BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

OCTOBER, 1944

A I—GENERAL, PHYSICAL, AND INORGANIC CHEMISTRY

CONTENTS

	a la contrata de la c	PAGE		PAGE
Ι,	Sub-atomics	209	vi, Kinetic Theory. Thermodynamics .	224
II,	Molecular Structure	211	vII, Electrochemistry	226
ш,	Crystal Structure	215	VIII, Reactions	226
IV,	Physical Properties of Substances		1X, Preparation of Inorganic Substances .	229
	(not included above)	219	$\dot{\mathbf{x}}$, Lecture Experiments and Historical .	
v,	Solutions, Dispersions, and Mixtures .	220	xI. Geochemistry	232

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BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A I-General, Physical, and Inorganic Chemistry.

OCTOBER, 1944.

I.—SUB-ATOMICS.

Ground triplet in bromine II. K. R. Rao (*Current Sci.*, 1944, 13, 42).—The fundamental inverted triplet term $4p^{3}P$ of Br II, involving -30 lines in the vac. grating region, has been established. The intervals are $4p^3P_2 - 4p^3P_1 = 3147$, and $4p^3P_1 - 4p^3P_0 = 695$ cm⁻¹ The identification of $5s^1D_2$ is corr. from 65657.1 to 61179.5 cm⁻¹ N. M. B.

Absorption of the yellow line of the night sky by sodium vapour. J. Bricard and A. Kastler (*Compt. rend.*, 1943, 216, 878-880).---Na vapour absorbs the yellow line of the night sky completely if the temp. is sufficiently high. There is partial absorption when the v.p. corresponds to a temp. of 149°, and complete absorption at 209°. A. J. M.

Experimental determination of the energies of atoms multiply ionised in deep levels, by crystal spectrography. (MIIe.) Y. Cauchois (Compt. rend., 1943, 216, 801-804).—L spectra of heavy elements comprise frequencies which cannot be reconciled with the energy schemes of a singly ionised atom. These are satellites of more schemes of a singly ionised atom. These are satellites of more intense radiations, and five groups are recognised. The *L* satellites of heavy elements are, with few exceptions, of greater ν than the principal radiation. The three groups L_{a_1} , L_{β_2} , and L_{β_3} , which have their origin in the transitions 2p 3d - 3d 3d, 2p 3d - 3d 4d, and 2p 3d - 3d 5d, are examined, and by consideration of the structure of the doublets it is possible to arrive at the multiple-ionisation levels which give rise to them. Thus, if δ is the difference of ν of a satellite and the parent radiation $\delta \alpha = (2c) 2d - 3d - 3d 3d = 2c$ ionisation levels which give rise to them. Thus, if δ is the difference of ν of a satellite and the parent radiation, $\delta a_1 = (2p 3d - 3d 3d) - (2p - 3d)$, $\delta \beta_2 = (2p 3d - 3d 4d) - (2p - 4d)$, $\delta \beta_5 = (2p 3d - 3d 5d) - (2p - 5d)$. If ΔL_{11f} , ΔM_V , ΔN_V , and ΔO_V represent the energy differences of a state of the multiply ionised atom and that of the singly ionised atom, $\Delta M_V = \Delta L_{11I} - \delta a_2$, $\Delta N_V = \Delta L_{11I} - \delta \beta_5$. $\Delta O_V = \Delta L_{11I} - \delta \beta_5$. To determine ΔL_{11I} the curve showing variation of δ as a function of E for the different levels M_V , N_V , and O_V is drawn and extrapolated to E = 0. Vals. are given for Th, Ra, Bi, Pb, Tl, Au, and Pt. New data relating to atoms of stamic number 92 (Pb) 91 (TI) and

New data relative to atoms of atomic number 82 (Pb), 81 (Tl), and 79 (Au). Weak *L*-emission and outer levels. (Mile.) Y. Cauchois (*Compt. rend.*, 1043, 216, 762—765; cf., A., 1942, I, 222, 349; 1944, I, 93).—The weak *L* emissions of Pb, Tl, and Au are investig-ated, and new data tabulated. The β_7 , β'_7 , γ_8 , and γ'_8 ($L_{II}N_{VI}$) doublets are resolved, and the vals. of O_I and N_{VI} , v_{II} are deduced. A. J. M.

New light effect; intensity variation by direct photo-electric measurements. P. G. Deo (*Current Sci.*, 1944, 13, 44).—The instantaneous diminution Δi , by irradiation, of the conductivity installations diminition I_{4} , by intallation, of the conductivity of Cl_2 and other gases under electrical discharge is not a linear function of the corresponding light intensity I. $I-\Delta i$ curves obtained by varying the distance of the light source depend on the nature of the irradiation; the curve for violet may lie above or below the curve for white light, according to initial intensity.

N. M. B.

Physical principles of betatron. D. W. Kerst (Radiology, 1943, 40, 115—119).—Electrons with velocity which may be close to that of light are shot from an electron gun or injector into a circular path within a doughnut-shaped vac. tube and accelerated by increasing the intensity of the magnetic fields between the poles of the electromagnet enclosing the vac. tube. Orbit-expanding coils are not energised until after the electrons have been accelerated. The electrons travel through distances of up to 200 miles before striking the target and producing X-rays of energies 2.3 and 20×10^6 v. At the lower energy the X-rays tend to go forward in the direction which the electrons had when striking the target; at the higher energy an output of 50 r. per min. has been produced at 70 cm. A.c. is used. E. M. J.

Electric breakdown and cumulative ionisation. B. Davidov (J. Physics U.R.S.S., 1943, 7, 196).—Mathematical. W. R. A.

New spiral form of the periodic table. E. I. Emerson (J. Chem. Educ., 1944, 21, 111-115).—The elements are arranged in the natural sequence of at. nos. on a plane spiral. The arrangement reflects the periodic occurrence of similar outer orbital configurations and the periodic occurrence of properties. L. S. T.

Energies and periods of a-disintegrations. I. Energies. II. Periods. A. Berthelot (J. Phys. Radium, 1942, [viii], 3, 17-28, 209 M (A., I.)

52-56).—I. The energy of a-disintegration of the natural radio-active elements is considered as a function of the no. of nuclear constituents. Using energy vals, for the β -disintegrations, the energy of binding of the last neutron to enter the nucleus is calc. for all isotopes having at. nos. 82—84. For at. nos. 82 and 86, discontinuities in the binding energy of neutrons occur when the no. of neutrons in the nucleus exceeds 126 and 134; for at. no. 82 the discontinuity is ~ 2.4 Me.v. The emission of energetic photons by Ra-C'' and Th-C'' depends on this discontinuity.

II. The frequency of a-disintegration of the natural radioactive elements is considered as a function of the energy change involved, the elements being grouped into families of isotopes. Evaluation of nuclear radii from these data leads to vals. intermediate between those of Gamow and those of Bethe. The significance of the energyperiod relationship is discussed with reference to the fine structure W. R. A. of nuclei.

Complexity of γ -radiation from Ra-D. S. T. Tsicn (*Compl. rend.*, 1943, 216, 765-767).—To verify the results of Amaldi *et al.* (*Ric. Sci.*, 1939, 10, 111) who showed that, contrary to former work, the γ -radiation from Ra-D is complex, the radiation is examined by means of an ionisation chamber filled with Ne at atm. pressure. This favours weak γ -rays because of its high coeff. of absorption. Secondary β -rays produced in the gas are completely absorbed. Secondary B-rays produced in the gas are completely absorbed. To distinguish rays of approx. the same energy, absorbents of rare-earth oxalates are used. The γ -radiation from Ra-D contains a ray (ray B) of energy 42:00-43:54 ke.v. The principal γ -ray of Ra-D (ray A) has energy 43:54-46:86 ke.v. The intensity ratio $I_A/I_B = 12\pm7$. $I_A = 3.8\pm0.8\gamma$, $I_B = 0.3\pm0.2\gamma$ per 100 dis-integrations. A. J. M.

Determination of radioactive period of vanadium of mass 52. J. Martelly (*Compt. rend.*, 1943, 216, 767—769; cf. Amaldi *et al.*, A., 1935, 910; Walke, A., 1938, I, 8).—The period of ⁵²V obtained by the reaction ⁵¹V (n, γ) ⁵²V, by irradiating V₂O₅ with slow neutrons, is 2.74 ± 0.01 million of the state is 3.74±0.01 min. A. J. M.

Determination of energy of γ -rays from the radioactive isotope of vanadium ⁵²V. J. Martelly (*Compt. rend.*, 1943, 216, 838-840).— The energy of γ -rays emitted from ⁵²V, determined by measuring the coeff. of absorption in Pb, Fe, and Cu, is 1.45 ± 0.05 Me.v. (cf. Vuece A 1944 L 24). Yuasa, A., 1944, I, 94). A. J. M.

Apparatus for counting electrons of small energy. Application to ⁸⁰Br (18 min.). A. Berthelot (*Compt. rend.*, 1943, 216, 806-808).— Absorption of electrons from ⁸⁰Br is very weak and shows no discontinuities, indicating the absence of conversion electrons of low energy. (Cf. C., 1944, Part 4.) A. J. M.

Investigation, by the absorption method, of radiation due to internal conversion, emitted by ⁸²Br (34 hr.) and ⁸⁰Br* (4.5 hr.). A. Berthelot (*Compt. rend.*, 1943, 216, 884—886).—Apparatus previously described (cf. preceding abstract and C., 1944, Part 4) has been described (cf. preceding abstract and C., 1944, Part 4) has been used to investigate conversion radiation associated with the transition ${}^{80}Br^* \rightarrow {}^{80}Br$ (18 min.). The thicknesses of Al absorbents required are 0.38, 0.95, 2.05, and 3.75 mg. per sq. cm., corresponding to energies determined by Valley *et al.* (A., 1939, I, 294) and to the Auger electrons. Using these energies the internal conversion energies of ${}^{82}Br$ (34 hr.) are 34 and 53 ke.v. A. J. M.

Cosmic rays. (Mlle.) T. Grivet (Ann. Physique, 1943, [xi], 18, 73-134).-A detailed experimental analysis is reported. Measurements are made at and below sea-level of the proportion of hard and soft rays, Rossi curves are traced, and the angle between rays in clusters is determined. Radiation which penetrates large thicknesses of earth consists of heavy electrons or mesons; the electrons are produced by decomp. of mesons in their passage through air or earth and by collisions of mesons with the atoms of dense screens. N. M. B.

Separation of electronic and non-electronic components of cosmic radiation by Bhabha's method. S. V. C. Aiya (*Proc. Indian Acad. Sci.*, 1944, 19, A. 177—181).—The theoretical prediction of Bhabha (A., 1944, I, 163) that Pb is more effective in cutting out electrons if split in the ratio $\sim 1:4$ (the thinner piece being used for shower production from high-energy electrons and the thicker piece absorbing the low-energy electrons) has been confirmed experimentally by observations at Ootacamund (geomagnetic latitude 1.7° N., 7200 ft. above mean sea level). Two Pb filters of total thickness 5.25 cm.

and five counters, three connected in coincidence and the other two in parallel and in anti-coincidence, were used; the total wt. of the apparatus was 4 oz. The hard component constitutes 66.3%W. R. A. of the total intensity.

Scattering of charged mesons under the influence of radiation damping. S. T. Ma and C. F. Hsüch (*Proc. Camb. Phil. Soc.*, 1944, 40, 167-172).—An alternative derivation of Waller's integral equation is given. The theoretical treatment of the scattering of charged vector mesons (A., 1944, I, 27) is extended to pseudoscalar H. J. W. mesons.

Representation of corpuscular interactions by means of a particle of spin 1. G. Petiau (Compt. rend., 1943, 216, 832-834).-Mathe-matical. A. J. M.

II.—MOLECULAR STRUCTURE.

Vibration frequencies of certain molecular groups (near infra-red). P. Barchewitz (Ann. Physique, 1943, [xi], 18, 167–189).—Certain bands in the near infra-red can be attributed, as a first approximation, to the presence of mol. groups (OH, NH_2 , NH, CH_3 , CH_2 , etc.). Conditions exist under which the bands characteristic of these groups are not revealed, and by modifying the experimental conditions (variation of temp., dilution, etc.) the max. reappear only in certain cases. From the data, considerations on mol. structure are deduced and discussed. N. M. B.

Ultra-violet absorption spectrum of diamond. (Mrs.) K. S. Bai (*Proc. Indian Acad. Sci.*, 1944, **19**, **A**, 253–260).—The ultra-violet absorption spectra in the region 3300–2200 A. have been investigated. With non-fluorescent and yellow-green-fluorescent diamonds the recorded spectra extend to 2250 A., requiring, however, long ex-posure with yellow-green-fluorescent specimens. Weakly blue-fluorescent diamonds show a cut-off at 3050 A., preceded by three sharp and intense bands at 3060, 3075, and 3157 A. In strongly blue-fluorescent diamonds these bands disappear, and the region of transmission extends to 2450 A., with step-like falls in intensity at 2845, 2715, and 2570 A. Diamonds exhibiting both types of fluorescence give absorption lines at 2359 and 2356:5 A. with five fluorescence give absorption lines at 2359 and 2356.5 A., with five bands at greater and three at shorter $\lambda\lambda$. Intensity of fluorescence varies with the intensity and breadth of these absorption lines and bands, which sharpen and shift towards shorter $\lambda\lambda$ at liquid-air W. R. A. temp.

Ultra-violet transparency patterns in diamond. G. R. Rendall (Proc. Indian Acad. Sci., 1944, 19, A, 293-297).—The ultra-violet transparency of crystals and cleavage plates of diamonds is examined by passing 2536 A. Hg radiation through the specimen and producing an image in a screen of U glass. A wide range of behaviour, from complete opacity to complete transparency, related to the lumin-escence properties of the individual diamond, has been observed. Transparency patterns of cleavage plates are in some cases similar to the luminescence patterns, but reversed; in other cases such a resemblance is not observed. The origin of these differences and similarities is discussed with reference to the intrusion of one diamond structure into another. W. R. A.

Relations between chemical activity and absorption in the ultra-violet of certain organic molecules. VIII. Absorption spectra of monochloro-derivatives of the amides of acetoacetic acid. IX. Absorption spectra of the *iso*nitro-derivatives of the amides of aceto-acetic acid. K. G. Naik, R. K. Trivedi, and B. N. Mankad (J. Indian Chem. Soc., 1943, 20, 407-408, 414).---VIII. Absorption is increased and shifted towards the use the use the second increased and shifted towards the visible by introduction of Cl into the CH₂ group of the anilide, m-4-xylylamide, and a-naphthyl-amide of CH₂Ac·CO₂H. IX. Conversion of the CH₂ group into C:N·OH in the same amides produces a marked shift of photontion towards the visible and a

produces a marked shift of absorption towards the visible and a smoothing out of the absorption max. L. I. I.

Absorption spectra of the simplest coloured compounds. A. Schwarzenbach, K. Lutz, and E. Felder (Helv. Chim. Acta, 1944, 27. 576-584) .- The extinction coeffs. of solutions of a no. of simple coloured compounds are measured at various $\lambda\lambda$ and the λ of the absorption max. is compared with the vals. $k'_p \sqrt{n} + k''_p$ and $k'_e n + k''_e$ (k'_p , k''_p , k'_e , k''_e = consts., n = no. of double linkings in the mol.) for polyene compounds and compounds with two canonical recomposed received. canonical resonance forms, respectively. I. W. S.

Spectrographic and kinetic study of the alkaline fading of tetra-iodophenolsulphonephthalein. E. S. Amis and T. Overman (J. Amer. Chem. Soc., 1944, 66, 941-945).—The absorption of alkalinefaded iodophenol-blue approximates to that of alcohol, acids, and H₂O, as would be expected if the carbinol is formed during fading. Spectra of the unfaded and regenerated acid solution are identical and the fading process, therefore, appears to be reversed in acid solution. The absorption band is not shifted but only lowered in intensity during fading. Addition of NaI influences the kinetics of fading by the Brönsted primary salt effect. Fading thus appears to consist of transformation from the quinonoid to the carbinol structure structure. W. R. A.

Ultra-violet absorption spectrum of ibogaine. V. Brustier, D. Vincent, and (Mile.) I. Sero (Compt. rend., 1943, 216, 909-911).-The ultra-violet absorption spectrum of ibogaine, the active principle of *Tabernanthe iboga*, shows marked similarity with that of quinoline. There is also a much weaker resemblance to the spectrum of indole, although chemical evidence (Raymond-Hamet, Bull. Soc. chim., 1942, [v], 9, 620) seems to indicate the existence of an indole nucleus in this alkaloid. The mol. probably contains a quinoline or isoquinoline nucleus and may also contain a subsidiary indole nucleus, the effect of the latter on the absorption spectrum being masked.

A. J. M. Hertzian spectra of solutions of alcohols. P. Girard and P. Abadie (*Compt. rend.*, 1943, 216, 836-838).—If a long-chain alcohol is diluted with various non-polar liquids (C_0H_6 , C_6H_{11} , vaseline), study of the Hertzian spectrum shows that the mol. undergoes a profound change of magnetizing for undergoes a profound change of geometrical form, varying with the diluent. The alcohol mol. appears to be very plastic and is readily deformed by hydrocarbon mols. The spectrum of solutions of $n-C_8H_{17}$ OH shows three clearly defined regions of dispersion, whereas that of the pure alcohol shows only two. The geometrical model of the mol. passes from an ellipsoid of revolution in the case of the pure alcohol, to an ellipsoid with three unequal axes in the case of solutions. The deformation is least marked in vaseline, probably because of its large mol. vol. The ratio of relaxation times indicates that the alcohol mol. is probably more extended in $C_{n}H_{14}$ than in vaseline. Dilution of the alcohol by $C_{n}H_{14}$ or $C_{n}H_{n}$ displaces the regions of dispersion towards short λ . This displace-ment is not $\infty \eta$ as required by Debye's theory. The spectrum of the alcohol in vaseline makes it clear that the η involved in dis-mention is not the which is ordinarily measured. persion is not that which is ordinarily measured. A. J. M.

