

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

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

APRIL, 1941.

I.—SUB-ATOMICS.

Paschen-Back effect. VII. Configuration interaction. J. B. Green (*Physical Rev.*, 1941, [ii], 59, 69—71; cf. A., 1939, I, 501).—The spectrum of Kr exemplifies well the effect of configuration interaction. The levels $3s_2$ and $4d_2$, belonging to configurations of the same parity, are $<1 \text{ cm.}^{-1}$ apart, and the Zeeman patterns of lines arising from them show large perturbations as regards both positions and relative intensities of the components. A semi-empirical theory leading to good agreement with experiment is discussed. N. M. B.

Zeeman effect of xenon. J. B. Green, E. H. Hurlburt, and D. W. Bowman (*Physical Rev.*, 1941, [ii], 59, 72—74).—Full Zeeman data for $\sim 125 \text{ Xe I}$ lines are tabulated. The g sum rule is violated by both of the completely known configurations, and in some cases may be accounted for by configuration interaction. N. M. B.

Photoconductivity of a natural willemite crystal. R. C. Herman and R. Hofstadter (*Physical Rev.*, 1941, [ii], 59, 79—84; cf. A., 1939, I, 60; 1940, I, 311).—Data for the dependence of the photoconductivity on the λ of the exciting light, temp., and time are plotted and discussed. The ultraviolet absorption spectrum of the crystal has been obtained. N. M. B.

Work function and temperature. S. Seely (*Physical Rev.*, 1941, [ii], 59, 75—78).—The change in height of the potential energy barrier at the surface of a metal with the expansion of the metal on heating is investigated, and the change of the normal max. energy of an electron in a metal is calc. as a function of temp. of the metal. Results show that the work function is a linear function of temp., and, with the thermionic emission equation, show that the thermionic emission const. is characteristic of the metal, and is no longer the same for all pure metals. Calc. consts. for C, Ca, Mo, Ni, Pt, and W show fair agreement with experiment. N. M. B.

Stationary electric and magnetic fields in beams of light. F. Ehrenhaft (*Nature*, 1941, 147, 25).—Experimental results show that every wave of light possesses a stationary field intensity in its direction of propagation, and also a stationary magnetic field. There is thus a p.d. between two points on the ray of light which has magnetising effects. L. S. T.

Abundance ratio $^{61}\text{Ni} : ^{64}\text{Ni}$. H. A. Straus (*Physical Rev.*, 1941, [ii], 59, 102—103).—In view of discordant available data, a new double-focussing mass spectrograph was used to separate the ions. The ratio obtained is 1.3. N. M. B.

Isotopic weights of nickel isotopes by the doublet method. T. Okuda, K. Ogata, H. Kuroda, S. Shima, and S. Shindo (*Physical Rev.*, 1941, [ii], 59, 104).—From mass differences obtained from doublet photographs, using a discharge through the vapour mixture $\text{Ni}(\text{CO})_4-n\text{C}_2\text{H}_4$, the following isotopic wts. and packing fractions, respectively, were obtained: ^{58}Ni $57.95967 \pm 4.1 \times 10^{-4}$, -6.97 ± 0.07 ; ^{60}Ni $59.94977 \pm 3.5 \times 10^{-4}$, -8.37 ± 0.06 ; ^{61}Ni $60.9540 \pm 15 \times 10^{-4}$, -7.5 ± 0.3 ; ^{62}Ni $61.94955 \pm 3.9 \times 10^{-4}$, -8.14 ± 0.06 ; ^{64}Ni $63.94740 \pm 5.6 \times 10^{-4}$, -8.22 ± 0.09 . The calc. at. wt. is 58.69, in exact agreement with the international val. N. M. B.

Radioactivity and the periodic table. J. F. King and P. H. Fall (*J. Chem. Educ.*, 1940, 17, 481—482).—A demonstration model is described and illustrated. L. S. T.

Neutro-electric effect. S. Kikuchi and H. Aoki (*Proc. phys.-math. Soc. Japan*, 1938, [iii], 20, 403—404; *Chem. Zentr.*, 1938, ii, 3783).—The effective cross-section of the Pb 93

atom for the neutro-electric effect is $0.5-1 \times 10^{-25}$ sq. cm. This val. accounts for the unexpectedly small no. of paired tracks obtained in Wilson chamber photographs (cf. A., 1938, I, 169, 289; 1939, I, 56). A. J. E. W.

Collisions of neutrons with deuterons and the nature of nuclear forces. H. S. W. Massey and R. A. Buckingham (*Nature*, 1940, 146, 776).—The angular distribution of 1.85-Mv . neutrons scattered by deuterons has been calc. for three assumed types of force, viz., (i) "mixed" exchange force, (ii) Majorana-Heisenberg exchange force, and (iii) "ordinary" force. Comparison with experimental results favours (i) or (ii), whilst evidence from the total collision area supports (i) strongly. Fundamental nuclear forces thus appear to be of type (i). L. S. T.

Scattering of α -particles in helium. J. A. Wheeler (*Physical Rev.*, 1941, [ii], 59, 16—26).—Mathematical. Deviations from the scattering expected from an inverse square law of force between α -particles are interpreted satisfactorily in terms of the influence on particles of 0, 2, and 4 units of angular momentum of a sp. nuclear interaction having a range $<9 \times 10^{-13}$ cm. The semistable state of the compound nucleus ^8Be found in certain disintegration experiments is found from the scattering analysis to have an energy $\sim 3 \text{ Me.v.}$, a mean life of 0.8×10^{-21} sec., and zero angular momentum. There is evidence for a semistable state of still shorter life, angular momentum 2, and energy 4—5 Me.v. N. M. B.

α -Particle model and the properties of the nucleus ^8Be . J. A. Wheeler (*Physical Rev.*, 1941, [ii], 59, 27—36).—Reasons are given for renouncing any attempt to interpret the scattering of α -particles in He in terms of a hypothetical law of force between α -particles. Available data and scattering analysis (cf. preceding abstract) lead to the following vals. for energy, width, life, and angular momentum, respectively, of ^8Be : normal state, 125 ke.v., $1-100 \text{ e.v.}$, $10^{-15}-10^{-17}$ sec., 0; first excited level, 2.8 Me.v., 0.8 Me.v., 10^{-21} sec., 0; second excited level, —, very great, —. Difficulties remain in the interpretation of the reaction of ^{11}B with protons to yield ^8Be . N. M. B.

Interaction of α -particles. H. Margenau (*Physical Rev.*, 1941, [ii], 59, 37—47; cf. Hafstad, A., 1939, I, 6).—Mathematical. An examination, on the basis of a Heitler-London analysis, of the forces between α -particles tends to discredit the α -particle model of the nucleus and to destroy the supposition that the forces are describable as a superposition of repulsive first-order and attractive second-order effects, or that the forces are additive. The range of the forces is approx. that of the forces between elementary nuclear particles. Results are applied to the problem of the scattering of α -particles in He. N. M. B.

Production of ^3He . R. D. Hill (*Physical Rev.*, 1941, [ii], 59, 103; cf. Alvarez, A., 1939, I, 590).—Assuming that the presence of ^3He in the atm. is due to transmutations involving cosmic rays, with the ^6Li slow-neutron reaction the most probable, the calc. no. of ^3He atoms in the air is $\sim 4 \times 10^{21}$. N. M. B.

Capture cross-section for C neutrons. R. D. O'Neal and M. Goldhaber (*Physical Rev.*, 1941, [ii], 59, 102).—Data obtained by the method of induced radioactivity are tabulated for N, F, Na, Mg, Al, Si, P, Cl, K, Ca, Ni, Cu, Ga, Sb, Tl, and Bi, and results are compared with available data. N. M. B.

Positrons from light nuclei. M. G. White, E. C. Creutz, L. A. Delsasso, and R. R. Wilson (*Physical Rev.*, 1941, [ii], 59, 63—68; cf. A., 1939, I, 592).—Four nuclei containing

one more proton than neutron (cf. Wigner, *ibid.*, 595) have been produced. Their half-lives and positron energies are: ^{30}P , 4.6 sec., 3.63 Me.v.; ^{31}S , 3.2 sec., 3.85 Me.v.; ^{33}Cl , 2.4 sec., 4.13 Me.v.; ^{35}A , 2.2 sec., 4.38 Me.v. Energies agree with calc. vals. and indicate that the π - π force exceeds the ν - ν force only by the Coulomb repulsion, nuclear vols. \propto at. wts., and nuclear charge is distributed uniformly through the vol. The half-life-energy relation agrees with the Fermi theory, with deviations as anticipated by the Gamow-Teller modification. N. M. B.

Branching ratios in the fission of uranium (235). H. L. Anderson, E. Fermi, and A. V. Grosse (*Physical Rev.*, 1941, [ii], 59, 52—56).—With a view to determining the probability (branching ratio) that when U fission occurs a given radioactive series will appear, a survey is reported of the % of slow neutron-induced U fissions that give rise to various series. The vals. found, 0.1—10%, were obtained by measuring the no. of β -disintegrations of a suitable member of the series after an irradiation under specified geometrical conditions and a quant. chemical separation. N. M. B.

Photo-fission of uranium and thorium. R. O. Haxby, W. E. Shoupp, W. E. Stephens, and W. H. Wells (*Physical Rev.*, 1941, [ii], 59, 57—62).—A full report of the discovery of photo-fission by γ -rays (cf. A., 1940, I, 341). The measured cross-section for the photo-fission of U and Th by γ -rays from F bombarded with protons is $3.5 \pm 1.0 \times 10^{-27}$ and $1.7 \pm 0.5 \times 10^{-27}$ sq. cm., respectively. N. M. B.

Equation of $^{235}\text{uranium}$ fission. A. V. Grosse (*J. Amer. Chem. Soc.*, 1940, 62, 3524—3525).—The fission products from ^{235}U can be classed in two groups, a heavy group containing elements of at. wt. 125—150 and a light group of elements having at. wt. 80—100. A provisional, but incomplete, "fission equation" for the amounts of various elements produced when 100 ^{235}U and 100 neutrons react is put forward on the basis of available data. It indicates that the discovery of additional fission fragments is to be expected. W. R. A.

Absorption of cosmic-ray protons in lead. G. D. Rochester and M. Bound (*Nature*, 1940, 146, 745—746).—Data obtained in a cloud-chamber investigation of the absorption of cosmic-ray protons in Pb are recorded and discussed. The interpretations put forward of the results depend partly on the assumed place of origin of the protons and partly on the form of their spectrum. L. S. T.

Possibility of detecting a doubly-charged proton by the photographic method. H. J. Taylor, D. Fraser, and V. D. Dabholkar (*Nature*, 1940, 146, 777).—The resolving power of the method of exposing Ilford "R" plates to cosmic rays at high altitudes is insufficient to reveal the existence of doubly-charged protons. A decision by means of this method is unlikely. L. S. T.

Penetrating cosmic-ray showers. L. Jánossy (*Nature*, 1941, 147, 56—57).—Transition curves of penetrating cosmic-ray showers (cf. A., 1940, I, 242) in Pb and Al are reproduced and discussed. The rays are produced probably by the soft component of cosmic rays. The possibilities that the showers are cascade showers, or are due to meson production or a related process, are discussed. L. S. T.

Electric fields produced by cosmic rays. F. Evans (*Physical Rev.*, 1941, [ii], 59, 1—7).—Mathematical. Assuming the existence in interstellar space of a finite density of matter, four assumptions concerning the flow of currents are postulated and justified. With the help of these it is deduced that charge density and c.d. vanish in interstellar space, and that the existence in such space of cosmic rays as charged particles predominantly of one sign will result in the production of negligible electric fields. N. M. B.

(A) East-west asymmetry of cosmic radiation at high latitudes. F. G. P. Seidl. (B) East-west asymmetry of cosmic radiation at high latitudes and the excess of positive mesotrons. T. H. Johnson (*Physical Rev.*, 1941, [ii], 59, 7—10, 11—15; cf. A., 1935, 1297).—(A) Results calc. from observed data are reported.

(B) The observed asymmetry is interpreted as due to the deflexion by the earth's magnetic field of the mesotron component while the rays are losing energy by ionisation in the atm. Assuming that deflexions without energy loss (as for the Lemaitre-Vallarta type primary rays) result in a

symmetrical distribution for the energy concerned, the asymmetry is traced to the difference between the actual deflexion and that of a ray which loses no energy. Calc. results agree with observed vals. N. M. B.

Excited states of nuclear particles in the meson-pair theory. C. L. Critchfield (*Physical Rev.*, 1941, [ii], 59, 48—52).—Mathematical. An improved meson-pair theory is developed without the use of perturbation calculations. N. M. B.

Protons of double charge and the scattering of mesons. H. J. Bhabha (*Physical Rev.*, 1941, [ii], 59, 100—101).—The consequences of a theory predicting the existence of protons of charge $2e$ and $-e$ (cf. A., 1940, I, 309) are discussed, and a new formula for the scattering of transversely polarised mesons caused by the spin of the heavy particles is presented. N. M. B.

Stability and magnitude of electronic charges. II. Scalar wave functions. A. Landé and L. H. Thomas (*J. Franklin Inst.*, 1941, 231, 63—70; cf. A., 1941, I, 70).—Mathematical. If the electronic particle has a fundamental length a , written in the form $a = \gamma e^2/mc^2$, then γ is found to have the val. $4 \times (\frac{2}{3})^{\frac{1}{2}}$ when a is the diameter of Thomson's cross-section σ of a free electric particle scattering infra-red light, or is found from the relation $a^2 = 2\sigma$, giving $\gamma = 4 \times (\pi/3)^{\frac{1}{2}}$, from which the Sommerfeld fine-structure const. $\alpha = \mu/\gamma = 1/137.1273$, where $\mu = amc/h$. The derivation of the proper vals. of μ is examined. N. M. B.

Upper limit of temperature. (A) C. Rosenblum. (B) F. G. Brickwedde. (C) W. Copulsky. (D) C. Rosenblum (*J. Chem. Educ.*, 1940, 17, 438, 543—544, 544, 544).—(A) The upper limit for at. H, calc. from the kinetic theory and the ideal gas law, is 3.58×10^{12} °K.

(B) A criticism and a discussion of temp. scales.

(C) Constancy of mass with increasing velocity cannot be assumed. The highest temp. which H can reach before being converted into radiant energy is 2.2×10^{12} °K.

(D) A reply to the above.

L. S. T.

Application of Mie's electromagnetic theory to the measurement of the size of small drops. G. R. Paranjpe and S. S. Lajami (*J. Univ. Bombay*, 1940, 9, Part 3, 38—54).—Mie's theory has been applied to the scattering of light by small drops, and the angles of the first min. of intensity in the forward direction are derived graphically. The results are compared with the corresponding vals. derived from Rayleigh's theory and the circular disc. theory. J. W. S.

General theory of spectra. II. M. H. Stone (*Proc. Nat. Acad. Sci.*, 1941, 27, 83—87; cf. A., 1940, I, 342).—Mathematical. The theory of lattice-ordered abelian groups is discussed and an integration-free treatment of Riesz's operational calculus in a linear lattice is derived.

W. R. A.

Modified atomic volume plots. T. Moeller (*J. Chem. Educ.*, 1940, 17, 441—442).—At. vols. are plotted against the long form of the periodic table. L. S. T.

II.—MOLECULAR STRUCTURE.

Potential energy functions for diatomic molecules. H. M. Hulburt and J. O. Hirschfelder (*J. Chem. Physics*, 1941, 9, 61—69).—Two additional spectroscopic consts., $\omega_e x_e$ and a_e , are used to improve the usual three-parameter Morse curves derived from D , r_e , and ω_e for diat. mol. (cf. A., 1929, 975). The improved potentials generally lie above the Morse curves and for fairly large internuclear separations the corrections may be 10% of the energy of dissociation.

J. W. S.

Band spectrum of BN. A. E. Douglas and G. Herzberg (*Canad. J. Res.*, 1940, 18, A, 179—185).—Two new band systems (a triplet and a singlet system) have been observed in a discharge through He containing traces of BCl_3 and N_2 . They are due to BN, and a vibrational and rotational analysis of the triplet system shows that it represents a $^3\Pi \rightarrow ^3\Pi$ transition, and is probably analogous to the Swan bands of C_2 . The vibrational frequencies in the upper and lower states are $\omega_e' = 1317.5$ and $\omega_e'' = 1514.6$ cm^{-1} . The rotational consts. are $B_e' = 1.555$, $B_e'' = 1.666$, $\alpha_e' = 0.010$, and $\alpha_e'' = 0.025$ cm^{-1} . The moments of inertia for the upper and lower states are 18.00×10^{-40} and 16.80×10^{-40} g. cm^2 , and the internuclear distances r_e' and r_e'' are 1.326 and 1.281 Å.

F. J. G.

Flame spectrum of carbon monoxide. A. G. Gaydon (*Proc. Roy. Soc.*, 1940, A, 176, 505—521).—The spectrum of CO burning in air and in O₂ at reduced pressure was photographed on high-contrast plates to display the band spectrum clearly. Analysis of the spectrum shows that the bands occur in pairs with a separation of about 60 cm.⁻¹; many of the strong bands are arranged in arrays with intervals of 565 and 2065 cm.⁻¹ The emitter of the spectrum is discussed; it seems unlikely that the bands can arise from either the suboxide C₃O₂ or the peroxide CO₃. CO₂ is the most likely emitter of the banded part of the CO flame spectrum; it is suggested that some of the peculiarities of the combustion of CO are due to a transition from a triangular electronically excited CO₂ mol. to the linear unexcited state, the mols. after this transition being left with very large vibrational energy.

G. D. P.

True measure of relative band intensities. N. R. Tawde and V. S. Patankar (*J. Univ. Bombay*, 1940, 9, Part 3, 16—23).—Various methods of measuring the relative intensities of the bands of a system are discussed. The ratio of the integrated to peak intensities has been determined for the second positive system of N₂. Agreement is good for bands of $\lambda >$ that of the (0,0) band (3371 Å.), but at lower λ the peak intensity vals. are $>$ the integrated intensities, probably owing to an over-estimate of the former due to the J -vals. for the heads increasing with decreasing λ .

J. W. S.

Absorption spectra of nitrogen dioxide, ozone, and nitrosyl chloride in the vacuum ultra-violet. W. C. Price and (Miss) D. M. Simpson (*Trans. Faraday Soc.*, 1941, 37, 106—113; cf. A., 1939, I, 298).—Absorptions have been measured down to 1000 Å. In NO₂ Rydberg-type bands were observed; these give 12.3 ± 0.2 v. for the ionisation potential, in which a $2p$ [O] non-bonding electron is concerned. O₃ is nearly transparent between 2300 and 1600 Å., below which absorption due to O₃ formed by photo-dissociation obscures that due to O₃. It is inferred that certain band systems having wide vibrational structure are due to the excitation of π bonding electrons. The spectra of several bent triat. mols. are compared and an attempt is made to correlate them with the respective heats of formation of the mols.

F. L. U.

Vibration energy levels and specific heat of ethylene. E. J. Burcik, E. H. Eyster, and D. M. Yost (*J. Chem. Physics*, 1941, 9, 118—119).—The Bonner assignment of the torsional level of C₂H₄ yields a more reasonable explanation of the weak combination and harmonic lines of the Raman spectrum than does Conn and Sutherland's assignment (A., 1939, I, 549). It also leads to vals. of the heat capacity in much better accord with measured vals. The theoretical heat capacities at 150—450° K. follow the empirical relation $C_p^0 = 9.638 - 3.109 \times 10^{-2}T + 1.551 \times 10^{-4}T^2 - 1.426 \times 10^{-7}T^3$.

J. W. S.

Light absorption of organic compounds. IX. Unsaturated carbonyl compounds and semicarbazones. A. Burawoy (*J.C.S.*, 1941, 20—24).—Vals. of the λ and extinction coeff. (ϵ) at the absorption max. are given for citral, citrylidene-acetaldehyde and -crotonaldehyde (I), β -cyclocitral (II), α -, β -, and ψ -ionone, their semicarbazones, and the phenyl-semicarbazones of (I) and (II); ϵ - λ curves are also given for $\lambda = 2000$ —4000 Å. The correlation of differences in absorption and structure is discussed.

A. J. E. W.

Vibration spectra of certain condensed gases at the temperature of liquid nitrogen. I. Experimental methods: (A) Infra-red spectra. G. K. T. Conn, E. Lee, and G. B. B. M. Sutherland. (B) Raman spectra. G. B. B. M. Sutherland and Cheng-Kai Wu. II. Infra-red and Raman spectra of hydro- and deuterio-chloric acid at liquid nitrogen temperatures. E. Lee, G. B. B. M. Sutherland, and Cheng-Kai Wu (*Proc. Roy. Soc.*, 1940, A, 176, 484—493, 493—504).—I (A). The infra-red spectrometer is described; it is of the Pfund-Barnes type designed for the investigation of mols. in the gaseous state at room temp. and the study of thin layers of solidified gases at low temp. The absorption cell, detector system, and calibration of the instrument are described.

I (B). The special Dewar vessel for the observation of Raman spectra at low temp. is described; it is especially suitable for small quantities of material.

II. The infra-red absorption spectrum of HCl was recorded at the temp. of liquid N about 20° below the transition point at 98° K. It consists of two bands with max. at 2701 and 2744 cm.⁻¹, each showing fine structure; there are indications of a third band. The Raman spectrum at the same temp.

D 2 (A., I.)

also shows a doublet structure, whilst at higher temp. only a single line is observed, the difference being due to the association of HCl mols. in the solid state. The absorption spectrum of DCl was observed under the same conditions; three max. and traces of other structure were recorded. The results are in agreement with the low symmetry of solid HCl revealed by X-ray analysis.

