals. of λ at ordinary temp. can be substituted for vals. at abs. zero (λ_0) in the derived equation $\lambda_0(T_s - T) = 2M\sigma T_s/\rho r$ where M and ρ have their usual significance.

C. R. H. Solid solutions of calcium and strontium orthosilicates. N. A. Toropov and P. F. Konovalov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 40, 155-157). — d_1^{20} and *n* data for solid solutions in the system Ca₂SiO₄-Sr₂SiO₄ are recorded. The solid solutions exist in a con-C. R. H. tinuous series.

Polymer chemistry of silicates, borates, and phosphates. S. B. Hendricks (J. Washington Acad. Sci., 1944, 34, 241-251).-An address. Patterns in which silicate, phosphate, and borate groups combine to form polymers are illustrated and discussed. The formation of a complete series of solid solutions between Ba2Si3O8 and $Ba_2Si_4O_{10}$ is explained as being due to addition of SiO_2 to the $(Si_3O_3''')_n$ chains of $Ba_2Si_3O_3$ to give the sheet polymer $(Si_4O_{10}''')_n$ of $Ba_2Si_4O_{10}$. An illustration of the possible structural relation between cryst. B_2O_3 and cubic HBO₂ is given. Discussion of the types of silicate systems in which liquid immiscibility occurs shows that immiscibility results from mutual insolubility of space and sheet polymers arising from their greatly different configurations. C. R. H.

System boron oxide-beryllium oxide-lithium oxide in glassy state. (Glasses transparent for X-rays.) L. J. Mazelev (J. Appl. Chem. Russ., 1940, 13, 1288—1303).—46 systems containing 2.5—15 wt.-% of BcO and 2.5—25% of Li₂O were examined. Transparent glasses are obtained at BeO <13% when the wt. ratio Li₂O: BeO is ~1 to 3. The softening interval of these glasses is very short; the softening temp. is ~440° for large [Li] and ~500° for small [Li]. d is the larger the smaller is [B], and is raised by Li more than by Be. Resist-ance to H₂O is small. it increases with [Bel and is lowered by B more ance to H₂O is small; it increases with [Be] and is lowered by B more than by Li. Thermal expansion increases with temp. and is the smaller the larger is [B]. n (1.52-1.57) is lowered by B and raised by Li. The crystals obtained on devitrification of the glasses had a com-position near 2BeO,B₂O₃. The glasses BeO 14.08, Li₂O 17.56, B₂O₃ 68.36 wt.-% and BeO 11.95, Li₂O 17.82, B₂O₃ 70.23 wt.-% are recommended for windows in X-ray tubes. J. J. B.

Thixotropy in silver amalgams. D. R. Hudson (Physical Rev., 1944, [ii], 65, 247-248).—There are small but definite peaks at 15% and 28% Ag in the density-composition curve. The sp. vol.composition curve consists of straight lines intersecting at min. to inposition the vector sites of straight lines intersecting at 13% and 25%; thus the partial sp. vols. are const. for both components over corresponding ranges of composition. Amalgams containing > 8% of Ag are quite fluid although they are heterogeneous, the solubility of Ag in Hg being 0.03% at room temp. Over the range 8–20% Ag the amalgams are plastic, and set hard on keeping, but the hardened material recovers its plasticity on kneading. Possible explanations of this thixotropic effect are N. M. B. discussed.

superstructures but gives results inconsistent with Cu-Mn binary alloy equilibrium systems. Slowly cooled and annealed samples both show a series of continuous Cu-Mn solid solutions, showing a face-centred cubic lattice with a parameter increasing with [Mn] from 0 to 60%. With 60-90% Mn the lattice is face-centred tetragonal. With 90-100% Mn the system shows a solid solution with 90% Mn, and an a-Mn phase. L. J. J.

Carbides in the iron-manganese-carbon system. E. Ohman (Jernkont. Ann., 1944, 128, 13-16; Bull. Iron Steel Inst., 1944, No. 102, 60A).—An X-ray study made by the author in 1926 of the carbides present in the above system revealed a hitherto unknown double carbide of Mn and Fe which has a monoclinic crystal structure. By dissolution of C in molten Mn carbides are produced which, according to X-ray powder photographs, are isomorphous with the Cr carbides $Cr_{23}C_6$ and Cr_7C_8 . As the powder photographs are in exact agreement with those obtained for the above Cr carbides the Mn carbides probably have the formula $Mn_{23}C_6$ and Mn_7C_8 . The latter has been observed only in alloys with >80% Mn, whilst $Mn_{23}C_6$ is found with up to 50% Fe and <6% C present. With >50% Fe cementite is the only carbide formed. Both cementite and $Mn_{23}C_6$ are present even when the Mn content is up to 70%. Mn can replace Fe in cementite to a considerable extent.

R. B. C.

Iron-nickel-aluminium-copper alloys with preferred magnetic orientation. W. Jellinghaus (Arch. Eisenhüttenw., 1943, 16, 247-251; Bull. Iron Steel Inst., 1944, No. 102, 54A).—A quinary Fe alloy containing Al 8—9, Co 23, Cu 3, and Ni 15% heat-treated in a magnetic field with subsequent tempering has preferred magnetic orientation and is the best known permanent-magnet material. A study was made of the structure and magnetic properties of a no. of alloys of the above composition except for Al, which varied between 5.7% and 16.7%. Specimens from all melts had as principal constituent one with a cubic body-centred structure. At the lower end of the Al range austenite was also present; only with the highest Al content was a cubic body-centred phase with superstructure observed. The temp.-coercivity relation showed that the intermediate, apparently homogeneous, structure consisted of > one phase. The explanation of the permanent magnetism is the same as that in the case of ternary Fe-Ni-Al alloys. Heattreatment in a magnetic field is effective only within a certain range of composition which is characterised by homogeneous solidification, a high Curie point, and the proximity of the solubility limit of austenite. R. B. C.

Solubility of hydrogen in molten copper-tin alloys.--See B., 1944, I, 373.

Setschenov's rule and the solubility of hydrogen sulphide in hydrochloric acid solutions. A. F. Kapustinski and B. I. Anvaer (Compt. rend. Acad. Sci. U.R.S.S., 1941, 30, 625-628).—The solubility of H_2S in HCl of concn. 16:5-34:9% has been determined. The results agree satisfactorily with the equation of Setschenov, $s = s_0 e^{-k\varepsilon}$, where $s_0 =$ solubility of gas in H_2O , s = solubility in electrolyte, and c = concn. of electrolyte. The solubility does not pass through a min. The solubility of H_2S in HCl solutions of ZnCl₂ and FeCl₂ has also been determined. ZnCl₂ causes an increase and FeCl₂ a decrease in the solubility. A. J. M.

Solubility of lithium carbonate. (Mlle.) L. Lagarde (Compt. rend., 1943, 216, 156–158).—The solubility of Li_2CO_3 in the presence of Li' and of CO_3'' has been determined by finding the solubility in presence of LiCl and of Na_2CO_3 . Addition of Li' gives an almost const. solubility product. The addition of CO_3'' affects the solubility of $\text{Li}_2\text{CO}_3 \ll \text{does that of LiCl}$. A. J. M.

Properties of freshly formed surfaces. II. Rate of adsorption of isoamyl alcohol at air-water surface. C. C. Addison (J.C.S., 1944, 252-256).—The vibrating jet technique (C., 1944, 43) has been used to study the rate of establishment of surface equilibrium of iso-C₆H₁₁·OH (I)-H₂O mixtures at air-liquid interfaces at 20°. From the variation in the lengths of successive waves in the jet the variation of the (I) mols. to the surface cale. as ~8.5 × 10⁻⁴ cm. per sec. The slight decrease in this velocity with increasing concn. is attributed to mutual interference between migrating mols. Surface equilibrium is established in <0.025 sec. and ~0.01 sec. in 0.122 and 0.812% solution, respectively. J. W. S.

Properties of freshly formed surfaces. III. Mechanism of adsorption, with particular reference to the sec.-octyl alcohol-water system. C C. Addison (J.C.S., 1944, 477–480).—The dynamic surface tension of aq. solutions of sec.- C_8H_{17} ·OH and the mean velocity (V) at which the alcohol mols. migrate to the surface have been determined. Surface ages ranged from 0.01 to 0.12 sec. The mean val. of V is > the val. for iso- C_8H_{17} ·OH (cf. supra) and is independent of concn. The variations of V with the distance of the mol. from the surface and with the free energy of the surface are discussed. The free energy of the surface is shown to be the major factor determining V, the distance of the mol. from the surface being insignificant.

Adsorption in relation to constitution. III. Adsorption of carbohydrates from aqueous solutions by charcoal. B. P. Gyani (*J. Indian Chem. Soc.*, 1944, 21, 79–82).—The adsorption by activated C of sugars from aq. solution is \gg with SiO₂ gel. The adsorption coeff. increases in the order arabinose < xylose < fructose < glucose <galactose < mannose < rhamnose < sucrose < maltose, adsorption coeffs. of sugars of the same family being close together. Rhamnose shows anomalous behaviour since with a lower mol. wt. than the hexoses it should have a lower coeff. than the latter. The coeffs. for tri- and poly-saccharides are high (100% for maltin) and conform to the general rule that adsorption increases with mol. complexity. C. R. H.

Kinetic studies of adsorption of phenol by activated carbon in packed towers. A. F. Tesi (Univ. Pittsburgh Bull., 1944, 40, 303— 310).—Adsorption of PhOH from its aq. solution by active C follows the Freundlich isotherm. In continuous flow through towers, the Schumann-Furnas treatment of heat transfer can be applied to transfer of PhOH. A const. mass-transfer coeff. is obtained over a wide range of conditions. L. J. J.

Efficiency of exchange, vapour pressure isotherms, and heats of wetting of technical hydrogen-ion exchangers. M. Trautz and H. Nienhaus (*J. pr. Chem.*, 1943, [ii], 162, 181–217).—The efficiency of exchange of H^{*} with Na^{*}, K^{*}, Mg^{**}, Ca^{**}, and Ba^{**} solutions, and the dependence of the v.p. of H₂O over the solid and ΔH of wetting on the H₂O content of 3 commercial exchangers, have been determined. W. R. A.

Thermodynamics and statistics of zeolitic solid solutions. R. M. Barrer (*Trans. Faraday Soc.*, 1944, 40, 374—384).—Occlusion isotherms are derived for solid solutions of the zeolitic type in which the occluded mols. possess various degrees of mobility within the lattice. Standard free energies and entropies of occlusion are calc., and compared with these quantities derived from experimental data. For various gas-zeolite systems, and for H₂-M systems (M = Ti, Zr, Th, V, Pd), good agreement between experimental and calc. quantities is found if the occluded mols. or atoms are treated as three-dimensional oscillators; in these systems the possibility that any large fraction of the occluded mols. possesses even one degree of translational freedom is excluded. When long-chain mols. are occluded there is loss of three translational and three principal rotational degrees of freedom, and of numerous possible gas-phase configurations. A thermodynamic criterion for the formation of new phases is given. F. L. U.

Surface tension of solutions. I. A. A. Shuchovitzki (J. Phys. Chem. Russ., 1943, 17, 313-317).—If the mol. fraction of the solute is N, the surface tension of the solution is $\gamma_0 - RTn \log_e[1 + N(C - 1)]$, γ_0 being the surface tension of the solvent, n a function of the size of the mol., and C the work of displacing a mol. of solvent by a mol. of solute in the surface layer, which is supposed to be unimol. I. I. B.

Calculation of the surface energy of non-polar substances from the heat of sublimation. R. Fricke (Z. physikal. Chem., 1942, B, 52, 284—294; cf. A., 1943, I, 86).—A method is given for calculating the total and free surface energies of the various surfaces of a nonpolar crystal from the surface energy obtained by Volmer *et al.*, from heat of sublimation at abs. zero. A special form of the third law of thermodynamics is developed for a series of cases, and the surface energies of a large no. of surfaces of metal crystals are evaluated. The total surface energy is const. over the whole range of accuracy of Dulong and Petit's law, and the free surface energy varies linearly with temp. over this range. A. J. M.

Rate of rise of water in capillary tubes. W. A. Rense (J. Appl. Physics, 1944, 15, 436-437).—Assuming the flow to be turbulent, the rate equation for the rise of H₂O in a capillary tube is derived, viz., $z = k_1 + k_2 \log t$ (z = height, k = const., t = time). This agrees with measurements obtained by photographing the rise in stroboscopic light, except for points near the end of the rise when turbulence ceases. The possibility of determining the Reynolds no. dynamically from such observations is indicated. J. H. Ba.

Formation of bubbles. R. B. Dean (J. Appl. Physics, 1944, 15, 446-451).—The efficiency of various substances as nuclei for the formation of gas bubbles is said to be due to the presence of absorbed or trapped gases. It is shown experimentally that many surfaces, when treated to remove such gases, lose their ability to form bubble nuclei. The very low pressures or high superheating necessary to produce gas bubbles in H_2O are compared with the ease of formation by mechanical shock or turbulent flow. Pressure-lowering in sound waves produced by shock is not sufficient to cause cavitation and hence bubbles, and it is suggested that disturbances give free vortices which produce sufficient tension to rupture the liquid.

I. H. BA.

Wetting and swelling of graphite. P. Tschugunov and B. Bruns (Acta Physicochim. U.R.S.S., 1943, 18, 351-357).—Measurements of the contact angle (a) of H_2 bubbles on the surface of polished graphite under $n-H_5O_4$, -KCl, -KBr, -KI, -NaOH, and -Na₂SO₄ show that a_{max} occurs when the polarisation of the graphite is ~ -0.2 v. referred to the Hg₂Cl₂ electrode. The highest val. of a is 36° (in H₂SO₄) and the lowest 21° (in NaOH), the val. in the salt solutions being $\sim 28^\circ$. Graphite was treated with a mixture of H₂SO₄ and HNO₃ and excess of acid washed out of the swollen graphite. The amount of O_2 evolved on immersion in alkali is equiv. to the amount of fixed H₂SO₄, assuming the formation of an acid salt. Similar results are obtained by anodic oxidation of graphite in 50% H₂SO₄. C. R. H.