Fluorescence and absorption spectra of diamond in the visible. (Miss) A. Mani (Proc. Indian Acad. Sci., 1944, 19, A. 231-252). Fluorescence and luminescence spectra in the visible have been investigated at room and liquid-air temp. for 32 diamonds of widely varying luminescence colour and intensity. The spectra are related with respect to both their general character and their intensities. All the spectra consist mainly of the electronic bands at 4152 and 5032 A., which comprise a set of lines, bright in fluorescence, dark in absorption and lattice lines appearing at greater bin fluorescence. in absorption, and lattice lines, appearing at greater λ in fluorescence. With blue fluorescence the 4152 A. system is the more prominent, and with yellow fluorescence, the 5032 A. system, but, generally, the two systems appear with comparable intensities. 36 electronic lines, other than 4152 and 5032 A., are recorded. The 4152 A. line appears in most diamonds as a doublet the width and second appears in most diamonds as a doublet, the width and separation of the two lines increasing with intensity of blue fluorescence. The 5032 A. line shows no such changes. Differences in ν between the main lines at 4152 and 5032 A. and the associated lattice lines lie in the infra-red and represent the vibration $\nu\nu$ of the diamond lattice. Δv are the same in both systems, but the degree of sharpness and intensity distribution vary. 25 vv are derived, constituting the lattice spectrum of diamond. W. R. A. the lattice spectrum of diamond.

Fluorescence of naphthalene crystals. I. V. Obreimov and C. G. Schabaldas (*J. Physics U.R.S.S.*, 1943, 7, 168–178).—The fluorescence spectrum of cryst. $C_{10}H_8$ has been investigated at 20° K. It is similar to the resonance spectrum of gases, and contains practically all the Raman and some non-Raman vibrational vv. Four electronic transitions were found. W. R. A.

Theory of the influence of concentration on the fluorescence of solutions. S. I. Vavilov (J. Physics U.R.S.S., 1943, 7, 141-152).-A migration of energy between mols. must occur if there exists a quantum-mechanical resonance between the excited and nonexcited mols. in a solution; when the distances between them are great the migration will lead to depolarisation. At small distances when there is considerable resonance coupling between mols. the migration may be accompanied by noticeable quenching of fluorescence. The theory of the influence of concn. on fluorescence is developed and formulæ are given for the yield, degree of polarisation, and lifetime of the excited state which are confirmed by the available experimental data. W. R. A.

Influence of temperature on the quenching of active nitrogen at various pressures. S. S. Joshi and A. Purushotham (*Proc. Indian Acad. Sci.*, 1944, 19, A, 159—162).—Quenching of the afterglow of active N is dependent on temp. and occurs at a definite temp, which is the higher the higher is the streaming pressure of the gas. Vals. at 15 and 33 mm. Hg are 215° and 330° . Existence of a chemically active form of N, which exhibits no afterglow, is considered improbable. W. R. A. Influence of temperature on the quenching of active nitrogen at

Mechanism of luminescence of phosphors. II. V. V. Antonov-Romanovski (*J. Physics U.R.S.S.*, 1943, 7, 153-167).—Using the experimental observation that the displacement of a thermal electron of the KCl + Tl phosphor between two consecutive trap-pings is small and of the order of the lattice const. (A., 1943, I, 114: 1944, I, 3), a theory of recombination luminescence is developed 114; 1944, I, 3), a theory of recombination luminescence is developed. This theory explains the shape of the decay curve and its dependence on conditions of excitation and decay, and is used to estimate the magnitudes of the diffusion coeff. and the mobility of the electrons.

It is shown that a unimol. decay process and spontaneous radiation are possible in the initial stages of the process. W. R. A.

Chemiluminescence. W. G. Leedy (J. Chem. Educ., 1944, 21, 142-144).—Reactions involving chemiluminescence, the chemiluminescence of 3-aminophthalhydrazide, and the interpretation of chemiluminescence are described. L. S. T.

Raman spectrum of diamond. R. S. Krishnan (Proc. Indian Acad. Sci., 1944, 19, A, 216–223).—The Raman spectrum of the ultra-violet-transparent type of diamond has been investigated using the Hg line 2536 A. In addition to the displacement of 1332 cm.⁻¹ displacements of 1925, 2176, 2245, 2267, 2301, 2467, 2495, 2518, 2610, and 2665 cm.⁻¹ are recorded. These are identified as the harmonics and combinations of the eight fundamental oscillation frequencies of the diamond according to the Raman theory of crystal dynamics (A., 1944, I, 143). W. R. A.

Calculation of the elastic constants of quartz at room temperature from Raman effect data. B. D. Saksena (*Proc. Indian Acad. Sci.*, 1944, **19**. A, 357–369).—That the Si-O bonds in *a*-quartz are largely covalent is shown from the crystal structure and high frequency of vibration. Consequently, it may be assumed that in a homogeneous strain the distance from the basis to basis is altered as if the basis was rigid and attached at one point in the continuum subjected to strain, and thus changes in bond distance and bond angles may be derived from the known crystal structure. The four force consts. for Si-O valency, O-O repulsion, and Si-O-Si and O-Si-O deformations have been computed from Raman spectral data, and from these the potential energy per unit vol. and, hence, elastic consts. can be calc. in good agreement with observed vals.

W. R. A.

Raman effect in crystals. Lines due to ClO_3' ion in the Raman spectrum of a crystal of sodium chlorate. A. Rousset, J. Laval, and R. Lochet (*Compt. rend.*, 1943, **216**, 886–888).—A more complete list of Raman lines for cryst. NaClO₃ is given. Theoretical predictions based on the structure of ClO_3' are confirmed. A. J. M.

Raman spectra of acetylenes. VII. Symmetrical-top acetylenes. F. F. Cleveland and M. J. Murray (*J. Chem. Physics*, 1944, 12, 320).—Erratum (cf. A., 1944, I, 3). L. J. J.

Raman spectra of acetylenic bromides, iodides, and ketones and of some cyclic compounds. M. J. Murray and F. F. Cleveland (J. Chem. Physics, 1944, 12, 156—159).—Raman spectra are listed for CEt CBr, CEt CI, CPr CBr, CPr CI, CBu CBr, CBu CI, $C_{\delta}H_{11}$ C CBr, $C_{\delta}H_{11}$ CI, CPh CBr, a-phenyl- Δ^{α} -butinen- γ -one, Δ^{γ} -hexinen- β -one, Δ^{γ} -octinen- β -one, Δ^{δ} -noninen- γ -one, ascaridole, 1:3-dioxan, p- $C_{\delta}H_{\delta}$ Me SO₃Et, and cis- and trans-1:2-diacetoxycyclohexane. Depolarisation factors and relative intensities are given in some cases. L. J. J.

Molecular structure and thermodynamics of propane. Vibration frequencies, barrier to internal rotation, entropy, and heat capacity. K. S. Pitzer (*J. Chem. Physics*, 1944, 12, 310—314).—The vibrational assignment of Wu and Barker (A., 1941, I, 397) is extended and slightly revised to give definite vals. to all normal modes, correct within 2%, and in agreement with experimental entropy and heat capacity vals. Free energy, heat content, and heat capacity functions are calc. over the range 180—1500° K. Fundamental r^{ν} are evaluated from infra-red and entropy data, and force consts. calc. The apparent increase in potential barrier from C₂H₆ to C₃H₈ arises from interaction of H atoms of Me groups. For the torsional mode in C₃H₈, where such interaction does not arise, the force const. is the same as for C₂H₆, viz., 0.74 × 10⁻⁶, compared with 0.71 × 10⁻⁶. L. J. J.

Vibrational spectrum of pyridine and thermodynamic properties of pyridine vapours. C. H. Kline, jun., and J. Turkevich (J. Chem. Physics, 1944, 12, 300–309).—Fundamental $\nu\nu$ and thermodynamic properties of C_sH_sN are calc. ($S = 68.6 \pm 0.7$ c.u. per g.-mol. at 25° and 1 atm. as ideal gas) from infra-red and ultra-violet absorption spectra and Raman spectra. L. J. J.

Electrostatic contribution to hindered rotation in certain ions and dipolar ions in solution. IV. T. L. Hill (J. Chem. Physics, 1944, 12, 147—156; cf. A., 1944, I, 118).—Kirkwood and Westheimer's models of mol. cavities (A., 1938, I, 574) are adapted to the considerations of earlier papers. The effective dielectric consts. are no longer const., but vary with inter-charge distance. L. J. J.

Depolarisation factor of Rayleigh radiation for water and solutions of electrolytes. J. P. Mathieu and (Mlle.) G. Lelong (Compt. rend., 1943, 216, 800-801).—The depolarisation factor, ρ , for the Rayleigh radiation of H₂O and solutions of electrolytes (NaNO₂, Na₂SO₄, and NaCl of various concns.) has been determined by Cornu's method. For H₂O, $\rho = 0.066$, and the optical anisotropy, $\delta = 5.9 \times$ 10^{-2} . For NaNO₃ the vals. agree with those of Sweitzer (A., 1927, 510, 932), but for Na₂SO₄ and NaCl they are considerably smaller (0.044-0.066, 0.062-0.071). A. J. M.

Effect of non-homogeneity of mol. wt. on the scattering of light by high polymer solutions. B. H. Zimm and P. M. Doty (*J. Chem. Physics*, 1944, 12, 203-204).—The treatment given previously by M 2 (A., I.) the authors (A., 1944, I, 175) is generalised to predict an observable effect depending quantitatively on the non-homogeneity of mol. wt. L. J. J.

Influence of thin films on the magneto-optical Kerr effect. J. Frenkel (J. Physics U.R.S.S., 1943, 7, 192-195).—Theoretical. Criticism of the interpretation given by Noskov (A., 1944, I, 53) to his experimental data on the influence of a thin film of a dielectric on the angle through which the plane of polarised light is rotated. The theory now put forward is in better agreement with the experimental data. W. R. A.

Single bond energies. V. Association of ketyls. H. E. Bent and A. J. Harrison (J. Amer. Chem. Soc., 1944, 66, 969-973).—The ketyl formed when fluorenone is treated with Na-Hg does not associate to a pinacolate at room temp. or at -112° . The shape of the absorption curve for Na fluorenone is a function of temp. and, consequently, the mol. extinction coeff. at one temp. cannot be used to calculate the fraction dissociated at another temp. COPh₂ forms a ketyl which is largely associated at room temp. to a pinacolate and the dissociation const. at 20° is $4\pm1 \times 10^{-6}$. The Na derivative of COPh₂ in Et₂O has an apparent mol. extinction coeff. which decreases rapidly as temp. is lowered. When such data are combined with dilution data the temp. coeff. of the dissociation const. and the heat of dissociation (4 ± 1 kg.-cal.) can be calc. W. R. A.

Molecular constants and kinetic theories. I. The parachor (molecular volume). II. Additive molecular constants and chemical structures. R. Samuel (J. Chem. Physics, 1944, 12, 167-179, 180-202).—I. The parachor is an example of an additive mol. const. which is unable to distinguish between different possible structures of a mol. or the different conflicting chemical theories on which they are based. A new set of at. parachors is calc. on the basis of classical chemical formula without invoking different types of linkings having characteristic parachor consts., and ascribing instead different consts. to the same atom in different valency states. N₂, O₂, N₂O, CO₂, CO, SO₂, and the azides are no longer anomalous.

Minimum 20, N_2O , CO_2 , CO_2 , CO_3 , SO_2 , and the azides are no longer anomalous. II. Mol. refractivity, dipole moment, bond distance, and bond energies may be separated into at. or bond contributions according to different proposed structures of a covalent mol., giving selfconsistent results. They therefore have no diagnostic value as regards the nature of covalent linkings, and can agree with the older classical formulæ, *e.g.*, those involving 5-covalent N. L. J. J.

Thermodynamic properties and potential energy of solid argon. O. K. Rice (*J. Chem. Physics*, 1944, 12, 289–295).—The Debye characteristic temp. and the potential energy of solid A are calc., on the assumption that Debye's theory holds at all temp., from experimental data on sp. heat at low temp. and the equation of state at high pressures. On this basis a consistent series of thermodynamic data for solid A is obtained, but the interat. potential curve is different from that obtained by an earlier method (A., 1941, I, 106), showing extreme change of curvature near its min., rendering the theory of small vibrations inapplicable. L. J. J.

Orientation phenomena in nematic liquids. New method of measuring surface tension applicable to these liquids. V. Naggiar (Ann. Physique, 1943, [xi], 18, 5-55).—Nematic threads always accompany vortices in nematic liquids (e.g., p-azoxyanisole) and the nuclear structure represents the position of optical axes in a vortex movement. The homotropic structure is the only structure determined by the boundaries. In an electric field, the nematic threads are only a secondary effect which disappears at low frequencies. In a magnetic field, the action of surface forces causes an orientation tangential to the first mol. layers at the free surface. For a sufficiently strong field a deformation of structure is observed which allows determination of the order of magnitude of the orientation couples taking part in the nematic structures. (Cf. C., 1944, Part 4.) N. M. B.

Parachor of potassium chromate. W. V. Bhagwat, V. A. Moghe, and P. M. Toshniwal (*J. Indian Chem. Soc.*, 1944, **21**, 53—54).—The parachor of K_2CrO_4 in aq. solution is ~195. The calc. val. is 347.6. The difference is partly, but not completely, accounted for by supposing that at. and ionic parachors are not the same.

Parachor of potassium dichromate and constitution of dichromic acid. W. V. Bhagwat, V. A. Moghe, and P. M. Toshniwal (*J. Indian Chem. Soc.*, 1944, 21, 61-62).—The parachor of $K_2Cr_2O_7$ has been determined in aq. solution at different temp. Vals. range from 401.7 to 504.8. The calc. val. is 468, but if the mol. contains two polar and four semi-polar bonds, the theoretical val. is 458.4. Parachor observations support the view that chromic acid exists in solution largely as $H_2Cr_2O_7$, and that there is an equilibrium $H_2Cr_2O_7 + H_2O \rightleftharpoons 2H_2CrO_4$. The occurrence of $H_2Cr_2O_7$ in solution is also confirmed by conductivity experiments. A. J. M.

Organic parachors. VI. Supplementary series of tertiary alcohols. O. R. Quayle and (Miss) K. O. Smart. VII. Series of saturated hydrocarbons. O. R. Quayle, R. A. Day, and G. M. Brown (J. Amer. Chem. Soc., 1944, 66, 935–938, 938–941).—VI. Vals. of n, p, γ , and parachor of nine tert. alcohols are found in close agreement with calc. vals. Tables for the estimation of parachors of tert. alcohols, and more particularly position vals. of CH_2 in alkyl chains, are given. Modifications in the bubbler for measuring γ are described.

VII. Vals. of ρ , γ , and parachor of 13 paraffin hydrocarbons are given. Parachor vals. are given for CH₂ (40), H (15.5), and C (9.0). The val. for CH₂ is not changed by chain length up to C₁₂H₃₆. Chain-branching does not produce uniform effects, but the data are inadequate to evaluate variations in the effect.

W. R. A.

III.—CRYSTAL STRUCTURE.

Method of calculating the integral breadths of Debye-Scherrer lines: generalisation to non-cubic crystals. A. R. Stokes and A. J. C. Wilson (*Proc. Camb. Phil. Soc.*, 1944, 40, 197-198).—An extension of work previously reported (A., 1942, I, 318). H. I.'W.

Scattering of X-rays in polycrystalline substances. I. [Theory.] II. Application to liquids. L. M. Brechovskich (*J. Physics U.R.S.S.*, 1943, 7, 179—188, 180—191).—I. A theory of X-ray scattering by polycryst. substances is developed which takes into account the thermal vibrations of atoms. The ratio of the intensity of the scattered radiation to the Laue part is > for single crystals and the Debye background depends on the size of the grain in the same way as the scattered radiation.

II. An extension of the theory to liquids, based on the concept of the liquid as a finely-powdered polycryst. specimen, has been made and is applied with fair success to liquid Na. W. R. A.

X-Ray topographs of diamond. G. N. Ramachandran (*Proc. Indian Acad. Sci.*, 1944, 19, A, 280-292).—Topographic maps representing the variation in intensity of X-ray reflexion over the area of a crystal plate are obtained by photographing the Laue reflexion from any set of crystal planes. White X-radiation, diverging from a pin hole, is used. Lateral distortion of the particular Laue spot examined is eliminated by tilting either the photographic or the crystal plate. Topographs of 18 cleavage plates of diamond are given and are of three types: (i) those exhibiting a uniform distribution of relatively weak reflexion intensity over the whole area and characteristic of the blue-fluorescent diamonds which are opaque in the ultra-violet and show no birefringence; (ii) those having a strong reflexion intensity and showing parallel lines running in different directions over the whole crystal area (ultra-violet-transparent non-luminescent diamonds showing an intense birefringence are characteristic of this group); (iii) an apparent co-existence of types (i) and (ii), giving a uniform weak reflexion overlaid by some regions of intense reflexion. The latter appear as small areas of uniformly high intensity, as a few fine streaks running through the crystal, or as a combination of these two effects. Type (iii) has properties intermediate between those of types (i) and (ii). Correlations with luminescence, ultra-violet transparency, and birefringence patterns confirm the suggestion that type (i) belongs to the tetrahedral structure, type (ii) to the octahedral, and type (iii) is an interpenetration of the tarahedral and octahedral types. W. R. A.