G. D. P.

Polymerisation of dyes in solution. Thionine and methylene-blue. E. Rabinowitch and L. F. Epstein (*J. Amer. Chem. Soc.*, 1941, 63, 69—78).—The extinction curves of thionine (Thio) and methylene-blue (MB) have been determined at different concns. and temp. in H₂O, EtOH, and EtOH-H₂O mixtures. The curves indicate that the spectra are made up by the superposition of two bands, the M -band which for H₂O is more prominent in dil. solution, and the D -band stronger in conc. solution. In H₂O deviations from Beer's law appear even at the lowest concns. ($< 10^{-6}$ mol. per l.) and are explained quantitatively by the formation of dimeric ions Thio₂⁺⁺ and (MB)₂⁺⁺ to which the D -band is ascribed, the M -band being ascribed to the monomeric ions Thio⁺ and (MB)⁺. In H₂O and dil. EtOH, increase of temp. has a similar effect to dilution, the intensity of the M -band increasing, whilst in more conc. EtOH mixtures a reverse effect is observed. Dissociation consts. and heats and entropies of formation of the dimerides in H₂O have been calc. Dimerisation does not occur in pure EtOH and is reduced considerably in EtOH-H₂O mixtures. Dimeric ions do not fluoresce, hence self-quenching of fluorescence at higher concns. of dye is attributed to dimerisation; no self-quenching, however, occurs in EtOH. Dimerisation is considered a universal property of org. dyes fundamentally associated with the property of colour and can be interpreted quantitatively on London's theory of intermol. forces. Potential energy curves are given for the interaction of two Thio⁺ ions in H₂O and in EtOH and, because of the ionic coulombic repulsion, dimerisation requires an activation energy. Other properties of dye solutions (oxidation-reduction potentials, conductivity, osmotic pressure) are in accord with the dimerisation hypothesis.

W. R. A.

Ultra-violet absorption in a series of chloropyrimidines in the vapour state and in solution. F. M. Uber and R. Winters (*J. Amer. Chem. Soc.*, 1941, 63, 137—141).—Broad bands are exhibited, between 2100 and 3000 Å., prominently in the vapour state and less prominently in solution by pyrimidine and its Cl₂-, Cl-, and Cl₃-derivatives. With increasing no. of Cl absorption max. shift to longer λ and mol. extinction coeffs. increase.

W. R. A.

Carcinogenic hydrocarbons. V. Comparison of the intensity of fluorescence of cholanthrene and its homologues. W. F. Bruce (*J. Amer. Chem. Soc.*, 1941, 63, 304—305; cf. A., 1941, II, 92).—The intensity of fluorescence (detailed) of cholanthrene is $<$ that of its 20-Me derivative, thus paralleling the carcinogenic activity, but that of the 20-Et and -Pr ^{β} derivatives is only slightly lower.

R. S. C.

Absorption spectra of derivatives of 1:2-benzanthracene. R. N. Jones (*J. Amer. Chem. Soc.*, 1941, 63, 151—155).—Absorption spectra for 21 derivatives of 1:2-benzanthracene and their fluorescence in the solid state and in solution are reported and qualitatively discussed.

W. R. A.

Absorption spectra of alkylchrysenes. R. N. Jones (*J. Amer. Chem. Soc.*, 1941, 63, 313—314).— λ and intensities of max. in the region 2700—3800 Å. have been determined for solutions in EtOH of 5-methyl- (I), 4:5- (II) and 5:6-dimethyl- (III), and 4:5-methylene-chrycene (IV). (I) and (II) give spectra closely resembling that of chrycene but (III) shows less similarity. In the spectrum of (IV) increased fine structure is shown in agreement with the corresponding increased amount of fine structure which is found for 1:2 benzanthracene derivatives containing a bridge methylene group (cf. preceding abstract).

W. R. A.

Spectroscopic properties of $\beta\beta\beta'$ -trichlorotriethylamine.—See A., 1941, II, 35.

Induction, resonance, and dipole moment. C. P. Smyth (*J. Amer. Chem. Soc.*, 1941, 63, 57—66).—The dipole moments in the vapour state are recorded for Bu ^{α} Cl 2.09, Bu ^{β} Cl 2.04, sec.-BuCl 2.12, Bu ^{γ} Cl 2.13, MeNO₂ 3.5, Pr ^{α} NO₂ 3.72, Pr ^{β} NO₂ 3.73, Bu ^{γ} NO₂ 3.71 D. These data, combined with existing dipole moment data for vapours, are used to extend previous conclusions on the inductive effects in straight and branched C chains. No detectable differences in μ exist corresponding

with differences in chemical reactivity between halogens or H on primary, *sec.*, and *tert.* C atoms. The moments of fluoromethanes and fluorochloromethanes should not be appreciably affected by polar structures containing doubly-bonded halogen, the contributions of such structures being masked by inductive effects. From the vals. of μ for solutions of Ge and Pb halides the bond moments of Ge-Cl and Pb-Cl are calc. to have min. vals. of 2.0 and 4.1 D. Using these vals. with the val. for Sn-Cl and μ for KCl, KI, and NaCl, the amount of ionic character in each of these bonds is computed and is in fair agreement with vals. calc. from electronegativities derived from thermal data. The amounts of double bond character in C-halogen bonds in monohalobenzenes have been calc. from observed μ vals. but are < those computed from bond lengths. The amounts of resonance contributions calc. from μ vals. cannot be ascertained with great exactness.

W. R. A.

Dipole moment and molecular structure of higher fatty acids. G. R. Paranjpe and P. Y. Deshpande (*J. Univ. Bombay*, 1940, 9, Part 3, 24—37).—From ϵ and n_D measurements on C_8H_{16} solutions, and on the assumption that the at. polarisation is 15% of the electronic polarisation, the following dipole moments (in D.) at 25° have been determined; lauric acid 0.75, myristic acid 0.77, palmitic acid 0.77, trilaurin 2.59, and palmitone 2.12. The vals. for the acids, which apply to dimeric mols., lead to a structure of the CO_2H groups in such mols. in which the H of one mol. is chelated to the O of the other, the O-H-O, O-C-O, and C-O-H angles being 180°, 125°, and 110°, respectively.

J. W. S.

Dipole moments and resonance in the tetrionic acids. W. D. Kumler (*J. Amer. Chem. Soc.*, 1940, 62, 3292—3295).—The following vals. of dipole moments in dioxan have been measured at 25°: tetrionic acid (I), 4.72; α -chlorotetrionic acid, 5.69; α -bromotetrionic acid, 6.00; Me α -bromotetrate, 6.19; α -iodotetrionic acid, 5.59; Me α -iodotetrate, 6.12; *l*-ascorbic acid, 3.93 D. Tetrionic acids are possibly keto-enol tautomers. Calc. vals. for possible mol. configurations are given and it is concluded that (i) (I) is essentially in the enol form in dioxan, (ii) a resonating form involving a separation of charge contributes to the structure of the mol., and (iii) the OH is fixed in the plane of the ring with the H of the OH oriented toward the α -C. These conclusions are substantiated by the results for α -halogen-substituted acids and by the Me esters. The apparently low val. for ascorbic acid compared with that for (I) is explained on the basis of resonating forms of α -diketones, β -ketonic esters, and β -ketonic γ -lactones.

W. R. A.

Densities and refractive indices of liquid paraffin hydrocarbons. M. L. Huggins (*J. Amer. Chem. Soc.*, 1941, 63, 116—120).—Recent data for ρ for normal paraffin hydrocarbons yield the equation $V_n = 26.96 + 16.49n + (29.0/n)$ for the calc. molal vol. of a mol. containing n C atoms; molal vols. of non-normal paraffins are represented by $V = V_n + \text{const.}$ Mol. refractions for normal paraffins are given by $R_n = 2.12 + 7.815n$ and the vals. of $R - R_n$ are const. for series of non-normal paraffins. The bond refractions of C-C and C-H depend on the no. of C and H atoms attached to each C of the linking. Equations for computing R from their formulæ are given.

W. R. A.

Effect of the rotation of groups about bonds on optical rotatory power. W. Kauzmann and H. Eyring (*J. Chem. Physics*, 1941, 9, 41—53).—A comparison of the mol. rotations, $[M]_D$, of various optically active cyclic and open-chain compounds shows that $[M]_D$ is reduced markedly if the groups surrounding the asymmetric atoms possess a threefold axial symmetry about the bonds uniting them to the asymmetric atom, this symmetry being either inherent in the groups or acquired by them through free rotation about these bonds or by their orienting themselves equally in each of the three possible equilibrium positions about each bond. $[M]_D$ is thus a measure of the freedom of orientation about single bonds of the groups in an asymmetric mol. This has an important effect on the temp. coeff. of $[M]_D$ and accounts for the large differences observed between the $[M]_D$ for liquids and cryst. solids. This theory is applied to the elucidation of the structures of certain S compounds, polypeptides, and proteins.

J. W. S.

Dispersion of magnetic double refraction in the short infra-red spectrum. F. J. Davis (*J. Opt. Soc. Amer.*, 1940, 30, 488—494).—The dispersion of the Cotton-Mouton effect in CS_2 , C_6H_6 , PhCl, $PhNO_2$, PhMe, $C_6H_5MeNO_2$, and halowax

oil at 20° has been studied at $\lambda = 0.65$ — 1.6μ . For each liquid the ratio of the Cotton-Mouton const. (C) to the Kerr const. is const. within the experimental error ($\sim 1\%$). In general the observed C - λ curves are slightly less steep than those given by Havelock's law, but the observed and calc. C vals. differ by $> 6\%$; the agreement shows that the magnetic and optical anisotropies of the liquids are approx. independent of λ .

A. J. E. W.

Momentum distribution in molecular systems. I. The single bond. C. A. Coulson. **II. Carbon and the C-H bond.** C. A. Coulson and W. E. Duncanson. **III. Bonds of higher order.** C. A. Coulson (*Proc. Camb. Phil. Soc.*, 1941, 37, 55—66, 67—73, 74—81).—I. The momentum distribution in mols. in which only single bonds occur is dealt with, using the Dirac transformation theory of space wave functions. Two approximation methods are employed, the mol. orbital method, in which single electron momentum functions are calc., and the electron-pair method. In each case, the presence of the bond decreases the mean component of the velocity in the direction of the bond, increases the mean component of velocity perpendicular to the bond, and increases the mean momentum averaged over all directions. The theory is applied to H_2^+ and H_2 . Contours of const. momentum density are obtained for H_2^+ . The mean radial distribution functions for the two mols. are given, and the mean momentum for both is calc. The results are discussed in connexion with the experimental results of Hicks on the Compton line and scattering of fast electrons in H_2 (A., 1937, I, 580).

II. The momentum distribution for an electron in one of the hybridised orbitals of a C atom is calc., and is obtained as a function of the degree of hybridisation. The mean momentum increases with increasing coeff. of mixing (σ). The momentum of the C-H bond is also considered on the assumption that the bond is homopolar. This momentum also depends on the degree of s - p mixing, an increase in the proportion of p -binding increasing the mean momentum, but the effect is < in the case of the isolated at. orbital. The mean momentum for the C-H bond is < for the isolated C at. orbitals, but > for an isolated H atom over the greater part of the range of σ .

III. The momentum distribution of double bonds and conjugated bonds is considered, with special reference to C_2H_4 , C_6H_6 , and $(CH_2)_n$. The mean radial distribution function shows that the mean momentum of the electrons is < if they were rigidly attached to their own particular nuclei. Polar diagrams (contours of const. probability) indicate that the component of momentum perpendicular to the bond is > that along it, and if electron mobility is high in any direction in a mol., momentum is usually small in that direction.

A. J. M.

Revisions of the covalent radii and the additivity rule for the lengths of partially ionic single covalent bonds. V. Schomaker and D. P. Stevenson (*J. Amer. Chem. Soc.*, 1941, 63, 37—40).—For essentially covalent single bonds bond lengths are given by the sum of the appropriate covalent radii but certain mols., e.g., F_2 , N_2H_2 , H_2O_2 , show deviations. The length of a single bond A-B is given by $r_{AB} = r_A + r_B - \beta(x_A - x_B)$ (i), where r_A and r_B are normal covalent bond radii, β is a const. = 0.09, and $x_A - x_B$ is the difference between the Pauling electronegativities of A and B. Therefore, $-\beta(x_A - x_B)$ is a measure of the extra ionic character of the bond A-B. Vals. of covalent single bond radii are calc. for about 20 atoms and compared with the Pauling-Huggins vals. Observed bond lengths in diat. mols. (alkalis, alkali hydrides and halides, H halides) are compared with vals. calc. from $r_A + r_B$ and from equation (i). With polyat. mols. the vals. for diat. bond lengths calc. by equation (i) are compared with experimental vals. and with $r_A + r_B$ and Pauling-Huggins vals. from covalent radii. Generally the additivity of bond radii is valid only when correction is made for the ionic character of the bond. New vals. of normal covalent single-bond radii for H, N, O, and F are given which are consistent with ascertained bond lengths in H_2 , N_2H_2 , H_2O_2 , and F_2 .

W. R. A.

Hyperconjugation. R. S. Mulliken, C. A. Rieke, and W. G. Brown (*J. Amer. Chem. Soc.*, 1941, 63, 41—56).—Hyperconjugation (A., 1939, I, 353), the conjugation of a group such as Me with other groups containing double or triple bonds, has been investigated by quantum-mechanical computations on typical mols. using the mol. orbital (MO) method. The at. orbital method (AO) can also be applied but is more cumbersome. From the MO viewpoint the Me group can be written as $-C \equiv H_3$ and compared with $-C \equiv N$ and $-C \equiv CH$. Differ-

ences in conjugating power are quantitatively expressible in terms of a parameter related to the strength of the triple bond. Although $C\equiv H_3$ is more saturated than $C\equiv C$ and therefore has less tendency to conjugate, it still has considerable power of conjugation as indicated by calculations from thermal and bond distance data. Three general types of conjugation are recognised: (a) ordinary (first-order) conjugation as in $HC\equiv C-C\equiv CH$ or $N\equiv C-C\equiv N$; (b) second-order conjugation (first-order hyperconjugation) as in $H_3\equiv C-C\equiv CH$ or $H_3\equiv C-C\equiv N$; (c) third-order conjugation (second-order hyperconjugation) as in $H_3\equiv C-C\equiv H_3$. Accordingly all saturated org. mols. are stabilised by (c). The single and multiple bonds of a conjugated system are classified as acceptor and donor bonds, respectively; type (a) conjugation causes a shortening of acceptor and a lengthening of donor bonds. There is thus a net energy of conjugation (resonance energy) and this has been shown to be the sum of a positive, stabilising energy located in acceptor bonds and a negative energy located in donor bonds. In type (c) conjugation in saturated hydrocarbons C-H bonds are donor and C-C bonds predominantly acceptor, *i.e.*, simultaneously donor and acceptor but with acceptor properties the more pronounced; the gains in stability by acceptor bonds are quite large but the losses by donor bonds are very small. Energy of conjugation is regarded as energy of delocalisation resulting from the passage from localised MO's to non-localised MO's. MO's are derived by the linear combinations of at. orbitals (LCAO) method. Observed energies of conjugation and hyperconjugation agree well with val. calc. on the theory advanced provided that two parameters (characteristics discussed) are suitably chosen. One of these parameters has hitherto been regarded as the resonance integral but is shown to be only $\sim 10\%$ of the val. of the resonance integral and for $C=C$ bond distance of 1.33 Å. is ~ 45 kg.-cal. per g.-mol. Type (c) conjugation is considered to be present in all org. mols. and reduces bond lengths. Normal C-C bonds have $\sim 11\%$ double bond character and normal, unconjugated C=C bonds $\sim 12\%$ triple bond character as a result of hyperconjugation. Conjugation energies have been computed for CMe_2CH , C_2H_6 , $(CH_2C)_2$, $(CH_2CH)_2$, C_2H_6 , C_2H_4 , C_6H_6 , and $(CMe)_2$. Type (b) conjugation energies between Me or CH_2 groups and double bonds are given for 14 mols. and the relation between bond length and bond order is discussed. The theory is used to explain the observed decrease in the heats of hydrogenation of unsaturated compounds on Me substitution.

W. R. A.

Molecular structure of myosin.—See A., 1941, II, 56.

Structure of molecules and aggregates of molecules. J. G. Kirkwood (*J. Chem. Physics*, 1941, 9, 1—2).—Methods of investigating mol. structure and the applications of these measurements are discussed.

J. W. S.

Molecular distribution. J. E. Mayer and E. Montroll (*J. Chem. Physics*, 1941, 9, 2—10).—Functions by means of which the distribution of mols. in a system may be described are defined, and the relations between them are derived. Equations for the calculation of these functions from the mutual potential energy between pairs of mols. are also derived. Methods for the numerical evaluation of the functions are discussed.

J. W. S.

Theory of the transition in KH_2PO_4 . J. C. Slater (*J. Chem. Physics*, 1941, 9, 16—33).—Different possible arrangements of the H atoms in KH_2PO_4 crystals result in different orientations of the H_2PO_4 dipoles. As these have min. energy when oriented along the crystal axis there is a tendency for spontaneous polarisation, resulting in a transition, with polarisation, below the Curie point. The statistical theory is developed and found to predict a phase change of the first order. It is suggested that the change observed is a broadened first-order transition, the broadening being due to irregular shifts of the transition temp. due to stresses in different regions of the crystal. In general accord with experiment, the theory predicts that the magnetic susceptibility above the Curie point is 4.33 times the val. predicted by the Weiss theory. The predicted entropy change (0.69 unit) is $<$ the observed val. (~ 0.8 unit).

J. W. S.

Force constants in some organic molecules. B. L. Crawford, jun., and S. R. Brinkley, jun. (*J. Chem. Physics*, 1941, 9, 69—75).—The possibility that in a series of mols. involving the same bonds, the bond force consts. are only slightly changed from one mol. to another is investigated. In HCN,

C_2H_2 , C_2H_6 , CMe_2CH , $(CMe)_2$, and MeCN the bond structures demand 20 different bond consts., with which the 52 fundamental frequencies fit satisfactorily. The application of the treatment to Me halides is also investigated. The structural significance of force consts. is discussed.

J. W. S.

Mathematical methods for the study of molecular vibrations. E. B. Wilson, jun. (*J. Chem. Physics*, 1941, 9, 76—84).—Methods to simplify the calculation of vibration frequencies of complex mols. (A., 1940, I, 11) are described and illustrated by application to the MeCl mol.

J. W. S.

Theory of antiferromagnetism. J. H. Van Vleck (*J. Chem. Physics*, 1941, 9, 85—90).—By means of the Dirac vector model, expressions for the magnetic susceptibility (χ) of a medium with antiferromagnetic exchange coupling are derived. The theory predicts a Curie temp. above which the internal field disappears and at which χ is a max. (1.5 times its val. at 0° K.). This accords with experimental data on MnO but not with those on MnSe. The relation of this theory to previous theories, of which it is a generalisation, is discussed.

J. W. S.

Molecular fields of force. S. Chapman (*Nature*, 1940, 146, 747).—A correction (cf. A., 1941, I, 30).

L. S. T.

III.—CRYSTAL STRUCTURE.

Diffuse reflexions on Laue photographs. K. Lonsdale (*Nature*, 1940, 146, 806).—Raman and Nilakantan's claims (A., 1941, I, 30) cannot be admitted. Photographs taken at liquid air temp. show that for KCl, $NaNO_3$, $CaCO_3$, and org. compounds the diffuse reflexions almost or completely disappear at -180° , while the Laue spots increase in definition and no. For the diamond, the diminution of intensity at liquid air temp. is slight, but the characteristic temp. of the diamond is high and a change of 200° relatively unimportant. The temp. changes are completely reversible, and it is unnecessary to suppose the phenomenon to be other than a temp. effect.

L. S. T.

Diffuse reflexions from diamond. H. A. Jahn and K. Lonsdale (*Nature*, 1941, 147, 88—89; cf. A., 1940, I, 348).—The changes in shape of modified (111) reflexions that occur when the orientation of the diamond crystal is varied have been investigated. When the crystal is rotated about the $[1\bar{1}0]$ axis so that reflexion occurs from the other side of the vertical (111) plane, the angle of incidence, θ , is -21.9° , and for vals. of $\theta >$ or $<$ -21.9° , the modified reflexion is a triangle of three small spots surrounding a diffuse centre. For $\theta -26.8$ to -16.5° , the position of the centre of this triangle agrees with the Faxén formula $d_{111} \sin(\theta + \phi) = \lambda \cos \phi$, where λ is the wave-length, and ϕ the angle of reflexion. The radial apex of the triangle always points away from the accompanying Laue spot, and the triangle increases in size as θ departs from the Bragg angle, -21.9° . All three spots and the diffuse centre are due to characteristic radiation, and the modified reflexions, whether of these or other shapes given in other crystal orientations, are only slightly reduced in intensity by a lowering of temp. of 200° . The Faxén-Waller theory can give detailed agreement with experiment.

L. S. T.

Quantum X-ray reflexion in diamond. (Sir) C. V. Raman and P. Nilakantan (*Nature*, 1941, 147, 118—119; cf. A., 1940, I, 403).—The (111) reflexions of diamond fit the formula $2d \sin \psi \sin(I + \epsilon) = n\lambda \sin I$, when ψ is the glancing angle of incidence, ϵ is the angle between the static and dynamic stratifications, and I the inclination of the phase-waves of the lattice vibration to the static crystal planes. $I, 55^\circ \pm 1^\circ$, is one half the tetrahedral valency angle, indicating that the phase-waves of the lattice vibration giving the modified reflexions from the (111) planes of diamond are parallel to the (100) planes of the crystal lattice. It has been confirmed experimentally that, as expected, the intensity of the reflexions is practically unaffected by cooling to liquid air temp.

L. S. T.

Extra spots in Laue photographs. G. E. M. Jauncey (*Nature*, 1941, 147, 146).—A discussion of explanations proposed by Preston, Zachariasen, and Raman and Nath of the formula recently derived by Bragg for the intensity of X-rays scattered from a group of 8 point atoms at the corners of a cube, and of an expression for the position of the secondary max. intensity of the modified Bragg spot.