Surface viscosity and the structure of monolayers of higher alcohols. A. A. Trapeznikov (Compt. rend. Acad. Sci. U.R.S.S., 1941, 30, 321-326).— η of an octadecyl alcohol (I) monolayer was determined at various temp. The formula of Fourt and Harkins (A., 1938, I, 615) for η determined by a disc viscometer requires correction as the monolayer entrains measurable quantities of the substrate. The surface pressure (F) was also determined. The curves of η against F are given for monolayers of (I) on 0.01N-HCl, 0.01N-NaCl, and H₂O at different temp. The curves of F against area per mol. (a) are also given. Since the F-a curves do not change their form to any great extent over a 10° range, it might be expected that the η -F curves would take identical courses at different temp. There is, however, a great difference in the form of the η curves at temp. between 15° and 22°. At low temp. the abs. η in the "solid" condensed state region (F > 13.4 dynes per cm.) is < in the "liquid" state region (F < 13.4 dynes per cm.). η varies with F in a similar manner in both regions. After passing through a max. η rapidly decreases. The relation between F and η is very nearly linear for F > 13.4 dynes per cm. and at the lower temp. The position of the max. in the two pressure regions varies with temp. The divergence between contraction and expansion curves increases as temp. rises, but generally η is greater during expansion than contraction, especially at the transition boundary between the two regions.

A. J. M.

Pure and mixed monolayers of dilauryl maleate and fumarate. J. L. Shereshefsky and A. A. Wall (J. Amer. Chem. Soc., 1944, 66, 1072-1076).—The surface pressure-area relationships have been determined for dilauryl maleate and fumarate films at different temp. and for the mixed esters at 25°. The consts. in the Langmuir equation of state of duplex films for these substances have been evaluated. Area consts. agree with X-ray dimensions of maleic and fumaric acids. The relation between the val. of the dipole moment of the head group and the tendency to form expanded films and the relation between stability and surface potentials are discussed. Raoult's law can be applied to the pressure of head groups in mixed duplex films. W. R. A.

Solutions of problems relating to media in contact by the method of wave-trains. G. Green (*Phil. Mag.*, 1944, [vii], 35, 519-531).---Summations of wave-train effects for two media in contact are tabulated for the cases of a source in either medium or at the boundary. Applications are given to the solution of problems involving the transmission of elastic and thermal vibrations (cf. *ibid.*, 1940, [vii], 29, 100). H. J. W.

Theory of filtration of aerosols. I. Role of van der Waals forces. N. N. Tunitzkii and I. V. Petrianov (*J. Phys. Chem. Russ.*, 1943, 17, 408—413).—It is assumed that between aerosol particles and solid surfaces an attraction exists which accelerates the filtration of aerosols through porous filters. The attraction is calc. for a force α (distance)⁻⁶. J. J. B.

Foaming properties of soap solutions.—See B., 1944, II, 320.

Use of low temperatures in the study of colloids. A. Boutaric (*Compt. rend.*, 1943, 216, 379—380).—The stability of org. and inorg. colloidal solutions on storage is considerably greater at 0° than at higher temp. L. J. J.

Examination of some carbons by X-ray diffusion at very small angles. H. Brusset, J. Devaux, and A. Guinier (Compt. rend., 1943, 216, 152—154).—Various specimens of C when examined by X-rays show a central diffusion spot as well as the rings due to graphite structure. This diffusion spot is characteristic of the disperse state, and if the intensity (1) diffused at angle ε is measured, the curve of log I against ε^2 tends towards a straight line for small ε . From the slope, a no. characteristic of the size of the particles can be obtained. Almost all the lignites examined gave a central diffusion spot. They contain micelles of various dimensions. Bitumen is intermicellar. A similar micellar dispersion was obtained for samples of anthracite. A sample of humic products, containing a large proportion sol. in bases, gave results very similar to those of lignite. Aq. solutions of NH₄ humate and of Na humate do not show the central diffusion spot. In the case of various active carbons the nature of the central spot varied considerably with the treatment. Activation causes breakdown into a very finely divided state. A. J. M.

Viscosities of pectin solutions. H. S. Owens, H. Lotzkar, R. C. Merrill, and M. Peterson (*J. Amer. Chem. Soc.*, 1944, **66**, 1178—1182).— The relative η of pectin (I) solutions varies with concn. similarly to other ionisable hydrophilic colloids. In dil. solutions η attains a max. at pH ~6 but can be reduced to a min. by adding NaCl or an acid; CO(NH₂)₂ has little effect. As the concn. of (I) is increased to >0.5%, the relative η is unaltered by varying pH between 1 and 7. The η -concn. curve follows the Arrhenius equation to <0.1% (I), when pH is 1 or 2 or when <0.9% of NaCl is present. This permits the calculation of vals. of intrinsic η which may have some relationship to mol. wt. The η -concn. curves for Na, NHMe₂, NH₂·[CH₂]₂·NH₃, (OH·CH₂)₂CMe·NH₃, and NEt₄ pectinates are practically identical. Temp. (0-30°) has little effect on η -concn. curves for solutions containing <0.05% of (I), but above 0.05% η decreases with rising temp. A tentative explanation is advanced.

Viscosimetric determination of the degree of polymerisation and the shape of polyamides in solution. A. Matthes (J. pr. Chem., 1943,[ii], 162, 245-278).—The relation between intrinsic viscosity, $[\eta]$, and degree of polymerisation, P, of an ε -aminohexolactam polymeride (I) has been determined in conc. and 40% aq. H₂SO₄; $[\eta] = KP^{\alpha}$ (K and a are consts.), K = 0.0281, $\alpha = 0.668$ in conc. H₂SO₄, K = 0.0268, $\alpha = 0.510$ in 40% aq. H₂SO₄. The relation has been used in a viscosimetric study of the depolymerisation of (I) in 40% aq. H_2SO_4 . All available evidence points to a long unbranched and coiled chain as the shape of polyamide mols. The amount of coiling varies with the solvent. W. R. A.

Electrical and elastic properties of amorphous polar polymers. R. F. Tuckett (*Trans. Faraday Soc.*, 1944, **40**, 448—462).—The deformation of an amorphous polymer under const. stress is examined theoretically with reference to a spring-dashpot model, and it is shown that, whilst the rate of ordinary elastic deformation is characterised by a true relaxation time related to the ordinary macroscopic viscosity, the rate of highly elastic deformation is characterised by an "orientation time," τ , as expressed by $D_t = D_{1-\infty}(1 - e^{-t/\tau})$, which is related to the modulus of high elasticity by a friction const. that is \ll the ordinary viscosity and to which no definite physical meaning can be assigned. In this latter respect the theory diverges from Debye's treatment of dipole rotation. If a dipole is attached to the main chain in an amorphous polymer, both dipole rotation and highly elastic orientation are affected to the same extent by intermol. forces, and both processes should have the same time consts. This hypothesis is supported by some experimental evidence and by a consideration of energies of activation of various mol. rate-processes. Orientation-time distributions are also discussed. F. L. U.

Interaction between rubber and liquids. V. Osmotic pressures of polymer solutions in mixed solvents. VI. Swelling and solubility in mixed liquids. G. Gee (*Trans. Faraday Soc.*, 1944, 40, 463–468, 468–480).—V. An expression is obtained for the free energy of dilution of a ternary mixture of polymers + two liquids by one of the liquids, and is applied to the osmotic equilibrium between a solution of a polymer in the two liquids and a second phase containing only the two liquids. The osmotic behaviour of the ternary solution is very similar to that of a solution of the polymer in a single liquid, and van 't Hoff's law holds at infinite dilution. The distribution of the two liquids in the solvent and solution phases is calc. This is identical only if the heat of mixing of the three components is zero and if the two liquids have equal mol. vols., whilst for fairly large heats of mixing the % difference between the mol. ratio of the liquids in the solution.

VI. The solvent properties of a mixture of two liquids are intermediate between those of the constituents only when these mix ideally; the larger is the heat of mixing, the greater is the solvent power of the mixture relative to those of the components. Hence over a certain concn. range a mixture of two non-solvents may be a solvent. The same principle applies to the swelling of a crosslinked polymer. Methods of estimating the val. of the consts. in the equations derived in the preceding paper are discussed. Experimental data for the crit. solubility limits of unvulcanised rubbers and the swelling of vulcanised rubbers are semi-quantitatively explained from the measured heats of mixing of the three binary mixtures, and qualitatively from the cohesive energy densities of the three separate components. F. L. U.

Ordered swelling state of nitrocellulose. G. V. Schulz (Z. physikal. Chem., 1942, **B**, 52, 253—256).—If the effect of concn. of cellulose nitrate (I)-COMe₂ mixtures on the entropy of swelling is determined, it is found that the entropy is negative for a degree of swelling (q) (vol. to which 1 c.c. swells) <3, and positive above that. This is in agreement with the work of Kratky, Sekora, and Treer, who have shown that at comparatively high q of (I) in COMe₂, definite lattice structures exist, as shown by X-ray analysis. The upper limit for the occurrence of these structures is q = 3. The limit between the two regions appears also in mechanical properties of the mixture. The process of swelling can be explained on the basis of these observations. For comparatively small amounts of the swelling agent, the forces between the components are strong enough to maintain the solid, lattice arrangement. With the addition of more of the swelling agent, the distances between the components increase, the binding energy of the (I) mols. decreases, and the lattice breaks down. A. J. M.

Structure and properties of cellulose ester films. II. Structure change of cellulose nitrate films during their relaxation. V. A. Kargin, P. V. Kozlov, and R. V. Zueva (*J. Phys. Chem. Russ.*, 1943, 17, 318-325).—When cellulose nitrate films (from COMe₂) were stretched and then released, a part (about $\frac{1}{2}$) of their birefringence disappeared rapidly (some hr. at room temp., and some sec. at 100-150°) but the rest of it remained for days. The orientation shown by X-rays was permanent at room temp. but disappeared at 100-150°. Stretched and then released benzylcellulose films lost their birefringence completely after heating at 100°; no orientation as shown by X-rays occurs in these films. It is concluded that relaxation of stretched films takes place in two distinct stages.

J. J. B. Kinetics of isothermal coagulation of non-colliding particles. N. N. Sirota (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 40, 234-238).—Mathematical. The isothermal coagulation of a solid dispersion phase (spheroidal cryst. particles) dispersed in a solid matrix is regarded as consisting of dissolution of the particles of the disperse phase and their growth. W. R. A.

Electrokinetic phenomena in relation to electrodialysis. I. I. Shukov (Uspechi Chim., 1943, 12, 265-286).—The transference no. of Cl' in KCl is not affected by collodion membranes with large pores (radius $r > 10^{-5}$ cm.), but is reduced to <0.3 when r is $<10^{-7}$ cm. For a given r the reduction is the larger the more dil. is the KCl solution; this is explained by a contraction of the double layer in higher concn. The ζ -potential has a max, when $r = 10^{-5}$ cm. and is very small at $r < 10^{-7}$ cm.; it is a definite function of the permeability of the membrane for H₂O. For electrodialysis the transference nos. n in the membranes are more important than the ζ -potentials. According to the vals. of n in the membranes of a two-membrane electrodialyser the middle portion can be diluted or conc. Positive collodion membranes are obtained by incorporating in the collodion quininc' or nigrosine, and negative ones, by incorporating Baden-blue. The smaller is r, the larger is the difference between the n of different ions. J. J. B.

VI.—KINETIC THEORY. THERMODYNAMICS.

Fugacities in gas mixtures. M. Temkin (J. Phys. Chem. Russ., 1943, 17, 414—423).—A thermodynamic equation for the fugacity of a component of a gas mixture is derived; it can be applied if the pressure of the mixture is known as a function of temp., vol., and composition. Solutions are given for equations of state of the van der Waals and Kammerlingh-Onnes types. J. J. B.

Dimerisation in perfect solutions. Analysis of data of Brown and Bury. W. F. K. Wynne-Jones and G. S. Rushbrooke (*Trans. Faraday Soc.*, 1944, 40, 345–352).—The cryoscopic measurements by Brown and Bury (cf. A., 1926, 675) for several solutes in dry PhNO₂ are reconsidered. By avoiding one approximation used by these authors in their calculations, and by using a new formula involving activity coeffs., evidence is obtained for dimerisation of acids (EtCO₂H, CH₂Ph·CO₂H) and probably of β -C₁₀H₇·OH, but not of alcohols (CH₂Bu β ·OH, CH₂Ph·OH). F. L. U.

Properties of reversible micelle formation from the viewpoint of the law of mass action. O. Lamm (Arkiv Kemi, Min., Geol., 1944, 18, A, No. 9, 22 pp.).—The theory of simple micelle formation (the aggregation of low-mol. particles with increasing concn.) is developed on the basis of the law of mass action. The more complex case where the equilibrium const. varies with particle size is also considered, assuming a statistical distribution of particle size. If for a given concn. there is a statistical distribution of particles, this is true for all concns. Sedimentation and diffusion and their connexion with micelle formation are discussed. The treatment is applied only to non-electrolytes. A. J. M.

Strengths of six monocarboxylic acids in 25% aqueous acetone and 20% aqueous sucrose. I. Davey and J. F. J. Dippy (J.C.S., 1944, 411-415).—Dissociation consts. at 25° have been determined by a conductivity method for EtCO₂H, BzOH, CH₂Ph·CO₂H, CHPh₂·CO₂H, Ph·[CH₂]₂·CO₂H, and CHPh:CH·CO₂H. With the exception of CHPh₂·CO₂H, the order of strengths is the same as for aq. solutions. The strengths in aq. sucrose are > those in H₂O despite the lower dielectric const. of the sucrose solution. CHPh₂·CO₂H is anomalous since the strength in aq. COMe₂ is < instead of > that of BzOH, and the strength in aq. Sucrose is < in H₂O. C. R. H.

Binary system P_2O_6-2CaO,P_2O_5 . W. L. Hill, G. T. Faust, and D. S. Reynolds (*Amer. J. Sci.*, 1944, 242, 457-477).—Data from quenching experiments are recorded and phase diagrams presented for the equilibrium relationships between P_2O_5 and $Ca_2P_3O_7$. Eight cryst. phases are stable at liquidus temp., viz., tetragonal (?) $(P_2O_5)_n$ with a triple point at 580° and 555 mm.; CaO,2P_2O_5, m.p. 810°; 2CaO,3P_2O_5, incongruent m.p. 774°; β -CaO,P_2O_5, m.p. 977° (metastable); a-Ca metaphosphate, m.p. 984°; trömelite, observed as a series of solid solutions ranging from ~32 to 37% CaO, which is metastable below 915° and melts incongruently at 985°; β -2CaO,P_2O_5; and a-2CaO,P_2O_5, m.p. 1353°. The $a \rightleftharpoons \beta$ inversion points of CaO,P_2O_5 and 2CaO,P_2O_5 lie at 963° and 1140°, respectively. L. S. T.