X-Ray reflexion and structure of diamond. G. N. Ramachandran (*Proc. Indian Acad. Sci.*, 1944, **19**, **A**, 304—309).—Laue photographs, taken with the X-ray beam normal to the (111) planes, have been investigated for two blue-fluorescent diamonds with greatly different fluorescence intensities but similar in other respects. Microphotometric determination of the peak intensity of the various spots shows that, although the intensity is greater for the fluorescent diamond, the intensity ratio (r) of the various spots differs. (r - 1) or the product of the structure factor, the λ reflected, and a function of the angle of incidence. W. R. A.

Intensity of X-ray reflexion of diamond. P. S. Hariharan (Proc. Indian Acad. Sci., 1944, 19, A, 261-264).—The intensity of X-ray reflexion from the (111) planes of several diamonds is studied. With blue-fluorescent diamonds the intensity of X-ray reflexion increases with intensity of fluorescence, whereas with yellow-green-fluorescent diamonds the reverse is shown. The order of intensity of X-ray reflexion is : non-fluorescent > yellow > blue. This behaviour is correlated with the views advanced by Raman (see below) on the crystal structure of real diamonds. W. R. A.

Experimental evidence for the existence of the four possible types of diamond. R. S. Krishnan (*Proc. Indian Acad. Sci.*, 1944, 19, A, 298—303).—X-Ray and spectroscopic studies of diamond provide experimental evidence for the existence of four diamond structure types. Co-existence of the two tetrahedral types is inferred from the increased intensity of X-ray reflexion in such diamonds. The Bragg reflexions of a diamond consisting of alternate layers of the two octahedral types, examined by the oscillating-crystal method, exhibited a periodicity consistent with a difference of 0-05% in crystal spacing of the two types. The Raman displacement corresponding with the fundamental lattice vibration shows, for the octahedral type of diamond, a width equal in order of magnitude to the expected vibration frequency difference of the two octahedral structures. W. R. A. **Crystal symmetry and structure of diamond.** (Sir) C. V. Raman (*Proc. Indian Acad. Sci.*, 1944, **19**, **A**, 189—198).—The C atoms in diamond may be oriented in space in four different ways, positive or negative tetrahedral or octahedral forms. A fundamental vibration of the diamond lattice, $\nu = 1332$ cm.⁻¹, should appear in both Raman and infra-red spectra if the crystals are tetrahedral, but only in the Raman spectrum if the crystals are octahedral. This behaviour has been observed in the common (tetrahedral) and rarer (octahedral) types by Robertson *et al.* (A., 1934, 583). The two tetrahedral types have identical properties and interpenetrate freely, but composition planes result from the intertwinning of the two octahedral forms, appearing as a lamellar structure parallel to the octahedral planes. Intertwinning of

Crystal forms of the Panna diamonds. S. Ramaseshan (Proc. Indian Acad. Sci., 1944, 19, A, 334-342).—The external forms and surface characters of 29 Panna diamonds have been examined. The surfaces of the crystals are divided into 24 segments of sharply defined edges. In the best specimens these segments are triangles, the edges meeting at points and vertices in groups of four and six. Measurements of curvature show that this is highly variable, even in an individual diamond. W. R. A.

X-Ray studies on orthorhombic lead monoxide. A. Byström (Arkiv Kemi, Min., Geol., 1944, 17, B, No. 8, 6 pp.).—From X-ray measurements by the powder method the lattice dimensions of orthorhombic PbO are a 5.48, b 4.74, c 5.88 A., in accord with the measurements of Halla and Pawlek (A., 1927, 924) but, contrary to their interpretations, evidence is obtained that the Pb atoms are arranged in approx. face-centred positions, and each O atom in contact with three others, yielding a structure with sheets of Pb atoms in the (001) plane and puckered O layers in every second interspace. This provides three O atoms linked by coordinate linkings to the Pb and with the 2s electrons of the latter completing an octet of electrons around the Pb atom. The space-group is probably C_{2w}^{0} —Pba. Hydrated PbO, prepared by hydrothermal synthesis at 270°, is orthorhombic with a 14.08, b 5.71, c 8.70 A. and space-group probably either D_{2h}^{11} or C_{2w}^{0} . J. W. S.

X-Ray analysis of antimony trifluoride. A. Byström and A. Westgren (Arkiv Kemi, Min., Geol., 1943, 17, B, No. 2, 7 pp.).— Crystals of SbF₃ are orthorhombic, with 4 mols. per unit cell, spacegroup C_{20}^{10} —Ama. Each Sb is situated on top of an approx. equilateral triangle of F atoms. Parameters have been derived: Sb—F 2·0 A. within a mol.; three other F, each belonging to different mols., neighbour each Sb, two at 2·55 and one at 2·92 A. Sb—F angles are 81·9° (one) and 104·3° (two). F—F distances from mol. to mol. are 2·73, 2·73, and 2·99 A. W. R. A.

Crystal structure of ZnSb₂O₄ and isomorphous compounds. S. Ståbl (*Arkiv Kemi*, *Min.*, *Geol.*, 1943, 17, B, No. 5, 7 pp.).—MgSb₂O₄, MnSb₂O₄, FeSb₂O₄, CoSb₃O₄, NiSb₂O₄, and ZnSb₂O₄ were prepared by heating the metallic oxides with Sb₂O₃ or the metal with Sb₂O₄ in a vac. The lattice consts. of these compounds as determined by the powder method are recorded. ZnSb₂O₄ has a structure similar to that of Pb₃O₄ with space-group D_{44}^{13} —P4/mbc. J.W.S.

X-Ray analysis of $CrVO_4$ and isomorphous compounds. K. Brandt (Arkiv. Kemi, Min., Geol., 1943, 17, A. No. 6, 13 pp.).—CrVO_4 is orthorhombic with space-group D_{24}^{7} —Cmem. The unit cell has $a 5\cdot568$, $b 8\cdot208$, and $c 5\cdot977$ A. and contains 4 mols. The Cr atoms are surrounded by distorted octahedra of O atoms, which, sharing two edges with each other, form long, slightly staggered strings parallel with the (001) plane. These strings are bound together by forming slightly irregular tetrahedra of O atoms around the V atoms. NiCrO_4, CoCrO_4, CuCrO_4, ZnCrO_4, and CdCrO_4 have a similar structure and their lattice consts. are recorded. J. W. S.

Tungsten oxides.—See A., 1944, I, 183.

Oxygen positions in tungstates and molybdates with the scheelite structure. L. G. Sillén and (Miss) A. L. Nylander (Arkiv Kemi, Min., Geol., 1943, 17, A. No. 4, 24 pp.).—On the assumption that the ions are rigid spheres, parameters of isomorphous compounds MXO_4 (M = Ca, Sr, Pb, Ba; X = W, Mo), crystallising in the space-group C_{4A}^6 , are deduced which agree well with experimental vals. These derived vals, give insight into which interat, contacts are really essential to the stability of the lattice. Applications of the method to other structures are suggested. W. R. A.

X-Ray analysis of twinned MnP crystals. K. E. Fylking (Arkiv Kemi, Min., Geol., 1943, 17, A, No. 7, 9 pp.).—X-Ray investigation by the powder method indicates that MnP is orthorhombic, with a 5 905, b 5 2 4 9, $c 3 \cdot 167$ A. The ρ (5 $\cdot 49$) corresponds to 4 MnP mols. per unit cell. Rotation X-ray diffraction photographs with single crystals in some cases show additional lines attributable to twinning. J. W. S.

Structure of natrophilite, NaMnPO₄. A. Byström (Arkiv Kemi, Min., Geol., 1943, 17, B, No. 4, 4 pp.).—X-Ray investigations by the powder method indicate that the most probable space-group of NaMnPO₄ is D_{24}^{16} —Pnma. The cell dimensions are a 10.52, b 6.32, and c 4.97 A. J. W. S. **Crystal structure of Ni, Mo.** D. Harker (*J. Chem. Physics*, 1944, 12, 315–317).—A. Ni-Mo alloy containing ~20 at.-% Mo exists as a cubic close-packed structure at temp. >900°. Quenching and annealing at <840° leads to a slight tetragonal distortion of the cubic structure. The resulting tetragonal cell has 2.5 times the vol. of the distorted face-centred cubic cell, and corresponds to space-group C_{44}^5 —I4/m, unit cell a_0 5.720, c_0 3.564 A., c_0/a_0 0.6231, with 2 Mo in 2(a), 8 Ni in 8(h), x = 0.200, y = 0.400. L. J. J.

Binary system Cd[Hg(CNS)₄]-Co[Hg(CNS)₄].—See, A. 1944, I, 221.

Structure of collagen fibres.—See B., 1944, II, 226. Structure of wool fibre.—See B., 1944, II, 225, 226.

Electron diffraction of sulphur nitride, arsenic disulphide (realgar), arsenic trisulphide (orpiment), and sulphur. C. S. Lu and J. Donohue (J. Amer. Chem. Soc., 1944, 66, 818—827).—From electron diffraction measurements the S₈ mol. has a regular puckered ring with S—S $2 \cdot 07 \pm 0 \cdot 02$ A. and angle S–S–S $105 \pm 2^{\circ}$, and shows rather large amplitude of thermal vibrations; As₄S₆ has As—S $2 \cdot 25 \pm 0 \cdot 02$ A., angles As–S–As $100 \pm 2^{\circ}$ and S–As–S $114 \pm 2^{\circ}$. Mol. structures of As₄S₄ and S₄N₄ could not be unequivocally established, but cradle-shaped configurations of an alternating eight-ring are satisfactory. In S₄N₄ there is a bisphenoid of S and a square of N atoms with N—S $1 \cdot 62 \pm 0 \cdot 02$, S—S $2 \cdot 60$ A., angles S–N–S 112° and N–S–N 106° , whereas As₄S₄ has a bisphenoid of As and a square of S atoms with As–S $2 \cdot 23 \pm 0 \cdot 02$, As—As $2 \cdot 49 \pm 0 \cdot 04$ A. and angles As–S-As $101 \pm 4^{\circ}$, S–As–S 93° , and S–As–As 100° . The structures, and more particularly those of As₄S₄ and S₄N₄, are discussed in relation to their chemical properties. W. R. A.

Magnetic susceptibility of diamond. A. Sigamony (Proc. Indian Acad. Sci., 1944, 19, A, 310—314).—The magnetic susceptibility, χ , of 40 Indian and S. African diamonds was determined by the Curie method. No systematic changes in χ with changes in colour, absorption, luminescence, and photoconductivity were observed. Vals. of χ ranged between -0.456 and -0.411×10^{-6} . No change in χ was observed when two highly fluorescent diamonds were exposed to intense radiation from a C arc, filtered free from infra-red. W. R. A.

Magnetic susceptibility and anisotropy of carborundum. A. Sigamony (*Proc. Indian Acad. Sci.*, 1944, **19**, **A**, 377–380).—The magnetic susceptibility, χ , and the anisotropy of SiC have been investigated by the Curie method. Black crystals are diamagnetic but show irregular behaviour. A green, translucent, hexagonal plate of SiC behaved regularly and gave $\chi - 12.8 \times 10^{-6}$ and anisotropy 0.82 $\times 10^{-6}$. W. R. A.

Principal magnetic susceptibilities of metal crystals. S. R. Rao (*Current Sci.*, 1944, 13, 125-126).—Determinations of χ_{II} and χ_{L} on single crystals of Bi, Zn, Cd, and Te by Krishnan's torsional method (A., 1935, 924) give, respectively: Bi -1.058, 1.405; Zn -0.206, -0.147; Cd -0.234, -0.159; Te -0.342, -0.289 (all $\times 10^{-6}$), in agreement with existing published vals. by other methods.

L. J. J. Photoconductivity of diamond. I. Experimental. II. Theoretical. D. D. Pant (*Proc. Indian Acad. Sci.*, 1944, **19**, **A**, 316—324, 325—333). —I. The photoconductivity of 36 diamonds, mostly polished cleavage plates, has been measured with Hg illumination parallel and perpendicular to the polished plane faces. The diamonds fall into three poorly-defined groups giving photocurrents of 10^{-8} , 10^{-9} , and 10^{-10} amp. No clear-cut division into diamonds of high and low conductivity, as suggested by Robertson *et al.* (A., 1934, 583), is possible. Diamonds highly photoconducting in the ultra-violet exhibit similar properties in the visible. Strongly photoconducting diamonds exhibit the red-light effect but this is not observed with lower photoconductivities. Such diamonds also exhibit a secondary current on long illumination which persists after the light is extinguished. Illumination with red light increases the current when the diamond is in this state, the increase being quantitatively related to the magnitude of the secondary current without illumination. The relations between photoconductivity and other optical properties are discussed.

II. Variations in photoconductivity in diamonds are due to variations in crystal structure, assuming that non-homogeneities and irregularities in the crystal produce the photoelectrically active centres. Other features of photoconductivity, *e.g.*, the spectral distribution curves (particularly the rise for $\lambda\lambda < 3000$ A.), the absence of a definite threshold frequency, the effect of red light, and the secondary current, are explained. The relation between the magnitude of the dark secondary current and that produced by red-light excitation is derived theoretically. W. R. A.

Lattice spectrum and specific heat of diamond. B. Dayal (*Proc. Indian Acad. Sci.*, 1944, **19**, **A**, 224—230).—The bulk modulus of diamond, calc. from the spectroscopic data of Krishnan (A., 1944, I, 213) and of Mani (*ibid.*, p. 212) by the method of Nath (A., 1935, 1058), is $5 \cdot 9 \times 10^{13}$, in good agreement with experimental vals. Vals. of C_{v} have been calc. from spectroscopic data, the three degrees of freedom not covered by these data being considered as an elastic spectrum and represented by a term of the Debye type having a

characteristic temp. of 820°. Observed and calc. vals. agree well, particularly in the range 200—1100° K. W. R. A.

Nature and origin of the luminescence of the diamond. (Sir) C. V. Raman (*Proc. Indian Acad. Sci.*, 1944, **19**, **A**, 199—215).—The luminescence of several specimens of Indian and S. African diamonds, both natural crystals and cleavage plates, has been studied. Many cleavage plates show luminescence patterns which, together with the transparency patterns in the ultra-violet at $\lambda < 3000$ A. and the patterns of structural birefringence between crossed polaroids, are due to the lamellar twinning of the various crystal structures of diamond (cf. A., 1944, I, 216). Interpenetration of the positive and negative tetrahedral forms results in a blue luminescence without structural birefringence and opacity to ultra-violet radiation. Interpenetration of tetrahedral and octahedral structures gives rise to a yellow luminescence, a banded structural birefringence, and imperfect ultra-violet transparency. Interpenetration of the two octahedral forms gives no luminescence, but produces ultra-violet transparency and a characteristic finely-streaked birefringence. The emission and absorption spectra in the visible region, and the reflecting power of the lattice planes for X-rays, confirm the physical nature of the luminescence. W. R. A.

Evaluation of the specific heat of rock salt by the new crystal dynamics. B. Dayal (*Proc. Indian Acad. Sci.*, 1944, **19**, **A**, 182–187).—By the Raman dynamics of crystal lattices the rock salt structure has nine distinct $\nu\nu$ of vibration, representing 45 of the 48 degrees of freedom of the 8 Na' and 8 Cl' ions in a super-lattice cell. These $\nu\nu$ are evaluated and agree well with the experimental vals. from the Raman spectrum. The other three degrees of freedom representing the spectrum of the elastic vibrations of the lattice are calculable from known elastic consts. Vals. of C_{ν} calc. from these data agree satisfactorily with experimental vals. W. R. A.

Birefringence patterns in diamond. (Sir) C. V. Raman and G. R. Rendall (*Proc. Indian Acad. Sci.*, 1944, **19**, **A**, 265—273).—The structural or geometric birefringence of several diamonds is investigated. This birefringence results from the co-existence in the crystal of structures with different properties and crystal spacings. Diamonds of the blue-luminescent, ultra-violet-opaque type are isotropic, whereas those of the non-luminescent, ultra-violet-transparent type exhibit birefringence. X-Ray studies point to a difference in crystal spacing between the two octahedral structure types present in the non-luminescent diamonds, which results in the laminar birefringence of such diamonds. The production of birefringence patterns by the intrusion of the octahedral type structure into diamonds having tetrahedral structure is confirmed by variations of luminescence, ultra-violet transparency, and X-ray reflexion over the specimen. W. R. A.

Luminescence patterns in diamond. K. S. Bai (*Proc. Indian* Acad. Sci., 1944, **19**, **A**, 274—279).—The patterns of intensity and colour in the luminescence of cleavage plates of diamond, produced by long-wave ultra-violet illumination, are studied. Lines in the pattern frequently run parallel to the natural faces of the crystal. Blue-luminescent diamonds may show no pattern, whereas patterns are always observed with mixed blue and yellow luminescence. Yellow luminescence is characterised by several bright parallel lines, sometimes in > one direction. Local variations in the ultra-violet absorption spectrum show that the patterns arise from the intrusion of a diamond structure having properties different from those of the rest of the crystal. W. R. A.

Variation of birefringence of gypsum and barytes with temperature. J. Jaffray (Compt. rend., 1943, 216, 814—816).—For gypsum, the birefringence (b) of cleavage laminæ is a linear function of temp., and $db/d\theta$ is negative, decreasing regularly with decreasing λ between 8500 and 3500 A. For barytes cut perpendicularly to the acute bisector of the optic axes, the birefringence is also a linear function of temp., but $db/d\theta$ is positive and increases as λ decreases over the range 9000—3800 A. A. J. M.