L. S. T.

Photographic Fourier syntheses. M. L. Huggins (*J. Amer. Chem. Soc.*, 1941, **63**, 66—69).—The photographic method, proposed by Bragg (A., 1930, 479), for making a Fourier summation from crystal diffraction data has been extended to give increased accuracy and more quant. results. In its present form it is applicable only to summations having a centre of symmetry. W. R. A.

X-Ray comparison of natural and synthetic starch.—See A., 1941, II, 60.

Reaction of formaldehyde with amino-acids. X-Ray diffraction study.—See A., 1941, II, 60.

Structures of complex fluorides. Stereochemistry of fluoborate and oxyfluoborate complexes. Crystal structure of potassium oxyfluoborate-potassium hydrogen fluoride, $K_3NbOF_5 \cdot KHF_2$. J. L. Hoard and W. J. Martin (*J. Amer. Chem. Soc.*, 1941, **63**, 11—17).—Equimol. aq. solutions of NbF_5 and KF yield $K_3NbOF_5 \cdot H_2O$, which is monoclinic and isomorphous with $K_3TiF_6 \cdot H_2O$ and, therefore, possibly has an octahedral $NbOF_5$ group. When aq. NbF_5 and excess of aq. KF react K_3NbOF_5 is formed which is isomorphous with K_3ZrF_7 , and has, as preliminary X-ray diffraction work confirms, a cubic system. A limited amount of HF added to an aq. solution of NbF_5 and excess of KF gives a cryst. compound of empirical composition K_3HNbOF_7 , actually an aggregate of K' , HF_2' , and octahedral $NbOF_5''$ and, therefore, having the salt-like structure $K_3NbOF_5 \cdot KHF_2$. In the presence of larger concns. of HF monoclinic K_3NbF_7 crystals are formed in which the symmetry of the NbF_5'' group is C_2 (A., 1939, I, 359). The 7-co-ordination groups NbF_7'' and $NbOF_6'''$ have quite distinct geometrical configurations. The ion NbF_8''' appears to be non-existent but the analogous TaF_8''' ion is known in Na_3TaF_8 . $K_3NbOF_5 \cdot KHF_2$ is monoclinic, with a 8.82, b 14.02, c 6.82 Å., β 86° 34', space-group C_{2h}^2 — $C2/c$, 4 mols. per unit cell. The Nb—F and Nb—O distances are 1.88 Å. and F—F separations from nearest neighbours \sim 2.65 Å. in the $NbOF_5''$ group and \sim 2.30 Å. in the F_2' group. The compound is isomorphous with $K_2SnF_6 \cdot KHF_2$ and $K_2PbF_6 \cdot KHF_2$. W. R. A.

Crystalline behaviour of linear polyamides. Effect of heat-treatment. C. S. Fuller, W. O. Baker and N. R. Pape (*J. Amer. Chem. Soc.*, 1940, **62**, 3275—3281).—X-Ray studies of unoriented polyhexamethylene sebacamide and adipamide, solidified from melts at different cooling rates, indicate that the degree of polycrystallinity and perfection of the crystal lattice depend on the rate of cooling. Annealing completely quenched specimens, oriented and unoriented, restores the crystal lattice arrangement to an extent which increases with increasing annealing temp. The macromol. behaviour has been related to that of ordinary monomeric systems. A continuous increase in Young's modulus with decreasing rate of cooling has also been observed, indicating an increased degree of crystallinity. These results suggest that segments of the mols. may exist as cryst., mesomorphic, or amorphous regions in the solid polymerides and imply a considerable rotational freedom of chain mols. in the solid state. The data are discussed in terms of the segment theory of chain polymerides. W. R. A.

Determination of molecular symmetry in the $\alpha\beta$ -diethylbenzyl [$\gamma\delta$ -diphenylhexane] series. C. H. Carlisle and (Miss) D. Crowfoot (*J.C.S.*, 1941, 6—9).—X-Ray crystallographic measurements are carried out on $\gamma\delta$ -diphenylhexane (I), m.p. 89—90°, and the isomeric 4:4'-(OH) $_2$, -(NH $_2$) $_2$, and -(CO $_2$ Me) $_2$ -derivatives. (I) and its 4:4'-(NH $_2$) $_2$ -derivative have mols. containing a centre of symmetry, since both crystallise with 2 mols. in the unit cell and space-groups requiring four asymmetric units. (I) and its three derivatives belong to the *meso*-series. The isomerides of lower m.p. derived from the liquid form (II) of (I) all show crystal structures in which the asymmetric unit may well be the mol. itself and are racemic. Stereochemical arrangement of the atoms in the above *meso*-series is closely related to the form deduced for the natural sex hormones. Diagrams are shown. Disposition of atoms about the central C—C is of the *trans*-type characteristic of the junction between rings b and c of the sterol sex-hormone series. X-Ray data are also recorded for $\alpha\beta$ -diethylstilbene, $\alpha\beta$ -diethylstilbæstrol (+C $_6$ H $_5$) $_2$, 4:4'-dimethoxy- $\alpha\beta$ -diethylstilbene, $\alpha\beta$ -diethylstilbæstrol dipropionate, and 4:4'-dihydroxy- $\gamma\delta$ -diphenyl- Δ^8 -hexadiene. A test for polarity was positive only in the

case of 4:4'-diamino- $\gamma\delta$ -diphenylhexane, m.p. 97—98° [*i.e.*, derived from (II)].

Relationships between lattice types and Brillouin zones. G. V. Raynor (*Phil. Mag.*, 1941, **31**, [vii], 131—138).—Theoretical. Processes are described by which the approx. form of the Brillouin zones can be deduced for a variety of lattice types, including complex structures to which it would be difficult to apply rigidly the more formal methods.

Brillouin zone for the gallium structure. G. V. Raynor (*Phil. Mag.*, 1941, [vii], **31**, 139—143).—From the structure data of Laves and Bradley for the Ga lattice, the dimensions of Brillouin zones containing 5.4 and 3 electron states per atom are obtained. L. J. J.

Crystal structure of aluminium-black. W. O. Milligan and A. B. Focke (*J. Physical Chem.*, 1941, **45**, 107—108).—Al distilled under a pressure slightly > that required to form an Al mirror gives a black, soot-like deposit termed Al-black. An X-ray diffraction study of the deposit shows it to consist of colloidal Al of the same crystal structure as massive Al. The X-radiograms are the same whether the Al is deposited in air or in H $_2$, indicating that there is no reason for assuming that the colloidal particles are stabilised by traces of Al $_2$ O $_3$. C. R. H.

Crystal structure of iodic acid. M. T. Rogers and L. Helmholz (*J. Amer. Chem. Soc.*, 1941, **63**, 278—284).—Cryst. HIO $_3$ has space-group D_2^2 — P_{212121} , a_0 5.525 \pm 0.010, b_0 5.855 \pm 0.010, c_0 7.715 \pm 0.010 Å., 4 HIO $_3$ mols. per orthorhombic unit cell. Patterson and Fourier projections are discussed. Pyramidal IO $_3$ groups exist in the crystal with I—O distances 1.80, 1.89, and 1.81 Å., O—O distances 2.78 Å., and O—I—O angles 96°, 98°, and 101°. Other three O atoms are in positions approx. opposed to the three O in I—O linking and at distances of 2.45, 2.70, and 2.95 Å. making a distorted IO $_6$ octahedron with three strong and three weak linkings. The hydroxyl O has two nearest O neighbours at 2.78 Å. and thus two H bonds for each IO $_3$ group forming a moderately strong bifurcated bond. I atoms are surrounded by distorted octahedra of O atoms and the O atoms are in a nearly closest packed arrangement. The I atoms are not in the perovskite arrangement. W. R. A.

Crystal structures of heterocyclic organic compounds of analogous constitution. III. Phenazine and diphenylene dioxide. R. G. Wood and G. Williams (*Phil. Mag.*, 1941, [vii], **31**, 115—122; cf. A., 1941, I, 76).—Crystallographic, optical, and X-ray measurements on phenazine (I) and diphenylene dioxide (II) are recorded. The results are in agreement with a planar structure for both mols. (I) forms monoclinic holohedral crystals with $a:b:c = 2.61:1:1.39$, $\beta = 108^\circ 55'$; the unit cell contains 2 mols., with a 13.2, b 5.07, c 7.12, space-group $P2_1/a$ (C_{2h}^2); the refractive indices and optical axial angle are $n = 1.73$, $\beta = 1.82$, $\gamma = 1.96$, $2V = 83^\circ$. (II) forms similar crystals with $a:b:c = 2.99:1:2.30$, $\beta = 100^\circ 20'$; the unit cell has 4 mols. with a 15.2, b 5.07, c 11.7 Å., and is centred in the (100) plane; the space-group is Aa (C_2^2) or $A2/a$ (C_{2h}^2). A table is given summarising the principal data for eight mols. dealt with in this series of papers. L. J. J.

Electron diffraction intensities. S. Fordham (*Nature*, 1940, **146**, 807).—Variations in extinction due to irregular crystal shape or to anisotropy will explain, at least qualitatively, many of the differences between calc. and observed electron diffraction intensities. L. S. T.

Structure of the hydrides of boron. VI. AlB $_3$ H $_2$. J. Y. Beach and S. H. Bauer (*J. Amer. Chem. Soc.*, 1940, **62**, 3440—3442).—From electron diffraction measurements AlB $_3$ H $_2$ is planar except for the H atoms. 3 BH $_2$ groups are attached to the central Al at angles of 120°. B atoms are located near the centres of trigonal bipyramids formed from the 4 H and the Al. The interat. distances are Al—B = 2.14 \pm 0.02, B—H = 1.27 \pm 0.04 Å. and from these vals. an electron configuration has been deduced. W. R. A.

Polishing of solids and the mechanism of sliding on ice and snow. F. P. Bowden (*Soc. Chem. Ind. Victoria*, 1940, **40**, 240—250).—A lecture reviewing recent work on the production, nature, and properties of the Beilby layer. A. R. P.

Electron diffraction investigation of the molecular structures of tetrahydrofuran, 2:5-dihydrofuran, furan, dioxadiene, and

p-dioxen. J. Y. Beach (*J. Chem. Physics*, 1941, **9**, 54—55).—The C—O and C—C distances in tetrahydrofuran (I) and 2:5-dihydrofuran (II) are those predicted by the table of covalent radii (A., 1934, 350), viz., 1.43 and 1.54 Å., respectively. In furan (III) the C—O and C—C distances are 1.40±0.03 and 1.46±0.03 Å. if the C=C distance is assumed to be 1.35 Å., whilst in dioxadiene (IV) the C—O and C=O distances are 1.41±0.03 and 1.35±0.03 Å., respectively. The C—O—C angles are (I) 111±2°, (II) 110±3°, (III) 107±3°, and (IV) 116±4°. J. W. B.

Influence of intramolecular atomic motion on electron diffraction diagrams. P. Debye (*J. Chem. Physics*, 1941, **9**, 55—60).—The influence of at. vibrations and of free or hindered rotations of mol. groups on the scattering properties of mols. is discussed, and the radial distribution curve is calc. J. W. S.

Magnetic and thermal properties of crystalline copper sulphate at low temperatures. K. S. Krishnan (*Nature*, 1941, **147**, 87—88).—A discussion of recent results. L. S. T.

Dynamical determination of the elastic constants and their temperature coefficients for quartz. J. V. Atanasoff and P. J. Hart (*Physical Rev.*, 1941, [ii], **59**, 85—96).—A mathematical theory giving the relations between the elastic const. and the frequencies of piezoelectric vibration for an infinite homogeneous anisotropic plate is developed, and its adaptation to finite plates is examined. Experimental results show that the method of using high-order harmonics eliminates edge effects and leads to accurate data. The calc. elastic const. and their temp. coeffs. show a small unexplained divergence from classical theory. Observations for 0—80° are reported, and additional data give results up to the α - β transition point. N. M. B.

The C_{14} elastic constant for β -quartz. J. V. Atanasoff and E. Kammer (*Physical Rev.*, 1941, [ii], **59**, 97—99).—The method previously described (cf. preceding abstract) gives the val. 35.75×10^{10} dynes per sq. cm. This differs by a factor of ~ 2 from the only other available val., but is justified by a study of its behaviour in the range 0—650° and the consistency of the val. from different cuts from different crystals. N. M. B.

Plastic and allotropic forms of sulphur. H. F. Schaeffer and G. D. Palmer (*J. Chem. Educ.*, 1940, **17**, 473—475).—A review. L. S. T.

IV.—PHYSICAL PROPERTIES OF PURE SUBSTANCES.

Resistance measurements on very pure silver, molybdenum, palladium, and platinum in the temperature range 1.2—273° K. K. Steiner and E. Fünfer (*Actes VII Congr. int. Froid*, 1937, **1**, 388—397; *Chem. Zentr.*, 1938, ii, 3787).—The resistance (R) of specially purified specimens has been measured at nine temp. R is approx. $\propto T^4$ at 8—40° K., but with Ag and Pt, and probably with Mo and Pd, the exponent deviates to vals. < 4 . The R - T curves for Ag and Pt are similar to those of Meissner and Voigt (A., 1931, 292). A. J. E. W.

High-frequency resistance of superconducting tin. H. London (*Proc. Roy. Soc.*, 1940, **A**, **176**, 522—533).—The high-frequency resistance of Sn in the superconducting state ($T < 3.7^\circ$ K.) was measured at λ 20.5 cm. The resistance falls gradually as the temp. falls below the transition point in contrast with the sudden drop which occurs with d.c. The experimental results are in agreement with theory, which assumes the simultaneous presence of normal and superconducting electrons. In the normal state at low temp. ($T > 3.8^\circ$ K.) the conductivity for high frequencies is $<$ that for low frequencies. This result may be caused by the mean free path of the electrons becoming $<$ the penetration depth due to skin effect under the conditions of high conductivity and high frequency. G. D. P.

Decrease in resistance of constantan with a magnetic field at temperatures between 1° and 20° K. W. F. Giauque and J. W. Stout (*J. Amer. Chem. Soc.*, 1940, **62**, 3516).—The effect of a magnetic field on the resistance of constantan has been investigated at 1.47°, 4.29°, 10.67°, and 20.34° K. at each of the field strengths, $H = 850, 1600, 3000, 4100, \text{ and } 8300$ gauss. The resistance decreases with magnetic field strength, the change being $\propto H^n$, where n is slightly > 1 at low field strengths and slightly < 1 at higher fields. At the temp. of liquid air the change is $\propto H^2$. W. R. A.

Thermal data. XIII. Heat capacities and entropies of creatine hydrate, dl-citrulline, dl-ornithine, l-proline, and taurine. H. M. Huffman and S. W. Fox (*J. Amer. Chem. Soc.*, 1940, **62**, 3464—3465).— C_p vals. from 87° to 300° K. have been measured for creatine hydrate, dl-citrulline, dl-ornithine, l-proline, and taurine and from these data vals. of $S_{298.1}$ are computed and are, respectively, 56.0, 60.8, 46.2, 40.8, and 36.8 g.-cal. per degree per mol. W. R. A.

Simultaneous determination of adiabatic and isothermal elasticities. H. F. Ludloff (*J. Chem. Physics*, 1941, **9**, 119—120).—The effects of the frequency (ν) and type of vibration and the form of the sample on the adiabatic or isothermal character of a proper vibration are discussed. If all three dimensions of the sample are equal, isothermal vibrations occur only at $\nu\nu <$ the first proper ν or $> 10^{11}$ cycles per sec. If, however, one dimension is small relative to the others, vibrations antisymmetrical relative to the longitudinal mid-plane of the sample are isothermal at low ν , whilst the symmetrical vibrations are all adiabatic. This should permit the simultaneous study of the two elastic moduli through the temp. range of phase transitions. J. W. S.

Homologous series of alkanes. Density and its temperature coefficient. G. Calingaert, H. A. Beatty, R. C. Kuder, and G. W. Thomson (*Ind. Eng. Chem.*, 1940, **33**, 103—106; cf. A., 1936, 309).—Selected, smooth vals. of the temp. coeffs. of the density for normal and branched-chain alkanes are obtained from literature data. The mol. vols. of the n -alkanes from C_4H_{10} to $C_{20}H_{42}$ in the liquid state at 20° are expressed by: $V = 30.392 + 16.375n + 74.44/n^2$ ($n = \text{no. of C atoms}$). Selected literature vals. and calc. vals. of d^{20} are in close agreement. Mol. vols. at 20° in any given homologous series of branched-chain alkanes, with the possible exception of the initial member in each series, differ from the vals. of corresponding n -isomerides by a const. amount, characteristic of the series. The use of this alignment method to detect doubtful vals. of d^{20} in the literature is illustrated. A. T. P.

Entropy of fusion of argon. O. K. Rice (*J. Chem. Physics*, 1941, **9**, 121).—From the Debye theory, an expression is obtained for the complete partition function per atom for the thermal motion in liquid A at the m.p. Combining this relation with the observed vals. of the vol. change during fusion, X-ray data for the liquid, and the d of the solid at the m.p., it is shown that the co-ordination no. in the liquid is 10 (cf. A., 1940, I, 17) and the entropy of fusion is 3.5 assuming no disorder in the solid or 3.1 corr. for disorder, as compared with an experimental val. of 3.35 entropy units. J. W. S.

Stability of crystal lattices. V. Experimental evidence on recent theories of the equation of state and the melting of solids. R. Fürth (*Proc. Camb. Phil. Soc.*, 1941, **37**, 34—54).—A no. of general rules concerning the mechanical and thermal behaviour of solids can be derived from Born's new theory of thermodynamics and the melting of crystals. A summary of the theory is given. The laws of Grüneisen and Lindemann for the normal m.p. can be deduced from the theory, and the effects of pressure on m.p., and of pressure and temp. on compressibility and elasticity coeffs. predicted by the theory are in satisfactory agreement with experiment. The connexion between breaking and melting is discussed, and a thermodynamical theory of the phenomenon is developed. An equation connecting heat of fusion and heat of sublimation is deduced on the basis of the "theory of holes" in liquids. The relation is approx. satisfied by most elements. A. J. M.

Interatomic potential curve and the equation of state for argon. O. K. Rice (*J. Amer. Chem. Soc.*, 1941, **63**, 3—11).—The relationships between the interat. potential energy (U) curve and the properties of solid A have been investigated from 0° to m.p. and a $U-r^3$ curve is derived and compared with similar curves obtained by previous investigators. The effects of disorder (premelting) distribution of frequencies of the normal modes of vibration of the solid on its physical properties, and possible deviations from Debye theory, are considered. The new $U-r^3$ curve gives a val. for the second virial coeff. of A in good agreement with the experimental val. W. R. A.

Critical constants and van der Waals' equation. R. R. Evans (*Chem. and Ind.*, 1941, 90—91).—The relation derived by Copley (A., 1941, I, 78) has no theoretical significance. A. J. E. W.

Thermal conductivity of liquids. M. R. Rao (*J. Chem. Physics*, 1941, 9, 120—121).—Assuming a liquid to comprise a no. of linear harmonic oscillators, each vibrating with the same frequency about a displaced equilibrium position, and assuming that thermal energy is transmitted during the very brief period of contact between mols., an expression can be derived for the thermal conductivity (K) of a liquid. With the simplifying assumption that transmission of thermal energy between mols. occurs when the energy difference of the two mols. has a const. val., it follows that $K = Ae^{B/T}$, where A and B are consts., independent of temp. Consequences of this relation are discussed. J. W. S.

Adiabatic cooling [of air] consequent on the work done when it rises. F. Morán (*Anal. Fis. Quím.*, 1940, 36, 5—19).—Decrease of temp. of a rising column of air is due, not to expansion, but to adiabatic cooling, although the mathematical result is the same in either case. Expansion can occur without cooling if no work is done. F. R. G.

V.—SOLUTIONS AND MIXTURES (INCLUDING COLLOIDS).

Viscosities of aqueous solutions. G. S. Kasbekar (*J. Univ. Bombay*, 1940, 9, Part 3, 55—62).—The viscosities (η) of various aq. solutions of $ZnCl_2$, $Ca(CNS)_2$, $Zn(CNS)_2$, and H_3PO_4 have been determined by the Ostwald viscometer method. d^{25} vals. for the $Ca(CNS)_2$ and $Zn(CNS)_2$ solutions are also recorded. The variation of η with the molality (m) of the solution is represented satisfactorily by Arrhenius' empirical relation $\eta = A^m$, where A is a const. With $ZnCl_2$ and H_3PO_4 solutions the vals. of $(\eta - 1)/m$ pass through a min. J. W. S.

Experiment illustrating diffusion. J. H. Gardner (*J. Chem. Educ.*, 1940, 17, 494).—Gelatin (I) in a test-tube is covered by an equal vol. of (I) coloured by the addition of a small crystal of fuchsin (II). The coloured gel is covered with paraffin to prevent putrefaction. Diffusion of (II) into the lower layer of (I) becomes apparent in 1 hr. L. S. T.

Specific gravity of the ternary $CaO-Na_2O-SiO_2$ glasses. XVIII. Specific gravity [and viscosity] of the glasses at 1000—1350° by the Stokes method. S. Inoue and I. Sawai (*J. Soc. Chem. Ind. Japan*, 1940, 43, 325—328B).—Data on ρ and η for $CaO-Na_2O-SiO_2$ glasses at 1000—1350° are recorded. ρ is not a linear function of temp. At const. $[SiO_2]$ η increases with increasing $[CaO]$, and at const. $[CaO]$ or $[Na_2O]$, η increases with increasing $[SiO_2]$. F. J. G.

Application of X-rays to the study of alloys. H. Lipson (*Nature*, 1940, 146, 798—801).—A review. L. S. T.