Three-phase pressures for solid salt-solution-vapour. I—III. (Miss) A. E. Korvezee and P. Dingemans (*Rec. trav. chim.*, 1943, 62, 625—638, 639—652, 653—657).—I. The "characteristic coeff." (k) of Kume (A., 1936, 1197) depends on temp, and is therefore not a characteristic const. for each substance. This variation may be small (resorcinol) or large (NaBr), and is related to the variation of the activity of H₂O with the molar concn. Moreover, discontinuities in the k-temp. curves occur at transition temp. The v.p. of the saturated solutions relative to that of pure H₂O at the same temp. varies approx. linearly with temp. along the threephase pressure curves. An expression is given for the activity of the H₂O in the saturated solution in terms of the relative v.p. II. For salts having two cryst. forms with a transition temp.

II. For salts having two cryst. forms with a transition temp. there are three types of pressure-temp. curves possessing either two stable max. or one stable and one metastable max. Equations are given for the relative v.p.-temp. curves for three saturated solutions, from which the max, in the pressure-temp, curves can be calc, with an accuracy ~1%. The heat of transition between two cryst, forms can be obtained from the differences in slopes of the relative v.p. curves at the transition temp, and also from the difference in the heat of crystallisation of the two forms at the temp. of the max. Data and calculations are given for the systems $H_2O-NH_4NO_3$, $H_2O-AgNO_3$, and $H_2O-KCNS$ which exemplify the three types mentioned. III. Expressions are derived for ideal systems connecting the

III. Expressions are derived for ideal systems connecting the m.p. of substance and the temp. at which a max. occurs on the three-phase pressure curve solid-saturated solution-vapour, and for the distances between the temp. of the two max. on the three-phase pressure curves when the solid occurs in two modifications. Compared with all the known systems salt-H₂O, they show an error $\sim 1\%$. J. O'M-B.

Mineralogical aspects of the system FeO-Fe₂O₃-MnO-Mn₂O₃. B. Mason (Stockholms Hogsk. Min. Inst., Rept. 150; Geol. Foren. i Stockholm Forh., 1943, 65, 97-180; Bull. Iron Steel Inst., 1944, No. 102, 32A).—Chemical, physical, and mineralogical studies of the system were made to determine the phase relations with the view of defining the limits of the different mineral species and elucidating their mutual relations. The mineral species in the system are: magnetite, Fe₃O₄; hæmatite, a-Fe₂O₃; maghemite, γ -Fe₂O₃; manganosite, MnO; hausmannite, Mn₃O₄; bixbyite, a-Mn₂O₃, with up to ~60% of Fe₂O₃ in solid solution; jacobsite, (Fe,Mn)₃O₄ (Mn₃O₄ 16·7-54%); and vredenburgite (Mn,Fe)₃O₄ (Mn₃O₄ 54-91%). The literature is critically reviewed. R. B. C.

91%). The literature is critically reviewed. R. B. C. Application of free energy equations to the study of the synthesis of hydrocarbons from carbon monoxide and hydrogen. W. W. Myddleton (J. Inst. Petroleum, 1944, 30, 211—224).—The vals. of the consts. A, B, etc. and of the integration const. (I) in the general free energy equation $\Delta G_T = \Delta H_0 + AT \log_0 T + BT^2 + CT^3 + \dots + IT$, where ΔH_0 is regarded as the change in heat content in hypothetical reaction at abs. zero, have been calc. from known thermal data and derived equations for the reactions $nCO + (2n + 1)H_2 \rightarrow C_nH_{2n} + (2 + n)H_2O$ and $2nCO + (n + 1)H_2 \rightarrow C_nH_{2n+2} + nCO_2$ over the range 25—250°. Terms in D contribute <0·1%, those in C + D < 2%, and those in B + C + D < 10% to the total free energy. Vals. for the latter are given for the lower parafins and olefines. The reaction in which CO₂ is formed has a higher negative free energy than that producing H₂O, and the formation of CO₂ would be expected to accompany the latter reaction. Special conditions at the catalyst surface are suggested as a reason for the inhibition of CO₂ formation. CO may be adsorbed by the catalyst by either dual attachment, when H₂O is formed by reaction with H₂, or single attachment, when H₂ forms CO₂ and CH₂ groups which are converted into CH₄ by the action of chemi-sorbed H. Dual attachment does not occur with Fe catalyst. The appearance of traces instead of large amounts of C₂H₄ is accounted for by the incorporation of C₂H₄ actually formed into the building up of hydrocarbon chains. The free energy relations predict appreciable quantities of *iso*-parafins, and modifications in catalyst and in reaction conditions may be able to increase the yield. Conditions which favour aromatic hydrocarbon formation are less likely to be attained.

C. R. H.

Bond energy of organic compounds. J. K. Sirkin (J. Phys. Chem. Russ., 1943, 17, 347-380).—The heats of formation of org. compounds are discussed. They can be considered as sums of bond energies; new vals. for these energies are calc. They often appear to be identical in compounds in which the lengths of the bond are different, and sometimes they are different in compounds having equal bond lengths (e.g., in lower and higher paraffin hydrocarbons). The groups CHMe: or CMe: have a greater energy content than $^{\rm CH}_2$ ·CH₂· or :CH·CH₂·. The largest deviations from additivity are due to resonance. J. J. B.

Thermochemistry of formaldehyde, hexamethylenetetramine, and their derivatives. M. Delépine and M. Badoche (*Compt. rend.*, 1942, **214**, 777—780).—Heats of combustion have been redetermined by an accurate bomb method, giving the following mol. vals. at const. vol. and const. pressure : $\frac{1}{3}(CH_2O)_3 120.9$, 120.9; $1/n(CH_2O)_n$ (polyoxymethylene) 120.3, 120.3; $\frac{1}{4}[(CH_2O)_n, H_2O]$ 120.05, 120.05; $(CH_2)_8N_4 1003.0$, 1003.6; $(CH_2)_8N_4, 2HNO_3 953.6$, 952.2; $C_3H_1O_2N_8$ (dinitrosopentamethylenetetramine) 866.1, 865.2; $C_3H_6O_3N_8$ (trinitrosotrimethylenetriamine) 557.9, 556.2; $C_3H_6O_8N_8$ (trimethylenetriamine) 506.6, 503.9 g.-cal. L. J. J.

Heats of transformation in the systems wurtzite-sphalerite, and cinnabar-metacinnabarite. A. F. Kapustinski and L. G. Tschentzova (Compt. rend. Acad. Sci. U.R.S.S., 1941, 30, 489-490).—The heats of dissolution of synthetic wurtzite and sphalerite in HCl have been determined by means of an adiabatic calorimeter to be 17.4 and 50.2 g.-cal. per g., respectively. These vals. give 3190 g.-cal. per g.-mol. for the heat of transformation ZnS (sphalerite) \rightarrow ZnS (wurtzite). The heats of dissolution of synthetic cinnabar and metacinnabarite in aq. K₂S (38%) and KOH (2%) were 12.4 and 16.5 g.-cal. per g., respectively, giving 950 g.-cal. per g.-mol. for the heat of transformation HgS (cinnabar) \rightarrow HgS (metacinnabarite).

A. J. M.

Exact calculation of heats of dissolution from solubility data. A. T. Exact calculation of heats of dissolution from solubility data. A. T. Williamson (*Trans. Faraday Soc.*, 1944, **40**, 421-436).—Exact thermodynamical treatment leads to the general equation $\Delta H = \nu R T^*(dm/dT)_{\text{sat.}}[(\partial \log_{\varphi} \gamma/\partial m)_T + (1/m)_{\text{sat.}}]$ for the heat of dis-solution, where ν is the no. of ions per mol. of an electrolyte, *m* is the molality of the saturated solution, and γ the mean activity coeff. of an electrolyte (for non-electrolytes $\nu = 1$ and $\gamma = f_2$, the fugacity of the solute). Vals. of ΔH calc. from data for KCl, Ba(NO₃)₂, Na₂CO₃, NaOH, and CO(NH₂)₂ agree well with calori-metric determinations. An appendix contains alternative forms of the equation for use with different kinds of experimental data (solvent activities, osmotic coeffs.) and for solvated solutes. (solvent activities, osmotic coeffs.) and for solvated solutes.

F. L. U. Energies of solution of silica in water and hydrochloric acid. P. G. Nutting (J. Chem. Physics, 1944, 12, 347–348).—Energy relations relating to Si(OH), solutions are calc. from the solubility of pure SiO₂ in H_2O and HCl solutions. Most of the energy change is due to the first H O taken on during hydrotion of the SiO theorem. the first H_2O taken on during hydration of the SiO₂, the second H_2O differing little in energy from the solvent. L. J. J.

Calorimetric study of the absorption of acetone by β -methyl-glucose tetranitrate and β -methylcellobicse heptanitrate. E. Calvet E. Calvet and A. Maurizot (*Compt. rend.*, 1943, 216, 51—52).—The heat of absorption of COMe₂ by β -methylglucose tetranitrate (I) and β -methylcellobiose heptanitrate (II) has been determined. The results methylcellobiose heptanitrate (II) has been determined. The results are expressed as the amount of heat given out when n mols. of COMe₃ attach themselves to a C₆ group. For n < 1, (I) and (II) adsorb COMe₂. For n = 1, a liquid phase appears. The solid phase disappears when n = 5 for (I), and when n = 3 for (II). The curve of heat of adsorption against n is linear up to n = 3, and there is a max. at n = 6 for both (I) and (II). This max. is 5750 g.-cal. for (II) and 5400 g.-cal. for (I). The heat of dissolution per C₆ group is -4000 g.-cal. for both. Comparison is made with the results for the cellulose nitrates (III), where a max. is also obtained for n = 6. The form of the curve of heat of absorption against n is also the same, The form of the curve of heat of absorption against n is also the same, but in the case of (III) the max. heat evolved is ~ 4 times > that for (I) and (II), and the total heat of dissolution is positive. The difference is due to the fact that (I) and (II) are cryst., and dissolve readily in $COMe_2$, the dispersion in the solvent (negative thermal effect) taking place at the same time as gelatinisation (positive effect), whereas in (III) the dispersion does not occur at the outset of gelatinisation. A. J. M.

VII.—ELECTROCHEMISTRY.

Electrical conductance of aqueous solutions. I. Sodium and potassium bromates at 25°, and the conductance of the bromate ion. J. H. Jones (J. Amer. Chem. Soc., 1944, 66, 1115—1116).—Vals. of Λ have been measured at 25° for aq. KBrO₃ (0.0005—0.15M.) and aq. NaBrO₃ (0.0005—0.5M.) and ρ of aq. NaBrO₃ (0.0005—0.3M.) have been determined at 25°. Λ_0 for BrO₃' at 25° is 55.78 ±0.05.

W. R. A.

Electrical conductivity of the thoria-ceria system. M. Fox. (Compt. rend., 1943, 216, 443-445).—The conductivity of ThO_2 -CeO₂ mixtures has been measured at 800° and 1200° in atm. of O₂, N₂, and H₂, and in a vac. Max. resistivity is found with 1 mol.-% CeO₂ in N₂ and in a vac.; in O₂ a flat max exists with 1--2 mol.-% CeO_2 , whilst in H₂ no max. is found, the resistivity decreasing continuously with increasing $[CeO_2]$. Outside this range resistivity decreases with increasing $[CeO_2]$ in all cases, but in O₂ that of CeO_2 is slightly decreased by addition of 1-5 mol.-% ThO₂. L. J. J.

Physical properties of isomeric oximes. I. Molecular conductivities in liquid sulphur dioxide of isomeric aldoximes. N. K. Patwardhan and S. S. Deshapande (J. Indian Chem. Soc., 1944, 21, 135-138).—Mol. conductivities for liquid SO₂ solutions of benzaldoxime and its o-, m-, p-NO2- and p-OMe-derivatives and of furfuraldoxime and cinnamaldoxime have been measured. The β -aldoximes have higher conductivities than the *a*-aldoximes, sug-gesting that the β -forms are "*anti*" and the *a*-forms "syn." C. R. H.

Effect of adsorbed layers of molecules of dielectrics on the contact potential difference between two metals. J. H. von Duhn (Ann. Physik, 1943, [v], 43, 37–52).—Contact p.d. of Ni, Cu, Ag, Ta, and Pt surfaces, saturated with vapours of parafins, aliphatic alcohols, and C_4H_8 , PhMe, and PhCl at a pressure of 2–10⁻⁴ mm. Hg, and measured against a normal electrode, are $\sim \pm 0.8 v$. The p.d. varies with the adsorption pressure, the electron structure of the metal, and the mol. refraction of the adsorbate, but not with the dipole moment of the latter.

Applicability of Nernst formulæ to amphoteric adsorbents. A. N. Frumkin (Compt. rend. Acad. Sci. U.R.S.S., 1941, **30**, 417-419).— The p.d. between the surface of an amphoteric non-conducting adsorbent and the solution can be expressed by the same relation as for a H electrode provided that the no. of adsorbing groups on the surface is great enough. W. R. A.

Theory of hydrogen ion discharge. III. Palladium. A. Frumkin and N. Aladjalova (*Acta Physicochim.*, 1944, 19, 1-35).—The properties of Pd electrodes depend largely on the nature of their

surface. Experimental results indicate that the overvoltage of Pd during evolution of H consists of two parts. One of them is almost independent of the nature of the solution, and is slowly attained after switching on the current. It also disappears slowly when the current is switched off, and can be transmitted to the diffusion side of the electrode. This indicates that it is an equilibrium potential between H, dissolved in the metal and that in the electrolyte. The other part of the overvoltage, which may reach high vals. in alkaline solutions, is not connected with evolution of H, but depends on the This electrochemical reaction itself quite apart from the electrodes. overvoltage is not affected by transition of Pd from the a to the β phase. It is independent of the area of Pd covered by the H₂. overvoltage is not affected by transition of 1 d nom the u could p phase. It is independent of the area of Pd covered by the H₂. The mechanism of the process accounting for these facts is based on the theory of slow discharge. Equations are deduced showing the overvoltage to be composed of two parts, one depending on the intensity of current, the other on the equilibrium potential of adsorbed H₂, in accordance with the experimental facts. The theories of Farkas (A., 1937, I, 75, 253) and of Hickling *et al.* (A., 1943, I, 18) are discussed in the light of the experimental results. The poisoning of Pd electrodes is briefly considered. A. I. M. A. I. M. The poisoning of Pd electrodes is briefly considered.