Photodichroism of thin coloured sheets of sodium chloride. S. Nikitine (Compt. rend., 1943, 216, 758-760).—A section of synthetic NaCl crystal, initially colourless, coloured by irradiation with X-rays for the first time, shows photodichroism when exposed to rectilinearly polarised white light. If the same section, partly decolorised and rendered anisotropic by the action of the polarised white light, is to be used again for the same experiment, it must first be completely decolorised, and then re-coloured by X-rays. It will then show the photodichroism again, and this can be repeated indefinitely. However, after each treatment the crystal shows a fatigue effect, evidenced by a decrease in the photodichroism, although the crystal is submitted to identical conditions. To study this in greater detail, the effect of irradiating coloured crystals with polarised monochromatic light preferentially absorbed by the F centres (blue light) or the F' centres (yellow and orange light) has been investigated. It is thus shown that a crystal showing fatigue contains both F and F' centres, whilst a new crystal contains only F centres. The fatigue effect is due to the production of an increasing no. of F' centres on each exposure of the crystal to X-rays. A. J. M.

218

Thermodynamics of crystal lattices. IV. Elastic constants of a face-centred cubic lattice with central forces. (Miss) M. M. Gow (Proc. Camb. Phil. Soc., 1944, 40, 151-166).—The isobars, isotherms, and the dependence of the elastic consts. on temp. are calc., using inverse-power law attractions and repulsions. Results are tabulated for five sets of vals. of the indices in the potential. H. J. W.

Polymorphism of s-mono-oleyl-disaturated triglycerides.—Sec A., 1944, II, 287.

IV.--PHYSICAL PROPERTIES OF SUBSTANCES.

Magnetic properties of oxygen adsorbed on activated charcoal. C. Courty (Compt. rend., 1943, 216, 769-771).—The susceptibility, χ , of O₂ adsorbed on C is 107-5 × 10⁶, which does not differ greatly from the val. for ordinary O₂. It is possible to determine χ conveniently for a gas by adsorbing it on activated C, since a large mass of gas is conc. into a small vol. A. J. M.

Magnetic properties of hæmatite powders : influence of grain size. R. Chevallier and (Mlle.) S. Mathieu (Ann. Physique, 1943, [xi], 18, 258-288).—Magnetisation curves were found with increasing and decreasing fields up to 6500 gauss for samples of uniform microcryst. powders of average grain size d. The coeff. of initial magnetisation falls rapidly with decrease of d, and $\chi \times 10^6$ varies from ~400-500 to 25-30 for grain sizes $300-1\mu$. and is ~1750 for very thin films of artificial hæmatite. The true coeff. of magnetisation decreases with increase of field and approaches, for all powder samples, the limiting val. $\chi = 20 \times 10^{-6}$. N. M. B.

Magnetic susceptibility and constitution of nitroso-pentammine cobalt salts. S. P. Ghosh and P. Ray (J. Indian Chem. Soc., 1943, 20, 409—413).—Redetermination of the magnetic moment of the black and red isomerides of $[Co(NH_3)_6(NO)]^{++}$ salts gives a paramagnetic moment of 1.5 Bohr magnetons for the black chloride and a diamagnetic val. for the red nitrate. The electronic structure of the complexes is discussed. L. J. J.

High-temperature heat contents of magnesium nitrate, calcium nitrate, and barium nitrate. C. H. Shomate (J. Amer. Chem. Soc., 1944, 66, 928—920).—High-temp. heat content measurements on $Mg(NO_3)_2$ (399—623° K.), $Ca(NO_3)_2$ (403—815° K.), and $Ba(NO_3)_2$ (411—862° K.) are used to derive equations for heat content and C_p and vals. of entropy (S) for 50° intervals from 350° K. W. R. A.

Melting of crystalline polymers. (Miss) E. M. Frith and R. F. Tuckett (*Trans. Faraday Soc.*, 1944, 40, 251-260).—On the basis of a fringed micelle model a thermodynamic relation is obtained between the m.p. and the proportion θ of amorphous material in the structure. The convergence of m.p. in a homologous series and the existence of a range of melting in materials containing cryst. and amorphous parts in equilibrium are necessary consequences of the theory. Calc. vals. of the cryst.-amorphous equilibrium over a range of temp. agree with experimental data for rubber and polyethylene. Extension of the treatment to stretched polymers is in qual. agreement with observation for rubber. F. L. U.

ment with observation for rubber. Dissociation of ammonium chloride. C. C. Stephenson (J. Chem. Physics, 1944, 12, 318-319).—The standard free energy of dissociation of NH₄Cl into NH₈ and HCl, calc. from dissociation pressures and heat capacities and from solubility and activity coeffs. of aq. solutions, gives the vals. 21,860 and 21,780 g.-cal. per g. mol., respectively, at 298·1° K., in agreement with the assumption of complete dissociation in the vapour phase. The corresponding vals. for ΔH at 298·1° K. are 42,160 and 42,260 g.-cal. per g.-mol., respectively. The standard entropy of aq. NH₄' at 298·1° K. is calc. as 26·5 and 27·1 g.-cal. mol.⁻¹ deg.⁻¹, respectively, from the above sets of data. L. J. J.

Entropy values in homologous series of salt-like solid materials. W. D. Treadwell and B. Mauderli (*Helv. Chim. Acta*, 1944, 27, 567-571).—Comparison of the entropy vals. (S) of various series of elements and compounds indicates that for the corresponding compounds of a group in the periodic classification S increases linearly with the mol. wt. of the compound and can be expressed as $S_{298} = a (\log M_e + \beta \log M_a) + b$, where M_e and M_a are the mol. wts. of the cation and anion, respectively, $\beta =$ valency of cation/valency of anion, and a and b are const. for the particular series but vary with the series. J. W. S.

Thermal expansion of plastic materials.-See B., 1944, II, 207.

Van der Waals' cohesion constant. F. C. Auluck and R. N. Rai (*Current Sci.*, 1944, 13, 126–127).—Solving the Schrödinger equation for a hole in a liquid leads to expressions for the van der Waals const. $a = 2 \cdot 4 v^2 \sigma (\sigma \rho / h^4)^{1/7}$ and the intrinsic pressure $p_0 = 2 \cdot 4 \sigma (\sigma \rho / h^4)^{1/7}$ in terms of the mol. vol. V, the surface tension σ , and the density ρ . L. J. J.

Attempt to define a perfect liquid. J. P. E. Duclaux (Ann. Physique, 1943, [xi], 18, 209—215).—Theoretical considerations are based on a comparison of the known properties of various liquids in order to determine those of a perfect liquid. N. M. B.

Rheochor and its application. W. V. Bhagwat, P. M. Toshniwal, and V. A. Moghe (*J. Indian Chem. Soc.*, 1944, 21, 29-31).-Vals.

for at. rheochors have been calc., the substitution of $\eta^{\frac{1}{2}}$ for $\gamma^{\frac{1}{2}}$ in the parachor being used (cf. A., 1943, I, 301). The vals. obtained are H 1.77, C 6.44, O 6.02, S 11.28, Cl 11.6, Br 13.8, and Hg 8.75. When substituted for various org. liquids, these vals. reproduce the rheochors of the compounds with fair accuracy; alcohols and aromatic hydrocarbons show marked deviations. The formula $R_m = R(1-x) + xR_x$, where R_m , R, and R_x are the rheochors of solution, solvent, and solute, respectively, and x is the mol. fraction of the solute in solution, extends the calculation to solutions, e.g., of sucrose. L. S T.

Viscosity of methyl dilinoleate.—D. W. Young and R. E. Biertuempfel (J. Amer. Chem. Soc., 1944, 66, 843—844).—Vals. of η are given for the range -40° to 100°. W. R. A.

Viscosimetric behaviour of malt extracts.—See B., 1944, III, 158. Thermoplastic flow of polystyrene.—See B., 1944, II, 207.

V.—SOLUTIONS, DISPERSIONS, AND MIXTURES.

Molecular state of mixtures. F. Michaud (*Compt. rend.*, 1943, 216. 840—842).—It is shown theoretically that in binary mixtures the relative lowering of v.p. of the two components is the same for that concn. which corresponds to max. free energy, and this is confirmed by vals. taken from "International Critical Tables," which show that the free energy of a binary mixture is a max. when the concns. are equimol. Exceptions occur when the two mols. tend to combine in some ratio other than 1:1. A. J. M.

Diffusion equations, their representation by models, and diffusion experiments with silica gels. III. Diffusion in a defined space with initial local differences of concentration. A. Dobrowsky (Kolloid Z., 1943, 105, 149–160).—The diffusion equations are solved to give the concn. gradients and amounts of substance diffusing after any time, in defined vols. of uniform cross-section, with various boundary conditions. The equations are verified by experiments on the diffusion of aq. $Na_2Cr_2O_7$ in SiO₂ gels, and by hydraulic models (cf. A., 1944, I, 197). J. H. BA.

Dielectric properties of dipolar ions in mixed solvents. G. Oster (J. Amer. Chem. Soc., 1944, 66, 948—951).—A theory of the decrease in dielectric increment of dipolar ions with decrease in ϵ of the solvent mixture is developed. On the basis of electrostatic theory dipolar ions would be expected to sort out the solvent constituent of higher ϵ , thus producing a shell of material of greater ϵ which would act as an electrostatic shield decreasing the effective dipole moment and dielectric increment of the dipolar ion and becoming more pronounced as the difference in ϵ of the shell surrounding the dipolar ion and that of the liquid in the bulk of the solutions widens. The theory is in general accord with observed results. W. R. A.

Dielectric constants of solutions of glycine and pyridine betaine in water-dioxan mixtures. G. Oster, (Miss) D. Price, L. G. Joyner, and J. G. Kirkwood (J. Amer. Chem. Soc., 1944, 66, 946—948).—Vals. of ϵ for solutions of glycine and pyridine betaine (I) in H₂O-dioxan mixtures at 25° are given. The dielectric increments of both solutes show a regular decrease with decreasing ϵ of the solvent mixture, similar to that exhibited by glycine betaine and the benzbetaines. The possibility of the reversion of (I) to the nonionised form is examined and calculations have shown that the charged groups could approach each other, and thus account for the experimental results, only if valency bonds were greatly distorted. W. R. A.

Viscosity of aqueous solutions of electrolytes as a function of the concentration. VIII. Potassium ferricyanide. G. Jones and S. M. Christian (J. Amer. Chem. Soc., 1944, 66, 1017-1019).—Data for ρ and η of aq. $K_3Fe(CN)_6$ up to saturation are recorded. Equations connecting ρ , η , and $1/\eta$ with concn. are given. $K_3Fe(CN)_6$ solutions verify the predictions of Falkenhagen and Vernon. W. R. A.

Existence of an intermediate precipitated phase in the decomposition of the solid solution of aluminium and magnesium. P. Lacombe (Compt. rend., 1943, 217, 175-177).-If the Al-Mg system is annealed at a low temp. (<280°) and if the re-dissolution of the pptd. phase with rise of temp. is followed by dilatometry or conductivity, there is an anomaly in the curve at 280°. If the duration of annealing is prolonged the anomaly disappears. There is no anomaly if the annealing is carried out at temp. >280°. This is due to an intermediate pptd. phase, the occurrence of which has also been followed by X-ray analysis. This indicates that below 280° a phase different from Al₃Mg₃ exists, but if the alloy is heated at >280° for a few min. the pptd. phase disappears and the normal diagram for the β phase is obtained. This result is confirmed by thermal analysis. A. J. M.

Phase diagram of the copper-iron-silicon system from 90 to 100% copper. A. G. H. Andersen and A. W. Kingsbury (*Amer. Inst. Min. Met. Eng., Tech. Publ.* 1510, 1942, 10 pp.; *Metals Tech.*, 9. No. 6).—Cu-Fe and Cu-Fe-Si alloys were examined by the X-ray powder method after quenching from $400-1025^\circ$. Fe-rich phases were identified by chemical analysis after removal of the Cu-rich phase with HNO₃. Isothermal sections of the three-component

diagram are given for temp. between 500° and 875°, and diagrams showing the effect of Si on Cu containing 0.5 and 2% Fe, based on the authors' and previous work. R. KE.

Rate of precipitation of silicon from solid solution of silicon in aluminium. L. K. Jetter and R. F. Mehl (Amer. Inst. Min. Met. Eng., Tech. Publ. 1508, 1942, 16 pp.; Metals Tech., 9, No. 6).— Using a new dilatometer (cf. C., 1944, Part 4) measurements were made for isothermal ageing at temp. of $196-236^{\circ}$ for five quenched alloys containing 0.41-1.23% Si. The effect of rate of quenching is also described. The rate of dilation increases with increase in solute concn. and with increasing temp. and also with rate of quenching owing to the nucleating effect of the quenching strain. The results are treated theoretically, assuming that the pptn. is due to formation and growth of nuclei. R. KE.

Constitution of lead-rich lead-antimony alloys. W. S. Pellini and F. N. Rhines (Amer. Inst. Min. Met. Eng., Tech. Publ. 1506, 1942, 7 pp.; Metals Tech., 9, No. 6).—The solidus and eutectic temp. were determined with a specially designed apparatus by observing the temp. at which a slowly heated lightly loaded specimen was ruptured. The solid solubility limit is 3.5% Sb at the eutectic temp., $251.5 \pm 0.5^{\circ}$. R. KE.

Solubility products of copper oxides and hydroxide and the solubility of copper hydroxide in sodium hydroxide solution. W. Feitknecht (*Helv. Chim. Acta*, 1944, 27, 771–775).—The energy of formation of $Cu(OH)_2$ is recalc.' from other thermal data as $\Delta A = -85.41$ kg.-cal. From this and other data the following solubility products (S) are calc. $S_{Cu_00} = [Cu''][OH'] = 1.26 \times 10^{-15}$, $S_{Cu0} = [Cu''][OH']^2 = 1.0 \times 10^{-20}$, $S_{Ou(OH)_2} = [Cu''][OH']^2 = 1.6 \times 10^{-19}$. From the Cu remaining in solution immediately after a little $Cu(NO_3)_2$ is treated with an excess of N-NaOH and the amount remaining after the solution has been kept for 4 months so as to cause pptn. of CuO the equilibrium consts. of the reactions $Cu(OH)_2 + 2OH' \rightleftharpoons Cu(OH)_4''$, $CuO + H_2O + 2OH' \rightleftharpoons Cu(OH)_4''$, and $Cu(OH)_4'' \rightleftharpoons Cu'' + 4(OH)'$ are calc. as 5.3 $\times 10^2$, 6.5×10^3 , and 7.5 $\times 10^{-17}$, respectively. J. W. S.

Effect of sulphide ion hydrolysis on the solubility-solubility product relationship of metallic sulphides. P. van Rysselberghe and A. H. Gropp (J. Chem. Educ., 1944, 21, 96—99).—A theoretical treatment in which the extensive hydrolysis of S'' is taken into account in establishing the correct relationship between the solubility and the solubility product of sparingly sol. sulphides. The formation of complex ions is the probable explanation of the lack of agreement between simple theory and facts for ZnS, CdS, and CuS. L. S. T.

Mutual solubility in the ternary system cadmium-cobalt-zinc mercurithiocyanates. I. Binary system Cd[Hg(CNS)₄]-Co[Hg(CNS)₄]. M. Straumanis and W. Stahl (Z. physikal. Chem., 1943, A. 193, 97-111).—Co[Hg(CNS)₄] (I), Zn[Hg(CNS)₄], and Cd[Hg(CNS)₄ (II) all crystallise as tetragonal bisphenoidal (S_4) , body-centred. The space-group is therefore S_4^2 , with 2 mols. per unit cell. Lattice consts. at room temp. are, respectively: a 11.0868, 11.0616, 11.4403, c 4.3652, 4.4287, 4.2043 A., c/a 0.3937, 0.4002, 0.3675, v 536.56, 541.90, 550.26 A.³ The (I)-(II) system shows complete miscibility by exchange between Co^{*}₂ and Cd^{*}₂ with deformation of the crystal. The Vegard additivity law holds within experimental error. L. J. J.

Solubilities of high mol. wt. symmetrical normal aliphatic tertiary amines. A. W. Ralston, C. W. Hoerr, and P. L. Du Brow (J. Org. Chem., 1944, 9, 259-266).—Solubilities of $N(C_8H_{17})_3$ (I), $N(C_{12}H_{28})_3$ (II), and $N(C_{18}H_{37})_3$ (III) have been determined at 10° intervals between -60° and 60° in C_8H_6 , cyclohexane (IV), CCl₄, CHCl₃, Et_2O , EtOAc, BuOAc, COMe₂, COMEEt, MeOH, 95% EtOH, Pr⁸OH, and Bu^aOH. The solubility curves are generally similar to those of the corresponding primary and sec. amines (cf. A., 1944, I, 123; II, 248), from which the *tert*. amines differ in being more sol. in (IV) than in C_6H_6 . (III) differs from all other amines studied in being less sol. in CHCl₃ than in CCl₄ at lower concns. (I), (II), and (III) form simple eutectics with C_6H_6 , (IV), and CCl₄. With increase in polarity of the solvent solubility decreases markedly, especially at lower temp., and in several solvents a region of two immiscible solutions appears. H. W.