Precipitation in copper-beryllium alloys. F. W. Jones and P. Leech (*J. Inst. Metals*, 1941, 67, 9—24).—Alloys of Cu with 2—2.6% of Be consist of $\alpha + \beta$ phases when quenched from $>600^\circ$; on reheating at 2° per min. the β phase disappears at $175-200^\circ$, but the γ phase cannot be detected microscopically or by X-rays below 350° . At 620° a heat absorption of 1.6 g.-cal. per g. takes place corresponding with the re-formation of β from $\alpha + \gamma$. Max. hardness is obtained by reheating at 380° , at which temp. pptn. of γ is practically complete. Sp. heat-temp. curves for alloys quenched from $600-840^\circ$ show either two or three min. or inflexions, suggesting that pptn. proceeds in several stages which overlap, but no evidence as to the nature of these can be obtained by X-ray examination. Crystals of β or γ do not seem to serve as nuclei for pptn. when quenched supersaturated α alloys are reheated. Pptn. occurs at temp. well below those expected, using normal vals. for the activation energy of diffusion; Becker's theory of nuclei formation does not explain this fact. A. R. P.

System platinum-mercury. I. N. Plaksin and N. A. Suvorovskaja (*J. Appl. Chem. Russ.*, 1940, 13, 677—685).—The temp.-composition curve suggests the compounds $PtHg$, decomp. at 159.1° , Pt_2Hg , decomp. at 236° , and Pt_3Hg , decomp. at 485.1° . The solubility of Pt in Hg rises from 0.02% at 17° to 1.2% at 172° . R. T.

Structure and properties of iron-nickel alloys.—See B., 1941, I, 107.

Some properties of quaternary alloy equilibrium diagrams. A. J. C. Wilson (*Proc. Camb. Phil. Soc.*, 1941, 37, 95—101).—The geometrical rules which must be obeyed by equilibrium

diagrams of quaternary alloys are considered. The properties of the regions of existence of one-, two-, three-, or four-phase systems are discussed. A. J. M.

Solubility of methyl chloride in certain solvents. J. G. Mamedaliev and A. Kuliev (*J. Appl. Chem. Russ.*, 1940, 13, 735—737).—The corr. solubilities of MeCl at 20° are: C_6H_6 , 47.23, CCl_4 , 37.56, $AcOH$ 36.79, $EtOH$ 34.70, H_2O 3.03 vols. of MeCl at n.t.p. per vol. of solvent. R. T.

Hydrogen bonding and the solubility of alcohols and amines in organic solvents. XIII. M. J. Copley, E. Ginsberg, G. F. Zellhoefer, and C. S. Marvel (*J. Amer. Chem. Soc.*, 1941, 63, 254—256; cf. A., 1940, I, 438).—Solubilities of numerous volatile amines and alcohols in non-volatile polyhydric alcohols, polyethylene glycols and amines, amides, esters, and ethers are recorded. High solubilities of alcohols in polyethylene amines and *tert.* amides and of amines in polyhydric alcohols indicate that the $O-H \leftarrow N$ is much stronger than the $O-H \leftarrow O$ linking. R. S. C.

Theory of adsorption of gases on solids when the potential energy varies continuously over the surface. A. R. Miller and J. K. Roberts (*Proc. Camb. Phil. Soc.*, 1941, 37, 82—94).—The theory of adsorption in which it is supposed that there is a definite no. of adsorption sites on a surface, and that there is a fixed interaction energy between two particles adsorbed on neighbouring sites, but a negligible interaction between particles further distant, is extended by making the model approach more nearly to an actual surface. A one-dimensional film is considered, in which the potential energy of a single adsorbed particle varies continuously and periodically with its position on the surface, and where there is a repulsive force between adsorbed particles varying with their distance apart according to an inverse power law. The variation of the heat of adsorption with the fraction of sites occupied is considered, and it is shown that there is much less difference between the behaviour of mobile and immobile films than is indicated by the fixed interaction model. A. J. M.

Adsorption of vapours at solid surfaces and change of surface electrical potential. A. A. Frost and V. R. Hurka (*J. Amer. Chem. Soc.*, 1940, 62, 3335—3340).—The change of surface electrical potential of paraffin, collodion, and $p-NH_2 \cdot C_6H_4 \cdot NO_2$ caused by adsorption of inorg. and org. vapours has been investigated by two different methods. The vac.-tube electrometer method gives direct qual. results; the vibrating electrode method proves more satisfactory and yields quant. observations of change of potential with v.p., the curves obtained being similar to adsorption isotherms. The potential changes are attributed to dipole orientation at the surface and it is suggested that symmetrical mols., such as CCl_4 and C_6H_6 , on adsorption acquire induced dipoles. The observed potential changes vary from 5 to 500 mv. W. R. A.

Dynamics of adsorption of acetylene by silica gel from oxygen-nitrogen mixtures. I. P. Ischkin and P. Z. Burbo (*J. Appl. Chem. Russ.*, 1940, 13, 1022—1027).— C_2H_2 is removed from its solutions in liquid O_2-N_2 by filtration through SiO_2 gel. The process is one of adsorption. R. T.

Adsorption of acetylene on selective adsorbents. S. Bresler (*Acta Physicochim. U.R.S.S.*, 1940, 12, 783—785).—The possibility of selective chemisorption of C_2H_2 on ketones of high mol. wt. has been investigated. $n-C_{15}H_{31} \cdot COMe$, if pptd. from an alkaline medium, readily takes up 1—1.8 mols. of C_2H_2 per mol., the sorption being largely reversible. The activity of the adsorbent slowly decreases on keeping, and more rapidly on warming. Specimens pptd. from acid media have only a very low activity, suggesting that the active adsorbents are in the enol form, and that the loss of activity on keeping is due to a change to the keto-form. F. J. G.

Structure of adsorption layers. A. Buzágh (*J. Hungarian Chem. Soc.*, 1940, I, No. 1, 3—4).—A new method is described for research on the structure of border phases between solids and liquids and for analysis of the nature and quantity of active forces regulating the stability or coagulation of colloid solutions. The method is also adapted for continuous measuring of the "breaking angle" (crit. angle at which the particles of a suspension deposited on a special wall of a container just fall away by slow overturning of the container), the sine of which angle is a measure of the adhesive force. Adsorption layers are found to be possibly >1 mol. thick. Experimental evidence is quoted of adhesion being due,

not to mass action, but to surface action based on the interaction of adsorption layers, and governed by the same rules as govern the formation, stability, and cessation of disperse systems. Experimental evidence is also quoted that adhesion of particles is determined by electric properties, viz., (a) thickness and electric charge of an electric double layer consisting of oriented dipoles, (b) orientation of mols. Further experiments are mentioned concerning the mechanism of coagulation of fibrous gels caused by dil. electrolyte solutions in emulsions of compounds of high mol. wt., especially proteins. It is inferred that fibre formation occurs, not at the isoelectric point where adhesion is max., but near this point, when the adhesive force is not yet strong enough to prevent free organisation of the particles. E. A.

Relationships between the adsorption isotherm and the spreading force. W. B. Innes and H. H. Rowley (*J. Physical Chem.*, 1941, **45**, 158—165).—Mathematical. Consideration of two methods of forming a film on a surface, by adsorption and by spreading from one part of the surface to another, both methods being reversible, leads to a relation between spreading force and adsorption isotherm data. A two-dimensional equation of state corresponding with the Langmuir adsorption isotherm gives a plot similar to that expected for a real two-dimensional gas. This equation of state is independent of the adsorption equilibrium const. in the Langmuir equation, indicating that where the latter equation applies, the equation of state is independent of attractive forces between adsorbent and adsorbate. C. R. H.

Internal surface of cellulosic materials. A. J. Stamm and M. A. Millett (*J. Physical Chem.*, 1941, **45**, 43—54).—Data for the selective adsorption of stearic acid (I) from org. solvents and of PhOH from H₂O by filter-paper and by cross-sections of sugar pine have been obtained. (I) is positively adsorbed from C₆H₆ solutions whereas the solvent is selectively adsorbed from solutions of (I) in EtOH and COMe₂. A polar solute, e.g., PhOH, when dissolved in a non-polar solvent is unable to enter the cell-wall structure. PhOH-H₂O solutions, however, are more readily adsorbed than H₂O alone. Vals. for the internal surface of cellulosic materials have been calc. from these data and from data for heats of swelling and adhesion tension. The internal surface of microscopically visible capillary structures calc. by various methods yields vals. of the same order of magnitude, viz., $\sim 2 \times 10^3$ sq. cm. per g., whereas the internal surfaces of swollen cell-wall structures are $\sim 3 \times 10^6$ sq. cm. per g. C. R. H.

Theoretical and experimental analysis of the capillary-rise method for measuring the surface tension of solutions of electrolytes. G. Jones and L. D. Frizzell (*J. Chem. Physics*, 1940, **8**, 986—997).—Langmuir's theory (A., 1939, I, 140) of the cause of the Jones-Ray effect (A., 1937, I, 126) is analysed and one of its premises is found to be inconsistent with experimental evidence that a solution-air interface is electrically charged. The apparent relative surface tensions of ThCl₄ solutions show normal behaviour over the concn. range 10^{-2} — 5×10^{-6} M., in spite of the fact that a max. exists in the ζ -potential-concn. curve. Also, contrary to Langmuir's theory, the addition of 10^{-6} M.-ThCl₄ does not eliminate the Jones-Ray effect with KCl solutions, and the capillary rise in distilled H₂O is independent of the CO₂ content. J. W. S.

Surface tension of different dilutions of Boys' soap solution. N. Ramlal and S. B. Nizami (*J. Osmania Univ.*, 1939, **7**, 16—18).—Surface tensions of 0—30% Na oleate solutions in 25% aq. glycerol, determined by a dynamic (ripple) method, agree with vals. obtained by Mahajan (A., 1931, 1366) using a static method. F. L. U.

States of monolayers. W. D. Harkins and E. Boyd (*J. Physical Chem.*, 1941, **45**, 20—43).—General phase diagrams for monolayers on a liquid subphase afford evidence for the existence of two and possibly three phases exhibiting η relations attributed in three dimensions to the liquid state, and also a gas and a liquid phase. The transition from one to another of these five phases, the nature of triple points, the relation between mol. dimensions and the phase of a monolayer, changes from two- to three-dimensional systems, the compressibility of monolayers, and kindred subjects are discussed theoretically. C. R. H.

State of monolayers adsorbed at the interface solid-aqueous solution. F. M. Fowkes and W. D. Harkins (*J. Amer. Chem. Soc.*, 1940, **62**, 3377—3386).—By means of an improved

apparatus (described) contact angles between a liquid and the plane surface of a solid have been measured using the principle of the tilting plate. A theory is presented by which the film pressure can be determined. Adsorbed films consisting of NH₂Bu^a, AcOH, Pr^aCO₂Na, Bu^aOH, Pr^aCO₂H, and EtCO₂H are two-dimensional imperfect gases on paraffin, stibnite, graphite, or talc. The areas of the films at the solid-liquid and liquid-vapour interfaces are practically identical. Pressure-area relationships and wetting characteristics of the films depend on the type of polar group in the mols. The effect of chain length is discussed. All the films are unimol. layers. W. R. A.

Thermodynamics of films: energy and entropy of extension and spreading of insoluble monolayers. W. D. Harkins, T. F. Young, and E. Boyd (*J. Chem. Physics*, 1940, **8**, 954—965; cf. A., 1939, I, 467).—Equations are given for the entropy increase, heat absorption, heat content increase, and internal energy increase during the expansion of insol. monolayers. The two-dimensional phases are classified as gas, liquid expanded (L_1), intermediate, liquid condensed (L_2), and solid. They differ from three-dimensional systems in that the mean mol. distances can be increased considerably without destruction of the liquid state. The change from solid to L_2 exhibits zero latent heat, and hence is a phase change of the second order. The increase in heat content when the monolayer of C₁₁H₂₃CO₂H (I) spreads over unit area is ~ 400 ergs per sq. cm. for a solid film, zero for the L_2 phase, rises gradually in the intermediate phase to an almost const. val. of 300 ergs per sq. cm., and decreases to ~ 50 ergs per sq. cm. in the L_1 phase. The heat content increase during the spreading of 1 g.-mol. of (I) at 18° is ~ 0.2 kg.-cal. for the solid phase, 8.3 kg.-cal. for the intermediate phase, and very small for the L_1 phase. At 25° the vals. for the intermediate and L_1 phases are ~ 4.6 and 1.0 kg.-cal., respectively. J. W. S.

Unimolecular films of saccharase [invertase]. H. Sobotka and E. Bloch (*J. Physical Chem.*, 1941, **45**, 9—19).—Experimental methods for the prep. and measurement of the thickness, area, and activity of films of highly purified yeast invertase (I) are described. Stable films on H₂O are possible when salts of Al, Fe, La, Zr, and especially Ce and Th are present. Built-up (I) films >45 Å. thick retain the full enzymic activity of the material from which the film has been made. It is possible that fractionation takes place to form an inactive fraction which is sol. and an active fraction which concentrates in the film layers. Wt. for wt. this second fraction may be more active than the original (I). C. R. H.

Laminar systems. XIV. Mechanism of the formation of thin films of copper sulphide on the surface of solutions. S. G. Mokruschin, V. A. Kosheurova, and I. A. Blum (*Kolloid. Zhurn.*, 1940, **6**, 119—127; cf. A., 1941, I, 39, 45).—Films of Cu₂S (or CuS) produced by gaseous H₂S on the surface of Cu salt solutions consist from the beginning of colloid particles as distinct from unimol. layers. When the duration t of the reaction increases the film becomes denser but not thicker. This is shown by measuring the area-pressure curve for films at various t . The shorter is t , the more compression is necessary to reach the pressure of 17 dynes per cm., but at this pressure the films crumble irrespectively of t ; their thickness is, therefore, independent of t . The mass of the film $S = S_0 kt / (1 + kt)$, S_0 and k being consts. This equation indicates that the rate of reaction is determined by that of the dissolution of H₂S. The final thickness is for 0.8N-, 0.08N-, and 0.008N-Cu(NO₃)₂, 44, 80, and 138 Å., respectively, and for 0.7N- and 0.07N-CuSO₄ 65 and 109 Å., since the particle size increases with dilution. J. J. B.

Statistical theory of duplex films. L. S. K. Feng and W. Band (*J. Chem. Physics*, 1940, **8**, 977—980; cf. A., 1940, I, 159, 209).—The dissociation treatment of condensing systems is applied to duplex films, and by making certain simple assumptions agreement is obtained with existing data on the saturated state of myristic acid films (A., 1926, 348; 1939, I, 467). J. W. S.

Structure of multilayers. I. G. Knott, J. H. Schulman, and A. F. Wells (*Proc. Roy. Soc.*, 1940, **A**, 176, 534—542).—Multilayers of long-chain compounds deposited on a transparent base have been examined microscopically and by X-rays. An X-ray photograph of a stationary multilayer of Et stearate is identical with that obtained by rotating a single crystal of β -Et stearate about the long axis of the cell.

The experiments show that the multilayer consists of micro-crystals all oriented with one axis normal to the surface on which the multilayer is deposited. The single crystals grow right through the layer ~ 1000 mols. thick. G. D. P.

Nature of foam. VII. Foam formation of mixed aqueous solutions of saponin and ethyl alcohol. T. Sasaki (*Bull. Chem. Soc. Japan*, 1940, 15, 449—454; cf. A., 1939, I, 520).—The persistence of foam produced in aq.-EtOH solutions of saponin (0.009085 and 0.001820 g. per l.) shows a max. at [EtOH] ~ 0.257 g.-mol. per l. It decreases rapidly with increasing [EtOH] > 0.77 g.-mol. per l. It is assumed that at lower [EtOH] the foam production and stabilisation are due to the saponin and EtOH, respectively, but that at higher [EtOH] both actions are due to EtOH, owing either to its preferential adsorption in the foam film or to its causing dehydration of the saponin particles. The effects noted are compared and contrasted with those observed with hydrophilic and hydrophobic colloids. J. W. S.

Foam stability. Foam produced in aqueous extract of the root of *Acanthophyllum paniculatum*, Rgl. K. N. Arbuzov (*Kolloid Shurn.*, 1940, 6, 63—69).—Roots of *Acanthophyllum* (grown in Turkestan) contain 22% of saponin (I) and 4% of sapogenin. The foaming capacity of an aq. extract from dried root is almost identical with that of purified (I) at an equal concn. The rate of draining of the foam is high (e.g., 10% per min.) at low concns. (0.25%), and low (e.g., 1% per min.) at high concns. (5%); for a given concn. it shows a max. when 30—50% of the foam has drained away. The root extract may be used industrially instead of pure (I). J. J. B.

Red gold sols. A. L. Elder (*J. Chem. Educ.*, 1940, 17, 512).—Borovskaja's method of prep. is preferred to that of Zsigmondy. 1 c.c. of 1% AuCl_3 is added to 95 c.c. of H_2O , and heated to 90—95°. 2.5—5 c.c. of 1% Na citrate (I) are added, and the solution is boiled for 1—1.5 min. A light cherry-red sol is obtained. Colour can be varied by changing the concn. of (I) and time of boiling. L. S. T.

General and electrochemical properties of Raffo's sulphur sols. A. Charin (*Acta Physicochim. U.R.S.S.*, 1940, 12, 703—721).—A no. of properties of the S sols obtained by addition of $\text{Na}_2\text{S}_2\text{O}_3$ to H_2SO_4 have been studied. The micelles contain considerable amounts of polythionate ions, but the intermicellar liquid is almost free from these at first. On keeping, the adsorbed polythionate ions are slowly liberated, this being accompanied by crystallisation of the S. Electro-metric titration curves with HCl, BaCl_2 , and MgCl_2 show that cation exchange occurs in the outer layer, with quant. equivalence. The sols have high vals. of ζ , which are markedly diminished by addition of BaCl_2 , owing to the strong adsorption of Ba^{++} ions, but less so by addition of HCl or NaCl. This electric charge is the main stabilising factor, but the disappearance of cataphoretic mobility before complete coagulation shows that hydration also plays a part. F. J. G.

Ion antagonism in Raffo's sulphur sols. A. Charin (*Acta Physicochim. U.R.S.S.*, 1940, 12, 722—736).—It has been shown by direct analysis that adsorption of Cl^- and SO_4^{--} ions by these sols (cf. preceding abstract) does not occur. HCl diminishes the adsorption of Ba^{++} ions, and still more that of Mg^{++} ions, and this is parallel to the antagonistic effect of HCl on the coagulation of the sols by MgCl_2 and BaCl_2 . Cation exchange plays an important part in the coagulation by BaCl_2 in the presence of small concn. of HCl or NaCl, but increase of [NaCl], or to a smaller extent of [HCl], diminishes the importance of this. Addition of EtOH or COME_2 renders the sols sensitive to NaCl, but not to HCl. The greater antagonistic effect of HCl as compared with NaCl is ascribed to its greater hindering effect on the adsorption of bivalent ions, to a stronger binding of H_2O mols. in the micelle in presence of H^+ , and to a weaker dehydrating influence of HCl. F. J. G.

Chromium hydroxide sols. D. S. Datar and M. Qureshi (*J. Osmania Univ.*, 1939, 7, 5—11).—Changes in $\text{Cr}(\text{OH})_3$ sols caused by exposure to ultra-violet light were studied by measuring the extinction coeff. (ϵ) and electrical conductivity (κ). Short exposures lead to a decrease in p_H and an increase in κ , both of which effects are reversed by long exposures; ϵ vals. are increased. This behaviour may be explained by an increase in the hydrolysis of CrCl_3 adsorbed on the micelle, followed by an increase in particle size. Decrease of κ after

long exposure is due to the photochemical destruction of the HCl liberated by hydrolysis. F. L. U.

Colloidal clays. II. E. A. Hauser and D. S. Le Beau (*J. Physical Chem.*, 1941, 45, 54—65; cf. A., 1939, I, 23).—The cataphoretic velocity (v), η , and apparent ρ of purified, colloidal monodisperse fractions of Wyoming bentonite (I) have been determined. For concns. $< 0.5\%$ v is const. for a given particle size and increases with decreasing particle size. At higher concns. v decreases, the decrease being most marked with the smallest particle size fractions. This decrease in v occurs when the average distance between the particles is ~ 5.5 times the apparent diameter of the particles. ρ of (I) dispersed in H_2O is lower for extreme dilutions and higher for concns. $> 0.5\%$ than that of dry (I). The smaller the particles are the lower is the concn. needed to exceed ρ for the dry (I). At low concns. H_2O causes swelling of the crystal lattice but as the concn. is increased a compression of the ionic atm. occurs which is synonymous with a decrease in swelling and an increase in the ρ of adsorbed H_2O . This in turn accounts for an increase in the apparent ρ of (I). In dil. solutions η is independent of particle size, but at higher concns. ($> 0.5\%$) η increases with concn. and with increase in particle size. The type of H_2O -adsorption in or around the particles and the gelation of systems of very low concn. are discussed. C. R. H.

Hydration of clay in water vapour and in liquid water. V. S. Scharov (*Kolloid. Shurn.*, 1940, 6, 3—14).—The v.p. of wet clay is already equal to that of H_2O at low H_2O contents, and the thermodynamical rule of a strict interdependence between H_2O content and v.p. breaks down for hysteresis of drying, syneresis, etc. Thermodynamic equations assuming a complete equilibrium should not be applied to H_2O -clay mixtures. J. J. B.

Influence of hydrophilic colloids on the rate of dissolution of metal oxides in acids. J. N. Berg and M. N. Vischniakov (*Kolloid. Shurn.*, 1940, 6, 71—78).—The rate of dissolution of CuO is reduced by colloids. The effect in N-HCl decreases in the order gelatin (I) $>$ agar (II) $>$ starch (III) $>$ gum arabic (IV), and in $\text{N-H}_2\text{SO}_4$ in the order (I) $>$ (IV) $>$ (II) $>$ (III); the effect is stronger in HCl than in H_2SO_4 . The effect on the rate of dissolution of $\text{Fe}(\text{OH})_3$ in HCl is small; it decreases in the order (I) $>$ (III) $>$ (II) $>$ (IV). It increases with the amount of colloid added, indicating an adsorption of the colloid by oxides. J. J. B.