Effect of temperature on the discharge of N₃' ions and OH' ions in solutions of azides. E. T. Verdier (Compt. rend., 1943, 216, 183–185; cf. A., 1942, I, 268).—In order to confirm the equation $\Delta N = \frac{1}{2} \frac{1}{2}$ $kK_{Ae}^{-W|R^{-}e^{b}Y|}$ (K_{A} is a factor depending on the principal optical absorption of HN₃. W is energy of activation of the photogenic reaction, V = potential, I = intensity of current) for the intensity (ΔN) of the ultra-violet ray emitted at the anode in the electrolysis of HN3 and NaN3, the effect of temp. on the radiation has been investigated. The curve of log (K/K_A) against (1/T) $(K = kK_A e^{-W/RT})$ shows two straight lines separated by discontinuities at 12° and 18°. The slopes of these lines give energies of activation of 9500 g.-cal. $(0-12^{\circ})$ and 5500 g.-cal. $(18-40^{\circ})$. It appears that OH' alone are discharged at temp. <12° and N₃' only above 18°. A. J. M.

Influence of the anion on the capacity of a mercury electrode in dilute solutions. M. Vorsina and A. Frumkin (Acta Physicochim. U.R.S.S., 1943, 18, 341-350).-As an extension of an earlier investigation (cf. A., 1943, IS, 341–350).—As an extension of a Hg electrode in solutions of H_2SO_4 , NaOH, Na₂SO₄, HCl, KCl, HBr, and KBr has been measured. The val. of C_{\min} is > the val. calc. according to the Stern double layer theory when sp. adsorption is neglected. The magnitude of C_{\min} and the corresponding val. of the potential depend on the adsorbability of the anion, increase in the latter being accompanied by an increase in C_{min} . Where anion adsorption is strong, as, e.g., with appreciable concns. of I', Cmin. disappears C. R. H. altogether.

Polarographic reduction of rhodium compounds. J. B. Willis (J. Amer. Chem. Soc., 1944, 66, 1067–1069).—Rh complexes formed between RhCl₃ and KCN, KCNS, KCl + C_5H_5N , and NH₄Cl are stable towards Hg and give well-defined polarographic steps. Each reduction takes place from Rh^{III} to Rh^{III} and in no case, except possibly with KCNS, was the $Rh^{III} \rightarrow Rh$ step observed. There is evidence that the reducible ions formed are $[Rh(CN)_{d}]^{\prime\prime\prime}$, $[Rh(CNS)_{d}]^{\prime\prime\prime}$, $[Rh(C_{s}H_{s}N)_{d}]^{\prime\prime}$, and $[Rh(NH_{3})_{s}CI]^{\prime\prime}$. Some Rh complexes show no polarographic steps. W. R. A.

Reduction of quinaldinic acid at the dropping mercury cathode. J. T. Stock (J.C.S., 1944, 427-430).—Current-voltage curves of 0.001M-quinaldinic acid (I) in well-buffered aq. solutions at 25° over the pH range 1.5-12 have been obtained. (I) is reducible over the entire range, the principal product being dihydroquinaldinic acid. At low pH the curves consist of two waves separated by a max. As pH is increased the lower wave is shifted towards more negative potentials, the upper wave decreases in height, finally vanishing at pH 4, and the max. broadens. This max. can be completely suppressed by addition of 0.02% of gelatin, but at the same time the lower wave moves to more negative potentials and the upper wave disappears. Up to pH 6 the relation $\vec{E}_{\frac{1}{2}} = -(0.52 + 0.06\text{pH})$ v. holds for the lower wave. The height of the wave is c concn. of (I), and measurement of wave heights provides a means C. R. H. of determining (I) polarographically.

Polarographic investigation of cysteine, glutathione, and ascorbic acid. R. G. Rieser (Univ. Pittsburgh Bull., 1944, 40, 220-226). Half-wave potentials and diffusion coeffs. for reduction of cysteine and oxidised glutathione are calc. from polarographic data. The latter gives normal diffusion current-voltage curves from pH 9.3 to 2N-H₂SO₄. At pH 1.0 and 2.2 the diffusion current is ∞ the concn. Dehydroascorbic acid does not give a reduction polarogram concn. Dehydroascorbic acid does not give a reduction polarogram at pH 3·1-10·6. Reduction of cysteine and dithiodiglycollic acid at pH 3·1—10·6. Reduction of cysteine and difficulty only and shows similar mixed potential polarograms. $CH_2I \cdot CO_2H$ with the appropriate thiol compound at pH 1·0 gives a quant. yield of cysteine. L. J. J.

Ohmic resistance of local cells in the process of dissolution of metals in acids. B. Levitsch and A. Frumkin (Acta Physicochim. U.R.S.S., 1943, 18, 325-340).—The conditions determining the behaviour of the cathode of a local cell are considered on the assumptions that the cathode is an inclusion having the shape of a disc. anode potential is zero, anode polarisation is neglected, and the

cathode is strongly polarised. The max. sp. resistance per unit area opposed to the current flowing to the centre of the cathode discis $2r_0/\pi\chi$, where r_0 is the radius of the disc and χ is the conductivity of the electrolyte. As examples, the effect of inclusions of Sb in Pb and Ni in Zn when H_2SO_4 is the solvent has been calc. In the first case the ohmic potential drop may be neglected even for large inclusions and in the second it is $\Rightarrow 13$ mv. if r_0 is $\sim 10^{-4}$ cm. Where the ohmic potential drop cannot be neglected, changes in electrolyte concn. at the cathode surface should be taken into account.

C. R. H.

Graphical method of calculating polyelectrode electrochemical systems as applied to corrosion processes. N. D. Tomaschov (Compt. rend. Acad. Sci. U.R.S.S., 1941, 30, 621-623).—Comparison of cathode and anode polarisation curves makes it possible to calculate the work of each separate electrode in a polyelectrode system with any no. of electrodes. The relative surface area of each electrode in the system must be known, and the cathode and anode polarisation curves (c.d. against potential) under conditions close to the working conditions of the system must be plotted for each component of the system separately. The assumption is then made that the effective potentials of all the electrodes of the system become equal as the result of polarisation. This is usually the case if the total ohmic resistance is small. The c.d.-potential curves are replotted on a general current-potential diagram. The general potential of the system is the potential at which the sum of all the cathode currents equals the sum of all the anode currents. The curve indicates which electrodes will act as cathodes and which as anodes. In some cases the polarisation curves for the individual electrodes can be calc. but they usually have to be obtained experimentally. A. J. M.

VIII.—REACTIONS.

Explosives reactions. I. Chain reactions and gaseous explosions. M. F. R. Mulcahy and A. Yoffe (*J. Proc. Austral. Chem. Inst.*, 1944, 2, 106—120).—An introduction to the theory of chain reactions and gaseous explosions. C. R. H.

Temperature gradients in gaseous explosions. A. S. Leah (*Nature*, 1943, 152, 303-340).—Mean gas temp. in the burnt portion of explosive mixtures may be obtained by photographically recording flame travel and simultaneously measuring pressure rise by a diaphragm type of indicator; a large spherical explosion vessel, with central ignition, is used. Experiments with $10\% O_2 + 90\%$ CO indicate a rise in temp. as the flame travels outward from the spark, thus confirming David's theory that the latent energy decreases in the same direction. E. R. R.

Temperature of flame gases. W. T. David (*Nature*, 1943, 152, 278).—Considerable differences in temp. indicated by thermometric substances immersed in CO-air and CH₄-air mixtures are observed when bare and quartz-covercd Pt-Rh wires were used. The differences are largely due to the recombination of abnormally dissociated products on the surface of the wire. In CO-rich mixtures this effect is apparently suppressed. E. R. R.

Theory of slow combustion. L. Landau (Acta Physicochim., 1944, 19, 77-85).—The transference of heat from burning products of combustion to unburnt gas is usually assumed to be by simple thermal conduction. The stability of such a system is considered, and it is shown that the above assumption is not justified, as convection also plays a dominating part. The combustion of liquids is also considered. A. J. M.

Ignition of carbon and kinetics of its reaction with oxygen. Z. Klibanova and D. Frank-Kamenetzki (Acta Physicochim. U.R.S.S., 1943, 18, 387-405).—The kinetics of the reaction between C and O_2 at ordinary pressure and at high temp. have been measured by a method based on the determination of the temp. which a C filament must attain before it ignites in a stream of air or other O_2 -containing gas. The abs. reaction velocity at ~1200° K. is ~10⁻⁴ mol. per c.c. per sec., a val. of the same order as is obtained by other methods. The present data show a temp.-dependence which suggests an activation energy \gg energies previously reported. The present val. is 75—135 kg.-cal. per mol., corresponding with a reaction order 0.4—0.8, and definitely <1. C. R. H.

Oxidation of earbon. Z. F. Tschuchanov (Compt. rend. Acad. Sci. U.R.S.S., 1940, 28, 32-36).—Velocities of oxidation of electrode C at 720—770° x. (Chaikina, A., 1938, I, 628) correspond with energies of activation 43,000 and 37,000 g.-cal. per g.-mol. for the reactions $3C + 2O_2$ (ads.) = C_3O_4 and $C_3O_4 + C + O_2$ (gas) = $2CO + 2CO_2$, respectively. Corresponding vals. from the velocity of oxidation of active wood charcoal (Tschuchanov, A., 1941, I, 272) at 873— 973° x. are ~19,000 and ~27,000 g.-cal. per g.-mol. Divergent results obtained by other authors in different temp. ranges are explained by the simultaneous variation of the velocity coeffs. of the above two reactions with temp. L. J. J.

Reaction of unsaturated halides with sodium vapour. A. G. Evans and H. Walker (*Trans. Faraday Soc.*, 1944, 40, 384-397).— Speeds of reaction of a no. of org. halides with Na have been measured, and the velocity coeffs., together with calc. collision nos. and activation energies, are recorded. In many cases the velocity is > would be expected from the corresponding C-halogen bond strength, and the possibility of accounting for these anomalies by extra resonance forms in the transition state is discussed. F. L. U.

Kinetics of anionotropic rearrangement. I. Rearrangement of propenylethynylcarbinol. E. A. Braude and E. R. H. Jones. II. Medium effects in the oxotropy of propenylethynylcarbinol. Determination of isodielectric energies of activation. E. A. Braude (J.C.S., 1944, 436-443, 443-449).—I. The acid-catalysed anionotropic rearrangement reaction CHMc:CH-CH(OH)-C:CH (I) \rightarrow OH-CHMe-CH:CH-C:CH (II) is of the first order (in 20% aq. EtOH) for (I) concns. ranging from 0.02 to 0.15 mol., the velocity coeff., k, decreasing slightly at higher (I) concn. k vals. were measured from the changes in absorption of ultra-violet light. (II) is formed to an extent >98%. k is α stoicheiometric acid concn., C_A , when C_A is <0.1 Å.; at higher C_A vals. k becomes α Hammett's acidity function, (H_0) . Catalysis was studied over the concn. range 0.02-4M. for HCl and 0.02-2M. for H₂SO₄. An attempt was made to compare catalytic activity of different concns. of buffered solutions of AcOH of const. pH with catalytic activities of unbuffered AcOH solutions. Variation of k with the acid dissociation const., K_A , was studied for 8 acids used in 1M. concn., the K_A vals. ranging from 1.2×10^{-4} to 1.8×10^{-5} . The salt effect is positive and α (H_0). Vals. of E over the temp. range $0-60^{\circ}$ for different acids and acidities vary from 19,000 to 24,000. In 0-4M-HCl the vals. of k as measured from the change of optical rotation in a solution of a resolved sample of (I) ($[a]_D^{\circ} + 45^{\circ}$) and that obtained from the light absorption changes are respectively $27.5 \pm 1.5 \times 10^{4}$ min.⁻¹ and $.32.8 \pm 0.6 \times 10^{4}$ min.⁻¹ Reaction mechanism is interpreted in terms of a reversible electronic rearrangement, followed again by a reversible decomp. of the oxonium ion into (II) + H^{+}, the process being named " oxotropy."

process being named "oxotropy." II. Variation of k with change in the EtOH/H₂O ratio (between 20 and 100% EtOH) has been studied over a wide range of HCl concns. $(0\cdot1-4M.)$ and of temp. $(30-60^{\circ})$; the variation is also recorded for $0\cdot2M$ -H₂SO₄, M-H₂PO₄, and M-AcOH, all at 60°, the changes in the EtOH/H₂O ratio being between 0 and 100% EtOH in the case of AcOH. k decreases with increasing proportion of EtOH. For EtOH $\geq 80\%$ in HCl, the results are accurately represented by the equation log k = mD + n, where D is dielectric const., m and m being const. for a given acid concn. and temp.; at EtOH >90% k rapidly increases again. The equation does not apply in H₃PO₄ or AcOH when EtOH is >60%, and when 4M-HCl is used. The vals. of E (Arrhenius) range from 22,000 for 20% EtOH to 25,700 for 80% EtOH in the case of 0·1M-HCl; the corresponding vals. for 0·4M-HCl and M-HCl and for M-HCl (100% EtOH) are respectively 23,500 and 27,500; 24,200 and 26,500; and 22,500. The isodielectric energies of activation (energies of activation for a solvent of temp.-invariant dielectric const.) are adduced in the discussion of reaction mechanism. Experimental results are discussed in relation to work done by other investigators; the various modern concepts used point to rearrangement rather than to proton transfer as the rate-determining step. J. LE.

Influence of alkyl groups on reaction velocities in solution. V. Formation of phenyltrialkylammonium iodides in methyl alcohol. D. P. Evans (J.C.S., 1944, 422—425).—Reaction rates of MeI with NPhMc₂ (I), NPhMeEt (II), NPhMeBu^a (III), and NPhBu^a₂ (VII) were found to be of the second order; those of MeI with NPhEt₂ (IV), NPhEtPr^a (V), and NPhPr^a (VI) showed slight autocatalysis. Vals. of *E* for (I), (II), (III), (IV), (V), (VI), and (VII) are respectively: 15,200, 15,400, 15,430, 18,000, 19,030, 19,060, 19,000; those for log *PZ* are: 6.9, 6.9, 6.7, 7.7, 8.2, 8.1 and 8.1; the temp. ranges of reactions are: 25—65°, 45—84°, 45—84°, and 65—100° for the rest. The large increase in both the *E* and the log *PZ* vals. in passing from methylalkylanilines to higher alkylanilines is noteworthy; the possible causes of this effect are discussed, the likelihood of steric effect being emphasised. The comparison of dialkylaniline-MeI reaction velocities (in MeOH, at 65°) with those of dialkylaniline-allyl bromide (in EtOH, at 40°) shows that the variation in velocity from base to base is independent of the alkyl halide and is governed by the nature of the alkyl groups in the base; the velocity coeffs. of the two sets of reactions decrease in the order Mc₂ > Me Et > Me Pr > Et₂ > Et Pr > Pr₂. J. LE.