Solubilities of high mol. wt. normal aliphatic primary alcohols. C. W. Hoerr, H. J. Harwood, and A. W. Ralston (*J. Org. Chem.*, 1944, 9, 267—280).—Solubilities of the alcohols with 10, 12, 14, 16, and 18 C have been determined between -40° and 50° in the solvents used for tert. amines (preceding abstract), and in EtNO₂ and MeCN. The behaviour of the alcohols is similar to that of other long-chain compounds studied, and their solubility curves resemble those of the nitriles and acids (cf. A., 1944, I, 122; 1943, I, 87), which have a similar degree of polarity. Simple eutectics are formed with CeHe, *cyclohexane*, and CCl, in which the solubilities decrease in the order given. With increasing polarity of the solvent the solubilities decrease at lower and increase at higher temp. In highly polar solvents two immiscible solutions appear over considerable ranges of concn., as with the tert. amines; an exception to this behaviour is provided by C₁₈H₃₂°OH and C₁₈H₃₂°OH in EtNO₂. With increase in the mol. wt. of the alcohol the solubility curves become steeper at low and flatter at higher concns. The behaviour cannot be accounted for by mol. association alone. H. W.

Accommodation coefficients on gas-covered platinum. I. Amdur, M. M. Jones, and H. Pearlman (*J. Chem. Physics*, 1944, **12**, 159– 166).—At room temp., accommodation coeffs. (a) on a completely gas-covered Pt wire are: He 0.403 \pm 0.001, Ne 0.700 \pm 0.002, A 0.847 \pm 0.002, Kr 0.844 \pm 0.002, Xe 0.858 \pm 0.002, H₂ 0.312 \pm 0.001, D₂ 0.393 \pm 0.001, N₂ 0.769 \pm 0.002, CO 0.772 \pm 0.002, O 0.782 \pm 0.002. Temp. is without influence at 18.9–30.5°. a increases with pressure up to ~0.1 mm. and then remains const. throughout the range of free mol. conduction. Results are corr. for radiation, wire conduction, and free mol. conduction effects on temp. distribution along the Pirani gauge wire used. L. J. J.

Adsorption analysis. I. A. Tiselius (Kolloid-Z., 1943, 105, 101-109) .- When a solution is passed through an adsorbent, e.g., activated charcoal, the solute is adsorbed so that pure solvent passes until the adsorbent is saturated with solute, after which the solution appears separated by a sharp boundary from the solvent. In a solution having several solutes, several boundaries are obtained. In the apparatus described an interferometer is used for observing these boundaries and three methods of application are described. In "front" analysis the vol. of solvent passed before the appearance of the solution front (retardation vol., v_r) is measured. v_r (when corr. for solvent initially present on the adsorbent) is equal to the adsorption coeff. an at the concn. used, and the method can be applied in certain cases to the determination of adsorption isotherms. Retardation vols. are given for various sugars (in 0.2%aq. solution), amino-acids, and peptides (in 0.5% aq. solution). In the case of mixed solutes mutual influence on the vals. of a_A is observed unless the individual a_A are widely different. This inter-ference occurs in a mixture of lauric and palmitic acids. In elution analysis the adsorbed solute is washed through by a solvent, which produces zones of the solutions travelling with speeds dependent on α_A . Zone spreading introduces difficulties, but the method gives useful results when the solute is weakly adsorbed. In displacement analysis the adsorbed solute is displaced by another solute (e.g., PhOH), in which case the zones are usually well defined. A separation of such similar substances as sucrose and maltose is observed by this method. Difficulties arise with very weakly adsorbed solutes (zone spreading) and displacement is not usually quant., but it can be made so by preliminary treatment of the adsorbent adsorbent. J. H. BA.

Water sorption by maize starch.-See B., 1944, III, 157.

Elucidation of dyeing processes. R. Haller (Kolloid-Z., 1943, 105, 47-149).—Consideration of the data on the dyeing of Al_2O_3 (produced by anodic oxidation or suspended in H_2O) shows that the dyeing efficiency depends on the degree of dispersion of the Al_2O_3 and of the dye. Even if the dyeing process is a chemical reaction, as for certain animal fibres, it may in certain conditions be based on adsorption. J. H. BA.

Surface of solids. X. Extension of the attractive energy of a solid into an adjacent liquid or film, the decrease of energy with distance, and the thickness of the film. W. D. Harkins and G. Jura (J. Amer. Chem. Soc., 1944, 66, 919-927). --Practically every film adsorbed on the surface of non-porous solids has been found to be highly multimol. at v.p. slightly < saturation. The effect of distance on the intermol. attraction between a solid and an adjacent liquid or an adsorbed layer has been determined in energy units. The energy decays exponentially with distance. The energy of vaporis-ation of H_2O at 25° (Q) is 10,540 g.-cal. per mol., but if the water is adsorbed on a clean surface of cryst. TiO₂ (anatase) this energy is increased by amounts depending on the no. of layers of H_2O adsorbed, the water for any two three four and four layers being 650, 1200 the vals. for one, two, three, four, and five layers being 6550, 1380, 450, 80, and 40 g.-cal. per mol. > Q. Consequently at least 5 mol. layers of H₂O should be adsorbed on anatase before saturation of the vapour is attained and experimental evidence shows thicknesses of >15 A. With N₂ at -195.6° the measured thickness is 36 A. (10 mol. layers). At 0° n-C₄H₁₀ attains a thickness of 64 A., but the thickness of the first mol. layer is \sim 4 A. since the mols, lie flat on the surface. Until about the seventh layer the degree of orientation is small but thereafter the surface of the film should exhibit practically the same orientation as liquid $n-C_4H_{10}$. These results are not in accord with Langmuir's theory of unimol. layers, or with the combined monolayer plus capillary condensation theory. They show that films adsorbed on plane surfaces usually attain greater thicknesses than on porous solids, but PreOH on BaSO, is an exception and H_2O on hydrophobic solids should also be an exception. Whilst these results show general agreement with the multi-mol. theory of Brunauer, Emmett, and Teller (A., 1938, I, 190), the assumption in the theory that the energy of vaporisation of the second adsorbed layer is \Rightarrow the energy of vaporisation of the liquid is shown to be incorrect. Capillary condensation does not appear to play an important rôle in the sorption with cryst. powders of the type used. W. R. A. exception and H₂O on hydrophobic solids should also be an excep-

Surface tension and van der Waals' equation. F. C. Auluck and R. N. Rai (J. Chem. Physics, 1944, 12, 321-322).—Fürth's " hole "

treatment of liquids (A., 1941, I, 369) leads to a connexion between the van der Waals const. *a* and the surface tension (γ). The treatment gives the relation $a = 1.3 V^2 [\gamma^{3/2}]/(kT)^4$]. Vals. calc. for a no. of liquids differ from the corresponding vals. of *a* from gas data by a nearly const. factor of ~2. A similar degree of agreement is given by vals. of *a* calc. from γ and ρ vals. by means of the Schrödinger equation. L. J. J.

Pseudo-optics in capillary phenomena. II. R. E. Liesegang (Kolloid-Z., 1943, 105, 98-101; cf. A., 1944, I, 58).—The method of analysis of mixtures by means of capillary rise on unglazed paper is extended by applying it to small drops of mixture solution previously dried on the paper, and allowing the capillary rise of H₂O to take place first in one direction, followed by drying, and then in the direction at right angles. Pseudo-optical effects produced by pore blocking and cuts in the paper tend to obscure the resulting picture, but any confusion can be overcome by marking the water line at intervals. J. H. BA.

Structure of the collodion membrane and its electrical behaviour. **VIII.** Quantitative studies concerning the acidic properties of collodion and their correlation with membrane structure and activity. K. Sollner and J. Anderman. **IX.** Water uptake and swelling of collodion membranes in aqueous solutions of organic electrolytes and non-electrolytes. K. Sollner and P. W. Beck (J. Gen. Physiol., 1944, 27, 433—449, 451—460).—VIII. A no. of collodion (I) preps. were brought into the state of free acids by exchange of all other cations for H' and their acid nos. in the dissolved state and their base-exchange capacities in the fibrous state were determined. The acid no. is lowest for highly purified (I) and highest for highly oxidised (I), but the ratio of the extremes of acid nos. is only 1: 3.3, corresponding with a mean equiv. wt. ratio of 100,000: 30,000. Base-exchange capacities vary considerably, the ratio of the lowest and highest vals. being 1: 200. In electrochemically inactive (I) only one in 770 acid groups is available for base exchange, whereas in the most active (I) one group in 13 is available. The high vals. obtained for oxidised (I) are due not so much to the high acid nos. as to their more open micellar structure. This structural difference is ascribed to the presence of a small fraction of low mol. wt. which inhibits normal formation and arrangement of micelles. There is reasonably good correlation between acid no. and electrochemical activity, low acid nos. being found with the least active preps., but correlation between base-exchange capacity and activity is poor, low capacity vals. being accompanied by low as well as high activity. although high capacities are always associated with high activity.

IX. The swelling of dried (I) in aq. solutions of org. electrolytes and non-electrolytes depends on the nature of the solute. No significant swelling occurs with hydrophilic solutes, e.g., EtOH, PhSO₃H, 2-C₁₀H₇·SO₃H, glycerol, glucose, citric acid, but with carbophilic solutes, e.g., higher alcohols and fatty acids, where swelling effect increases with increasing mol. wt., PhOH, m-NO₂·C₆H₄·OH, the swelling is > in absence of solute. The amount of H₂O taken up by (I) in presence of some solutes is \ll the amount taken up in absence of solute; (I) which has thus accumulated a significant quantity of org. solute has probably a different structure from (I) wetted with H₂O only. C. R. H.

Diffusion of gaseous hydrocarbons through rubber membranes. L. Long (J. Chem. Educ., 1944, 21, 139–141).—Apparatus, method, and results for diffusions of C_7H_{16} and of iso- C_8H_{16} through various diaphragms of rubber and neoprene under different conditions of temp. and pressure are described. L. S. T.

Effects of pressure on the properties of liquids and solutions of electrolytes. B. B. Owen (J. Chem. Educ., 1944, 21, 59-63, 84; cf. A., 1943, I, 298).—The dependence on pressure of the partial molal vols. of the components of ionic reactions is discussed, and a correlation of their behaviour in terms of ionic dimensions is attempted, the equations of Tait and of Born and Tammann's hypothesis being used for the purpose. A relationship between ϵ and sp. vol. of the pure solvent is derived. L.S.T.

Magnetic rotativities. III. Ionic (heteropolar) associations. R. de Mallemann (Ann. Physique, 1943, [xi], 18, 56-72; cf. ibid. 1942, [xi], 17, 360).—A theoretical examination of rules for mixtures, and electrolytic solutions. Conclusions based on considerations of available data are discussed. N. M. B.

Effect of the colloidal state or suspensions on the transmission of infra-red up to 20,000 A. through substances. M. Déribéré (Compt. rend., 1943, 217, 201-211).—The transmission of infra-red rays by a suspension of bentonite has been studied. Thin sheets of bentonite were also prepared. The leaflets transmitted infra-red radiation much better than the suspensions. The Brownian movement thus affects the transmission considerably. A. J. M.

Structure of highly purified sulphide sols. III. Structure and temporary reactions of highly purified sulphur sol. W. Pauli, E. Russer, and P. Balog (*Helv. Chim. Acta*, 1944, 27, 585-612; cf. A., 1937, I, 237, 514).—S sol, prepared by interaction of conc. H_3SO_4 and conc. aq. $Na_2S_2O_3$, pptn. with saturated aq. NaCl and agitation of the ppt. with H_2O , followed by electro-dialysis, is yellow by reflected and orange yellow by transmitted light. The [H']

calc. from the conductivity of the sol is < that determined by conductometric titration with NaOH or $Ba(OH)_2$ but increases gradually when the sol is kept. From the Ag' consumed and H' liberated when the sol is treated with AgNO₃ and immediately titrated with NaOH the amounts of $H_2S_2O_3$ and polythionic acids (I) present have been determined. Results on a coagulum obtained by freezing the sol indicate that the $H_2S_2O_3$ is firmly bound to the S, whilst (I) is an impurity in the aq. phase. The sol gradually reacts directly with AgNO₃, I, and NaOH and the reactions involved are discussed. The case of coagulation by electrolytes follows the normal order of cations and anions, excepting that increase in [H'] has a stabilising effect. The markedly hydrophilic character of the sol is accounted for by the high proportion of stabilising electrolyte, ~1 mol. of $H_2S_2O_3$ to 4 atoms of S. J. W. S.

Variation of magnetic properties of ferric hydroxide sols on addition of hydrochloric acid. A. Boutaric and (Mlle.) P. Berthier (Compt. rend., 1943, 216, 757—758).—Making use of the law of addition of magnetic properties it is possible to obtain the susceptibility (χ) of Fe(OH)₃ sols, and its variation with the addition of various amounts of HCl (0.05—0.5N). χ increases with [HCl], and with time, approaching the limiting val. +193 × 10⁻⁶. This is of the same order as χ for Fe^{III} salts in solution. The method makes it possible to follow the progressive breakdown of micelles of Fe(OH)₃.

Precipitation of proteins by synthetic detergents. F. W. Putnam and H. Neurath (J. Amer. Chem. Soc., 1944, 66, 692–697).— Anionic detergents ppt. proteins only in the cationic form, no pptn. occurring at pH > the isoelectric point of the protein. In the system cryst. horse serum-albumin-Na dodecyl sulphate pptn. is related to protein-detergent wt.-concn. ratio, pH, temp., and ionic strength. When protein-detergent complexes are dissociated by Ba salts the recovered protein is in a regenerated state, as indicated by diffusion, viscosity, and electrophoresis studies. The mechanism and applications of the methods are discussed. W. R. A.

Effect of polyhydric alcohols on the solubilisation of proteins in an organic medium. J. Loiseleur (*Compt. rend.*, 1943, 216, 904– 905).—The addition of $(CH_2 \circ CH)_2$, like that of the aliphatic acids, aids dissolution of proteins in org. solvents (A., 1931, 166). Unlike the acids, polyhydric alcohols do not greatly assist the direct dissolution of dry proteins, but when added to an aq. solution of a protein they prevent its pptn. by EtOH, $COMe_2$, $CCl_3 \cdot CO_2 H$, $OH \cdot C_6 H_2 (NO_2)_3$, etc. Dilution of these "protected" solutions with H_2O causes immediate pptn. of the protein. The dielectric const. of the protein solution is considerably decreased by the addition of the polyhydric alcohol. This affects the dissociation of the protein, favouring formation of the zwitterion. This fact alone is insufficient to explain the phenomenon, but there may be some physical association of the polyhydric alcohol with the protein. A. J. M.

VI.--KINETIC THEORY. THERMODYNAMICS.

Strength of strong acids. J. V. Chodakov (Compt. rend. Acad. Sci. U.R.S.S., 1943, 41, 117—119).—The author's semi-empirical formula for the dissociation const. of an acid in terms of its anionic radius r (in crystals) is $1\cdot32/r \approx 0.84 - 0.042 \log k$, giving $k = 10^{3\cdot5}$ for H₂SO₄ and $10^{2\cdot5}$ for HCl. Evidence supporting a higher strength for H₂SO₄ than for HCl is reviewed. L. J. J.

Effect of substituents on the dissociation constants of carboxylic acids. J. N. Sarmousakis (J. Chem. Physics, 1944, 12, 277–288).— Vals. of log K_{AxB0} , the ratio of dissociation const. of a substituted acid to that of the parent acid, are calc. for p- and *m*-substituted benzoic acids, by means of the Kirkwood-Westheimer theory on the basis of an oblate spheroidal mol. model. Agreement with experimental vals. is good for the *m*-acids, but the *p*-acids show differences which are ascribed to resonance affects. The differences vary very little with the single-component hydroxylic solvent used. L. J. J.

Ionisation constants of very weak acids. Acetoxime, methyl ethyl and diethyl ketoximes. C. V. King and A. P. Marion (*J. Amer. Chem. Soc.*, 1944, 66, 977–980).—The rate of decomp. of nitrosotriacetonamine, catalysed by OH', has been measured as a function of ionic strength (μ) at 24.9° up to [OH'] = 0.05 and μ = 0.22 and may be expressed as $k = (1\cdot209-0\cdot479 \ \mu)$ [OH']. The acid dissociation consts. of the ketoximes have been determined as a function of μ , using the catalytic reaction above to measure the [OH'] of NaOH partly neutralised by ketoxime. W. R. A.

Steric strain and the anomalous base strength of normal aliphatic amines. H. C. Brown and M. D. Taylor (*J. Amer. Chem. Soc.*, 1944, 66, 846-847).—The base strength of *n*-aliphatic amines referred to BMe_3 as standard acid increases from NH_3 to NH_2Me , decreases with NH_2Et , and then increases regularly, thus displaying a very close similarity to *n*-aliphatic acids. It is suggested that this behaviour results from steric interference, and that the point in the series at which weakening is exhibited will depend on the size of the mol. of the reference acid; the larger is the acid the earlier in the series will weakening be shown. W. R. A. Effect of sodium chloride on the pH of p-phenolsulphonate buffers from 9° to 60°. R. G. Bates and S. F. Acree (J. Res. Nat. Bur. Stand., 1944, 32, 131—143).—E.m.f. measurements on mixtures of p-OH·C₈H₄·SO₃K, NaOH, and NaCl have been made over the range 0—60°. For a given composition pH decreases with temp., and for a given temp. pH decreases with increase in [NaCl]. The effect of NaCl on pH is satisfactorily accounted for solely by the change in ionic strength and activity coeffs. on addition of a third ionised component to the buffer. Abnormal and sp. effects due to Na^{*} and Cl' appear to be absent. Equations permitting the calculation of the effect of NaCl on pH are given. A method for the calculation of the ionic strength and pH of unknown mixtures of sulphonate and NaOH by determining the e.m.f. in presence of two different concns. of NaCl has been devised. C. R. H.