Ageing of sols and gels. VIII. Alcosols of mercury acetamide. E. M. Preis (*Kolloid. Shurn.*, 1940, 6, 57—62; cf. A., 1941, I, 11).—Gelation of EtOH solutions of $(\text{NHAc})_2\text{Hg}$ (I) can be caused not only by nitrates etc. but also by chlorides, iodides, etc. which in aq. solution decompose (I). Salt concns. needed to induce gelation increase with the H_2O content of EtOH; e.g., for the three solutions 0.3N-(I) + 0.008N- NaNO_3 in abs. EtOH, 0.3N-(I) + 0.1N- NaNO_3 in 96% EtOH, and 0.3N-(I) + 0.1N- NaNO_3 in 75% EtOH, the gelation time is a few sec., 2 min., and 45 min., respectively; in 70% EtOH the mixture 0.3N-(I) + 0.1N- NaNO_3 does not gel at all. J. J. B.

Interaction of cellulose acetate with organic solvents. T. A. Granskaja and A. I. Kaliteevskaja (*Kolloid. Shurn.*, 1940, 6, 145—152).—Sorption by cellulose acetate (I) of C_6H_6 from mixtures of C_6H_6 and light petroleum (II) (b.p. 47—50°), and that of PhMe from PhMe-(II) mixtures, increases when the concn. of (II) decreases. The solubility of (I) in these mixtures is insignificant. The heat of sorption (wetting) rises from 0.42 cal. per g. in (II) first rapidly and then slowly towards the val. of 8.8 cal. per g. for C_6H_6 . It is concluded that the "solvation layer" is multimol. and the intensity of attraction is highest near the solid surface. J. J. B.

Polymerides. I. Highly elastic deformation in polymerides. A. P. Alexandrov and J. S. Lazurkin. **II. Dynamic method for the study of elastic materials.** J. S. Lazurkin. **III. Technique of mechanical testing of soft and hard rubber and plastics.** G. Gurevitsch and P. Kobeko (*Acta Physicochim. U.R.S.S.*, 1940, 12, 647—668, 669—680, 681—702).—I. Highly elastic deformation involves re-orientation of the mols. under the imposed stress, and may be considered kinetically as a relaxation process associated with a relaxation time $\tau = Ae^{U/kT}$ where U is the potential barrier between the two configurations. The total deformation after time t is $D = D_{el.} + D_{h.c.} (1 - e^{-t/\tau})$, where $D_{el.}$ is the ordinary

elastic deformation and $D_{h,el,\infty}$ the final equilibrium val. of the highly elastic deformation. For a periodic stress of frequency ω this gives $D = D_{el} + D_{h,el,\infty} / (1 + i\omega\tau) = D_{el} + D' + D''$, D' and D'' being real and imaginary components. Experimental results for rubber and various high polymerides show a qual. agreement with this expression, at $\omega = 1 - 1000$ and $T = -80^\circ$ to 200° .

II. In view of the importance of time and temp. with regard to highly elastic deformation (see above) it is desirable to study the response of plastic materials to periodic stresses over a wide range of frequency and temp. An apparatus for this purpose is described. At room temp. the deformation of rubber is almost independent of ω ($\omega > 2000 \text{ min.}^{-1}$). The temp. at which the deformation becomes half that at room temp. depends on ω , according to $\log t_0/t = B(1/T_0 - 1/T)$ where $t = 1/\omega$.

III. The total elastic deformation of rubber subjected to a static stress for a limited time decreases with increasing degree of vulcanisation, but the initial deformation is almost unchanged. The usual methods for testing the mechanical properties of plastic materials fail to allow for the influence of time and temp. on the highly elastic deformation.

F. J. G.

Lyophilic system albumin-pectin. A. P. Saltschinkin and F. L. Movshovitsch (*Kolloid. Shurn.*, 1940, 6, 15—27).—The ovalbumin (I) used had 0.2% of ash, p_H 6, and a negative cataphoretic mobility; the pectin (II), prepared from sugar beet, had 3.5% of ash, p_H 5, and was positive. Mixtures of (I) and (II) in H_2O were coagulated by warming for 5 min. at 60° if they contained 2—14 parts of (II) for 100 parts of (I); this was presumably due to the acid reaction of (II). The osmotic pressure of a mixture of 5 g. of (I) + 5 g. of (II) per l. is < that of 5 g. of (II) alone; this indicates formation of a complex between (I) and (II). The viscosity of (I) + (II) + H_2O , or of (I) + (II) + glucose + H_2O , or of (I) + (II) + starch + H_2O is raised by a short heating at 60° ; this may be due to a complex formation or to a denaturation of (II) which also increases η . Electrical conductivity of (I)-(II) mixtures is additive. Some mixtures of (I) + (II) + glucose + H_2O gel after heating at 70° .

J. J. B.

X-Ray examination of the structure of gelatin. I. I. Sokolov (*Kolloid. Shurn.*, 1940, 6, 99—108).—Gelatin boiled with H_2O for 3 hr. shows only an "amorphous circle"; the spacings 2.8 and 11 Å. disappear almost completely. Further heating for 45 hr. has no additional effect. Neither stretching of, nor addition of electrolytes to, this thermolysed gelatin affects its X-ray pattern. Treatment with CH_2O gives three spacings (2.79, 3.92, and 12.45 Å.) but they disappear on washing with H_2O . Ordinary gelatin when treated with CH_2O or electrolytes gives distinct spacings, e.g., with H_2SO_4 2.91, 3.01, 4.26, 7.35, and 10.55 Å., and with $NaOH$ 2.79 and 3.00 Å. (and two "amorphous rings"). AcOH has no effect on the pattern of ordinary gelatin.

J. J. B.

Mutual coagulation of colloidal solutions. IV. Interaction of zinc ferrocyanide and (a) ferric hydroxide, (b) thorium hydroxide, and (c) ceric hydroxide. P. M. Barve, V. C. Vora, and B. N. Desai (*J. Univ. Bombay*, 1940, 9, Part 3, 69—75; cf. A., 1939, I, 255).—As in systems investigated previously, the width of the zone of mutual coagulation of $Fe(OH)_3$, $Th(OH)_4$, and $Ce(OH)_4$ sols by $Zn_2Fe(CN)_6$ sols is a min. when the charge on the particles is a max. The min. val. of the width of the zone in different pairs appears to depend also on the hydration of the hydroxide particles.

J. W. S.

Rhythmic precipitation. T. Moeller (*J. Chem. Educ.*, 1940, 17, 519).—Banded structures of $Co(OH)_2$ in gelatin are illustrated. 5 ml. of 0.1M- $Co(NO_3)_2$ are added to 30 ml. of hot 10% gelatin in a test-tube; after setting, the gel is covered with 10 ml. of 0.2M-aq. NH_3 , and set aside.

L. S. T.

VI.—KINETIC THEORY. THERMODYNAMICS.

Equilibrium constant equation. W. A. Dow (*J. Chem. Educ.*, 1940, 17, 439—440).—A theoretical demonstration.

L. S. T.

Ethane-ethylene-hydrogen equilibrium. E. A. Guggenheim (*Trans. Faraday Soc.*, 1941, 37, 97—105).—The equilibrium const. K_p for the reaction $C_2H_4 + H_2 \rightleftharpoons C_2H_6$ is calc. by the methods of statistical mechanics from spectroscopic and thermal data. The calc. vals. agree completely with

3 out of 4 sets of experimental data over the range 673 — 973° K. Formulæ are given for K_p over the same range.

F. L. U.

Effect of solvation on the dissociation of acetone cyanohydrin. T. D. Stewart and B. J. Fontana (*J. Amer. Chem. Soc.*, 1940, 62, 3281—3285).—The dissociation $OH\cdot CMe_2\cdot CN$ (I) \rightleftharpoons $COMe_2 + HCN$ is catalysed by amines in all solvents. The reaction is immeasurably rapid in H_2O and the lower alcohols, measurable in Bu^oOH , CCl_4 , C_6H_6 , and $CHCl_3$, and extremely slow in dioxan. In the presence of amine, the degree of dissociation is (a) increased in H_2O because of possible formation of an amine-HCN complex (II), (b) totally unaffected in nine different alcohols for which there is little evidence for the formation of (II), and (c) decreased in CCl_4 , C_6H_6 , $CHCl_3$, and dioxan, probably owing to formation of a cyanohydrin-amine complex which more than compensates for any formation of (II) (cf. A., 1938, I, 81). The pure solvents with or without a trace of catalyst affect the rates and equilibria of dissociation in a manner which can be correlated with their capacities to form H bond complexes and to act as proton donors. The heats of dissociation of (I) in H_2O , $EtOH$, C_6H_6 , and $CHCl_3$ are calc. and vary from 8400 to 10,400 g.-cal. per mol.

W. R. A.

Constitution of alkaline-earth aluminate solutions. G. Maekawa and T. Arimori (*J. Soc. Chem. Ind. Japan*, 1940, 43, 315b).—Vals. of p_H for Ca aluminate solutions have been determined, and compared with those for solutions of $Ca(OH)_2$ so as to find the concn. of free $Ca(OH)_2$. In this way the ratio (combined CaO)/ Al_2O_3 is shown to be ~ 1 , so that the solutions contain salts of $HAIO_2$. Similar results were obtained for Sr and Ba aluminate solutions.

F. J. G.

Dissociation constant of hypochlorous acid. G. Holst (*Svensk Kem. Tidsskr.*, 1940, 52, 258—261).—The p_H of chloride-free $NaOH$ - $HOCl$ mixtures has been determined at 25° with the glass electrode, $[HOCl]$ being determined by $I-Na_2S_2O_8$. Const. vals. of K are calc. for the p_H range 4—9, giving $K_{25} = 6.8 \times 10^{-8}$.

M. H. M. A.

Thermodynamic study of bivalent metal halides in aqueous solution. VII. Activity coefficient of barium bromide at 25° . R. A. Robinson (*Trans. Faraday Soc.*, 1941, 37, 82—84; cf. A., 1940, I, 359).—Osmotic and activity coeffs. determined by the isopiestic method are tabulated for $BaBr_2$ over the range 0.1—2.4M. The γ -concn. curve is considerably higher than that for $BaCl_2$, and no reversal in order of the chloride and bromide occurs as it does with Rb and Cs salts.

F. L. U.

Physicochemical studies on the alkali carbonates. II. Calculation of activity coefficients of sodium and potassium carbonates in aqueous solution. L. Lortie and P. Demers (*Canad. J. Res.*, 1940, 18, B, 373—385).—The usual equation for calculating the mean activity coeff. (γ) of an electrolyte from the depression of the f.p. (θ) has been modified so as to take account of the variation of the no. (ν) of ions per mol. resulting from hydrolysis or from secondary ionisation; the modification requires the assumption that the individual activity coeffs. of the ions are all equal. The modified equation is $\log \gamma_\theta = -j/2.3026 - \int_0^M j d \log \nu M + b \int_0^M (\theta/\nu M) d\theta$, where $M = \text{concn.}$, $b = 0.00025$, $j = 1 - \theta/\nu\lambda M$, and $\lambda = 1.858$ and where ν is a variable function of M and θ . Using this equation, vals. of γ for K_2CO_3 and Na_2CO_3 have been computed. At each concn. γ for K_2CO_3 is $>$ for Na_2CO_3 . At high dilution the curves approach the limiting law for uni-univalent rather than that for uni-bivalent salts.

F. J. G.

Changes in chemical equilibria in liquid interfaces. G. J. Szasz (*J. Amer. Chem. Soc.*, 1940, 62, 3520—3521).—An unsuccessful attempt has been made to explain the colour changes produced when an aq. solution of a dye is shaken with equal vols. of an immiscible liquid (cf. Deutsch, A., 1928, 1183). Various concns. of dye were employed at a given p_H and the concn. at which the most pronounced colour change occurred has been determined for 5 dyes. Me-violet in 0.1N-HCl changes from blue to purple. Tropæoline OO gives a distinct colour change in the foam at p_H 2.28, but not in the liquid phases. Data are given for malachite-green base in 0.4N-HCl, brilliant-green base in 0.25N-HCl, bromothymol-blue in H_2O , thymolsulphonphthalein in 0.0016N-HCl, and rhodamine O in C_6H_6 .

W. R. A.

Iodine monochloride. III. Systems iodine monochloride-acetic acid and iodine monochloride-carbon tetrachloride. J. Cornog and L. E. Olson (*J. Amer. Chem. Soc.*, 1940, **62**, 3328—3330).—The ICl-AcOH system is of the simple binary type with a eutectic at -35° containing 60 mol.-% of AcOH. ICl-CCl₄ forms a series of solid solutions. The liquidus curve is S-shaped. A eutectic point occurs at -26.4° and of 98.2 mol.-% of CCl₄ between solid solutions and another solid phase of undetermined composition. A metastable double layer liquid system is also found with crit. temp. $\sim 14^\circ$. The f.p. of ICl is 27.3° , i.e., $0.1^\circ >$ the accepted val.

W. R. A.

B.p.-composition diagram of immiscible and partly miscible liquid systems. M. Randall and W. Avila (*J. Chem. Educ.*, 1940, **17**, 536—537).—Diagrams for the systems C₆H₆-H₂O and NH₂Ph-H₂O are reproduced and discussed.

L. S. T.

Solubility product. Demonstration introducing the common ion effect and formation of complex ions. S. Zuffanti (*J. Chem. Educ.*, 1940, **17**, 433).—The use of AgOAc for this purpose is described.

L. S. T.

Effect on the solubility of precipitates of ions of the same charge in absence of a common ion. R. N. Golovati (*J. Appl. Chem. Russ.*, 1940, **13**, 586—591).—At 18 – 20° the solubility of PbI₂ is min. in 0.01N-KI, and is raised by KNO₃ or Ca(NO₃)₂, to an extent \propto their concn.; at the same time the [KI] at which solubility is least rises. Analogous results are obtained for the systems PbF₂-KF-KNO₃ and PbSO₄-K₂SO₄-KNO₃. The solubility of CaSO₄ is min. in 0.08N-K₂SO₄; in presence of 0.01–0.1N-HNO₃ it is higher, but falls with increasing [K₂SO₄], whilst in 0.1N-KOH it rises. The solubility of PbSO₄ is least at p_H 7; it falls with increasing [K₂SO₄] at $p_H < 7$, and rises at $p_H > 7$. The effect of a common ion is to depress solubility in absence of complex formation; where complexes are formed the action of salts not having a common ion is unpredictable, and depends largely on the properties of the complex.

R. T.

Solubility of salts in acids. P. A. Epik (*J. Appl. Chem. Russ.*, 1940, **13**, 857—865).—Tananaev's formulæ (A., 1937, I, 135) are based on erroneous assumptions, and are not valid. Those of Babko (A., 1936, 41) are applicable to appropriate cases. Formulæ for calculation of solubility of ppts. of the type M_mA_n, in presence and absence of excess of H, M, or A ions, are derived.

R. T.

Ternary systems ZnSO₄-H₂SO₄-H₂O from -5° to 70° and ZnO-SO₃-H₂O at 25° . L. C. Copeland and O. A. Short (*J. Amer. Chem. Soc.*, 1940, **62**, 3285—3291).—The system ZnSO₄-H₂SO₄-H₂O has been investigated over the temp. range -5° to 70° and from 0 to 60% H₂SO₄, and at 25° up to 97% H₂SO₄. Trilinear plots at 15° , 25° , and 45° are presented. A three-dimensional model over the temp. range -4.5° to 65° is given, the projection of the model on the 0% H₂SO₄ face showing the solubility of ZnSO₄ in H₂O and the variation of the four-phase systems (two solid, one liquid, and one vapour) with temp. By extrapolation it is shown that at 21° a quintuple point exists where ZnSO₄·xH₂O (x = 7, 6, and 1) are in equilibrium with saturated ZnSO₄ solution (ZnSO₄ 21.5%, H₂SO₄ 23.5%) and vapour. Isothermal invariant points for ZnSO₄·7H₂O = ZnSO₄·6H₂O + H₂O and ZnSO₄·6H₂O = ZnSO₄ + 5H₂O exist at 30° and 60° , respectively, the data for 21° and 39° being substantiated by v.p. and decomp. pressure measurements. At 25° and up to 97% H₂SO₄ anhyd. ZnSO₄ exists and possibly ZnSO₄·H₂SO₄. The study of the system ZnO-SO₃-H₂O at 25° indicates that the solid phase in equilibrium with the ZnSO₄ solution is a basic salt and is represented as 3Zn(OH)₂·ZnSO₄·4H₂O. The results obtained are compared with existing data.

W. R. A.

Sulphuric acid treatment of phosphates. IV. System CaSO₄-H₃PO₄-H₂O. A. A. Taperova (*J. Appl. Chem. Russ.*, 1940, **13**, 643—652).—At 25° the stability of various cryst. forms of CaSO₄ varies according to the [H₃PO₄], in the orders CaSO₄·0.5H₂O (I) < anhydrite (II) < gypsum (III) at [P₂O₅] < 33.75%, (I) < (III) < (II) at [P₂O₅] 33.75–49%, and (III) < (I) < (II) at [P₂O₅] > 49%. At 80° (II) is the sole stable phase.

R. T.

Bunsen's salt. H. Irving and G. W. Chery (*J.C.S.*, 1941, 25—30).—The only double compound occurring in the system NH₄Cl-(NH₄)₂Fe(CN)₆-H₂O at 25° or 40° is Bunsen's salt, 2NH₄Cl·(NH₄)₂Fe(CN)₆ (I). The existence of a tri-

hydrate (Hözl, *Sitzungsber. Akad. Wien*, 1928, **137**, IIb, 1110) could not be confirmed. The grounds for Hözl's formulation of (I) as containing 8-covalent Fe are false, as the defects which he observed in the linearity of the conductivity with the mol. ratio in this system are predicted on general grounds. X-Ray examination indicates that the hexagonal unit cell of (I) has a_0 9.24, c_0 18.92 Å. The Fe-Cl distance is ~ 6 Å., thus precluding the possibility of a covalent link between these atoms.

J. W. S.

Carbamide. IV. System carbamide-gypsum-water. W. Sakai (*J. Soc. Chem. Ind. Japan*, 1940, **43**, 318—319B).—When gypsum is heated at 80° with CO(NH₂)₂ (I), the yield of CaSO₄·4(I) increases with increasing humidity, the presence of adsorbed H₂O being necessary for reaction. The 25° and 30° isotherms of the system CaSO₄-(I)-H₂O are given. At 30° a solution in equilibrium with CaSO₄·4(I) is nearly saturated with (I), so that to prepare CaSO₄·4(I) through the solution phase it is necessary to cool a solution saturated at a higher temp.

F. J. G.

Calorimetric investigations of organic reactions. II. A new calorimeter. Mutarotation of α - and β -D-glucose. J. M. Sturtevant (*J. Physical Chem.*, 1941, **45**, 127—147).—An adiabatic calorimeter particularly suitable for heat measurements in very rapid reactions and for reactions where the heat changes are slight is described. Errors in temp. measurement and in timing, and errors due to lag and other causes, are discussed. The use of the instrument in the measurement of the mutarotation of α - and β -D-glucose at 25° and 35° has shown that the heat change accompanying α (solid) \rightarrow β (solid) is 4874 and 4955 joules per mol. at the two temp. respectively, the heat change vals. for each step at the same temp. being α (solid) \rightarrow α (aq.) 10,716, 12,222; α (aq.) \rightarrow β (aq.) -1162, -1282; β (aq.) \rightarrow β (solid) -4680, -6015 joules per mol. The ratio of the two equilibrium consts. $K_{35}/K_{25} = 1.595/1.677 = 0.949$. The theoretical val. for the ratio is 3.7% higher, a discrepancy sufficiently large to suggest that additional forms of glucose are involved. The data of other investigators support this view.

C. R. H.

Heats of dilution of amino-acids. J. M. Sturtevant (*J. Amer. Chem. Soc.*, 1940, **62**, 3519—3520).—An aq. solution of an NH₂-acid contains only zwitterions if the solution is conc. On dilution some zwitterions will change to positive and negative ions and H₂O will dissociate. The thermal effects thus produced should be subtracted from the observed heat of dilution of NH₂-acids in order to obtain the true heat of dilution of zwitterions. Equations are developed which, in conjunction with data for glycine, yield a val. of 20 joules per mol. for the ionisation heat effect, of which ~ 15 joules per mol. are accounted for in changes occurring between 10^{-2} and 10^{-4} M.

W. R. A.

Entropy of dilution of strong electrolytes in aqueous solutions. H. S. Frank and A. L. Robinson (*J. Chem. Physics*, 1940, **8**, 933—938).—The relative partial mol. entropy of H₂O in aq. solutions of various salts is calc. from the relative partial mol. heat content of the H₂O and its activity, and is correlated with changes in the structure of H₂O in the solutions. Cations of small radii and ions capable of forming H-bonds with the H₂O (H₃O⁺, OH⁻, and NH₄⁺) stabilise the H₂O structure, whilst large ions and ions of non-spherical and non-tetrahedral shapes have the reverse effect. In dil. solution the entropy of dilution depends largely on the ionic strength. In all cases deviations from the Debye-Hückel limiting law are positive.

J. W. S.

VII.—ELECTROCHEMISTRY.

Sign of electrode potential. C. S. Hoyt (*J. Chem. Educ.*, 1940, **17**, 530—532).—A convention for the sign of the potential of a galvanic cell based on free energy changes at the electrodes is presented. It is independent of the direction of current flow, and applies uniformly to all cases. Examples of its application are quoted.