Kinetics of aromatic sulphonation reactions. Sulphonation of pnitrotoluene and of chlorobenzene by sulphur trioxide. K. D. Wadsworth and C. N. Hinshelwood (J.C.S., 1944, 469–473; cf. A., 1939, I. 570).—The sulphonation reactions of p-C₆H₄Me·NO₂ (I) and of PhCl were found to be of the second order with respect to SO₃, the velocity coeffs. being determined from the initial reaction rates at different SO₃ concens. Both reactions show strong retardation with time, being in this and other respects similar to the PhNO₂ sulphonation with SO₃. The kinetic data for PhNO₂, (I), and PhCl sulphonations are respectively : E = 11,400, 11,025, and 7720; $\log PZ = 3.91, 4.79, \text{ and } 5.14$; the probability factor $P = 1.9 \times 10^{-7}$, 1.65×10^{-6} , and 3.2×10^{-6} ; the temp. ranges of reactions were $25-100^{\circ}, 0-60^{\circ}$, and $0-40^{\circ}$. The retardation of reactions is ascribed to the formation of a complex $[Ar \cdot SO_{3}H, SO_{3}]$; the second order may be due to 2 SO₂ mols. reacting either singly or as a dimer, S₂O₆. The reactions were carried out in PhNO₂; the reaction rates were retarded by H₂SO₄ at low, but were little influenced at higher, temp. J. LE.

Comparative study of the kinetics and mechanisms of formation of the phenylhydrazone, semicarbazone, and oxime of d-carvone. G. H. Stempel, jun., and G. S. Schaffel (J. Amer. Chem. Soc., 1944, 66, 1158—1161).—The reactions between NH_2OH , $NHPh\cdot NH_2$, and semicarbazide (I) and d-carvone proceed by the same mechanism, are acid-catalysed, show no salt effect, and have velocities ∞ the concus. of the ketone and the carbonyl reagent. Data agree with Hammett's mechanism for the (I) reaction. W. R. A.

Velocity and yield in continuous reaction systems. K. G. Denbigh (Trans. Faraday Soc., 1944, 40, 352-373).—Two types of process are considered, one (tubular reactor) in which the reactants flow in uniform motion through a single vessel, with no mixing between different points on the line of flow, the second in which the reactants flow continuously through a series of tanks, in each of which a uniform concn. is maintained by stirring. The kinetics of processes of the latter type are often susceptible of much simpler mathematical treatment than are those of the former, since the evaluation of integrals is not involved. Equations giving the size of reaction space required for a given rate of output of reaction product are given. Where unwanted side reactions occur the tubular reactor gives the higher yield when the useful reaction is of higher order than the wasteful reaction, whilst in the opposite case the stirred tank reactor is to be preferred. In reversible consecutive reactions, the highest yield in a given time is obtained when the val. of some parameter, such as temp., is so adjusted that the reaction velocity is the max. possible at every moment. This principle is applicable to such processes as the catalytic oxidation of SO₂ and the synthesis of NH₃, and the latter is given a detailed numerical treatment.

Analytical expressions of kinetic curves of phase transformations accounting for the dimensionality of growth of transformation products and the magnitude of three-dimensional nuclei. N. N. Sirota A. (Compt. rend. Acad. Sci. U.R.S.S., 1942, 36, 175--179)...-From Tammann's concept of a phase transformation as a process of creation of centres of new phases and the growth of these, kinetic expressions for phase transformations are deduced on the assumption that the transformations are isothermal and that the vol. of the growth of the centres of the transformation products and of the size of the three-dimensional nuclei is taken into account. For a small linear velocity of growth of the new phase (I) and a large velocity of the formation of centres, the magnitude of the threedimensional nuclei must be considered. If the linear growth ceases the kinetics are similar to those of a first-order change. Except for the case of (I), the velocity coeff. is c the power of the time to the dimensionality of the growth. Variation of the probability of is formation of two- and three-dimensional nuclei cases the exponent of the time to vary. The theory is briefly applied to a transformation of over-cooled austenite. J. O'M-B.

Mechanism of enzyme-inhibitor reactions.-See A., 1944, III, 766.

Velocity of tarnishing on metals as influenced by supersonic waves. J. A. Hedvall and G. Ekwall. Supersonic wave apparatus. K. Dahr (*Arkiv Kemi, Min., Geol.*, 1944, 18, A. No. 11, 25 pp.).—The effect of supersonic waves on the tarnishing of Cu by I, and of Fe in O₂ at higher temp., has been investigated. In both cases the supersonic vibration resulted in a considerable increase in tarnishing velocity. The velocity of tarnishing was determined by optical interference methods. Local rise of temp. produced by the supersonic waves might be a contributory factor in the effect, but cannot completely account for it, as was shown by comparing the velocity of tarnishing of Fe at different temp. It is probably to be explained by enlargement of the reacting surfaces due to disturbances in the phase boundaries. The construction of the supersonic wave apparatus is fully detailed. A. J. M.

Catalytic decomposition of Tschugaev's pentammine $[(NH_3)_5CIPt]Cl_2$ A. M. Rubinschtein (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 28, 55–58).—Solutions containing $[(NH_3)_5CIPt]Cl_3$ and $(NH_3)_4PtCl_2$ (I) at $>100^\circ$ ppt. a yellow salt having the composition

30 - 30, 30 - 30,

Free radicals in polymerisation processes. S. Medvedev, O. Koritzkaja, and E. Alexeeva (J. Phys. Chem. Russ., 1943, 17, 391–407).—When CH₂:CCl·CH:CH₂ polymerises in vac. in presence of Bz_2O_2 or tetrahydronaphthalene hydroperoxide, the reaction mixture liberates I from HI in an amount > that corresponding with the peroxide present, and also binds I in CHCl₃; the I-binding capacity is ∞ the degree of polymerisation. This capacity is

attributed to the presence of free radicals, *i.e.*, long chains with nonsaturated ends, in the mixture; a mutual saturation of these ends does not occur because of the high viscosity of the mixture. If to the mixture more of the monomer is added, it polymerises although no peroxide is present. If the polymer is recryst, it ceases to add I. If the polymerisation takes place in solution, the η of which is < that of undiluted mixture, the mixture does not react with either HI or I. The simultaneous polymerisation of $(CH_2:CH)_2$ and $CH_2:CH:CN$ also forms free radicals. A theory of the rate of polymerisation is given; it assumes formation of free radicals and agrees with experiment. J. J. B.

Antioxidant properties of *d*-isoascorbic acid and its sodium salt.— See A., 1944, III, 825.

Temperature activation and inactivation of the crystalline catalasehydrogen peroxide system.—See A., 1944, III, 839.

Apparent heats of activation and surface activity in surface catalysis over wide ranges of temperatures. F. H. Constable (*Rev. Fac. Sci. Istanbul*, 1943, 8, A, 112—119).—Mathematical. An equation for the apparent heat of activation is derived, and the significance of one of the terms in the equation being negative, zero, or positive is discussed. This term is (1/h) - 1/RT, where h is the const. occurring in the author's equation connecting the no. of active centres in a catalyst surface with the heat of activation on each centre and which depends on surface conditions. C. R. H.

Kinetics of ammonia decomposition on iron catalysts. I. Chrisman and G. Korneitschuk (*Acta Physicochim. U.R.S.S.*, 1943, **18**, 420– 429).—Discrepancies observed in data on the kinetics of NH₃ decomp. on Fe catalysts are due to structural differences in the catalyst. If a const. catalytic surface is maintained, reproducible results can be obtained. On a promoted technical Fe catalyst of the type Fe-Al₂O₃-K₂O free from nitride the decomp. of NH₃ is ~100 times as fast as on promoted nitride of the type Fe₂N-Al₂O₃-K₂O. C. R. H.

Dendrite hypothesis of carbon deposition. Chemical behaviour of cyclohexane when in contact with electrically heated metallic coils. A. Balandin and N. Kotelkov (Acta Physicochim. U.R.S.S., 1943, 18, 406-419).—The catalytic dehydrogenation and decomp. of cyclohexane over Pt- and Pd-nichrome, nichrome, Cr-Fe, and Fe at 300-600° has been investigated. Nichrome, Cr-Fe, and Fe are inactive. Pd-nichrome is a poor catalyst. Pt-nichrome is a good catalyst at higher temp. The deposition of C does not diminish the dehydrogenation activity of the catalyst; on the contrary, the activity is increased. Deposition of C in the form of dendrites is suggested in explanation. C. R. H.

Formation of carbon dendrites by catalytic decomposition of alcohols on metals. A. A. Balandin and V. V. Patrikeev (Compt. rend. Acad. Sci. U.R.S.S., 1943, 40, 152—154).—The catalytic decomp. of $Pr\beta OH$ on a constantan wire leads to deposition of C in the form of dendrites. It is possible that a film of carbide is first formed on the metal which is subsequently decomposed to C and metal, the latter being in a looser form than originally. The dendrites start growing from the deposited metal crystals. This behaviour is not observed in similar experiments with *cyclo*hexane. The dendrites contain O and H corresponding with $C_{23}H_4O$. Calculation of the diameter of a crystallite gives d = 45 A., a val. intermediate between the vals. calc. for peat coke and C_2H_2 soot. C. R. H.

Catalysis in producing potassium and sodium sulphates from chlorides decomposed with sulphur dioxide in the presence of oxygen. S. I. Volfkovitsch (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 41, 21— 23).—The oxidation of SO₂ to SO₃ in the vapour phase in presence of H₂O (for conversion of KCl into K₂SO₄ with SO₂ in presence of O₄ at 500—550°) can be accelerated several hundred times by means of catalysts containing Fe₂O₃. Burnt pyrites refuse from H₂SO₄ manufacture is best used as a 1% admixture by wt. with the KCl. 90—95% recovery of K₂SO₄ is obtained with a reaction time of $\geqslant 1.5$ hr. and 40% utilisation of the SO₂ per passage. L. J. J.

Catalytic alkylation of hydrocarbons in the gas phase. G. L. Natanson and M. J. Kagan (J. Phys. Chem. Russ., 1943, 17, 381– 390).—Synthetic alumosilicates are catalysts at 400–430° for the reactions $C_6H_6 + C_2H_4 \rightarrow PhEt$ (yield, e.g., 17% of the C_6H_6 employed), PhEt $\rightarrow C_6H_6 + C_2H_4$ (yield, e.g., 25%), and PhMe \rightarrow $C_6H_6 + C_6H_4Me_2$ (yield, e.g., 15%). The mechanism of these reactions is discussed. J. J. B.

Preparation and reclamation of copper-chromium oxide catalyst [for the dehydrogenation of alcohols]. R. E. Dunbar and M. R. Arnold (*Ind. Eng. Chem. [Anal.*], 1944, 16, 441).—Celite Carrier Type VII (I) and Carborundum Brand porous aggregates are satisfactory new inert carriers for supporting this catalyst. (I) is a porous variety of pellets possessing greater mechanical strength than the granular Celite previously used. The customary AcOH leaching and washing of the catalyst can be substituted by careful heating in air at 150°. Cu-Cr₂O₃ catalyst that has become sluggish in action from prolonged use can be reactivated by heating to expel absorbed org. matter and to reoxidise the metals. Leaching with AcOH and washing then provides a catalyst as active as the original. Data showing the behaviour of six Cu-Cr₂O₃ catalysts supported on three inert materials are recorded for the dehydrogenation of Bu^aOH. L. S. T.

Magnetic studies of chromium oxide catalysts .--- See A., 1944, I, 272.

Catalytic aromatisation of branched chain aliphatic hydrocarbons. -See A., 1944, II, 357.

Action of chromia catalyst on aliphatic iso-alcohols.-See A., 1944, II. 357.

Catalytic vapour-phase oxidation of nicotine to nicotinonitrile.-See B., 1944, II, 301.

Chemical-catalytic liquid-phase oxidation of nicotine, β -picoline, and quinoline to nicotinic acid.—See B., 1944, I, 302.

Mechanism of electrolytic oxidation of aluminium. S. Anderson (J. Appl. Physics, 1944, 15, 477–480).—It is suggested that in anodic Al_2O_3 films on Al, the porous film of Al_2O_3 is separated from the Al surface by a compact barrier layer of Al_2O_3 which is continuous, unbroken, and the seat of growth processes from which is con-tinuous, unbroken, and the seat of growth processes from which the porous coating originates. The barrier layer is formed by diffusion of Al^{***} ions to the solution without remaining in the film. Electric conduction within the film allows O^{**} ions to pass O^{**} through spaces left by diffusion of Al^{***} ions through it. The theory accounts for the adherence, porosity, experimental ^{***} efficiency ratios,^{***} and unmineconne L. J. J. luminescence.

Structure of anodic coatings [on aluminium].—See B., 1944, I, 373.

Electrodeposition of brass.-See B., 1944, I, 373.

Electrochemical oxidation of *n*-butyl alcohol. II. I. Radt-schenko (*J. Appl. Chem. Russ.*, 1940, **13**, 1348—1354).—A solution of Bu^{\circ}OH in 4% H₂SO₄, or a two-phase mixture of these liquids, was oxidised at a Pb anode. When the ratio [Bu^{\circ}OH]: [H₂SO₄] values of the set of the child of PraCO₂H decreased from 23-42% to 4-6% and the yield of PraCO₂H decreased from 23-42% to 4-6% and the yield of PraCO₂Bu (I) rose from 18-42% to 40-52%. The effect of the c.d. (0.01-0.06 amp. per sq. cm.) on these yields was less definite. The yield of CO₂ increased with c.d. The formation of (I) takes place probably at the line between the U COL I was and the Drobably at the line between the COL I was an order where the U SOL I was a set of the conduction of the set of the conduction of th H_1SO_4 layer, the Bu^aOH layer, and anode, where the $[H_2SO_4]$ is very high. J. J. B.

Mechanism of formation and development of a latent photographic image. P. D. Dankov and A. A. Kotschetkov (Compl. rend. Acad. Sci. U.R.S.S., 1940, 26, 785-787).—The theory previously put forward (A., 1940, I, 124) requires for its verification the presence of orientational relations between crystals of AgBr and those of Ag. Evidence of this has now been obtained. Monocryst, films of AgBr were pricked with a blunt needle. Crystal deformation lines appeared in the form of rosettes. At liquid air temp. instead of rosettes, cracks were formed along the cleavage planes. The crystals were then developed. Ag crystals were formed, strictly oriented both in relation to the deformation figures obtained before development, and with regard to each other. When the AgBr was deformed at liquid air temp. the Ag crystals developed so that the [110] axis of the Ag coincided with the [010] axis of the AgBr. When a monocryst. AgBr film was partly reduced (1 min. in developer) the film was covered with very small regular crystals of Ag, but each crystal had a thin sinuous continuation. With further reduction the small crystals grow together and completely cover the A. J. M. surface.