Thermodynamics of azeotropic solutions. I. Shift of equilibrium in binary systems. O. Redlich and P. W. Schutz (J. Amer. Chem. Soc., 1944, 66, 1007—1011).—Since the azeotropic equilibrium of a solution of two miscible liquids is characterised by three intensive variables (temp., pressure, and composition), the shift in equilibrium is exhaustively described by two relations between the variables. Assuming that the vapour is a perfect gas mixture two expressions have been derived, in which relations between the variables are given in terms of ascertainable thermodynamic quantities. Azeotropic temp.-composition curves depend on whether one or both components are normal, dissociating, or associating. Dil. azeotropic solutions of a dissociating substance belong to the min. v.p. type. Only when a dissociating component is present does the temp.-composition curve increase or decrease without limit with decreasing conc. in dil. solutions. When the temp.-composition curve of a max. (min.) v.p. system extends to a pure component, this component is the more (less) volatile member. This rule holds for both upper and lower limits of the azeotropic temp. range. "Isobaric temp." is suggested for the temp. at which the v.p. of the pure components are equal. The slope of the temp.-composition curve is steep at this temp. if both components exhibit only small deviations from Trouton's rule. W. R. A.

System acetic acid-ammonia. A. W. Davidson, H. H. Sisler, and R. Stoenner (J. Amer. Chem. Soc., 1944, 66, 779–782).—The temp.-concn. curve of the system AcOH-NH₃ has been extended (cf. A., 1930, 406) to 100 mol.-% NH₃. The m.p. of NH₄OAC is 117°. Solid compounds, $5NH_3$, 4AcOH, $9NH_3$, AcOH, and (probably) $2NH_3$, AcOH have been shown to exist. Comparison with the H₂O-NH₃ system is made. W. R. A.

System sulphur dioxide-acetic acid. W. H. Scheub and C. R. McCrosky (J. Amer. Chem. Soc., 1944, 66, 841).—The m.p. curve shows the existence of the compound SO_2 , AcOH (m.p. -38°). The eutectic points are $-46\cdot1^{\circ}$ and $-80\cdot3^{\circ}$, corresponding with 13.2 and 78.4 mol.-% SO_2 . W. R. A.

Binary systems formed from nitriles and halides of titanium, tin, and antimony.—See A., 1944, II, 250.

Binary system tin tetrachloride-m-dinitrobenzene.-See A., 1944, II, 253.

Ternary system silver bromate-sodium bromate-water. J. E. Ricci and J. J. Aleshnick (J. Amer. Chem. Soc., 1944, 66, 980-983). —The system $AgBrO_3$ -NaBrO_3-H_2O has been investigated at 25° and partly studied at 0° and 50°. The compound $AgBrO_3$, NaBrO_3 (I) is formed. (I) forms a continuous solid solution with $AgBrO_3$. NaBrO₃ forms a solid solution containing up to 3.0% $AgBrO_3$. Ppts. of $AgBrO_3$ formed in the presence of Na^{*} and excess of BrO₃' ions must be contaminated with NaBrO₃; this would explain the difficulty of obtaining $AgBrO_3$ of const. solubility. The effect of these results on analytical procedures is discussed. The solubility of $AgBrO_3$ at 25° is 0.204%. W. R. A.

Ternary system barium bromate-barium chlorate-water at 25°. J. E. Ricci and S. H. Smiley (J. Amer. Chem. Soc., 1944, 66, 1011— 1015).—From solubility equilibrium relations at 25° of the system $Ba(BrO_3)_2$ -Ba(ClO_3)_2-H₂O the formation of a continuous solid solution of $Ba(BrO_3)_2$, H₂O-Ba(ClO_3)_2, H₂O is shown and this would explain why it is difficult to determine BrO_3' in the presence of ClO_3' by addition of a Ba salt. The system shows positive deviations from ideality (type II of Roozeboom's classification of solid solutions). The distribution const. for the two salts between their aq. solutions and the saturating solid solution was found to be log $K = 2 \cdot 0_6$, in fair agreement with the val. calc. from aq. solubilities of the salts, log $K = 1 \cdot 8_1$. The discrepancy is considered to result from the uncertainty regarding the val. of the activity coeff. of $Ba(ClO_3)_2$. W. R. A.

Systems $NaClO_3-NaBr-H_2O$, $NaClO_3-NaI-H_2O$, and $NaClO_3-NaNO_3-H_2O$ at 25°. J. E. Ricci (J. Amer. Chem. Soc., 1944, 66, 1015—1016).— Solubility measurements on the systems $NaClO_3-NaBr-H_2O$, $NaClO_3-NaI-H_2O$, and $NaClO_3-NaNO_3-H_2O$ at 25° indicate that these salt pairs do not form double salts or solid solutions at this temp. W. R. A.

Heat of formation of solid and liquid Mn(NO₃)₂,6H₂O. C. H. Shomate and F. E. Young (J. Amer. Chem. Soc., 1944, 66, 771773).—By measuring the heats of dissolution in N-H₂SO₄ at room temp. the heats of formation of $Mn(NO_3)_2, 6H_2O$ have been determined as (liquid) $-557,070\pm310$, (solid) $-566,680\pm310$ g.-cal. per g.-mol. The heat of fusion is 9610 ± 10 g.-cal. per g.-mol. W. R. A.

Heats of formation of $Mg(NO_3)_2$, $Mg(NO_3)_2$, $6H_2O$, $Ca(NO_3)_2$, $Ca(NO_3)_2$, $4H_2O$, and $Ba(NO_3)_2$. F. E. Young (J. Amer. Chem. Soc., 1944, 66, 773—777).—From measurements of heats of dissolution in N-HCl the heats of formation at 25° are calc. : $Mg(NO_3)_2 - 188,770 \pm 310$; $Mg(NO_3)_2$, $6H_2O - 624,410 \pm 310$; $Ca(NO_3)_2 - 224,050 \pm 360$; $Ca(NO_3)_2$, $4H_2O - 509,420 \pm 370$; $Ba(NO_3)_2 - 236,990 \pm 380$ g.-cal. per mol. W. R. A.

Heats of formation of $Al(NO_3)_{3,9}GH_2O$ and $Al(NO_3)_{3,9}GH_2O$. F. E. Young (J. Amer. Chem. Soc., 1944, 66, 777–779).—From measurement of the heats of dissolution of the nitrates and of Al in 4N-HCl the heats of formation at 25° are : $Al(NO_3)_{3,6}GH_2O = 680,890 \pm 460$ and $Al(NO_3)_{3,9}H_2O = 897,590 \pm 470$ g.-cal. per g.-mol. W. R. A.

VII.—ELECTROCHEMISTRY.

Redox potential of ferric solutions practically free from ferrous ions. (MIle.) D. Bézier (*Compt. rend.*, 1943, 216, 798-800).—The usual expression for the redox potential of a system, obtained by considering that both oxidised and reduced ions are present in considerable quantities, fails when applied to a solution containing only one type of ion. The potential curves as a function of pH have been obtained for solutions of Fe(ClO₄)₃ containing 10⁻¹ to 10⁻⁴ g.-ion of Fe per I. For a given solution at different pH vals. the potential is const. so long as [Fe^{...}] is const. It decreases when Fe(OH)₃ is pptd. In the region where the potential is const. it is given by $E = E_0 + 0.06 \log$ [Fe^{...}]. The method used shows at what pH vals. Fe(OH)₃ is pptd. At the pH at which pptn. commences all the Fe is in the form of Fe^{...} and not (FeOH)^{...} or (FeO)^{..}. The method also gives information concerning the formation of complexes by Fe^{...}. A. J. M.

Progressive decrease of current during electrolysis of acids and bases. P. Jolibois (Compt. rend., 1943, 217, 133-134).—When a strong acid or a strong base is electrolysed in a U-tube at const. p.d., the current progressively decreases until it is practically zero. This cannot be explained as due to polarisation, but an adequate explanation is given on the author's view of cataphoresis involving hydrated ions (A., 1944, I, 176, 178), according to which the acid becomes more conc. at the anode, whilst the cathode becomes surrounded with H_2O , the extent depending on time. In the case of a salt, e.g., K_2SO_4 , the current increases with time, as the electrolytes around the electrodes become H_2SO_4 and KOH, which conduct better than the original solution. A. J. M.

Anodic passification of copper in dilute sodium hydroxide solution. W. Feitknecht and H. W. Lenel (*Helv. Chim. Acta*, 1944, 27, 775– 789).—The c.d.-voltage and c.d.-time curves for Cu electrodes in 0.01—IN-NaOH show the usual course of anode processes leading to passification. The anodic films produced on the Cu have been examined by microscopic and X-ray methods. If the electrolyte is stirred during passage of the current a film of Cu₂O is first formed and this gradually passes into CuO. If this transition is completed a sudden rise in potential occurs at const c.d. If the electrolyte is not stirred a film of Cu(OH)₂ is formed over the Cu₂O. The thickness and structure of the surface film depend on the orientation of the crystallites. The possible anodic reactions are discussed.

J. W. S. **Polarographic examination of carbonyl compounds.** J. M. Lupton and C. C. Lynch (J. Amer. Chem. Soc., 1944, **66**, 697-700).— Reduction of aldehydes and ketones in acid N₂H₄ solutions has been carried out polarographically with Pr⁵CHO, COMe₂, COMe·CH₂Bu^a, and COMeBu^β from 0.0001 to 0.01M. Equations relating diffusion current and concn. are given. The precision is between 2 and 5%. W. R. A.

VIII.—REACTIONS.

Flammability limits in air [of] methyl chloride and its mixtures with dichlorodifluoromethane. K. S. Willson and W. O. Walker (Ind. Eng. Chem., 1944, 36, 466–468).—MeCl-air mixtures are flammable in the range 7.6—19.1% (v/v) of MeCl, but ignition does not occur in presence of <10% (v/v) of CCl₂F₂. MeCl-CCl₂F₂ mixtures containing >35.0% (w/w) of MeCl are non-flammable in air. The above vals. were obtained with a 15,000-v. spark, which gave the widest flammability range and is concluded to be the most reliable method. Igniting matches gave similar results, but low-voltage sparks gave ignition only within narrow limits, and ignition by flame was very variable. Ignition could not be obtained by red-hot wire or burning cigarette. M. H. M. A.

Influence of *n*-alkyl groups on the rate of a cyclisation reaction.— See A., 1944, II, 254.

Reaction of dibromides of mono-substituted ethylenes with potassium iodide. D. Pressman and W. G. Young (J. Amer. Chem. Soc., 1944, 66, 705-709).—Reaction rate coeffs. and heats and

entropy of reaction have been determined for the reaction between KI and CHRBr·CH₂Br (R = Pr, Ph, CH₂Ph, CH₂·OH, CO₂H, Br) in 99% McOH. Both Br atoms can react and do so with different rates and different heats of activation. Thus no significance may be attached to the effect of various substituents on the observed vals. W. R. A.

Relations between chemical activity and absorption in the ultraviolet of certain organic molecules. X. Velocity of hydrolysis of substituted amides of acetoacetic acid. XI. Velocity of replacement of chlorine atoms in the chloro-derivatives of the substituted amides of acetoacetic acid. R. K. Trivedi and B. N. Mankad (*J. Indian Chem. Soc.*, 1943, 20, 415-420, 421-423).—X. The relative rates of hydrolysis in acid and alkaline solutions of the anilide, o- and p-tolylamide, a- and β -naphthylamide, and m-4-xylylamide of CH₂Ac·CO₂H show a parallel effect of substitution on absorption spectrum and chemical reactivity; they indicate that reactivity is affected by the nature of the radicals attached to the •NH· group, and is enhanced by asymmetry of the mol.

XI. The velocity of replacement of Cl by H in the compounds referred to in Part VIII (A., 1944, I, 211) increases with the asymmetry of the mol., in the order anilide < m-4-xylylamide < a-naphthylamide. L. J. J.

Hydrolysis of trimethylethylene dibromide. Mechanism of ketone formation.—See A., 1944, II, 285.

Acetylenic ethers. IV. Hydration.-See A., 1944, II, 287.

Kinetics of polymerisation reactions. G. Gee and H. W. Melville (*Trans. Faraday Soc.*, 1944, 40, 240–251).—A general treatment of polymerisation kinetics is given for the extreme conditions where the half-life of the monomer is \gg and \ll the lifetime of chain growth, when the velocity coeffs. of propagation are independent of mol. size, and in the second case when they depend on mol. size. Size distributions are computed where possible. F. L. U.

Degradation of long-chain molecules. I. H. H. G. Jellinek (Trans. Faraday Soc., 1944, 40, 266—273).—The thermal degradation of polystyrene at $\sim 300^\circ$ in a vac. stops or slows down markedly when a certain chain length is reached, and the size distribution curve for the products is narrower than is predicted by the theory which assumes that each link is equally strong and equally accessible. The degradation of chains having equal nos. of weak links distributed at random is investigated theoretically, and the no. and wt. distribution functions, and the wt.-average chain lengths, are calc. In practice the condition that only weak links are ruptured will not usually be strictly fulfilled, and the required distribution functions must be obtained by combining the "weak link" theory with that dealing with chains having no weak links. F. L. U.

Study of the mechanism of polymerisation reactions by means of size distribution curves. E. F. G. Herington (*Trans. Faraday Soc.*, 1944, 40, 236–240).—The interpretation of size distribution curves is considered for polymerisations in which the mean life of active chain centres is very small compared with the half-life of the total reaction. If the degree of polymerisation is known and its extent small (>10% polymerised) information about the mechanism terminating the life of an active radical may be obtained from the form of the distribution curve. Three main types of curve are distinguished and discussed. Experimental complications often arise and the chief of these are indicated. F. L. U.

Nitration of cellulose. I.-See A., 1944, I, 174.

Induced oxidation of oxalic acid by dichromate with ferrous sulphate as inductor. C. R. Viswanadham and G. G. Rao (*Current Sci.*, 1943, 12, 327).—Oxalates interfere with the titration of FeSO₄ by dichromates. This is due to induction of the reaction between C_2O_4'' and Cr_2O_7'' by the rapid reaction of FeSO₄ with Cr_2O_7'' , FeSO₄ also induces the reaction between Cr_2O_7 and tartaric, citric, and malic acids, but not succinic acid. J. O'M-B.

Effect of dielectric constant and temperature on the catalysed decomposition of azodicarbonate ion. C. V. King and J. J. Josephs (J. Amer. Chem. Soc., 1944, 66, 767—771).—The rate of decomp. of the N₁(CO₂)₂" ion at five temp. from 15° to 35° in dil. aq. NaOH and in dil. aq. NaOH + dioxan (up to 60%) is determined. Molar H' catalysis consts. at zero ionic strength, calc. from rates, vary with ϵ of the medium, in satisfactory agreement with theoretical predictions. Temp. coeffs., energies and entropies of activation have been calc. and agree with those calc. by the Eyring " absolute rate " and collision rate theories. W. R. A.

Mechanism of peroxide-initiated styrene polymerisation. H. F. Pfann, D. J. Salley, and H. Mark (J. Amer. Chem. Soc., 1944, 66, 983-985).—The Br content in polymers obtained from liquid styrene and (p-C₈H₄Br·CO·O)₂ at various temp. has been determined gravimetrically and with the aid of Br^{*}. Vals. from the two methods agree and indicate between 1 and 3 Br atoms per chain. W. R. A.

Catalysis of the interaction between hydrogen sulphide and sulphur dioxide by silver sulphide. B. S. Rao (*Current Sci.*, 1943, 12, 323).— The reaction of H_2S and SO_2 is autocatalytic in presence of Ag owing to the formation of Ag_2S , the activity of which α the v.p. of H_2O in the system. The kinetics of the reaction can be examined in a glass apparatus if the v.p. is kept sufficiently low by means of an appropriate hygrostat. J. O'M-B.

Catalytic activity of silver sulphide. B. S. Rao and M. R. A. Rao (*Current Sci.*, 1943, 12, 323).—Ag₂S catalyses the decomp. of SO and its polymer, S_2O_2 . The reaction between H_2S and SO is catalysed in absence of H_2O (cf. preceding abstract). J. O'M-B.

Redistribution reactions in the halides of carbon, silicon, germanium, and tin. G. S. Forbes and H. H. Anderson (J. Amer. Chem. Soc., 1944, 66, 931-933).—With slightly moistened $AlCl_3$ as catalyst, mixtures of CCl_4 and CBr_4 , as well as CCl_3Br and CCl_2Br_2 , rearrange at 170° for 7 hr. until halogen atoms are distributed among the five members of the series according to the laws of probability. Corresponding rearrangements of Si chloro-bromides and -iodides without a catalyst are partial in 70 hr. at 140° but complete and rapid after passage through a tube at 600°. These random mixtures can be fully separated by fractional distillation at normal pressure without appreciable rearrangement. Distillation curves of the he tube product from GeCl₄ and GeBr₄ indicate the likely existence of GeCl₃Br (b.p. ~112°). Rapid redistribution takes place on redistillation of such a fraction. No irregularities are shown in the shape of the distillation curve of the Sn^{IV} chlorobromides near the b.p. calc. for the mixed compounds. The individual compounds could not be isolated, presumably because of redistribution during distillation, but some indication of redistribution was obtained. None of the phenomena observed was inconsistent with the hypothesis that all the chlorobromides of Ge and Sn^{IV} coexist in rearrangement decreases steadily from C to Sn. W. R. A.