L. S. T.

Potential of the Yb^{III}-Yb^{II} electrode. G. C. Walters and D. W. Pearce (*J. Amer. Chem. Soc.*, 1940, **62**, 3330—3332).—Aq. Yb(OAc)₃ was reduced electrolytically to the extent of $\sim 82\%$ and the product was used in the cell Pt|Yb^{III}, Yb^{II}; AcOH, N-KCl|N-KCl|N-KCl, Hg₂Cl₂|Hg, the e.m.f. of which was measured at different Yb^{III}/Yb^{II} ratios. The oxidation-reduction potential (E_0) is 0.578 v., a val. high compared with

0.43 v. for E_0 of $\text{Eu}^{III}-\text{Eu}^{II}$ (cf. McCoy, A., 1936, 1347). The lanthanide contraction creates greater stability in atoms in the normal trivalent state and is reflected in the magnitude of E_0 . It is predicted that Tm^{III} will be more unstable than Sm^{III} which will be more unstable than Yb^{III} or, in other words, E_0 for $\text{Tm}^{III}-\text{Tm}^{II} > \text{Sm}^{III}-\text{Sm}^{II} > \text{Yb}^{III}-\text{Yb}^{II}$.

W. R. A.
Mechanism of the glass electrode. G. Haugaard (*J. Physical Chem.*, 1941, 45, 148—157).—Conductivity experiments with glass electrodes have been made in conditions under which the electrodes normally operate. Na^+ are quantitatively responsible for the transference. They are displaced by H^+ which have a lower conductance. The potential of new glass surfaces in H_2O decreases with time, the val. at a given time having a linear relation to the log of the amount of H^+ adsorbed per unit area. The slope of the curve has a val. close to the val., 59.1 mv. at 25°, of the factor $RT/F \log e$ in the Nernst equation. H^+ adsorbed in the glass appear to be solvated to the extent of 0.5 mol. of H_2O per H^+ . Glass takes up both H_2O and EtOH from $\text{EtOH}-\text{H}_2\text{O}$ mixtures. It is suggested that Na_2SiO_3 is hydrolysed at the surface to form a skeleton of H_2SiO_3 in the surface layer. H^+ react with this surface and gain entrance to the glass. In the interior of the glass is a layer of unhydrolysed Na_2SiO_3 which moves to one side or another depending on the direction of the current.
 C. R. H.

Oxidation potentials of ketones and an aldehyde. R. H. Baker and H. Adkins (*J. Amer. Chem. Soc.*, 1940, 62, 3305—3314).—The method of establishing [by $\text{Al}(\text{O}i\text{Bu})_3$] and measuring the equilibrium $\text{CORR} + \text{CHR}'\text{R}''\text{OH} \rightleftharpoons \text{CHRR}'\text{OH} + \text{COR}'\text{R}''$ (Cox *et al.*, A., 1940, II, 90) is improved and the reversibility of the reaction is confirmed. Results are recorded for 23 ketones, 1 aldehyde, and 6 quinones. Fluorenone is used as standard because of its rapid rate of reaction. The rate of this reaction and the depolarisation potential at a dropping Hg cathode are not related to the relative reactivities. The results are used to calculate oxidation potentials. Unsaturation has little effect on the reactivity of a ketone. The high reactivity of $p\text{-O}_2\text{C}_6\text{H}_4\text{O}$ is due to the ready rearrangement of the primary reduction product to quinol.
 R. S. C.

Redox titrations of vat dye systems.—See B., 1941, II, 76.

VIII.—REACTIONS.

Temperature and latent energy in flame gases. W. T. David (*Nature*, 1941, 147, 89).—Additional experiments supporting the view that the temp. of the flame gases resulting from the combustion of an inflammable gaseous mixture increases, and the contained latent energy decreases, as the distances of flame travel from the igniting spark increases are discussed. They suggest also that this is because the mechanism of combustion in the early stages after spark ignition differs from that in the later stages.
 L. S. T.

Latent energy and dissociation in flame gases. W. T. David, A. S. Leah, and B. Pugh (*Phil. Mag.*, 1941, [vii], 31, 156—168).—Pressures < vals. calc. from thermal data, developed in CO -air explosions, are explained by postulating long-lived latent energy in the form of excess internal energy of the CO_2 mols. formed. The discrepancy between actual and theoretical flame temp. decreases with increasing distance of flame travel; it decreases when H_2 is mixed with the CO . The latent energy is emitted as after-glow and in contact with surfaces. Temp. measurements in explosions give higher vals. using a bare Pt-Rh wire than when a Pt-Rh wire coated with quartz is used, and the temp. is a max. for a lower percentage of CO in the mixture in the former case. This indicates abnormally high dissociation of CO_2 in the flame, recombination occurring on the bare wire, but not on the coated one.
 L. J. J.

Radiation of the low-temperature flame of carbon disulphide. V. Kondratev (*Acta Physicochim. U.R.S.S.*, 1940, 12, 637—646).—The dependence on the composition of the CS_2-O_2 mixture, and on temp., of the light output (i) of the low-temp. flame of CS_2 has been studied. With increasing $[\text{O}_2]$, i rises to a sharp max. at $[\text{O}_2]/[\text{CS}_2] \sim 6$ and then falls sharply, but without any abrupt change of reaction rate, so that a change in the reaction mechanism is probable. With rising temp. i decreases. The max. val. of i corresponds with evolution

of one quantum for ~ 40 mols. reacting. The radiation is purely chemiluminescent.
 F. J. G.

Surface as a limiting factor in the slow combustion of hydrocarbons. R. G. W. Norrish and J. D. Reagh (*Proc. Roy. Soc.*, 1940, A, 176, 429—448).—Rates of combustion of several hydrocarbons, both saturated and unsaturated, were determined in reaction vessels of widely varying diameter but approx. const. volume. When the diameter of the reaction vessel was sufficiently reduced the reaction rate fell to zero and the induction period increased towards infinity. In narrow vessels surface deactivation can predominate over other processes of deactivation, whilst in wider vessels surface and vol. deactivation occur to a comparable extent over a considerable range of pressure.
 G. D. P.

Relationship between initial conditions and pressure increase at explosion [of gas mixtures]. N. V. Tokarev and N. I. Nekrasov (*Acta Physicochim. U.R.S.S.*, 1940, 12, 573—588; cf. A., 1937, I, 247).—For NH_3-O_2 , NH_3 -air, and $\text{H}_2-\text{N}_2-\text{O}_2$ mixtures there is a linear relationship between the pressure increase Δp occurring when the mixture is exploded by a spark and its initial pressure, and between Δp and the initial temp. The straight lines representing these relations for any given mixture meet at a point where $\Delta p = 0$ and the initial pressure or temp. is that characteristic of the spontaneous inflammation of the mixture. Thus the vals. characterising spontaneous ignition can be approx. calc. from those characterising spark ignition.
 F. L. U.

Spontaneous inflammability of phosphine- and silane-acetylene mixtures.—See B., 1941, I, 94.

Reaction of methane with steam. II. Velocity of the reaction. A. Leibusch and G. Bergo (*J. Appl. Chem. Russ.*, 1940, 13, 1003—1013).—At 700—1050°, in SiO_2 reactors, CH_4 yields CH_2 , C_2H_6 , C_2H_4 , C_2H_2 , and C; all these products react with H_2O to give CO and H_2 . In the initial stages the velocity of the process is determined by that of the reactions $\text{CH}_4 \rightleftharpoons \text{CH}_2 + \text{H}_2$ (j) and $\text{CH}_2 + \text{H}_2\text{O} \rightleftharpoons 2\text{H}_2 + \text{CO}$. With increasing $[\text{H}_2]$ reaction (j) is reversed, and the dominating reaction then becomes $\text{CH}_4 + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}$.
 R. T.

Kinetics of thermal isomerisation of trans-dichloroethylene. J. L. Jones and R. L. Taylor (*J. Amer. Chem. Soc.*, 1940, 62, 3480—3485).—Thermal isomerisation of gaseous $\text{trans-C}_2\text{H}_2\text{Cl}_2$ into the *cis*-form has been studied in the temp. range 566—608° K. from 200 to 700 mm. The reaction is homogeneous of the first order, and with activation energy 41,900 g.-cal. which is considered to be localised in the internal degrees of freedom of the double bond and almost independent of the nature of the attached atoms. The isomerisation is thought to occur by the activation of the C:C double bond to form a single bond with two free valencies. Free rotation of the H-C-Cl groups takes place and a double bond is re-formed in the *cis*-mol. by an inversion of a free C valency. The activation energy compares favourably with those of the Me cinnamate and *isostilbene* isomerisations, and it is concluded that the reaction is almost independent of resonance effects.
 W. R. A.

Kinetics of the thermal decomposition of acetophenone. R. E. Smith and C. N. Hinshelwood (*Proc. Roy. Soc.*, 1940, A, 176, 468—473).—The reaction takes place predominantly by the step $\text{COPhMe} = \text{PhMe} + \text{CO}$, the PhMe undergoing a subsequent decomp. to C_6H_6 , CH_4 , and C. It differs from that of COMe_2 in yielding hardly any ketone. There is no retardation of the reaction by NO or by greatly increased surface, nor can an increased rate of reaction be induced by the presence of radicals from decomp. Et_2O . This indicates the absence of reaction chains. The contrast in behaviour between MeCHO and PhCHO is not found with the corresponding pair COMe_2 and COPhMe .
 G. D. P.

Homogeneous first-order gas reactions. XII. Decomposition of glyoxal tetra-acetate. J. C. Arnell, J. R. Dacey, and C. C. Coffin (*Canad. J. Res.*, 1940, 18, B, 410—413).—The decomp. of glyoxal tetra-acetate at 538—583° and at 4—40 cm. is homogeneous and unimol., with $k = 1.8 \times 10^{12} e^{-39,200/RT}$.
 F. J. G.

Chain reactions in aqueous solutions containing ozone, hydroperoxide, and acid. H. Taube and W. C. Bray (*J. Amer. Chem. Soc.*, 1940, 62, 3357—3373).—The interaction of O_3 and H_2O_2 in acid solution involves the reactions $\text{H}_2\text{O}_2 + \text{O}_3 = \text{H}_2\text{O} + 2\text{O}_2$ (A) and $2\text{O}_3 = 3\text{O}_2$ (B) (A., 1938, I, 147), both

of which are chain reactions. Both reactions are inhibited by Cl⁻ ions, aliphatic acids (except HCO₂H) and alcohols; (A) is also inhibited by Br⁻ ions. The effects produced by varying the concn. of Cl⁻ ions or of AcOH in HClO₄, HNO₃, and H₂SO₄ solutions have been investigated at approx. const. concns. of O₃, H₂O₂, and acid. The rates of both reactions in presence of the inhibitor in acid solution (0.1—0.4M-H⁺) at 0° are represented by differential equations. The chain reactions involve HO and HO₂ radicals which are formed in the bimol. reaction between O₃ and H₂O₂. HO reacts with O₃, H₂O₂, the inhibitors, and the acid anions (SO₄²⁻, NO₃⁻, and ClO₄⁻) but only O₃ reacts with HO₂. When AcOH is the inhibitor org. free radicals are formed and react with O₃ but not with H₂O₂. Cl⁻ ions give rise to Cl atoms which react more readily with H₂O₂ than with O₃. The predicted mechanism is: H₂O₂ + O₃ → HO + HO₂ + O₂; HO₂ + O₃ → HO + 2O₂; HO + O₃ → HO₂ + O₂; HO + H₂O₂ → HO₂ + H₂O; HO + inhibitor → radical + HO₂. The rates of reaction of HO with Cl⁻ > O₃ > H₂O > AcOH in 0.19M-H⁺ solution. The equilibrium Cl + Cl⁻ = Cl[·] has been detected. The reactions are catalysed by Ce³⁺, Pr³⁺, Co²⁺, Cu²⁺, Ag⁺, and Tl⁺ ions and by HCO₂H. The rate of decomp. of O₃ is greatly increased when O₃ oxidises Co²⁺ or Ce³⁺ ions or HCO₂H, which supports the view that HO and HO₂ radicals are intermediate products of both reactions.

W. R. A.

Quantitative study of the so-called "positive halogen" in ketones and esters.—See A., 1941, II, 67.

Velocity of reduction of phenols. I. Monohydric phenols.—See A., 1941, II, 94.

Rates of reaction of stereoisomeric oximes of cholestenone and of benzylidene-*p*-bromoacetophenone with iodine monobromide. J. O. Ralls (*J. Amer. Chem. Soc.*, 1940, **62**, 3485—3488).—The bromination of benzylidene-*p*-bromoacetophenone (I) and cholestenone (II) and their *anti*- and *syn*-forms of oximes, in CCl₄, AcOH, and CCl₄-AcOH solutions, with IBr, and the effect of direct bromination of oximes of (II) have been investigated. In CCl₄ the *anti*-form of the oximes is slightly more reactive than the *syn*-, whilst in pure AcOH and CCl₄-AcOH mixtures a marked depression in the bromination of (I) and its oximes and of the oximes of (II), but an acceleration of that of (II), was observed. The easy enolisation of (II) as compared with (I) is considered to account for the observed acceleration. In the direct bromination of the oximes of (II), the *anti*-form is more reactive than the *syn*-.

W. R. A.

Kinetics of reactions in heterogeneous systems. VI. Hydrolysis of acid halides by water. K. K. Dole (*J. Univ. Bombay*, 1940, **9**, Part 3, 76—93; cf. A., 1939, I, 270).—The addition of org. acid increases the velocity coeff. (*k*) of the hydrolysis of *o*-C₆H₄(CO₂H)₂ (I) at the interface between PhCl and H₂O, the increase being approx. \propto the concn. of the acid. Addition of Na₂SO₄ decreases *k* for (I) or *m*-NO₂·C₆H₄·COCl (II), this effect being attributed to a decrease in the solubility of the acid in H₂O, and consequent passage of the acid into the PhCl, where it is adsorbed in the interface, displacing acid chloride mols. and decreasing their concn. in the reaction zone. The rate of hydrolysis of an old PhCl solution of (I), when brought into contact with H₂O, is > for a fresh solution, owing to the slow hydrolysis by H₂O from the air yielding the acid. With *o*-C₆H₄I·COCl *k* decreases gradually for an old solution, but for a fresh solution it increases to a max. and then decreases. This is attributed to the lower solubility in H₂O of *o*-C₆H₄I·CO₂H, causing it to pass into the PhCl phase and to be adsorbed in the interface. Temp. coeff. measurements indicate that the reactions are composite, and that their courses are affected by both diffusion and adsorption phenomena. Except in the case of (II) the temp. coeffs. are increased by the addition of Na₂SO₄.

J. W. S.

Catalytic oxidation of phosphorus tribromide. C. R. Johnson and L. G. Nunn, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 141—143).—The oxidation of PBr₃ vapour by O₂ to POBr₃ at O₂ pressures from 150 to 700 mm. at temp. between 30° and 150° in the presence of N oxides takes place rapidly and non-explosively. It is catalysed by N₂O₄ but not by NO₂ and at <100° the velocity coeffs. at const. temp. \propto pressure of N₂O₄. Oxidation also \propto [O₂ pressure]^{1/2}.

W. R. A.

Oxidation-reduction reaction catalysed by iodine. Application to the detection of iodide. D. Hart and R. Meyrowitz

(*Ind. Eng. Chem. [Anal.]*, 1940, **12**, 774—775).—In presence of I⁻, addition of NO₂⁺ to a dil. HNO₃ solution of Pb arsenite ppt. PbHAsO₄ (I). This reaction forms the basis of a test for <0.2 μ g. of I⁻. Directions for using this as a drop reaction or on the macro-scale, and a modification in which Ag₃AsO₄ is pptd. instead of (I), are given. Sn²⁺, Sn⁴⁺, Fe²⁺, V, CNS⁻, ClO₄⁻, MnO₄⁻, IO₃⁻, BrO₃⁻, IO₄⁻, S₂O₃²⁻, and H₂O₂ give ppts. in absence of I⁻, and with Cr³⁺, Ag⁺, Hg²⁺, Hg²⁺, Fe³⁺, Be²⁺, Ir, Ru, F⁻, CN⁻, S²⁻, and S₂O₃²⁻ no ppt. is obtained in presence or absence of I⁻. A procedure which uses a Na₂CO₃ extract and detects 0.03 μ g. of I⁻ in presence of 50 mg. of interfering ions other than those of Hg, Ag, IO₃⁻, IO₄⁻, MnO₄⁻, S₂O₈²⁻, Au, Ir, and Ru, and H₂O₂ is described. Many other ions that do not interfere with the test are listed.

L. S. T.

Relation between the oxidising action and catalytic decomposition of concentrated hydrogen peroxide. I. Osmium tetroxide as a catalyst in the oxidation of acetic and propionic acids. L. M. Foster and J. H. Payne (*J. Amer. Chem. Soc.*, 1941, **63**, 223—225).—AcOH and EtCO₂H have been oxidised by 60% H₂O₂ catalysed by OsO₄ and the amount of oxidation, indicated by the amount of CO₂, and the decomp. of H₂O₂, indicated by the amount of O₂ evolved, have been determined simultaneously. The oxidation of EtCO₂H increases rapidly with increased amounts of OsO₄, whereas AcOH is influenced to a smaller extent. The decomp. of H₂O₂ is also catalysed by OsO₄.

W. R. A.

Poisoning of a palladium catalyst by carbon monoxide. M. G. T. Burrows and W. H. Stockmayer (*Proc. Roy. Soc.*, 1940, **A**, 176, 474—483).—Very small amounts of CO completely inhibit the combination of H₂ and O₂ at the surface of a Pd catalyst at low pressures and room temp. The poisoning effect is only temporary, the adsorbed layer of CO being removed by the O₂ in the mixture of H₂ and O₂. After an induction period combination proceeds at the normal rate. The length of the inert periods increases with the amount of CO in the system, and the rate of removal of CO increases as its pressure decreases, becoming comparatively great when the CO is insufficient to form a monolayer. The observations support the view that the catalysis is a process of alternate oxidation and reduction of the metal.

G. D. P.

Oxidation of sulphur dioxide at activated vanadium catalysts. II. Effect of alkali-metal salts and silicic acid on the catalytic activity of vanadium pentoxide. G. K. Borekov and V. P. Pligunov (*J. Appl. Chem. Russ.*, 1940, **13**, 653—662; cf. B., 1940, 736).—VOSO₄ is not formed when SO₂-O₂ is passed over V₂O₅ at 420—520°. The activation energy *E* of the reaction 2SO₂ + O₂ → 2SO₃ is 38 kg.-cal. Addition of SiO₂ to the V₂O₅ lowers its activity. That of 1 : 10 K₂SO₄-V₂O₅ in ten times that of V₂O₅ alone, at 500°, but is considerably smaller at <490° or at 520°; at the latter temp. conversion into VOSO₄ proceeds rapidly. At 500° olive-green crystals of a substance containing K₂O, V₂O₅, or V₂O₄, and SO₃ appear. 1 : 10 : 80 K₂SO₄-V₂O₅-SiO₂ mixtures are extremely active catalysts, being 20 times as active as V₂O₅ alone at 440—500°, and twice as active at 400°; the apparent *E* is 27 kg.-cal.

R. T. A.

Reaction between nitrous oxide and hydrogen on alumina. J. E. Vance and J. K. Dixon (*J. Amer. Chem. Soc.*, 1941, **63**, 176—181; cf. A., 1935, 829).—Rates and amounts of adsorption for H₂ and N₂O from 0° to 400° and the reaction between N₂O and H₂ at 330°, 403°, and 472° have been investigated on Al₂O₃ in a flowing system, the extent of the reaction being limited to ~10% at the highest temp. N₂O was adsorbed reversibly and instantaneously up to 250°, when it began to decompose at a rate \propto its pressure, the rate being reduced 25-fold by saturation of the Al₂O₃ with H₂O. Adsorption of H₂ was reversible and instantaneous up to 250°, when a slow activated adsorption became measurable. Between 300° and 400°, there appears to be a rapid initial adsorption followed by a very slow process, both of which are initially affected by addition of a small amount of H₂O vapour. The average measured rate of adsorption in the first 15 min. is 2700 times < the rate of reaction with N₂O and suggests that N₂O cleans up the most active surface for adsorption of H₂ at the rapid rate which is required to maintain the observed reaction velocity. The rate of decomp. of N₂O alone is 850 times < the rate of reaction with H₂. The rate of H₂O formation in the H₂O-H₂ reaction \propto [N₂O pressure]^{1/2} and \propto a fractional power of the H₂ pressure, which varied from 0.66 at 333° to 0.33 at 472°. Kinetic study suggests that part of

the reaction takes place on an unhydrated Al_2O_3 surface inhibited by H_2O and the remainder on a completely hydrated surface uninhibited by H_2O , the apparent activation energies on the two surfaces being 30.0 and 35.7 kg.-cal. per mol., respectively; the difference is attributed partly to the heat of adsorption of H_2O . The apparent activation energies of N_2O on Pt, Au, CuO, MgO, and CuO-MgO, and of the N_2O - H_2 reaction on Ag and Pt, are compared and shown to be of same order, except on Ag. The activity of Al_2O_3 in the dehydrogenation of hydrocarbons is briefly discussed. W. R. A.

Chromic oxide as a catalyst in potassium chlorate decomposition. M. Meyer (*J. Chem. Educ.*, 1940, 17, 494).— Cr_2O_3 (1–5%), or $\text{K}_2\text{Cr}_2\text{O}_7$, is the most efficient catalyst for the thermal decomp. of KClO_3 . Some Cl_2 contaminates the O_2 involved. L. S. T.

Charcoal catalyst for conversion of carbon monoxide.—See B., 1941, I, 99.

Electrolytic preparation of cerium amalgam. S. I. Skljarenko and B. A. Sacharov (*J. Appl. Chem. Russ.*, 1940, 13, 841–845).—Electrolysis of CeCl_3 in MeOH, EtOH, or MeOH-EtOH (Hg cathode, c.d. 0.05 amp. per sq. cm., at 30–40°) yields 0.5–1.2% Ce amalgams. R. T.

Electrolytic reduction of ferric sulphate in presence of titanium sulphate. IV. Nature of cathode polarisation. K. J. Gratshev (*J. Appl. Chem. Russ.*, 1940, 13, 516–520; cf. A., 1939, I, 480).—In electrolysis of aq. $\text{FeSO}_4\text{-Fe}_2(\text{SO}_4)_3$ at 20–50° (Pb anode, Cu cathode) only concentrational polarisation of the cathode is observed at c.d. < the limiting val. Polarisation is considerable with Pb cathodes at such c.d., owing to formation of a film at the metal surface. At c.d. > the limiting val. the polarisation potential at Pb is > at Cu cathodes as a result of the higher H overpotential on Pb. R. T.