Kinetics and mechanism of photographic development. I. Kinetics of development of single grains .- See B., 1944, II, 337.

Photochemical investigation of dark-coloured aniline. A. T. Vartanjan (Compt. rend. Acad. Sci. U.R.S.S., 1941, 30, 635-638). --Pure NH₂Ph kept in a high vac. (10⁻⁵ mm.) did not become discoloured on keeping in the dark or on exposure to diffuse daylight. It rapidly became coloured when exposed to Mg sparks filtered through Iceland spar or gelatin. Light of $\lambda \ge 2800$ A. is effective. Increase of temp. causes a considerable increase in the velocity of the photochemical reaction, and the walls of the vessel become covered with resinous products, consisting of a volatile and a non-volatile portion. H_2 and NH_3 are also formed. C_8H_6 could not be detected spectrographically owing to the extinction effect of NH_2Ph . Excitation of the vapour in a quartz vessel gives rise to a yellowish-green fluorescence with a continuous spectrum over the range 6300—3840 A. The carrier of the fluorescence is probably azophenine. The primary processes are the splitting off of NH_2 and H from the Ph radical, as is shown by the analysis of the absorption spectrum of NH_2Ph . The reactions are: $NH_2Ph + h_{\nu} =$ NHPh + H; $NH_2Ph + h_{\nu} = C_8H_4 \cdot NH_2 + H$; $NH_2Ph + h_{\nu} =$ $Ph + NH_2$. The radicals $C_9H_4 \cdot NH_2$, NHPh, and $C_6H_4 \cdot NH$ lead to the formation of azophenine. Increase of temp. causes a dis-placement of the predissociation limit and the continuous absorption towards longer $\lambda\lambda$. A. J. M. covered with resinous products, consisting of a volatile and a non-A. J. M. towards longer λλ.

Asymmetric photolysis of β -chloro- β -nitroso- $\alpha\delta$ -diphenylbutane with circularly polarised light. S. Mitchell and I. M. Dawson (*J.C.S.*, 1944, 452-454; cf. A., 1941, II, 349).—A resolution of the racemic

form of a chloronitroso-compound was accomplished using the phenomenon of "circular dichroism" which is of interest in connexion with the origin of optically active compounds in nature. CH2Ph·CCI(NO)·[CH2]2·Ph selected for photolysis satisfies the three of 2^{11} Control [C112] if it selected for photolysis satisfies the three photochemical requirements: (a) the main product of photolysis (in MeOH), CH₂Ph·C(:N·OH)·[CH₂]₂·Ph,HCl, contains no asymmetric C atom; (b) sufficiently high quantum efficiencies—these being per λ 6100 and 6580 A., 1·10 and 0·78, respectively, with the average of 0.94; (c) the absence of dark reaction. The progress of the photolysis was followed by means of a photoelectric colorimeter, the first stage of the decomp. being carried to the extent of 50%, while in each of the three subsequent stages 40% of the recovered compound was decomposed; the total decomp. was equal to 90% of the original material. The final specimen of the compound exposed to the right-handed light gave the polarimetric val. $a_{5300}^{20} = -0.10^{\circ}$, and the specimen exposed to the left-handed light gave $a_{5300}^{20} = +0.11^{\circ}$ (l = 1, c = 4%, in MeOH). J. Le.

Photochemical properties of 1 : 4-dimethoxy-9 : 10-diphenylanthr-acene. R. Audubert and C. Racz (*Compt. rend.*, 1943, **216**, 413— 414).—The threshold frequency for the photochemical reaction $R + O_2 \rightarrow RO_2$ has been determined for 1 : 4-dimethoxy-9 : 10-diphenylanthracene (0.018 g. per l.) dissolved in anhyd. Et₂O. The vidation reaction was followed photometrically. The threshold is oxidation reaction was followed photometrically. The threshold is 4550 A. (61,060 g.-cal.), giving 85,000 g.-cal. as an upper limit for the heat of dissociation of the oxide (energy of activation 24,000 g.-cal.). Hence mol. O_2 is liberated in the dissociation. L. J. J.

IX.—PREPARATION OF INORGANIC SUBSTANCES.

Reactions in the solid state. P. P. Budnikov and A. S. Bereshnoi J. Appl. Chem. Russ., 1940, 13, 1277-1287).-A review of recent German publications. I. J. B.

Complex compounds of cupric azide. III. Non-electrolytes with Complex compounds of cupric azide. III. Non-electrolytes with organic bases. A. Cirulis and M. Straumanis (J. pr. Chem., 1943, [ii], 162, 307-328).—The following compounds of general formula [Cu(amie)₂(N₃)₂] are prepared (a) from Cu(N₃)₂ (cf. Cirulis, A., 1939, I, 621) and the amine in boiling EtOH, or (b) from Cu(NO₃)₂ in MeOH, the amine, and NaN₃ (methods of prep. indicated in parentheses): bis-allylamine- (a, b), decomp. 179-180°, -benzyl-amine- [a, b; or from benzylamine azide and Cu(N₃)₂ in H₂O at the b.p.], m.p. 152°, -tetrahydro-\beta-naphthylamine- (b), m.p. 115°, -bornylamine- (b), decomp. 207-208°. -β-picoline- (I) (a, b), explodes 207-215° (preheated block) or on strong percussion, -2: 6-dimethylpyridine- (b), explodes 198-202° (slow heating) or 220-225° (preheated block), -piperidine- (a), m.p. 109°, -cyclohexylamine- (b), m.p. 134°, dimethylpyridine- (b), explodes 202-203°, -2: 4: 6-trimethylpyridine-(b), explodes 198-202° (slow heating) or 220-226° (preheated block), -piperidine- (a), m.p. 109°, -cyclohexylamine- (b), m.p. 134°, -2-aminothiazole- (b), decomp. 145-150°, -isoquinoline- (b), decomp. 197-200°, -6- (b), decomp. 210-213°, and -7-methylquinoline-diazidocopper (b), decomp. 138-140°. Compounds of formula [Cu(amine) (N₃)₃] are prepared similarly : o.,* m.-* and p-toluidine-(b), explode 123°, 157-160°, and 135° respectively, o-anisidine-(b), detonates 125° (preheated block), " 1: 4 : 5- " (b), explodes 130° (preheated block), and " 1: 3: 4- "xylidine- (b), decomp. 106-108°, ψ -cumidine- (b), m.p. 119° (decomp. 120°), benzidine- (b), amorphous, o-tolidine- (b), decomp. unsharply, o-dianisidine- (b), amorphous, o-tolidine- (b), decomp. unsharply, o-dianisidine- (b), decomp. 122-124°, p-nitrosodimethylaniline- (b), ignites 132°, a-picoline-* (a, b), detonates 204-205°, β-picoline-* [a, or from (I) in hot MeOH], explodes 210-211°, 2: 4-dimethylpyridine-* (b), explodes 208-209°, quinoline-* (a, b), explodes 207-208°, piperazine- (b), decomp. 150°, benziminazole- (b), decomp. 185° or on strong percussion, quinine-tetramine- (b), explodes 149-151°, quinidine- (b), explodes 152-154°, cinchonine- (b), decomp. 154-165°, cinchonidine- (b), inflames 169°, and brucine-tetra-azidocopper, (Cu₂N₃)₂O(C₄H₁₅O₃N₃] (b), m.p. 172°, is also prepared. The above compounds are green or brownish, insol. in and stable to cold H₄O, decomp. in bot H₂O; in most, Cu has co-ordination no. 3. The compounds marked * explode on percussion. E. W. W.

Magnesium and barium beryllates. (Mile.) M. L. Quinet (Compt. rend. 1943, 216, 297-299).-Addition of a Mg salt in aq. solution to an alkaline Be(OH)₂ solution gives a ppt. containing Mg₃BeO₄, nH₂O. No Mg can be detected in the solution. A similar reaction is found alkali concns., the solution contains Ba and Be in equimol. ratio, BaBeO₂ is also found in the ppt. and solution when $Be(OH)_2$ is added to $Ba(OH)_2$ solutions. with Ba-Be solutions >1 or <0.1N. in alkali. With intermediate

Precipitation of mercury from solutions of sulphides with amal-gamated zinc. I. N. Plaksin and L. D. Plaksina (Compt. rend. Acad. Sci. U.R.S.S., 1943, 40, 188–190).—Zn amalgam containing 4% of Hg ppts. up to 98.5% of Hg from Na₂S solutions in 12 hr. With a higher Hg : Zn ratio 99.9% of the Hg can be pptd. in 30 min. The temp. range $9-20^{\circ}$ is suitable. Pptn. of Hg from BaS solutions

with amalgamated Zn requires temp. $<10^{\circ}$ and alkalinity <0.5%. The consumption of Zn is 1.5-2 times the wt. of Hg recovered.

L. J. J. Etching figures on the surfaces of aluminium crystals. II. H. Mahl and I. N. Stranski (Z. physikal. Chem., 1942, B. 52, 257-262). --Etching of Al crystals with aq. or alcoholic HCl shows a cubic structure. If the etching is done by dry HCl at high temp., octa-hedra in combination with cubes are observed. This is in agreement with the theory that in the case of aq. and alcoholic HCl the etching figures are due to dissolution of a reaction product, whereas with dry HCl at the temp. used any AlCl_a produced would be volatilised off. A. J. M.

Aluminium orthohydroxide and its transformation into bayerite. H. Kraut, E. Flake, W. Schmidt, and H. Volmer (Ber., 1942, 75, [B], 1357–1373).—Al(OH)₃- C_a is obtained by the action of aq. NH₃ on Al₂(SO₄)₃,10H₂O and filtration of the ppt., which is agitated with successive amounts of H_2O over long intervals of time; the pH of the solution must be $\gtrsim 7.4$. The product usually contains SO₄", which can be removed only by very careful, prolonged washing. Such preps. are very rapidly sol. in 0.1% HCl but this property, which is very sensitive to pH, is immediately lost if pH reaches 8. The ageing of Al(OH)- C_a is followed by periodical determinations of H₄O and Debye-Scherrer X-radiograms, those of böhmite in its different stages of formation, bayerite-A, -B, and -C, and hydrargillite being determined for comparison. C_a shows no interferences. Pro-ducts undergoing ageing show the bohmite lines until the min. H₁O content is reached (poly-Al hydroxide-A gives well defined bohmite lines). The rate of alteration varies greatly with the details of prep. and, particularly, with the [NH₃] in the ultimate suspension. Further ageing causes the bayerite lines also to appear, with gradually increasing intensity, until they alone are observed. The H_2O content gradually increases. The hitherto unknown lattice of bayerite-C (prep. described) appears only when ageing of C_a occurs under NH₂.

Basic lanthanum nitrite. G. R. Sherwood (J. Amer. Chem. Soc., 1944, 66, 1228–1229).—La basic nitrite, prepared from LaCl₃ or La(NO_3)₃ by the method of Sherwood and Hopkins (A., 1933, 1008), liberated I from HI, reduced acidified KMnO4, and was thermostable up to the b.p. of conc. H_2SO_4 . The speed of pptn. increased with $[NO_2']$ and ppts. obtained using different initial $[NO_2']$ (0.5—2.0M.) gave identical analyses. With $[NO_2'] < 0.5M$. no nitrite was obtained; presumably only $La(OH)_3$ was pptd. To prevent formation of colloidal particles the $La(NO_3)_3$ should have an initial pH ~5. W. R. A.

Artificial production of diamonds. C. H. Desch (Nature, 1943, 152, 148-149) .- The conclusion that diamonds have not been prepared artificially is reviewed in the light of recent X-ray investig-É. R. R. ations of Hannay's artificial crystals.

Pure charcoal from cane sugar.-See B., 1944, I, 354.

Preparation of silicon tetrachloride and its use as a basis for obtaining silicie acid esters. K. Andrianov (Compt. rend. Acad. Sci. U.R.S.S., 1940, 28, 66-69).—Ferrosilicon containing 35-65% Si reacts with dry Cl₂ at temp. >200°. The reaction is thermally self-supporting. As by-products, FeCl₂ is formed in negligible amounts, and Si₂Cl₆ to the extent of 3—10% of the SiCl₄ at temp. <450°. No Si₂Cl₆ is formed above 450°. The yield of SiCl₄ reaches a max. val. of ~95% at 600°. Esters of Si(OH)₄ are prepared by adding SiCl₄ dropwise to the alcohol at 0°, stirring for 1 hr. at room temp., and heating at 80—90° for 2 hr. The best yield is obtained with >10% excess of alcohol. Insufficient proportions of alcohol give some Cl-ester. The yield is adversely affected by the presence of H₂O in the alcohol. 70-84% yields are quoted for Me, Et, and Bu esters. L. J. J.

Separation of oxygen isotopes by distillation of water. H. G. Thode, S. R. Smith, and F. O. Walkling (*Canad. J. Res.*, 1944, 22, **B**, 127-136).—The apparatus consists of three 25 ft. columns of b, far the appartus consists of three 29, I, 211). Mount-ing is staggered to facilitate pumping between shafts. Haydrite aggregate is a suitable packing material and could be used in the tubes of 2-3 ft. diameter. Only 15% of the liquid held drains immediately from such a packing; hence the columns can be closed for repair without complete mixing of all the column materials. The accuracy of the spectrographic examination of ^{18}O was >1%. The accuracy of the spectrographic examination of the mass spectrographic lines of $^{13}C^{16}O^{16}O$ and $^{12}C^{16}O^{17}O$. Distillation for 120 days produced 23 g. of ^{18}O in excess of normal, including 150 ml. of water enriched 6.5-fold in ^{18}O and 2.7-fold in ^{12}O . The v.p. of the H217O is the algebraic or geometric mean of the v.p. of H216O and H, 18O. Cohen's theory for the operation of packed fractionating and $H_2^{18}O$. Cohen's theory for the operation of packet fractionation columns explains the effect of rate of flow on equilibrium fractionation and agrees qualitatively with the production rates of ^{18}O . The 50% efficiency obtained is the same as that reported by Cohen in the chemical exchange process: (NaCN_{sol}-HCN_{gas}). J. O'M-B.

Oxidation of hydrogen sulphide by chromates in aqueous solution or suspension. H. B. Dunnicliff (J. Indian Chem. Soc., Ind. Ed.,

1944, 7, 43-46).-- A review. A full scheme of the reactions occurring is given. M. H. M. A.