Mutual effect of gas flow, diffusion, and chemical reaction in heterogeneous catalysis. C. Wagner (Z. physikal. Chem., 1943, A, 193, 1-15).—For the case of a reacting gas mixture flowing through a bed of compact, porous catalyst granules, differences in gas concn. between the interior and the exterior of the granules can be cale. from experimental data with the aid of the relations formulated by Damköhler, Thiele, and Zeldovitsch. Such differences are negligible in laboratory conditions, but are considerable in NH₃ synthesis, where diffusion into the catalyst grains is slight. With appreciable diffusion of N atoms, NH and NH₂ radicles, concn. differences may be negligible for granules of diameter $\gg 1$ cm.

L. J. J. Excess temperature in catalyst grains. G. Damköhler (Z. physikal. Chem., 1943, A, 193, 16–28).—The max. attainable excess temp. in a stationary catalyst granule is independent of the reaction velocity and the radius of the granule, and dependent only on the heat of reaction, the internal diffusion coeff., the internal thermal conductivity, and the exterior concn. of the reactants. Max. chemical utilisation of the interior of the granule is obtained when the interior excess temp. is a min. Vals. for max. excess temp. are calc. as 0.42°, 0.20°, 0.57°, 1.0°, and 3.0° for SO₂ + $\frac{1}{2}O_3$ at 1 atm. on V₂O₅ with ceramic support, N₂ + 3H₂ at 200 atm. on ZnO, and 4CO + 9H₂ \rightarrow C₄H₁₀ + 4H₂O at 1 atm. on Fe-Co-ThO₂, at 500°, 500°, 500°, 400°, and 304°, respectively. L. J. J.

Catalytic formation of methane from carbon monoxide and hydrogen. Nickel and nickel-alumina catalysts prepared from the hydroxide using potassium, sodium, and ammonium hydroxide as precipitants. K. M. Chakravarty and J. M. Sarker (*Current Sci.*, 1944, 13, 127).—Addition of $\Rightarrow 0.16\%$ of Al_2O_3 to a Ni catalyst increased the rate of the reaction $2CO + 2H_2 = CH_4 + CO_2$ relatively to that of $CO + H_2O = CO_2 + H_2$ in moist $H_2: CO$ (1:1) mixtures. Addition of traces of K_2CO_3 to catalysts promoted with Al_2O_3 preferentially accelerated the latter reaction. L. J. J.

Oxidation processes. XVII. Autoxidation of ascorbic acid in the presence of copper. A. Weissberger and J. E. Lu Valle (J. Amer. Chem. Soc., 1944, 66, 700-705).—The autoxidation rates of *l*-ascorbic acid (I) in presence of Cu throughout the pH range 2.59 to 9.31 is in accord with the assumption that 1 mol. of dehydro-ascorbic acid and one of H_2O_2 are formed from one of (I) and one of O_2 . The rate $(2 \times 10^{-5} \text{ g.-mol. per l.})$ is not ∞ (I) conc., but ∞ $[O_2]$; it ∞ increase in [Cu] at higher concns. of Cu, but at lower concns. it increases faster than [Cu]. The dependence of the rate on pH is caused by complex formation of some of the buffers with the Cu. Only the univalent ion of (I) acts as substrate of the Cu catalysis. A non-chain mechanism for the catalytic reaction is discussed. W. R. A.

Oscillographic polarography. J. Heyrovský and J. Forejt (Z. physikal. Chem., 1943, A. 193, 77-96).—Electrolytic polarisation phenomena can be very clearly demonstrated by means of a polarisable Hg electrode with an alternating e.m.f. and electron-beam oscillograph. Dropping and streaming Hg electrodes were used, the latter consisting of a jet of Hg forced under 1-2 atm. through a 0·1-mm. orifice obliquely through the solution examined. The action of depolarisers at concn. $< 10^{-4}$ N. can be studied by means of the first derivative of the potential-time curve, obtained oscillographically. Most metals are deposited at approx. the same rate,

and the more slowly the higher is the a.c. frequency. No deposition is observed at frequencies >1600 Hertz. The anodic reaction of Hg" with Cl' and CN' vanishes at 400 Hertz. Zn is deposited most rapidly from NH₃ solutions, less rapidly from acid and least from alkaline solutions. Cd is relatively slowly deposited from KCN solutions. Corresponding results are obtained by the use of amalgamated Hg dropping electrodes. L. J. J.

Mechanism of emission of ultra-violet radiation by anodic polarisation. R. Audubert (Compt. rend., 1943, 216, 880-882; cf. A., 1933, 764).—Ultra-violet light is emitted when an anode of Al, Ta, Mg, or Si is polarised. It is possible that this is due to reactions between activated and non-activated OH'. It is possible to calculate the ν of emission if the level of activation of the OH' is known. Reducing agents in the anode liquid suppress or weaken the luminosity. Possible reactions considered are: $OH + OH^* \rightarrow$ $H_2O_2 + h\nu_1$; $OH + OH^* \rightarrow H_2O + \frac{1}{2}O_2 + h\nu_2$; $OH^* + OH^* \rightarrow$ $H_2O_2 + h\nu_1$; $OH^* + OH^* \rightarrow H_2O_2 + \frac{1}{2}O_2 + h\nu_4$. The vals. of λ corresponding to the energy evolved in these reactions are 2187, 1895, 1458, and 1304 A., respectively. In the actual spectrum, investigated by means of a Cul counter, bands occur at 1950, 2190, 2390, and 2530 A., independent of the anodic potential, the nature of the electrode and the electrolyte. Two of these bands correspond with theory. It is possible that the third and fourth of the above reactions give out part of their energy thermally, the photon liberated being due to the deactivation of two OH*. This would give a band at 2370 A., which is in the neighbourhood of another of the observed bands. A. J. M.

Interpretation of photolysis of alkali azides in aqueous solution. M. Bonnemay (Compt. rend., 1943, 216, 882-884).—Possible reactions in the photolysis of azides in aq. solution are: $N_3' + h_{\nu} =$ $(N_3')^\circ$; $H_2O + (N_3')^\circ + h_{\nu} = N_2^* + NH + OH'$; $H_2O + N_2^* +$ $N_3' = N_2^* + N_2 + NH + OH'$; $H_2O + N_2^* + (N_3')^\circ = N_2^* +$ $N_2 + NH + OH'$; $(N_3')^\circ = N_3'$; $N_3^* = N_2 + h_{\nu_1}$. $(N_3')^\circ$ represents a form of N_3' which is directly decomposable and of which the life is ~5 min. The radicals (NH) react between themselves and with H_2O to give secondary products. Equations for the kinetics of these reactions are obtained which give results agreeing with experiment. A. J. M.

Photosensitised reactions of ethylene. D. J. Le Roy (Canad. Chemt., 1944, 28, 430–431, 451).—A review. The technique of photosensitisation is described, and the variation in results obtained by using Xe, Cd, Hg, Zn, and Na as photosensitisers is outlined. The Hg-photosensitised polymerisation of C_2H_4 (A., 1942, I, 151) is discussed. The Cd-photosensitised reaction produces little C_2H_2 and H_2 (Steacie et al., *ibid.*, 372). With Zn (${}^{1}P_1$) atoms the primary process is almost entirely Zn (${}^{1}P_1$) + $C_2H_4 = C_2H_3 + H + Zn$ (${}^{1}S_0$) (Habeeb et al., *ibid.*, 304). A. J. M.

Application of probability considerations to the mechanism of the photochemical polymerisation of acetylene. B. L. Dunicz (J. Chem. Physics, 1944, 12, 204).—Erratum (cf. A., 1944, I, 132).

Photochemical studies. XXXVII. Tests of mechanism for the photochemical decomposition of acetone. J. J. Howland, jun., and W. A. Noyes, jun. (J. Amer. Chem. Soc., 1944, **66**, 974–977).—The photochemical decomp. of COMe₂ has been investigated at 27° using $\lambda\lambda$ 2500—2700 and 3130 A., and various pressures. The quantum yield of COMe₂ decomposed diminishes with increasing intensity at all $\lambda\lambda$. Decrease in the size of the reaction vessel leads to an increase in C₂H₆/CO ratio; this ratio is diminished with increasing pressure at high intensity. These data are discussed in the light of the conflicting mechanisms proposed by Herr and Noyes (A., 1940, I, 417) and Spence and Wild (A., 1941, I, 480) and favour the former. W. R. A.

IX.—PREPARATION OF INORGANIC SUBSTANCES.

Non-stoicheiometric equations. O. F. Steinbach (J. Chem. Educ., 1944, 21, 66, 69).—Examples of chemical equations that can be made to balance algebraically by using different sets of coeffs. with only one set representing the stoicheiometric equation are given. The correct stoicheiometric coeffs. are obtained when the equations are balanced by either the valency-change or the ion-electron methods. L. S. T.

Existence of lithium hydrogen carbonate. (Mllc.) L. Lagarde (Compt. rend., 1943, 216, 810-812).—The solubility of Li_2CO_3 in H_2CO_3 has been studied for various pressures of CO_2 (5-800 mm.). Combining the law of mass action with Henry's law reasonably good vals. of the const. are obtained, indicating the existence of LiHCO₃ in solution. A. J. M.

Transformations of vitreous sodium metaphosphate. A. Boullé (*Compt. rend.*, 1943, 216, 890-892).—Na and K metaphosphates behave very differently when heated. In the case of Na, the insol. forms (referred to as B and D) and Graham's salt (metallic vitreous) always afford a sol. trimetaphosphate. When this is fused at 640° it gives a liquid metaphosphate formerly described (A., 1935, 571, 591, 944). In the case of K salts, the sol. forms (trimeta- and

tetrameta-) and the pptd. amorphous form are always converted into an insol. salt when heated. A. J. M.

Isotope enrichment by diffusion of copper into silver sulphide. A. Klemm (Z. physikal. Chem., 1943, A, 193, 29–39).—Isotope separation coeffs. are calc. for the general case of diffusion of an element across a plane boundary. A 5.5% change in the isotopic distribution ratio of Cu has been found after diffusion into Ag_2S at 450°. L. J. J.

Complex compounds of biguanide with tervalent metals. XI. Silver (Ag¹¹¹) ethylenedibiguanide hydroxide and its salts. P. Råy and K. Chakravarty (J. Indian Chem. Soc., 1944, 21, 47—50).—The composition of a complex silver ethylenedibiguanide hydroxide and its salts, in which the quadricovalent Ag shows a primary valency of 3, is $[Ag^{111} En(BigH^+)_2]X_3$, where $X = \frac{1}{2}SO_4$, NO₃, ClO₄, or OH and $En(BigH)_2 = 1$ mol. of ethylenedibiguanide, $C_8H_{16}N_{10}$. The salts are quite stable at ordinary temp. and the nitrate can be cryst. from warm dil. HNO₃. The compounds liberate 2 equive. of I for every atom of Ag from acidified KI solution. The new complex is diamagnetic. Ag¹¹¹ thus resembles Au¹¹¹ in forming quadricovalent planar complexes of the penetration class. F. R. S.

Calcium oxalates. (Dehydration curves, X-ray and infra-red studies.) J. Lecomte, (Mlle.) T. Pobeguin, and J. Wyart (Compt. rend., 1943, 216, 808—810).—The dehydration of four hydrates of CaC₂O₄ has been investigated. The hydrates were the monohydrate (I), and the three trihydrates, (II) (obtained by evaporation of solution in HCl), (III) (from aq. solution), and (IV) (the trihydrate of Jakob *et al.*). At ordinary temp. (I) and (II) do not lose H₂O over P₂O₅; (III) rapidly loses 4—5% in wt., but regains this on exposure to air; (IV) gradually loses wt. up to 18%. Loss of H₂O at higher temp. has also been studied. The distances between lattice planes in the anhyd. salt and the four hydrates, and a qual. estimate of the intensity of the spots in the Debye-Scherrer diagram, are given. The position and intensity of the infra-red bands are also given. The methods show clearly that the five substances considered are quite distinct. Part of the H₂O of (III) is less strongly held than the rest. Loss or gain of this H₂O does not affect the lattice. A. J. M.

Crystallographic structure of precipitated mixtures of calcium and strontium carbonates. Their fractional decomposition by heat. M. Guichard and J. Wyart (*Compt. rend.*, 1943, **216**, 844—846).— The X-ray structures of CaCO₃ and SrCO₃ are different when the substances are pptd. pure, and when they are pptd. together from mixed solutions of CaCl₂ and SrCl₂. In the latter case the diagram obtained depends also on the composition of the mixed solutions. It is possible to obtain a compound CaSr(CO₃)₂, which X-ray analysis shows to be orthorhombic. If a mixture of CaCO₃ and SrCO₂ prepared from the single substances is heated to 855° , the curve of loss of wt. with time is made up of two distinct parts. SrCO₃ begins to decompose at this temp. slowly, and only after all the CaCO₃ has been decomposed. When the ppt. obtained from the mixed solutions is heated, the curve of loss of wt. against time shows no discontinuity. There is, however, a decrease in velocity when ~85% of the CaCO₃ has been decomposed, but the substance decomposes as a whole. X-Ray diagrams of the substance obtained from a mixed solution which would give $3CaCO_3.2SrCO_3$ show the product to be a mixture of rhombohedral CaCO₃ and orthorhombic SrCa(CO₃)₂. A. J. M.

Crystalline magnesium and ferrous hydroxides. L. M. Clark, A. G. M. Hedley, and J. G. Robinson (*J.S.C.I.*, 1944, **63**, 208-210). --Cryst. Mg(OH)₂ can be prepared continuously by slowly mixing sufficiently dil. solutions of Mg^{**} and OH' in presence of brucite seed. Fe(OH)₂ can be similarly made, in the absence of O₂, from Fe^{**} and OH', using initially seed crystals of the isomorphous Mg(OH)₂. These cryst. products settle and filter well. The X-ray pattern of cryst. Fe(OH)₂ has been obtained, and from it the unit cell dimensions are deduced as a 3·24, c 4.47 A.

Basic magnesium nitrates. (Mme.) L. Walter-Lévy (Compt. rend., 1943, 216, 846—847).—The composition of the ppt. obtained by adding an alkali carbonate or hydroxide to fairly conc. solutions (4--5M.) of Mg(NO₃)₂ is const. no matter what precipitant is used, or what quantity, and corresponds to Mg(NO₃)₂,4Mg(OH)₂. The X-ray diagram of this compound is different from that of the nitrato-carbonate, Mg(NO₃)₂,2MgCO₃,8H₂O, and from that of brucite. When more dil. solutions are used, the stable solid phase is Mg(OH)₂. A. J. M.

Crystallised basic zinc chromates. O. F. Tarr, M. Darrin, and L. G. Tubbs (*J. Amer. Chem. Soc.*, 1944, **66**, 929–930).—Basic *Na*, *K*, and *NH*₄ Zn chromates were prepared by the reaction between an aq. suspension of ZnO and a solution of the appropriate tetrachromate ($K_2Cr_4O_{13}$). They were well-defined crystals having the composition $M_2O_4ZnO_4CrO_3, 3H_2O$. Corresponding alkaline-earth compounds were not obtained by this method. W. R. A.

"Sainte-Claire Deville hot-cold tube" and some of its applications. R. C. Young (J, Chem. Educ., 1943, 20, 378, 380).— The use of the hot-cold tube for the prep. of TiCl₃, ZrBr₃, Si₁₀Cl₂₂, TaBr₃, and TiBr₃ is described. L. S. T.

pH corresponding to the threshold of precipitation of rare-earth elements. (Mme.) M. Trombe (Compt. rend., 1943, 216, 888-890).-The pH at which pptn. of rare-earth elements first occurs has been The pH at which ppth, of rare-earth elements first occurs has been determined by slowly dissolving NH₃ in a solution of the nitrate of the element concerned. At first a colloid is obtained. At the moment of coagulation the pH falls suddenly, and then increases very slowly as the concn. of metal ions decreases. The pH for the threshold of ppth, of the Ce elements are > those obtained by Britton (A., 1925, ii, 1203) for the same concn. The change of threshold pH with concn. (Δ pH) varies for the different elements. In the range of concn. considered (0.5-0.005M.) Δ pH is La 1.44, Pr 0.85. Nd 0.65. Sa 0.39. Gd 0.80. Dv 0.75. Yb 1.25. Y 2.14. Pr 0.85, Nd 0.65, Sa 0.39, Gd 0.80, Dy 0.75, Yb 1.25, Y 2.14.

A. J. M.

A. J. M. Chloro(iso)cyanates of silicon, including rearrangements at high temperatures. H. H. Anderson (J. Amer. Chem. Soc., 1944, 66, 934—935).—The chloro(iso)cyanates SiCl₃(NCO), SiCl₂(NCO)₂, and SiCl(NCO)₃, b.p. 86.8°, 117.8°, 152.0°, have been prepared as colour-less liquids by (a) interaction of SiCl₄ and Si(NCO)₄ at 600°, (b) interaction of SiCl₄ and Si(NCO)₄ in a sealed tube at 135° for 70 hr., (c) gradual addition of AgNCO to a large excess of SiCl₄ in CS₂-EtBr (1:2). Vals of m.p., ρ^{25} n²⁰, and mol. vol. are given and com-pared with those of SiCl₄ and Si(NCO)₄. SiCl(NCO)₃ cannot be prepared by (c). Rearrangements at 600° without a catalyst dis-play random distribution. W. R. A.

Enrichment of ¹⁵N by chemical exchange. K. Clusius and E. Becker (Z. physikal. Chem., 1943, A. 193, 64-76).—Enrichment of ¹⁵N to 6.0% has been attained by means of the equilibrium ¹⁶NH₄ (liq.) + ¹⁴NH₃ (gas) \rightleftharpoons ¹⁴NH₄ (liq.) + ¹⁵NH₈ (gas) in two stages. 60% NH₄NO₃ solution is saturated with NH₃ at 90 mm. pressure in two packed towers in series, with gas and liquid flowing in the same direction. The NH₄NO₃ is continuously decomposed with NaCU and the NU pressure in NaOH and the NH_a recirculated. L. I. I.