Electrode polarisation in electrolytic preparation of potassium ferricyanide. O. Essin, S. Derendjaev, and N. Ladigin (*J. Appl. Chem. Russ.*, 1940, 13, 971–977).—In the electrolytic oxidation of $\text{K}_4\text{Fe}(\text{CN})_6$ to $\text{K}_3\text{Fe}(\text{CN})_6$ cathode polarisation is due entirely to concentrational factors, and is the same with Pt as with Ni electrodes. It is greatly diminished by stirring the electrolyte. R. T.

Recovery of cobalt from solutions of its sulphate by electrolysis.—See B., 1941, I, 111.

Replacement of cyanide in electrolytic baths.—See B., 1941, I, 109.

Production of ozone in the silent electric discharge. W. H. Otto and W. H. Bennett (*J. Chem. Physics*, 1940, 8, 899–903).—The rate of formation (v) of O_3 in a silent electric discharge with a 0.005-in. W wire as internal electrode is > with a 0.001-in. W wire. In each case the metal is oxidised. This action is prevented by using a 0.001-in. Rh-plated Ni wire, but the yield is reduced. With d.c., v is greatest when the inner electrode is negative, the difference being greater for the larger wire. With a.c. the yield is the mean of the two d.c. yields. It is inferred that the O_3 is formed principally through collisions between electrons and O_2 mols. at energies suitable for mol. dissociation. With the internal electrode negative, collisions occur at dissociation energies principally outside the ionising sheath but well inside the sheath where electrons excite the first crit. potential in O_2 and attach themselves to O_2 mols. When the electrode is positive, collisions at dissociation energies occur in a thin sheath adjacent to the electrode, and dissociations due to ultra-violet radiation of high energy also occur. J. W. S.

Mechanism of photographic development. III. Developing and non-developing reducing agents. T. H. James (*J. Amer. Chem. Soc.*, 1940, 62, 3411–3415; cf. A., 1940, I, 170).—The rate of formation of Ag in solutions of Ag salt complexes in the presence of Na_2SO_3 , Na_2SnO_3 , desylamine, and furoin has been studied. In Ag_2SO_3 complexes the rate is markedly increased by the addition of colloidal Ag or CuSO_4 and depends on $[\text{Ag}^+]$. Na_2SnO_3 reduces the $\text{Ag}_2\text{S}_2\text{O}_3$ complex without Ag catalysis whilst with AgI complex definite Ag catalysis is observed. Desylamine and furoin reduce Ag⁺ without Ag catalysis and at rates \approx their O_2 oxidation rates. W. R. A.

Photolysis of the aliphatic aldehydes. VIII. Acetaldehyde. F. E. Blacet and W. J. Blaedel (*J. Amer. Chem. Soc.*, 1940, 62, 3374–3377; cf. A., 1938, I, 366).—Redetermination of

the H_2 :CO ratio at 2654 Å. shows a max. at $\sim 30^\circ$ and it is found that on cooling to $< 0^\circ$ the ratio slowly diminishes with decreasing temp. In the condensable products Ac_2 , glyoxal, and CH_2O have been detected, particularly at lower temp., but COMe_2 and methylglyoxal were not found. The primary dissociation appears to be $\text{MeCHO} + h\nu \rightarrow \text{Me} + \text{HCO}$ (i) followed by $\text{MeCHO} + \text{HCO} \rightarrow \text{H}_2 + \text{CO} + \text{MeCO}$ (ii), $\text{MeCHO} + \text{Me} \rightarrow \text{CH}_4 + \text{MeCO}$ (iii), $\text{MeCO} + \text{MeCHO} \rightarrow \text{Me} + \text{CO} + \text{MeCHO}$ (iv), $2\text{MeCO} \rightarrow (\text{MeCO})_2$ (v), $2\text{HCO} \rightarrow (\text{HCO})_2$ (vi), and $2\text{HCO} \rightarrow \text{CH}_2\text{O} + \text{CO}$ (vii). W. R. A.

Chain photolysis of acetaldehyde in intermittent light. W. L. Haden, jun., E. P. H. Meiböhm, and O. K. Rice (*J. Chem. Physics*, 1940, 8, 998).—The decomp. of MeCHO in intermittent light, produced by the use of a rotating sector, has been investigated. Since the rate of decomp. is dependent on (light intensity)^{1/2}, the quantum yield (n) with a rapidly moving sector is > with a slowly moving sector. At 200° and 20 cm. pressure the change in n occurs with ~ 2 rotations per sec., indicating that the reaction chain lasts ~ 0.5 sec. Comparison with the data of Grahame and Rollefson (A., 1940, I, 170) indicates that under these conditions n is ~ 48 , and the chain length ~ 24 if two chains are initiated per quantum. Assuming the effective collision radius to be 3.5 Å, the Me radical makes $\sim 7 \times 10^8$ collisions in 0.5 sec., so one collision in $\sim 3 \times 10^{-7}$ results in reaction, this corresponding with a max. activation energy of 16 kg.-cal. per g.-mol. J. W. S.

Free radicals in the photolysis of propaldehyde. L. May, H. A. Taylor, and M. Burton (*J. Amer. Chem. Soc.*, 1941, 63, 249–254).—Free alkyl radicals are produced to approx. the same extent in the photolysis of EtCHO and of COMe_2 ; they have half-life vals. of 3.8 and 4.6×10^{-3} sec., respectively. Free formyl radicals are stable up to 100° and free H atoms comprise <2% of mirror-active particles produced by photolysis. Photolysis of EtCHO appears to be a chain reaction in which there are competing free radical decoms. W. R. A.

Photolysis of organic nitrogen compounds. III. Methyl isocyanate. D. A. Bamford and C. H. Bamford (*J.C.S.*, 1941, 30–34).—The absorption spectrum of MeNCO at 15° and 140° appears completely continuous at <2350 and <2400 Å., respectively. Analysis of the products of the Hg-sensitised photochemical decomp. of MeNCO in light of 2100–2400 Å. at 20–347° confirms that the initial decomp. involves dissociation in two distinct ways, yielding Me and NCO, and NMe and CO radicals, respectively, the former being the more important the higher is the temp. The quantum yield of CO from MeNCO at 307° is ~ 1 . High yields of H_2 and CO in the Hg-sensitised reaction at high temp., and particularly in the direct photolysis with a hot arc, indicate the formation of CH_2O , probably by interaction of NMe and MeNCO. In presence of NO the NCO and NMe radicals both react with this gas, forming N_2 and CO_2 , and Me radicals and N_2O , respectively. The fact that the decomp. of NCO into N_2 and CO is more important in the sensitised reaction than in the direct photolysis is attributed to the formation of HgNCO, as a radical, in the former reaction. This is assumed to be capable of decomp. in the same way as NCO but not to be so easily hydrogenated. J. W. S.

Photolysis of mercaptans. N. P. Skerrett and N. W. Thompson (*Trans. Faraday Soc.*, 1941, 37, 81–82).—MeSH vapour is decomposed when irradiated by Hg 2537 Å., giving chiefly Me_2S_2 and H_2 with small amounts of CH_4 and S, with a quantum yield ~ 1.7 . A mechanism involving the primary formation of MeS and H is proposed. These results agree with those obtained previously (cf. A., 1938, I, 633) in suggesting that the lower alkyl mercaptans are photolysed predominantly by the primary process $\text{RSH} \rightarrow \text{RS} + \text{H}$ and not $\text{RSH} \rightarrow \text{RH} + \text{S}$. F. L. U.

Photochemical decomposition of malonic acid. I. D. S. Rao (*J. Univ. Bombay*, 1940, 9, Part 3, 94–103).—From analyses of the products of the photochemical decomp. of aq. $\text{CH}_2(\text{CO}_2\text{H})_2$, irradiated by means of a SiO₂ lamp, it is inferred that the primary decomp. takes place in three ways, with formation of (a) $\text{H}_2\text{C}_2\text{O}_4$ and C_2H_4 , (b) $\text{H}_2\text{C}_2\text{O}_4$ and $(\text{CH}_2\text{CO}_2\text{H})_2$, and (c) CO_2 and AcOH. Secondary decomp. of $\text{H}_2\text{C}_2\text{O}_4$ yields CO_2 and HCO_2H , the latter in turn giving rise to CO and H_2O . J. W. S.

Effect of application of sonic energy to hydrolysis of potassium persulphate. W. C. Schumb and E. S. Rittner (*J. Amer. Chem. Soc.*, 1940, 62, 3416–3420).—The rates of hydrolysis

of $K_2S_2O_8$ at 60°, 70°, and 80°, and at 25°, 60°, and 70° with the application of sonic energy, have been investigated by the use of an improved apparatus. In the ordinary hydrolysis the unimol. reaction coeff. k decreased with increasing concn. except in the course of a single experiment at 60° over a period of 2 days when k increased with time. On the application of sonic energy and elimination of partly thermal effects and any catalytic effect due to metallic Ni, k increased with increased time of vibration, increasing vol. (concn. remaining const.), and with increasing $[K_2S_2O_8]$. The effect was too small to measure at 25°, but measurements at 60° and 70° indicate that the effect was slightly greater at 60° than at 70°.

W. R. A.

IX.—METHODS OF PREPARATION.

Acid-base reactions, their analogy to oxidation-reduction reactions in solution. T. H. Hazlehurst (*J. Chem. Educ.*, 1940, 17, 466—468).—A discussion in which acid-base reactions are shown to be closely analogous to oxidation-reduction reactions; they are not double decomp. reactions. Chemical reactions in general are classified. L. S. T.

Preparation of pure water. A. I. Baibaev (*J. Appl. Chem. Russ.*, 1940, 13, 499—505).—Conductivity H_2O is obtained in a single operation, using simple apparatus, by distillation of distilled H_2O from a non-volatile acid, with condensation at $<60^\circ$. R. T.

Comparison of methods of preparation of heavy water. A. I. Brodski (*J. Appl. Chem. Russ.*, 1940, 13, 670—676).—A crit. survey of methods, including fractional distillation, continuous electrolysis in cascade, and thermodiffusion of H_2O vapour or H_2 , leads to the conclusion that the ordinary method is at present the only practicable one, although in theory it is inferior to the others. R. T.

Technology of preparation of heavy water. V. A. Alexandrovitch and M. K. Scheludko (*J. Appl. Chem. Russ.*, 1940, 13, 483—498).—Electrolytic apparatus and methods of prep. of D_2O are described. R. T.

Oxygen exchange between anions and water. N. F. Hall and O. R. Alexander (*J. Amer. Chem. Soc.*, 1940, 62, 3455—3462).— H_2O containing excess of ^{18}O and having an excess ρ of 21.7 μ d was caused to exchange O with dissolved inorg. O compounds at 95—100° and under different conditions of time of contact, and p_H . The extent of exchange has been determined by measurement of ρ using the magnetically-controlled swimmer and it has been found to yield the most satisfactory data when used near the temp. of max. ρ . Complete exchange ($>95\%$) occurs with (min. time of contact in hr. in parenthesis) CrO_3 (5), $Na_2Cr_2O_7$ (5), Na_2CrO_4 (2), K_2MoO_4 (25), Na_2WO_4 (6), $NaBO_2$ (4), K_2CO_3 (22), KH_2AsO_4 (14), $KAsO_4$ (9), $NaMnO_4$ (?), $NaIO_3$ (48), Na_2SeO_3 (5), K_2SO_3 (8), $Na_2S_2O_3$ (5). KNO_3 , $NaNO_3$, $Mg(ClO_4)_2$, $Ba(ClO_4)_2$, $NaClO_3$, Na_2SeO_4 , and Na_2SO_4 show practically no exchange, whilst $NaBrO_3$, and possibly $NaIO_3$ and $NaMnO_4$, show partial exchange. Addition of NaOH does not appreciably affect the exchange with Na_2CrO_4 , K_2MoO_4 , Na_2WO_4 , $NaNO_3$, KH_2AsO_4 , $KAsO_4$, $NaMnO_4$, $Ba(ClO_4)_2$, $NaClO_3$, $NaBrO_3$, $NaIO_3$, Na_2SeO_3 , Na_2SeO_4 , and Na_2SO_4 but retards the exchange with K_2SO_3 and $Na_2S_2O_3$. Addition of acid accelerates for Na_2SO_4 and Na_2SeO_4 but appears to have little influence on $NaNO_3$ and $Mg(ClO_4)_2$. W. R. A.

Instability of silver perchlorate. S. R. Brinkley, jun. (*J. Amer. Chem. Soc.*, 1940, 62, 3524).— $AgClO_4$, recryst. from C_6H_6 and kept for 15 hr. in a desiccator at 10 mm., appeared to be superficially dry but caked. A violent explosion sometimes occurred when the cakes were broken by gentle pressure in a mortar. This detonation involves the $AgClO_4-C_6H_6$ additive compound and similar detonations are known to occur with the $AgClO_4-EtOH$ additive compound. The instability is unpredictable. W. R. A.

Bleaching powder.—See B., 1941, I, 99.

Metallo borohydrides. I. Aluminium borohydride. H. I. Schlesinger, R. T. Sanderson, and A. B. Burg. **II. Beryllium borohydride.** A. B. Burg and H. I. Schlesinger. **III. Lithium borohydride.** H. I. Schlesinger and H. C. Brown (*J. Amer. Chem. Soc.*, 1940, 62, 3421—3425; 3425—3429; 3429—3435).— Al_2Me_3 reacts with B_2H_6 thus: $Al_2Me_3 + 4B_2H_6 \rightarrow 2BMe_3 + 2AlB_2H_{12}$. A similar reaction takes place between $AlMe_3.Et_2O$ and B_2H_6 with formation of BMe_3

and other (unidentified) products. Before AlB_2H_{12} can be successfully prepared there must be excess of B_2H_6 ; otherwise a complex mixture of compounds of unknown composition is formed. AlB_2H_{12} appears to be a normal liquid, m.p. $-64.5 \pm 0.5^\circ$, v.p., $\log p = 7.808 - 1565/T$. It reacts readily with air, inflaming spontaneously with a very brilliant bluish-white flash. It hydrolyses rapidly thus: $AlB_2H_{12} + 12H_2O \rightarrow 12H_2 + 3H_3BO_3 + Al(OH)_3$, and with HCl, even at -80° , reacts readily thus: $2AlB_2H_{12} + 6HCl \rightarrow 6H_2 + 3B_2H_6 + Al_2Cl_6$. On heating H_2 is evolved and ultimately dark metallic crystals, possibly of AlB_2 , are formed together with an amorphous black solid which reacts with H_2O to give H_2 . Equimol. quantities of Me_2O and AlB_2H_{12} yield readily, even at -80° , a slightly volatile compound, $(AlB_2H_{12}.OMe)_n$. With NMe_3 at -80° a white cryst. compound, $AlB_2H_{12}.NMe_3$, m.p. 79° , is formed; at $\sim 100^\circ$ it yields borine trimethylamine and an oily liquid, possibly AlB_2H_6 . When AlB_2H_{12} is treated with excess of NMe_3 at -80° (1 : ~ 6) a compound (approx. 3 : 1), unstable to heat, is formed. Equimol. quantities of AlB_2H_{12} and NH_3 at -80° give a mixture of an amorphous white solid and crystals which in 0.5 hr. at 0° are completely converted into the amorphous solid. Attempts to prepare AlH_3X ($X = NMe_3$ or NH_3) were unsuccessful.

II. Interaction of $BeMe_2$ with excess of B_2H_6 yields Be borohydride, BeB_2H_8 , which reacts readily with air and H_2O , and with HCl at -80° gives H_2 , B_2H_6 , and chlorodiborane. The v.p. of BeB_2H_8 is given by $\log p$ (mm.) = $11.772 - 3240/T$; the m.p. could not be ascertained because of slight decomp. at 123° . NMe_3 and BeB_2H_8 ($\sim 6 : 1$) at -80° react to give a mixture of compounds, including $BeB_2H_8.NMe_3$ which is also formed from equimol. quantities of the reactants and reacts explosively with air or H_2O . V.p. of $BeB_2H_8.NMe_3$ from 65° to 140° are represented by $\log p$ (mm.) = $8.353 - 2909/T$. The NMe_3 is tightly held in the additive compound since this compound does not yield borine trimethylamine with B_2H_6 even at 70° . $BeB_2H_8.NMe_3$ reacts with NMe_3 to give $BeBH_2.NMe_3$ (I) and $BH_3.NMe_3$ (I) tends to lose NMe_3 and produces an oily material which with B_2H_6 gives BeB_2H_8 .

III. LiEt and B_2H_6 react at room temp. with formation of Et derivatives of B_2H_6 and a white, stable, non-volatile solid, m.p. $275-280^\circ$ (decomp.), which has been proved to be $LiBH_4$ by comparing the composition of the volatile products with that of the starting materials and by treating $LiBH_4$ with MeOH, when the following reactions occur: $LiBH_4 + 4MeOH \rightarrow LiB(OMe)_4 + 4H_2$; $LiB(OMe)_4 \rightarrow LiOMe + B(OMe)_3$. $LiBH_4$ reacts readily with HCl even at -80° giving $LiCl$, H_2 , and B_2H_6 but does not react with dry air. It also differs from AlB_2H_{12} and BeB_2H_8 in its salt-like character and in the fact that NMe_3 has no action on it. AlB_2H_{12} reacts with LiEt thus: $3LiEt + Al(BH_4)_3 \rightarrow 3LiBH_4 + AlEt_3$, indicating that the basic structures of Al, Be, and Li borohydrides are closely related and that the differences in chemical and physical properties arise from differences in the degree of polarisation or distortion of the BH_4 groups. BMe_3 , either in presence or in absence of a solvent, is absorbed by LiEt at room temp. yielding a white cryst. solid with empirical composition $LiEt.BMe_3$, which appears to be a quaternary B derivative. This compound is sol. in C_6H_6 , is stable to dry air, and dissolves in H_2O with slow evolution of gas. By comparing the reactions of the borohydrides described in these papers the tendency to react as BH_4 derivatives is for $Al(BH_4)_2 > Be(BH_4)_2 > LiBH_4$ and the tendency to react as BH_3 derivatives diminishes in the same sequence. Polar character increases: $B_2H_6 < Al(BH_4)_3 < Be(BH_4)_2 < LiBH_4$, and chemical stability increases in the same order. Whilst B_2H_6 is essentially an aggregate of 2 BH_3 groups and $LiBH_4$ is a true BH_4 derivative, the Al and Be compounds are equilibrium mixtures, $AlH_3.3BH_3 \rightleftharpoons Al(BH_4)_3$ and $BeH_2.2BH_3 \rightleftharpoons Be(BH_4)_2$. W. R. A.

Separation by thermal diffusion of mixtures of gases having the same molecular weight. F. T. Wall and C. E. Holley, jun. (*J. Chem. Physics*, 1940, 8, 949—953).—Using a thermal diffusion column comprising three concentric brass tubes 274 cm. long, with internal and external temp. of 235° and 21° , respectively, the separation of $CO_2-C_3H_8$, CO_2-N_2O , $N_2O-C_2H_6$, $CO-C_2H_4$, $CO-N_2$, and $N_2-C_2H_4$ mixtures has been investigated. Except for CO_2-N_2O mixtures, for which the separation is \gg the predicted val., the order of magnitude and the directions of the separations are in accord with those deduced theoretically on the assumption that the mols. behave as elastic spheres. J. W. S.

Action of phenolphthalein on insoluble hydroxides. G. Sachs (*J. Amer. Chem. Soc.*, 1940, **62**, 3514—3515).—The hydroxides of Pb, Cd, Co, Ni, Mn^{II}, Zn, and Mg are formed by phenolphthalein (I), whilst those of Sn^{II}, Sn^{IV} (?), Sb^{III} (?), Sb^V, Al, Fe^{III}, and Cr are not. With those of Cu and Bi coloration is obtained only when the hydroxide is prepared in excess of alkali. Development of colour is due to activated adsorption of (I) on the hydroxide. Those which are coloured are cryst. on formation according to X-ray evidence.

W. R. A.

Further concentration of ³⁴S. D. W. Stewart and K. Cohen (*J. Chem. Physics*, 1940, **8**, 904—907).—The exchange reaction between SO₂ and aq. NaHSO₃, carried out in three countercurrent fractionating columns, has been used to separate 55 g. of Na₂SO₃ containing 25% of ³⁴S. J. W. S.

Sulphuryl iodide. M. R. A. N. Rao (*Proc. Indian Acad. Sci.*, 1940, **12**, A, 354—356).—SO₂Cl₂ in CCl₄ (0.0005M.) reacts with dry KI in the dark to give I and SO₂ even at -10°. When a 0.005M. solution of SO₂Cl₂ in CS₂ is shaken with dry KI in the dark at -70° for 2—3 min. a violet solution is obtained. The intensity of the coloration increased on heating and continued to increase on subsequent cooling. Hence the SO₂I₂ primarily formed decomposes when heated to SO₂ and I which do not recombine. No alteration in coloration was evidenced when the original violet solution was maintained at -70°. SO₂I₂ is therefore probably colourless. Spectrograms of SO₂I₂, and of SO₂ + I₂ formed from SO₂I₂ and artificially mixed, are reproduced.

W. R. A.

Selenium iodide. M. R. A. N. Rao (*Proc. Indian Acad. Sci.*, 1940, **12**, A, 410—415).—When a dil. solution of Se₂Cl₂ in CCl₄ was shaken in the dark at -10° for 2 min. with dry KI the solution turned yellow and on exposure to light immediately became violet and deposited crystals of Se. At 25° the reaction took about 10—15 min. because Se and I were adsorbed on KI and reduced the effective area of the solid. When Se₂I₂, prepared by the above method, is shaken up with an aq. suspension of CdCO₃ two reactions occur: (a) Se₂I₂ → 2Se + I₂; (b) 2Se₂I₂ + 3H₂O → 3Se + H₂SeO₄ + 4HI. 10—15% of the Se₂I₂ hydrolyses whilst the remainder is decomposed according to (a). The decomp. has been followed by absorption spectra measurements. Freshly prepared Se₂I₂ absorbs all λ < 5900 Å., but as decomp. proceeds the solution becomes more transparent in the violet. The formation of Se₂I₂ from Se and I in CCl₄ is considered improbable.