Lower oxides of sulphur. I, II. P. W. Schenk (*Chem.-Zig.*, 1943, 67, 251-253, 273-276).—A review of published information on the prep., purification, and properties of SO, poly-S oxides, and S₂O₃. L. J. J

L. J. J. Normal and poly-molybdates of some complex cations and the composition and constitution of metamolybdates. P. Rây and B. Sarma (J. Indian Chem. Soc., 1944, 21, 139–144).—The prep. of the following is described : $[CoX_3]CIMoO_4$, $[CoX_3]_2[MoO_4]_3, 6:5H_2O$, $[CoX_3]_2[MoO_4]_3, 3H_2O$, $[NiX_2][MoO_4]_3, 3H_2O$, $[CiX_3][MoO_4]_3, 2:5H_2O$, $[CoX_3]_2[Mo_7O_{24}]_9, 9H_2O$, $[CoX_3]_2[HMO_2O_7]_6, 12:5H_2O$ (I), $[Co en_3]_2[HMO_2O_7]_6, 13:5H_2O$ (II), and $[Co en_3]_2[HMO_2O_7]_6, 11:5H_2O$ (III), where X = biguanide and en = $(CH_2 \cdot NH_2)_2$. (I), (II), and (III) lose their H₂O of crystallisation at 100°, leaving three mols. of combined H₂O. This is regarded as evidence in favour of Rosen-heim's structure for the metamolybdates, which are represented by

heim's structure for the metamolybdates, which are represented by R.H.[H2(MO2O7)6],aq. C. R. H.

Synthesis of ammonium phosphates from ferroferriphosphates. M. M. Bikov (Compt. rend. Acad. Sci. U.R.S.S., 1943, 40, 66-69). —The compound FeO,4Fe₂O₃,3P₂O₆,21H₂O has been obtained by natural oxidation (10 years) of Fe^{II} phosphate; oxidation of this or of natural β -kerchenite at 600° gives the compound 3Fe₂O₃,2P₂O₆. Crystal-optical data are given for these and (NH₄)₂PO₄,3H₂O. Fe phosphates may be converted into NH, phosphates by (NH,).S. W. R. A

W. R. A. Nickelocyanic acid and its salts. F. Feigl, V. Demant, and O. E. de Oliveira (Anais Assoc. Quím. Brasil, 1944, 3, 72-87).—K₂[Ni(CN)₄] with CuSO₄ gives $Cu[Ni(CN)_4], H_2O$, which with aq. NH₃ yields $[Cu(NH_3)_4][Ni(CN)_4]$. $Co[Ni(CN)_4], UO_2[Ni(CN)_4], Mn[Ni(CN)_4]$, $Fe[Ni(CN)_4]$, $[Fe^{II}\{2:2'-(C_5H_4N)_2\}_3][Ni(CN)_4]$ and $(pp'-NH_2\cdot C_6H_4)_2H_2[Ni(CN)_4]$ were also prepared. The compound of Bernoulli and Grether (A., 1901, i, 584) from Ni(CN)₂ and NH₃ is also obtainable from [Ni(NH₃)_4]Cl₂ and K₂[Ni(CN)₄] but is con-sidered to be a mixture of [Ni(NH₃)_4][Ni(CN)_4] and $[Ni(NH_4)_4][Ni(CN)_4]$. For a compound described by Hofmann and

sidered to be a mixture of $[Ni(NH_3)_4][Ni(CN)_4]$ and $[Ni(NH_3)_2][Ni(CN)_4]$. For a compound described by Hofmann and Küspert (A., 1897, i, 546) the formula $[Ni(NH_3)_2(C_6H_4)_2][Ni(CN)_4]$ is proposed. $Ni(CN)_4$ is considered to be $Ni[Ni(CN)_4]$ because with $(CH_2 \cdot NH_3)_2$ (en) it gives $[Nien_3][Ni(CN)_4], H_2O$. $[Ni(NH_2Ph)][Ni(CN)_4]$. $[Ni(2:2'-(C_5H_4N)_2)_2][Ni(CN)_4]$, and prob-ably $[Ni\{2:2'-(C_5H_4N)_2)_2][Ni(CN)_4]$ were also prepared. $K_2[Zn(CN)_4]$ with $NiSO_4$ gives $Ni[Zn(CN)_4]$ which in aq. suspension at 90° is converted into $Zn[Ni(CN)_4]$, also obtained from $K_4[Ni(CN)_4]$ with $ZnSO_4$, $Ni(CN)_2$ with $Zn(CN)_2$, $Ni(CN)_2$ with $Zn(NO_3)_2$, and $Zn(CN)_3$ with $Ni(NO_3)_2$. $Cd[Ni(CN)_4]$ is obtained by analogous methods even in the cold. F. R. G.

Pyridine complexes of rhodous halides.-See A., 1944, II, 377.

Thiosulphate compounds of palladium. D. I. Riabtschikov and A. P. Isakova (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **41**, 161— 164).—When acted on by S_2O_3'' , Pd salts react in an analogous manner to those of Pt. Equimol. quantities of $K_2[PdCl_4]$ (I) and $Na_3S_2O_3$ react to form a black ppt. of $PdS_2O_3 + PdS$. Pptn. of Pd is quant. With <2 mols. of $Na_2S_2O_3$, yellow $K_2[Pd(S_2O_3)_2]$, sol. in an excess of $Na_2S_2O_3$, is pptd. [PdCl_4][Pd4NH_3] dissolves readily in aQ, $Na_3S_2O_3$ at the ordinary temp. to yield an orange coloured

in an excess of Na₂S₂O₃, is pptd. [PdCl₄][Pd4NH₃] dissolves readily in aq. Na₂S₄O₃ at the ordinary temp. to yield an orange-coloured solution from which EtOH ppts. bright yellow [Pd(S₂O₃),][Pd4NH₃]₃. Aq. trans-[Pd2NH₃Cl₂] and aq. Na₂S₂O₃ form sparingly-sol., pale yellow [Pd2NH₃(S₂O₃,H₄O]. With aq. Na₂S₂O₃ and aq. [Pd4NH₃]Cl₂ the reactions [Pd4NH₃]Cl₂ + Na₂S₄O₃ \rightarrow [Pd4NH₃]Cl₂ the reactions [Pd4NH₃]Cl₂ + Na₂S₄O₃ \rightarrow [Pd4NH₃]S₂O₃ + 2NaCl, or [Pd3NH₃,S₄O₃] + 2NaCl + NH₃, or [Pd2NH₃,S₄O₃,H₂O] + 2NaCl + 2NH₃, can take place. With 2 mols. of Na₂S₂O₃, the reaction [Pd4NH₃]Cl₂ + 2Na₂S₂O₃ \rightarrow Na₄[Pd2NH₄(S₂O₃)₂] + 2NaCl + 2NH₃ occurs. The CS(NH₂)₃ de-rivative [Pd4CS(NH₂)₂]Cl₂ and Na₂S₂O₃ in conc. solution yield an orange-red ppt. of (Pd2CS(NH₂)₂,S₄O₃,H₆O] with CS(NH₂)₄ in the trans-position. With an excess of Na₂S₂O₃, the sol. product is Na₂[Pd2CS(NH₂)₂,2₅O₃], which crystallises with 6 H₂O on treat-ment with EtOH and evaporation over H₂SO₄ in an atm. of CO₂. The (CH₂'NH₂)₂ (en) compound [Pd2 en]Cl₂, prepared by heating (I) The $(CH_2 \cdot NH_2)_2$ (en) compound [Pd2 en]Cl₂, prepared by heating (I) with an excess of $(CH_2 \cdot NH_2)_2$, recats with Na₂S₂O₃ to give [Pd enS₂O₃] and Na₂[Pd en(S₂O₃)₂]. Excess of Na₂S₂O₃ displaces en completely from the inner sphere, S₂O₃ residues being substituted. L. S. T.

Compounds of palladium with carbon monoxide. A. Gelman and E. Meilach (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, **36**, 171–174).— By passage of CO for several days through $(NH_4)_2PdCl_4$ in conc. HCl the compound obtained is not $NH_4[PdCl_3CO]$ but $NH_4[PdCl_4CO]$. By metathesis reactions with $[Pt(NH_3)_4]Cl_2$ and with $(CH_2 \cdot NH_2, HCl)_2$ the compounds $[Pt(NH_3)_4][PdCl_2CO]_2$ and $(en H_2)[PdCl_2CO]_2$ have been isolated. The structure of these compounds is discussed in terms of the co-ordination theory and formulæ are advanced on the terms of the co-ordination theory, and formulæ are advanced on the assumption that the compounds are dimerides containing the ion -CI

CI

The instability of the Pd carbonyl halides

probably causes Pd to be tervalent in these compounds.

I. O'M-B.

X.---LECTURE EXPERIMENTS AND HISTORICAL.

Founders of the Italian school of chemistry. D. Marotta (Ber., 1942, 75, [B], 2095—2100).—An historical review dealing with the work of Piria, Cannizzaro, and Paternò. It is claimed that Paternò originated the hypothesis of the tetrahedral C atom. A. J. M.

William Albert Noyes. B. S. Hopkins (J. Amer. Chem. Soc., 1944, 66, 1045-1056).—Obituary notice. W. R. A.

XI.—GEOCHEMISTRY:

Chemistry of the earth. J. S. Anderson (*J. Proc. Roy. Soc. New South Wales*, 1943, 76, 329-344).—A lecture. Recent contributions of geochemistry to the problems of the relative and abs. abundance of the elements and their distribution are reviewed. C. R. H.

a-Helium method for determining geological ages. R. D. Evans and C. Goodman (*Physical Rev.*, 1944, [ii], **65**, 216-227).—New techniques for determining the rate of He production in igneous rocks by direct counting of the a-rays and the removal and measurement of He accumulated in rock during geologic time provide a direct, simple, and rapid physical method of He age analysis. Equations are derived relating the true rate of He production to the observed rate of a-particle emission from a thin source. Simple, accurate age corrections to the approx. age are derived. Agreement between "a-He" and "Rd-Tn-He" ages on the same samples indicates that the accepted decay consts. of the parent elements, Th and U, are correct to ± 5 -10%. Certain mineral constituents allow a significant amount of their radiogenic He to escape during geologic time. Magnetite is a suitable retentive mineral to serve as a basis for the revised He scale. The .a-activity of 81 rock specimens ranges from 0 to 5.8 with an average of 1.23 a-rays per hr. per mg. N. M. B.

Helium content of air. E. Glückauf (Trans. Faraday Soc., 1944, 40, 436—439).—A simple method is described in which He in air is determined with an accuracy of 1% by treatment with C cooled in liquid N₂ until all the Ne and part of the He has been absorbed. The residual He is measured, and the amount found is corr. for the absorbed fraction by means of a duplicate experiment with He-free air containing a measured quantity of He, carried out under identical conditions. The val. found is $5\cdot24\pm0\cdot03$ p.p.m. by vol., in good agreement with more exact determinations. F. L. U.

Hydrology of the Sierre (Valais) region. I. Relation between superficial and deep waters. II. Géronde lakes. J. P. Buffle (Arch. Sci. phys. nat., 1943, [v], 25, Suppl., 286-292, 292-295).-I. Chemical analyses of the H₂O of the Rhone, the sources of the Géronde lake, and various well waters are recorded and discussed.

II. Chemical analyses of the waters of the Rhône, and of the large and the small lakes of Géronde, are recorded. The lack of any direct relationship between the large Géronde lake and the Rhône is confirmed. The big difference in composition between the H_2O of the large Géronde lake and that of the H_2O of the small lakes east and west of it is discussed. L. S. T.

Source of supply of Blue lake near Kandersteg (Bernese Oberland). J. P. Buffle (Arch. Sci. phys. nat., 1944, [v], 26, Suppl., 18–22).— Chemical analyses of the lake H_2O and the H_2O of the River Kander are recorded. Comparison of the data excludes direct communication between the two, but the possibility of indirect communication is discussed. L. S. T.

Sodium sulphate waters of the Kungurian deposits at Levshino. A. M. Kuznetzov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **30**, 424– 427).—Analytical data on waters drawn from wells bored in different rocks to different depths are discussed and explanations of the base-exchange and other processes responsible for their formation are advanced. W. R. A.

Boron contents of some lakes of Western Kasakhstan. D. I. Kuznetzov (J. Appl. Chem. Russ., 1940, 13, 1332–1335).—KCl and B_2O_3 contents of 50 H_2O samples are given; the highest $[B_2O_3]$ was 0.053%. J. J. B.

Manganese in the sediments of polar seas. M. V. Klenova and A. S. Pachomova (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 28, 87— 89).—The Mn content of mud samples from the Barentz, Kara, and Greenland Seas ranged from 0.010 to 1.51%. The high concns. are found in separate areas of brown mud. In all cases the Mn content increases with the fineness of the sediment, and hence with the depth of the sea bed. The accumulation of Mn is favoured by oxidising conditions and high salinity gradients. L. J. J.

Phosphorus in sediments of polar seas. M. V. Klenova and M. L. Budianskaja (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, **28**, 82-86). —The P distribution in the upper layer of bottom deposits in Polar seas in stations distributed over the Barentz, Kara, and part of the Greenland Seas, was examined. P contents of sediments were in the region 0-0-32% (dry). No correlation with any single condition of sedimentation was found. L. J. J. Sediments of the Barentz Sea. M. V. Klenova (Compt. rend. Acad. Sci. U.R.S.S., 1940, 26, 796-800).—The sediments are classified according to particle size. The most widespread sediment is sandy mud. The most commonly occurring oxide in it is SiO_2 . The concn. of other oxides present varies with the grain size. Analyses are given. A. J. M.

Bacteria in the bottom sediments of the Dead Sea. B. Elazari-Volcani (*Nature*, 1943, 152, 274-275).—Profiles 10 to 170 cm. long were obtained from depths of 70 to 330 m. in the Dead Sea in December, 1941. The layers of colours, indicating zones of sedimentation, showed no seasonal repetition. S_2O_3 "-oxidising, cellulose-decomp., very active lactose- and glucose-fermenting, and denitrifying bacteria were found in enriched cultures. E. R. R.

Crude salt deposits in the separation pans of sea basins in the Kara-Bogas-Gol area. V. S. Egorov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 30, 505—508).—The sinking of the level of the Caspian Sea has resulted in a smaller inflow of H_2O into the basins of Kara-Bogas-Gol. This has resulted in a concn. of brine, and in 1039 the first crystallisation of NaCl was observed. Dilution of the brine is necessary for the deposition of sulphates. The increase in concn. of the solution leads to a decrease in separation of mirabilite. The cause of this is discussed. The effect of addition of fresh H_2O to brine on the order in which salts are deposited in the basin is considered. A. J. M.