Reactions of hyponitrites. I. Action of charcoal on sodium nitrite etc. T. M. Oza (J. Indian Chem. Soc., 1944, 21, 71-78).----When charcoal is heated with $NaNO_2$, $Na_2N_2O_2$ is produced to an appreciable extent as an intermediate product, although the quantity decreases at higher temp. The reaction consists of two concurrent reactions, the first being the thermal decomp. of NaNO₂, accelerated by C: $4NaNO_2 + 3C = 2Na_2CO_3 + CO_2 + 2N_2$. The second is the reduction of NaNO₂ to $Na_2N_2O_2$, and production of N₂O from the latter: $2NaNO_2 + C = Na_2N_2O_2 + CO_2$; $Na_2N_2O_2 + CO_2 = Na_2CO_3 + N_3O$. The last reaction occurs even at room temp. $Na_2N_2O_2$ will remove traces of CO_2 from air, and this is one reason why it is difficult to keep. The thermal decomp. of $Na_2N_2O_2$ has also been investigated. The decomp. proceeds readily at $334-336^\circ$. The primary reaction appears to be $3Na_2N_2O_2 = 2Na_2O + 2N_2 + 2NaNO_2$, but this is followed by the autoxidation of the NaNO₂: $5NaNO_2 = Na_2O + 3NaNO_3 + N_2$. A. J. M. appreciable extent as an intermediate product, although the quan-

Complex between sulphuric and nitric annyatures which dissolutes liberating nitric acid. M. Dodé (Compt. rend., 1943, 217, 153– 155).—When SO₃ is added to 100% HNO₃ at -10° , a cryst. com-pound, SSO₃,2N₂O₅,2H₂O, is formed, which when warmed dis-sociates into HNO₃ and not N₂O₅, although SO₃ is present. The reaction is $4(5SO_3,2N_2O_5,2H_2O) \rightarrow 6HNO_3 + 5(4SO_3,N_2O_5,H_2O)$. It is reversible. A. J. M. Complex between sulphuric and nitric anhydrides which dissociates

Effect of pH on the composition and physical appearance of potassium molybdates. H. Guiter (*Compt. rend.*, 1943, 216, 796—798; cf. *ibid.*, 1943, 216, 587).—The variation of p in the formula

798; cf. *ibid.*, 1943, **216**, 587).—The variation of p in the formula MoO₃, pK₂O with pH of the solution has been investigated. In presence of HCl, MoO₃, H₂O ppts. from N-K₂MoO₄ at pH <2.6. At pH -0.7 to 0.7 KCl appeared after 1—3 months. For negative vals. of pH a very viscous gum was formed after ~4 months. When dried this gave MoO₃. At pH 0.7—7, the *compound* 7MoO₃, 3K₂O,22H₂O (I) was obtained after 3 weeks, and KCl crystallised after 2 months. In presence of AcOH, (I) appeared in solutions of pH 2.8—7 after 3 weeks, and at pH 6.3—11.6 a white cryst. *compound*, 4MoO₃, 3K₂O,2H₂O, was formed after 2 months. In solutions of pH >7 the normal anhyd. K₂MoO₄ was formed. The largest crystals were obtained in a solution of pH 13.5. This behaviour is different from that of Na molybdates, with which This behaviour is different from that of Na molybdates, with which the K salts are not isomorphous. A. J. M.

The K saits are not isomorphous. A. J. M. Double molybdates and tungstates of alkali metals with lanthanum or bismuth. L. G. Sillen and H. Sundvall (*Arkiv Kemi, Min., Geol.,* 1943, **17**, **A**, No. 10, 18 pp.).—Two types of double salts with the general formula $AM(XO_4)_2$ (isomorphous with scheelite) and $A_sM(XO_4)_4$ (closely related to scheelite) have been prepared. The compounds with their lattice consts. (*a* and *c* respectively) are LiLa(MOO_4)_2 5·307, 11·670; NaLa(MOO_4)_2 5.328, 11·699; KLa(MOO_4)_2 5·420, 12·114; LiLa(WO_4)_2 5·335, 11·629; NaLa(WO(4)_2 5·345, 11·632; KLa(WO_4)_2 5·267, 11·552; KBi(MOO_4)_2 5·380, 11·916; Na_sLa(WO_4)_4 11·600, 11·546; Na_sBi(MOO_4)_4 11·444, 11·520; Na_sBi(WO)_4)_4 11·520, 11·402 A. C. R. H.

Extraction of uranium from Canadian pitchblende. A. Kuebel (J. Chem. Educ., 1944, 21, 148-149).—The laboratory procedure

described involves removal of U as crude sulphate from pitchblende concentrate and the purification of the crude sulphate. L. S. T.

Formation of iodous acid by the action of iodine on silver nitrate. (Mllc.) M. L. Josien (Compt. rend., 1943, 216, 842-844; cf. A., 1936, 438).—Aq. AgNO₃ is added to a solution of I in KI in sufficient quantity to remove all free I. When equilibrium has been established, the liquid is filtered and three separate portions are re-spectively titrated with $A_{S_2}O_3$ and with $Na_2S_2O_3$, and completely converted into HIO₃ and the oxidising power determined. Results indicate that HIO₂ exists together with HIO₃ and HOI in the product of the action of I on AgNO₃. A. J. M.

Action of hydrogen sulphide on permanganates. H. Potassium, ammonium, and barium permanganates. S. Mohammad and S. N. Bedi (J. Indian Chem. Soc., 1944, 21, 55-60; cf. A., 1942, I, 70).— When aq. H₂S is added to 1% aq. KMnO₄ until the colour just disappears, a neutral solution and a dark brown ppt. are obtained. The former contains 65% of the K as $K_2S_2O_3$, $K_2S_2O_4$, and K_3SO_4 . Further addition of H₂S after the decolorisation stage makes the solution alkaline owing to hydrolysis of permanganite. Excess of Further addition of H_2S after the decolorisation stage makes the solution alkaline owing to hydrolysis of permanganite. Excess of H_2S produces K polysulphides, and converts the dark brown ppt. into MnS. Similar results are obtained for the solutions produced with NH_4MnO_4 and $Ba(MnO_4)_2$. In the ppt. the ratio $K_2O/MnO_2 = 1/2$, but the ratios K_2O/MnO_2 . In the ppt. the ratio $K_2O/MnO_2 = 1/2$, but the ratios K_2O/MnO_2 , prepared as a dark brown ppt. by adding 2.5 c.c. of a 10% solution of glycerol to 50 c.c. of 1% KMnO₄, was also studied. The same products were obtained as with KMnO₄, but K_2SO_4 was absent from the solution before the polysulphide stage was reached. Similar results were obtained by adding H₂S stage was reached. Similar results were obtained by adding H_2S to BaO,2MnO₂, prepared by adding H_2O_2 to a 1% solution of Ba(MnO₄)₂ until just decolorised. In the action of H_2S on NH₄MnO₄, the ratio of $(NH_4)_2O/MnO_2$ in the ppt. is 1/1 instead of 1/2 with the other permanganates. A. J. M.

Influence of the atmospheric factors of production on the chemical activity and the grain distribution of powders. J. A. Hedvall and A. Lundberg (*Arkiv Kemi, Min., Geol.,* 1943, 17, A, No. 12, 11 pp.).— Previously published work on the effect of the gas pressure used in the prep. of powders on the chemical properties of the powders is reviewed, and new data on the properties of Fe_2O_3 and CaO prepared in vac. and under normal air pressure are presented. The vac.-prepared oxides give a smaller proportion of particles of grain size $0 - \sim 15 \mu$. and a larger proportion of particles of size $> \sim 15 \mu$. than do oxides prepared under ordinary pressure. The powders with the larger proportion of small particles are more reactive towards solvents than those with a smaller proportion. This difference in reactivity is not wholly accounted for by differences in surface area. C. R. H.

Reductions with nickel-aluminium alloy and aqueous alkali .-- See A., 1944, II, 258.

XI.—GEOCHEMISTRY.

Determination of the helium content of terrestrial materials. Goodman and R. D. Evans (*Rev. Sci. Instr.*, 1944, 15, 123–128).– Results obtained with 133 rocks of representative types are sum-marised; the He content ranges from 0.25×10^{-5} to 65×10^{-5} with modal and median vals. of 1.8×10^{-5} c.c. of He per g. There appears to be no correlation between He content and rock or mineral type, except for minerals in which U and Th are >0.1% (cf. C., 1944, Part 4).

Standard thermal dehydration curves of minerals. P. G. Nutting (U.S. Geol. Surv. Prof. Paper 197-E; Build. Sci. Abs., 1944, 17, No. 226) .- From several hundred curves obtained over a period of 15 years, 73 typical curves are chosen and reproduced in 9 main groups. Each mineral is described and similarities and differences groups. within the groups of curves are noted. J. A. S.

Occurrence of chloritoid in the Tumkur district, Mysore State. C. S. Pichamuthu (*Current Sci.*, 1943, 12, 332).—The Chitaldrug Dharwar schist belt in the Tumkur district contains chloritoid (I), bharwar schist beit in the rumkur district contains controlled (1), which occurs in disc-like, lenticular shape. It has almost perfect basal cleavage; imperfect prismatic cleavages intersect at angles of 120° and there is a parting parallel to 010. Crystalloblasts of (I) occur in the rock without relation to the direction of schistosity. (I) is poeciloblastic and contains much quartz and ilmenite. It is The product of the second sec J. O'M-B.

Unusual features in ejected blocks at Kilauea volcano. G. A. Macdonald (Amer. J. Sci., 1944, 242, 322-326).—Pictitic basalts near the feeding conduit of this volcano appear to have been reconstituted in solid state as a result of remaining at a high temp. for a long period, during which the original pigeonite broke down to give hypersthene and augite. A reddened picritic basalt shows deposition of Fe ore thoughout the olivine phenocrysts. L. S. T.



INDEX OF AUTHORS' NAMES, A I.

OCTOBER, 1944.

ABADIE, P., 212. Acree, S. F., 225. Aiya, S. V. C., 210. Aleshnick, J. J., 226. Alfrey, T., 224. Amdur, I., 222. Anders, S., 211. Anderson, J., 223. Anderson, H. H., 228, 231. Antonov-Romanovski, V. V., 212 Audubert, R., 229. Auduck, F. C., 222, 219.

Auluck, F. C., 222, 219. BAI, K. S., 211, 218. Barchewitz, P., 211. Bates, R. G., 226. Beck, P. W., 223. Beck, P. W., 223. Beck, F. W., 223. Beck, F. W., 223. Beck, F. W., 223. Beck, F. W., 223. Beck, T. S., 232. Bert, H. E., 214. Berthelot, A., 209, 210. Berthelot, A., 209, 210. Borther, D., 226. Bhagwat, W. V., 214, 219. Biertuempfel, R. E., 220. Bonnemay, M., 229. Boullé, A., 229. Boulard, A., 224. Brechovskich, L. M., 315. Bricard, J., 209. Brown, G. M., 214. Brown, H. C., 224. Brown, H. C., 224. Brown, H. C., 224. Brown, H. C., 224. Brown, M. A., 216.

CAUCHOIS, Y., 209. Chakravarty, K., 230. Chakravarty, K. M., 228. Chevallier, R., 219. Christian, S. M., 220. Clark, L. M., 230. Cleveland, F. F., 213. Clusius, K., 231. Courty, C., 219.

DAMKÖHLER, G., 228. Dartin, M., 230. Davidov, B., 209. Davidov, B., 209. Davidson, A. W., 225. Day, R. A., 214. Dayal, B., 217, 218.

de Mallemann, R., 223. de Mallemann, R., 223. Deo, P. G., 209. Déribéré, M., 223. Dobrowsky, A., 220. Dodé, M., 231. Donohue, J., 217. Doty, P. M., 213. Du Brow, P. L., 221. Duclaux, J. P. E., 219. Dunicz, B. L., 229.

EMERSON, E. I., 209. Evans, R. D., 232.

FEITKNECHT, W., 221, 226. Felder, E., 211. Forbes, G. S., 228. Foreit, J., 228. Frenkel, J., 214. Frith, E. M., 219. Fylking, K. E., 216.

GEE, G., 227. Ghosh, S. P., 219. Girard, P., 212. Goldfinger, G., 224. Goodman, C., 232. Gow, M. M., 219. Grivet, T., 210. Gropp, A. H., 221. Guichard, M., 230. Guiter, H., 231.

HALLER, R., 222. Harker, D., 217. Harkins, W. D., 222. Harkins, W. D., 222. Harkins, W. D., 222. Harkins, W. D., 222. Hedley, A. G. M., 230. Hedley, A. G. M., 230. Hedrall, J. A., 232. Herington, E. F. G., 227. Heyrovsky, J., 228. Hill, T. L., 213. Hoorr, C. W., 221. Howland, J. J., jun., 229. Hsüch, C. F., 211.

JAFFRAY, J., 218. Jellinek, H. H. G., 227. Jetter, L. K., 221. Jolibois, P., 226. Jones, G., 220. Jones, M. M., 222.

Josephs, J. J., 227. Joshi, S. S., 212. Josien, M. L., 232. Joyner, L. G., 220. Jura, G., 222.

KASTLER, A., 209. Kerst, D. W., 209. King, C. V., 224, 227. Kingsbury, A. W., 220. Kirkwood, J. G., 220. Klemm, A., 230. Kline, C. H., jun., 213. Krishnan, R. S., 213, 215. Kuebel, A., 231.

LACOMBE, P., 220. Lagarde, L., 220. Lagarde, L., 220. Laval, J., 213. Lecomte, J., 230. Lecoty, W. G., 213. Lelong, G., 213. Lenel, H. W., 226. Le Roy, D. J., 220. Liesegang, R. E., 223. Lochet, R., 213. Lochet, R., 213. Loiseleur, J., 224. Long, L., 223. Lundberg, A., 232. Lundberg, A., 234. Lundberg, A., 234. Lundberg, A., 234. Lundberg, A., 235. Lundberg, A., 236. Lundberg, A., 237. Lundberg, A., 238. Lundberg, A., 348. Lund

MA, S. T., 211. McCrosky, C. R., 225. Macdonald, G. A., 232. Mankad, B. N., 211, 227. Markad, B. N., 211, 227. Markad, B. N., 211, 227. Markelly, J., 210. Mathieu, J. P., 213. Mathieu, S., 219. Mathieu, S., 219. Mathieu, S., 219. Mathieu, F., 221. Mehl, R. F., 221. Mehl, R. F., 221. Moghe, V. A., 214, 219. Moghammad, S., 233. Murray, M. J., 213.

NAGGIAR, V., 214.

Naik, K. G., 211. Neurath, H., 224. Nikitine, S., 218. Noyes, W. A., jun., 229. Nutting, P. G., 232. Nylander, A. L., 216.

OBREIMOV, I. V., 212. Oster, G., 220. Overman, T., 211. Owen, B. B., 223. Oza, T. M., 231.

PANT, D. D., 217. Pauli, W., 223. Pearlman, H., 222. Pellini, W. S., 221. Pellini, W. S., 221. Piann, H. F., 227. Pichamuthu, C. S., 232. Pitzer, K. S., 213. Pobeguin, T., 230. Price, D., 220. Price, D., 220. Purushotham, A., 212. Putnam, F. W., 224.

QUAYLE, O. R., 214.

QUAYLE, O. K., 214. RA1, R. N., 219, 222. Ralston, A. W., 221. Ramachandran, G. N., 215. Raman, C. V., 216, 218. Ramasesban, S., 216. Rao, B. S., 227, 228. Rao, G. G., 227. Rao, K. R., 209. Rao, M. R. A., 228. Rao, S. R., 217. Ray, P., 219, 230. Reddlich, O., 225. Rendall, G. R., 211, 218. Rhines, F. N., 221. Ricc, O. K., 214. Robinson, J. G., 230. Russer, E., 223. Saksersa, B. D. 213.

SAKSENA, B. D., 213. Salley, D. J., 227. Samuel, R., 214. Sarker, J. M., 228. Sarmousakis, J. N., 224.

Schabaldas, C. G., 212. Scheub, W. H., 225. Schutz, P. W., 225. Schwarzenback, A., 211. Schwarzenback, A., 211. Schwarzenback, A., 211. Sero, I., 212. Shomate, C. H., 219, 225. Silden, L. G., 216, 231. Sisler, H. H., 225. Smart, K. O., 214. Smiley, S. H., 225. Sollner, K., 223. Stahl, S., 216. Stahl, W., 221. Stephenson, C. C., 219. Stephenson, C. C., 219. Stoenner, R., 225. Stokes, A. R., 215. Straumanis, M., 221. Sundvall, H., 231.

TARR, O. F., 230. Taylor, M. D., 224. Tisclius, A., 222. Toshniwal, P. M., 214, 219. Trivedi, R. K., 211, 227. Trombe, M., 231. Tsien, S. T., 210. Tubbs, L. G., 230. Tuckett, R. F., 219. Turkevich, J., 213.

VAN RYSSELBERGHE, P., 221. Vavilov, S. I., 212. Vincent, D., 212. Viswanadham, C. R., 227.

WAGNER, C., 228. Walker, W. O., 226. Walter-Lévy, L., 230. Weissberger, A., 228. Westgren, A., 216. Willson, K. S., 220. Wilson, A. J. C., 215. Wyart, J., 230.

Young, D. W., 220. Young, F. E., 225, 226. Young, R. C., 230. Young, W. G., 226.

ZIMM. B. H., 213.

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