Unusual occurrence of bedded thenardite. E. Spencer (Min. Mag., 1944, 27, 29—31).—Brine (NaCl 18.5, Na₂SO₄ 6.6, Na₂CO₈ 0.4, NaHCO₃ 0.4%) from shallow wells at Didwana, Jodhpur State, India, is evaporated in salt-pans dug on the surface of the ground, yielding a crop containing NaCl 87.2, Na₂SO₄ 11.2, Na₂CO₃ 0.2, NaHCO₃ 0.1, insol. 0.64, H₂O 0.66%. NaCl:Na₂SO₄ in the brine is 3 : 1, and in the salt 8 : 1. In the course of time large deposits of sulphate have accumulated beneath the salt-pans, containing Na₂SO₄ 91.9, NaCl 0.8, insol. 5.7%, etc. Optical data of the wellformed crystals are given. The crit. temp. for the formation of thenardite (anhyd. Na₂SO₄) from a saturated solution of NaCl is 18°, below which the temp. at Didwana rarely falls, when Glauber's salt would be formed. L. J. S.

Presence of leucitic rock in the Kolyma River basin. G. Bilibin (Compt. rend. Acad. Sci. U.R.S.S., 1940, 28, 79-81).—Results of examination of leucitites from the Kolyma River basin in the region of 67° 52' N. lat., 161° 39' E. long., are described. The leucities alternate with layers of tuff and tuffaceous breccia near a centre of eruptive activity. L. J. J.

Solfataric alteration of rocks at Kilauea volcano. G. A. Macdonald (Amer. J. Sci., 1944, 242, 496—505).—Solfataric alteration of olivine basalt lava and ash at Kilauea Caldera has produced rocks composed mainly of opal with some kaolin, ilmenite, and magnetite. Most of the MgO, CaO, and Na₂O, and much of the Al₂O₃ and Fe₂O₃, have been removed. The vol. and porosity of the rock are practically unchanged, and original structures and textures have been preserved. The alteration resembles that in areas of acid emanations in other volcanic districts. Alteration to limonite and goethite is less abundant. L. S. T.

Attempted revision of the formula of the mineral hibschite. D. S. Beliankin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **30**, 420-423).---From analytical data the formula

 $3(Ca,Mg)O,(A1,Fe)_2O_3,2(Si,Ti)O_2,2H_2O$ is proposed. W. R. A.

Pickeringite and ferropickeringite—minerals of the pyrite conflagrations in the Urals. G. N. Vertuschkov (Compt. rend. Acad. Sci. U.R.S.S., 1941, 30, 334—336).—Pickeringite (I) and ferropickeringite (II) are minerals produced by underground pyrite conflagrations. They are stable in air, but dissolve readily in H_2O . (I) shows a very thin, parallel, fibrous structure, low double refraction, and has n 1.479. When heated it dissolves in its own H_2O of crystallisation, and fuses to a white, lustrous, brittle bead, which is fairly hard, and has weak magnetic properties. The aq. solution is acidic. (II) forms friable, white, fibrous aggregates, of hardness ≥ 1 , d 1.79. It is readily fusible. After heating in the blowpipe flame, the residue is strongly magnetic. Its empirical formula is (Mg,Fe)Al₂(SO₄)₄,22H₂O. (II) can be distinguished from (I) and from halotrichite only by analysis. The origin of these minerals is discussed. A. J. M.

Occurrence in the Khalilovo iron ore deposits of magnetite formed from solutions of superficial origin at low temperature. B. P. Krotov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 26, 801-803).— The magnetite in these deposits is partly clastic, but pisiform grains, a continuous crust with regular crystals in the cavities at the surface of serpentinites, and veinlets are also found. The pisolitic structures have been formed by pptn. from solutions, part of the Fe₂O₃ having been reduced to FeO by decaying vegetable remains. The magnetite in veinlets originated at the epoch of diagenesis of the sediments of the basin (Jurassic) and their chloritisation. The magnetite in this area is thus of hypergene origin. A. J. M.

Mineralogical aspects of the system $FeO-Fe_2O_2-MnO-Mn_2O_3$.----See A., 1944, I, 282.

Binary system P₂O₅, 2CaO, P₂O₅, -Sec A., 1944, I, 281.

Phosphate-siderite rocks of the Turga horizon of Transbaikalia. K. S. Andrianov and A. I. Smirnov (Compt. rend. Acad. Sci. U.R.S.S., 1940, 28, 75-78).—Results of an investigation of the Zaza series in exposures along the Vitim and Zaza Rivers (Lower Cretaceous deposits in the Eravna district of the Buriat-Mongol Republic) are reported. Palæontological, geological, and mineralogical data for a no. of beds encountered are given. Phosphatised siderites and phosphorites have been formed in a fresh- H_2O lacustrian basin. This is possible in an alkaline reducing medium containing the ions concerned. Reducing conditions are evidenced by abundance of org. matter, pyrites, and bituminous shale. Phosphatised siderites form 24 bands with total thickness 2.5 m. L. J. J.

Ferruginous manganese rocks in the phosphorite-bearing beds of the Kara-tau. P. L. Bezrukov (Compl. rend. Acad. Sci. U.R.S.S., 1941, 30, 433-435).—The Cambrian deposits of Kara-tau show a combination of several chemical sediments : phosphate, siliceous, ferruginous, and Mn. The mode of their accumulation is discussed. W. R. A.

Genesis of the Mazul manganese deposit. G. D. Afanasiev, N. C. Aidinian, and I. V. Borisevitsch (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 26, 792-795).—The ores occurring in the Mazul deposit are and the process of ore formation is divided into four discussed, stages. The ores are chiefly carbonates, and oxidised with and re-ores. The origin of the deposit appears to be primarily sedimentary, with a subsequent superposition of regional metamorphism. A. J. M.

A. J. M.

Axinite from the mine "Julia " of the Khakas province." S. M. Kurbatov (Compt. rend. Acad. Sci. U.R.S.S., 1941, 30, 428-430) .-Analysis of axinite confirms Vernadski's formula, viz., $CaB_2Si_2O_8, 2Ca(Al,Fe)_2Si_2O_8, 2(Ca,Fe,Mn,Mg,H_2)_2SiO_4.$ W. R. A.

Alkaline rocks of the Kovdor-Ozero region of the Kola peninsula. J. P. Ivensen (Compt. rend. Acad. Sci. U.R.S.S., 1941, 30, 337-339).—The alkaline rocks in the neighbourhood of Lake Kovdor fall into two groups : (1) alkaline cancrinite and nepheline syenites, and (2) ijolite-urtites. The location of the rocks is given and their origin is discussed. A. J. M.

Relations of clinoenstatite to enstatite and diopside. D. S. Beliankin and B. V. Ivanov (Compt. rend. Acad. Sci. U.R.S.S., 1941, 30, 647-648).-Interaction of refractories in an open-hearth furnace gave rise to the formation of large skeleton crystals of clinoenstatite, the surface of which was overgrown with shells of enstatite-diopside (I) in a parallel crystallographic position, and at the edge, passing into yellowish-green augite. This shell-like crystallisation of (I) around clinoenstatite resembles that of microcline around plagio-clase. It is suggested that the sequence of crystallisation is governed by temp. A. J. M.

Mineralogy and geochemistry of the lead ore-bearing deposit Mirgalimsai in South Kazakhstan. E. V. Schevtschenko and V. K. Monitsch (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **41**, 30-32).— The Mirgalimsai deposit in the Djambul district contains fine-grained disseminated ores bedded in Upper Devonian limestones. The deposit is a telethermal type connected with the Variscian folding of the Karatau region. A detailed history of the mineralis-tion process is presented. Elements characteristic of the head ation process is presented. Elements characteristic of the basal magma (Ni, Co) are absent. Sn, Bi, and As, characteristic of Variscian deposits adjoining Uzbekstan and Kirghizia, are also absent. L. J. J.

Heats of transformation in the systems wurtzite-sphalerite and cinnabar-metacinnabarite.-See A., 1944, I, 282.

Nickel and cobalt in the manganese ores of Chiatura (Georgia). O. E. Zvjagintzev (Compt. rend. Acad. Sci. U.R.S.S., 1942, 36, 180– 181).—Recent analyses of the Mn ores of the Chiatura district having an accuracy of 0.0005% of the sample wt. show that both oxide and carbonate ores contain nearly const. amounts of Ni and Co slightly >, and in the ratio of, their Clarke nos. The concn. is independent of the type of ore and the Mn content. J. O'M-B.

Birefringence of gypsum and barytes in the extreme red and near infra-red. J. Jaffray (Compt. rend., 1943, 216, 409-410).—The birefringence $n_g - n_p$ of a sample of gypsum was 0.0092 for Na-D at 17°, and decreased from 0.00917 to 0.00865 over the λ range 6000—8800 A. at 17°. A barytes sample cut perpendicularly to the acute bisector of optic axes had $n_m - n_p$ 0.00116 for Na-D at 16°, decreasing from 0.001155 to 0.001046 between 6000 and 9000 A. at 16°. L. J. J.

Isomorphic substitutions in carbonate-apatite. I. Borneman-Starinkevitsch and N. Belov (Compt. rend. Acad. Sci. U.R.S.S., 1940, 26, 804–806).—The formula $xCa_{10}P_8O_{24}F_2 + yCa_{10}P_8CO_{23}(F,OH)_3$ corresponds with the % compositions of minerals of the carbonate-apatite class. There is $P \rightarrow C$ substitution. A. J. M.

New mineral species of the platinum group. O. E. Zvjagintzev Compt. rend. Acad. Sci. U.R.S.S., 1940, 26, 788-791).-Norilsk

Pt differs considerably from Ural Pt in containing a high proportion of Pd (2—14%), Fe (13—26%), Ni (>25.6%), Cu (>9.3%), and some Ag. It is probable that the Pt grains have cryst. out of a gaseous medium which contained carbonyls of Pt, Ni, Fe, Cu, and Pd. A. J. M.

Serpentine pseudomorphs after actinolite. V. N. Schtscherbina (Compt. rend. Acad. Sci. U.R.S.S., 1943, 41, 176-177),-An original mineral formation encountered in the Ebeita serpentinite massif is shown to be a large pseudomorph of serpentine after radial actinolite. Its mineralogy is described and its origin is discussed. L. S. T

Quantitative characteristics of the degree of uniformity of mineralisation, X a/b. I. S. Stepanov (Compl. rend. Acad. Sci. U.R.S.S., 1941, 30, 511-514).—The degree of uniformity of mineralisation is the ratio of the average metal val. to that of rich ores. The method of calculating this quantity, and some vals. for various deposits, are given. A. J. M.

Adsorption of hardness-reducers by rocks at different concentrations. M. V. Efimov (J. Appl. Chem. Russ., 1940, 13, 1336–1340).—Solu-tions of NaCl, MgCl₂, and AlCl₃ become alkaline in contact with powdered granodiorite (felspar + biotite + quartz), the [OH] being in AlCl₃ solution > MgCl₂ > NaCl. This is correlated with the acceleration of boring observed when NaCl, MgCl₂, or AlCl₃ is added to H O lubricating drille in Au minace added to H₂O lubricating drills in Au mines. J. J. B.

Content of radioactive elements in some soils of the U.S.S.R. V. I. Baranov and S. G. Zeitlin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **30**, 330–333).—Soils on lat. 40° N. were examined. The content of Ra and Th in all the soils investigated was of the same order, viz., 10^{-11} % Ra and 10^{-4} % Th. The ratio Th/Ra is approx. the same in all cases, the average being 6.9×10^6 , which is approx. the same as the Th/Ra ratio in rocks. The emanation power of the soils was also determined. They all emit an appreciable amount of Rn and Tn. The emanating power is, on the average, 41% Rn and 45% Tn. A. J. M.

Geological conditions of gas accumulations in coal deposits in the **Kuznetzk Basin.** A. I. Kravsov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 41, 27—29),—The Aralichevo coal deposit of the Stalinsk region is associated with alternating sandstones, aleurolites, argil-lites, and carbonaceous shales over a thickness of 375 m., containing 12 workable seams 1—8.4 m. thick. The coal contains 7—12% of volatile matter. The deposits are thrown into a large no. of folds and have a birth CH contant, increasing with depth and in folds and have a high CH₄ content, increasing with depth and in the anticlinal crests, and varying considerably from one fold to another. L. J. J.

Genetic classification of caustobiolites. A. F. Dobrjanski (J. Appl. Chem. Russ., 1940, 13, 443-446).—If the analyses of the org. part of wood and fossil fuels are represented in a triangular diagram with C, H, and (O + S + N) in the summits, it is seen that they form two distinct branches which touch each other at the beginning (at small C contents). To one branch belong wood, peat, lignite, coal, and anthracite; the other includes sapropel, oil shale, sapro-pelite, asphalt, petroleum, and asphaltites. These facts serve to solve the problem of the origin of petroleum and asphaltites. Petroleum is a derivative of sapropel, and asphaltites are formed by oxidation and evaporation of asphalts and petroleum. J. J. B.

Variation of Ishimbay oils. G. D. Halpern (Compt. rend. Acad. Sci. U.R.S.S., 1943, 41, 167-168).—The deposit is characterised by zonal oil distribution; ρ and η increase regularly from the centre to the periphery. The causes of the variation, and of the variations displayed by a single well at different periods of its life, are discussed. L. S. T.

Prognosis of oil deposits. S. F. Fedorov (*Compt. rend. Acad. Sci.* U.R.S.S., 1940, 28, 49-54).—Five factors are enumerated as important in forecasting the yield of oil-bearing strata: (i) oil is not found on a commercial scale in horizontally bedded deposits; (ii) the property of acting as an oil reservoir is determined by the "effective porosity" of strata, *i.e.*, the % of pores permitting free movement of oil; (iii) the presence of waters containing CaCl_a and alkali is characteristic of oil-bearing deposits; (iv) the reducing action of oil on rocks produces a fall in the redox potential of deposits as an oilfield is approached; (v) hydrocarbon gases are found in the soil above oil deposits. L. J. J.

Occurrence of oil as related to gravitational anomalies. L. V. Chmelevskaja (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, 36, 182— 184).—A review of the available data. It is concluded that the layers bearing oil in primary deposits are older than the orogenic phase in which the oil originated. Oil is found either on the out-skirts of some voung orogenic region in some of page time relation skirts of some young orogenic region in a zone of negative anomalies or on the outskirts of ancient orogenic regions in a zone of positive anomalies. In the latter case the oil was first deposited in rocks older than the orogenic phase responsible for the region. Recent movements causing dislocations in the border portion of ancient orogenic regions can change the sign of the anomaly. J. O'M-B.

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