W. R. A.

Existence of higher hydrates of ferric oxide as transition intermediates. L. A. Welo and O. Baudisch (*Phil. Mag.*, 1941, [vii], **31**, 103—114; cf. A., 1937, I, 474).—The transformation of γ-Fe₂O₃ into α-Fe₂O₃ in contact with H₂O has been followed at a series of temp. between 71.3° and room temp. by following the change in magnetic permeability. The transformation is of zero order at all the temp. used, abrupt changes in rate being found at most temp. It is concluded that the transformation takes place by a no. of alternative routes, all similar to that postulated for 136° in the authors' earlier paper, but involving a variety of higher hydrates of α- and γ-Fe₂O₃, besides α- and γ-FeOOH. The γ-α transformation of Fe₂O₃ in dry tubes may depend on the presence of traces of H₂O.

L. J. J.

Heating curves of iron ochre. V. E. Tartakovskaja and J. G. Chazina (*J. Appl. Chem. Russ.*, 1940, **13**, 866—868).—Two min. are observed in the heating curve, at 349° and 580°, and one max. at 980°. These are due, respectively, to dehydration of Fe hydroxides and of kaolin, and to an exothermic reaction of kaolinite at about 1000°. The fall in oil capacity following calcination of ochre is due to the diminution of active surface as a result of these reactions.

R. T.

Formation and stability of the halogen and cyanogen derivatives of the carbonyls and complex carboxyanides. II. B. Ormont (*Acta Physicochim. U.R.S.S.*, 1940, **12**, 759—771).—Theoretical. It is shown in terms of the author's theory (*ibid.*, 412) that compounds [Fe(CO)₅]_nX₂ (X = halogen) must be thermodynamically unstable with respect to [Fe(CO)₄X₂]. Possible structures for Fe(CO)₅X₂ are (a) Fe(CO)₅X₂, i.e., an additive compound, a mol. lattice; (b) [Fe₃(CO)₅X⁺X⁻]; (c) [Fe(CO)₅X]⁺X⁻, with an ionic lattice. Reasons for the instability of halogen derivatives of Co and Ni carbonyls, and the possibility of the existence of certain types of carbonyl cyanide derivatives, are discussed.

F. J. G.

X.—ANALYSIS.

Quantitative spectrographic analysis. J. T. M. Malpica (*Gen. Elect. Rev.*, 1940, **43**, 288—297, 333—335).—Special techniques and accessories for increasing the accuracy and sensitivity of quant. spectrography are discussed. A method of relative intensities with internal standards, developed to reduce the effect of the characteristics of the photographic plate in the intensity determinations, is shown to be independent of plate sensitivity, exposure, and time of development. However, the spectral response of the plate is not eliminated and the lines under comparison must be close to the λ scale. Accordingly, a method of relative intensity ratios with external standards has been developed to permit the making of intensity determinations completely independent of the photographic process.

R. B. C.

Phenolphthalein and methyl-orange. C. A. Peters and B. C. Redmon (*J. Chem. Educ.*, 1940, **17**, 525—528).—Electronic interpretations of the behaviour of these two indicators are presented.

L. S. T.

Sampling and analysis of feed and boiler waters.—See B., 1941, I, 82.

Silver phosphate in quantitative analysis. C. R. Johnson and L. G. Nunn, jun. (*J. Chem. Educ.*, 1940, **17**, 528—529).—Ag₃PO₄ (prep. described) is easily prepared in a form sufficiently pure to provide a satisfactory primary standard for Volhard determinations.

L. S. T.

Amperometric titrations. VI. Titration of sulphate and other anions with lead and the reverse titrations. I. M. Kolthoff and Y. D. Pan (*J. Amer. Chem. Soc.*, 1940, **62**, 3332—3335; cf. A., 1940, I, 131).—Sulphate has been titrated amperometrically with Pb(NO₃)₂ between 0.01 and 0.001M. in H₂O and H₂O—EtOH (20—30%) at a potential of the dropping Hg electrode of -1.2 v. in presence of indifferent electrolytes. The conditions for accurate titrations are described. Results of amperometric titrations of Pb with sulphate, oxalate, and iodate, and of oxalate and ferrocyanide with Pb are given.

W. R. A.

Titration of ammonia in presence of boric acid in the macro-, semi-micro-, and micro-Kjeldahl procedures, using methyl-red indicator and the colour-matching end-point. E. C. Wagner (*Ind. Eng. Chem. [Anal.]*, 1940, **12**, 771—772; cf. A., 1934, 47).—Details of prep. of the aq. H₃BO₃, and of the colour-matching titration with special reference to the semi-micro-procedure are given. Essential experimental conditions for the macro-, semi-micro-, and micro-Kjeldahl procedures are tabulated.

L. S. T.

Colorimetric determination of nitrite. M. B. Shinn (*Ind. Eng. Chem. [Anal.]*, 1941, **13**, 33—35).—Sulphanilamide (I) and NH₂·[CH₂]₂·NH·C₁₀H₇·2HCl are used in place of sulphanilic acid and α-C₁₀H₇·NH₂ in the determination of NO₂⁻. The colour develops more quickly (2 min.), is more stable (several hr.), and is less sensitive to variations in pH (acid concns. 0.1–1N.). Standard (I) is substituted as a primary standard for the less stable aq. NaNO₂. Details of procedure and test data are given.

L. S. T.

Organic reagents and methods involving their use. Indirect volumetric determination of metals precipitated by organic reagents of the oxime type. N. H. Furman and J. F. Flagg (*Ind. Eng. Chem. [Anal.]*, 1940, **12**, 738—740).—A BrO₃⁻·AsO₃^{'''} method for determining NH₂OH is described, and is applied to the determination of metals in various types of oxime ppts. NH₂OH is oxidised by a measured vol. of standard KBrO₃ in 3–4N-HCl, standard H₃AsO₃ is added, and the excess is determined by titration with KBrO₃ (Me-orange). The max. amount of NH₂OH permissible in any determination is 20 mg. A general procedure applicable to metal-oxime ppts. formed under the usual conditions and then dissolved in conc. HCl is detailed. Data for the determination of Cu pptd. with salicylaldoxime or α-benzoinoxime, and of Ni pptd. with dimethylglyoxime, are recorded. The method is suitable for semimicro-quantities of Cu⁺⁺.

L. S. T.

Enhancement by flotation of sensitivity of the reactions for phosphate and arsenate. A. M. Belousov and A. G. Belousova (*J. Appl. Chem. Russ.*, 1940, **13**, 594—595).—5 ml. each of N-(NH₄)₂MoO₄ and of 6N-H₂SO₄ are added to 3 ml. of solution at 35–50°, followed by 2–3 ml. of iso-C₆H₁₁·OH, and the solution is shaken, when a yellow pellicle forms at the phase

interface in presence of $\leq 0.1 \mu\text{g. PO}_4^{4-}$ per ml. 2 ml. of conc. HCl are added to 4 ml. of solution, H_2S is passed (2—3 min. at the b.p.), and the cooled solution is shaken at 50° with 1% CHCl_3 in *iso*- $\text{C}_2\text{H}_5\text{OH}$, when As_2S_3 collects at the phase interface ($\leq 2 \mu\text{g. AsO}_4^{4-}$ per ml.). R. T.

Determination of silicic acid. H. Gotô (*Sci. Rep. Tôhoku*, 1940, 29, 440—445).— SiO_2 is obtained in an insol. form which can be filtered and weighed by baking silicates with HCl and treating the residue with AcOH . If baking is carried out at temp. $\gt 150$ — 155° , Fe and Al remain in solution after this treatment. The prep. of collodionised filter-paper and its use in the determination of Zn by pptn. with H_2S and weighing as ZnSO_4 are described. O. D. S.

Determination of silicic acid in silicates. V. A. Smirnov and E. N. Isakov (*J. Appl. Chem. Russ.*, 1940, 13, 592—593).—A micro-method, differing from the ordinary micro-method in that the ppt. of SiO_2 is collected and washed on the centrifuge instead of on the filter, is described. R. T.

Determination of carbon monoxide in combustion gases by means of iodine pentoxide.—See B., 1941, I, 94.

Photometric determination of potassium with dipicrylamine. E. Amdur (*Ind. Eng. Chem. [Anal.]*, 1940, 12, 731—734).—A combination of Corning glasses No. 556 and 429 as light filters gives the best results in the photometric determination of K by means of dipicrylamine. A modification of the procedure described by Kolthoff and Bendix (A., 1939, I, 215) is given for K alone and in presence of Na. Li dipicrylamine saturated with K dipicrylamine is used as the reagent. Optimum amounts range from 0.3 to 0.8 mg. of K, but the method can be extended to 80 mg. of K. A Cenco—Sheard—Sanford photometer is used for measuring % transmission. L. S. T.

Use of borofluoric acid in micro-analysis. O. G. Scheintz (*J. Appl. Chem. Russ.*, 1940, 13, 1101—1103).—A drop of 2N- HBF_4 is added to a drop of solution on a slide, when characteristic micro-crystals form in presence of $\leq \text{K}^+$ 1.25, Rb^+ 0.65, Cs^+ 2.5, or Ba^{++} 0.06 $\mu\text{g. Mg, Li, Ca, Al, Fe, Cr, Ti, U, Mn, Zn, Co, Ni, Hg}^{II}, \text{Pb, Bi, Cu, Cd, Sb, Sn, Ag, Be, Zr, Th, Ce, Au, Pd, Pt, AsO}_3^{3-}, \text{AsO}_4^{3-}, \text{VO}_3^-, \text{WO}_4^{2-}$, and MoO_4^{2-} do not interfere. R. T.

Determination of potassium by silver cobaltinitrite method.—See A., 1941, III, 236.

Use of magnesium salt of hexanitrodiphenylamine in micro-analysis. O. G. Scheintz (*J. Appl. Chem. Russ.*, 1940, 13, 1098—1100).—A drop of saturated aq. $\text{Mg}[\text{N}(\text{C}_6\text{H}_4(\text{NO}_2)_3)_2]$ is added to a drop of test solution on a slide; characteristic micro-crystals form in presence of $\leq \text{Rb}^+$ or Cs^+ 0.04, Pb^{++} 0.25, Hg^{++} 0.5—1, or Ti^{++} 0.05 $\mu\text{g.}$ R. T.

Morin reaction for beryllium. E. B. Sandell (*Ind. Eng. Chem. [Anal.]*, 1940, 12, 762—764; cf. A., 1933, 269).—In 0.01—0.1N- NaOH under the conditions described, the sensitivity of the test is 0.01 p.p.m. of Be in daylight, and much greater in ultra-violet light. In 1—2 ml. of solution, 0.001 $\mu\text{g.}$ of Be can be detected. The sensitivity decreases with an increase in $[\text{NaOH}]$. $\text{Cu}^{++}, \text{Ag, Au, and Mn}$ are sufficiently sol. in NaOH to oxidise and destroy the reagent. In ultra-violet light, Li and Ca in alkaline solution give the same fluorescence as does Be, and that given by Zn is visible in daylight, but is \ll that given by Be. It is destroyed by addition of CN^- without effect on the Be fluorescence. The solubility of $\text{Sc}(\text{OH})_3$ in N- NaOH , and possibly that of $\text{Y}(\text{OH})_3$, is sufficient to give a faint fluorescence in daylight. Many other ions (listed) give no reaction. Metals that give hydroxides sol. in NaOH , with the exception of Zn, do not, in general, interfere with the test for Be in daylight. In presence of CN^- , 1 part of Be can be detected in presence of 2×10^4 of Zn. In daylight, 1 part of Be can be detected in presence of 10^5 of Al, and in ultra-violet light, in presence of 2×10^6 of Al. With metals giving hydroxides insol. in NaOH , Be can usually be detected if an excess of alkali is used, but sensitivity is reduced. Small amounts only of Ca can be prevented from interfering with the test for Be by adding $\text{Na}_2\text{P}_2\text{O}_7$. Alkali fluorides, phosphates, borates, and silicates do not interfere with the Be reaction. L. S. T.

Titan-yellow qualitative test for magnesium. E. B. Otto and C. E. Otto (*Ind. Eng. Chem. [Anal.]*, 1941, 13, 65—66).—An improved spot plate procedure which detects 0.01 mg. of

Mg per ml. is described. The reaction is not suitable for use on paper. A p_{H} of ~ 12.5 is necessary to produce the red colour, and it is better to dilute conc. solutions of Mg^{++} than to use high $[\text{NaOH}]$, which give a brownish-orange colour with the reagent, to attain this val. Under different conditions of p_{H} , concn. of ion, and of reagent, the following ions can interfere with the test for Mg^{++} : $\text{Ag}^+, \text{Hg}^+, \text{Hg}^{++}, \text{Cd}^{++}, \text{Ca}^{++}, \text{Co}^+, \text{Cu}^{++}, \text{Pb}^{++}, \text{Li}^+, \text{Mn}^{++}, \text{Ni}^+, \text{Cr}^{+++}, \text{Fe}^{++}, \text{Fe}^{+++},$ and MnO_4^- , and $\text{Al}^{+++}, \text{La}^{+++}, \text{NH}_4^+, \text{Zn}^{++}, \text{Sb}^{+++}, \text{Sn}^{++}, \text{Sn}^{+++}$, and As can prevent the formation of the red colour; tartrate and $\text{Fe}(\text{CN})_6^{4-}$ decrease sensitivity. L. S. T.

Separation method and qualitative test for cadmium ion involving alkaline tartrate complexes. J. P. McReynolds (*J. Chem. Educ.*, 1940, 17, 532).—Of the common cations only Cd, Fe^{+++} , Mg, and the alkaline earth ions are sol. in cold alkaline tartrate solutions and are reprecipitated on heating. To 1 ml. of the group II solution after removal of Pb is added 1 ml. of N-Rochelle salt; the solution is neutralised and made 0.5N. with respect to NaOH . On boiling, $\text{Cd}(\text{OH})_2$ is pptd., and can be confirmed as CdS. Alternatively, the procedure can be applied after separation of Bi^{+++} by means of aq. NH_3 . The test is sensitive to 1 part in 10^5 of Cd^{++} or 1 in 10^4 in presence of much Cu^{++} . L. S. T.

Slow and rapid autoelectro-analysis. J. Guzmán and S. A. Celsi (*Anal. Fis. Quim.*, 1940, 36, 26—32).—The term autoelectro-analysis is proposed for the determination of a metal by deposition on an electrode without the use of an external current. The determination of Cu can be carried out slowly using simple apparatus with Zn—Hg and Cu (or Pt) electrodes in 2N- H_2SO_4 ; errors are $\gt 0.2\%$. In the rapid determination of Ag the sol. electrode is of Cu and a third electrode of Pt is maintained at const. potential while the electrolyte is kept at 70° . Results by the latter method are less accurate. F. R. G.

Organic reagents for colorimetric analysis. Determination of metals and inorganic radicals. I—IV. N. L. Allport (*Ind. Chem.*, 1940, 16, 311—313, 318, 349—351; 1941, 17, 3—5, 47—48).—Working details of the most successful methods are given for the following: $\text{Al}^{+++}, \text{Be}^{++}, \text{Bi}^{+++}, \text{Ca}^{++}, \text{CrO}_4^{2-}, \text{Co}^+, \text{Cu}^{++}, \text{Fe}^{+++}, \text{Pb}^{++}, \text{Mg}^+, \text{Hg}^{++}, \text{Ni}^{++}, \text{Sn}^{++}, \text{Ti}^{+++}, \text{BO}_3^{3-}, \text{NO}_3^-, \text{NO}_2^-, \text{PO}_4^{3-}, \text{CS}_2$, and Cl_2 . L. S. T.

Determination of manganese by the silver—persulphate method. E. N. Denisov (*J. Appl. Chem. Russ.*, 1940, 13, 596—619).—100 ml. of solution of Mn salt in 2N- H_2SO_4 at 50 — 60° are added to a solution of 5 g. of $\text{K}_2\text{S}_2\text{O}_8$ in 100 ml. of 0.05N- AgNO_3 in 1.5N- H_2SO_4 at 50 — 60° , and this temp. is maintained until the colour changes from black to violet. MnO_4^- is then titrated. R. T.

Determination of cobalt as trioxalatocobaltate. G. H. Cartledge and P. M. Nichols (*Ind. Eng. Chem. [Anal.]*, 1941, 13, 20—21).—The method described is based on the spectrophotometric measurement of the absorption at 605 $\mu\mu$. due to $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$, which is produced by oxidation of Co^{++} by PbO_2 in presence of a weakly acid solution of $\text{K}_2\text{C}_2\text{O}_4$. Cu^{++} and Mn^{++} must be absent, but Ni, Fe, and Cr can be present in considerable amounts. A volumetric method, in which $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ is overtitrated with 0.05N- $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ and the excess of Fe⁺ determined by titration with $\text{K}_2\text{Cr}_2\text{O}_7$ (NHPh_2), is described. L. S. T.

Colour reaction for quadrivalent tin. V. I. Kuznetsov (*J. Appl. Chem. Russ.*, 1940, 13, 769—775).—To 1-aminoanthraquinone in conc. H_2SO_4 is added a solution of 2 g. of NaNO_2 in 10 ml. of conc. H_2SO_4 , and the diazo-salt obtained is coupled with NPhMe_2 in HCl, to yield 1-p-dimethylaminobenzene-azoanthraquinone, m.p. 243° [hydrochloride (I); hexachlorostannate]. Filter-paper is impregnated with a solution of 0.1 g. of (I) and 15 g. of NaCl in 200 ml. of 1% HCl in 30% EtOH; the colour of the paper changes from red to violet when a drop of solution containing $\leq 0.01 \mu\text{g.}$ of Sn^{IV} is placed on it (limiting dilution of Sn^{IV} is 10 p.p.m.). A similar reaction is given by much higher concns. of U, Nb (only in presence of tartrates), Zn, Cd, Hg^{II} , Pt^{IV} , Al, Sb^{III} , Mo, Au, Ir, and Ga; except in the cases of Sn^{IV} , U, and Nb the red colour is restored by placing a drop of dil. HF on the spot. U does not interfere except when $[\text{U}]/[\text{Sn}^{IV}] > 100$. R. T.

Dissolution of coal ash for determination of germanium. IV. I. P. Alimarin and B. N. Ivanov-Emin (*J. Appl. Chem. Russ.*, 1940, 13, 951—955).—Evaporation to dryness of solutions of GeO_2 in HF or HF—HCl— H_2SO_4 does not involve loss of Ge

as GeF_4 , owing to formation of a stable complex, H_2GeF_6 . However, in presence of alkali halides, considerable loss may occur, so that ash of a high Cl content cannot be analysed for Ge by this method. 3 g. of ash are heated with 10 ml. each of H_2SO_4 and HClO_4 and 25 ml. of HF, to evolution of SO_2 . 75 ml. of H_2O , 1 g. of H_2BO_3 , 2 ml. of Br, and 200 ml. of conc. HCl are added, the solution is distilled to half its vol. (receiver at 0°), when 150 ml. of HCl are added, and distillation is continued. Br in the distillate is reduced with NH_4OH , the acidity is adjusted to 4–5N. by means of aq. NaOH, 2 g. of H_2BO_3 are added, and the solution is saturated with H_2S . The ppt. is collected after 24 hr., washed, ignited with HNO_3 at $900\text{--}1000^\circ$, and weighed as GeO_2 . R. T.

Rapid determination of antimony, tin, and bismuth. S. Kallmann and F. Pristera (*Ind. Eng. Chem. [Anal.]*, 1941, 13, 8–11).—Details of new short methods for the accurate determination of Sb, Sn, and Bi in metals, alloys, and ores are given. Sb, Sn, and Bi are co-pptd. with MnO_2 formed from Mn^{++} and KMnO_4 in hot, dil. HNO_3 or H_2SO_4 . For Sb and/or Sn, the ppt. of MnO_2 is heated to fuming with H_2SO_4 , KHSO_4 , and $(\text{NH}_4)_2\text{SO}_4$, and to determine the Sb the solution is diluted with aq. SO_3 , boiled down with HCl, diluted, and titrated with KMnO_4 or KBrO_3 (Me-orange). The Sn is reduced by means of Ni and HCl in the solution after titration of the Sb, or in the solution containing the fumed MnO_2 ppt., and finally titrated with standard I. For Bi, the ppt. of MnO_2 is dissolved in dil. HNO_3 and H_2O_2 , and the Bi separated as basic nitrate by means of ZnO . This method eliminates the usual sulphide, carbonate, and basic nitrate separations. The basic nitrate is dissolved in HNO_3 , and the Bi finally pptd. and weighed as BiOCl . Test data and comparative analyses made by standard methods are recorded, and possible interferences are discussed. L. S. T.

Volumetric determination of bismuth. J. G. Carreró (*Anal. Fis. Quím.*, 1940, 36, 33–43).—A modification of the procedure proposed by Stamm and Goehring (A., 1939, I., 102) involves the titration of the CNS' solution either by Lang's method with KCN and KIO_3 , or by KBr and KIO_3 . Greater accuracy is obtained. F. R. G.

XI.—APPARATUS ETC.

High-output electric flask heater. H. A. Krantz and R. W. Huffer (*Ind. Eng. Chem. [Anal.]*, 1940, 12, 752–753).—A 3-l. flask is heated externally by means of three separate Ni–Cr heating units, supplemented by a Bunsen burner. The higher-boiling petroleum fractions ($>343^\circ$) can be distilled by means of this heating unit. Details of construction are given. L. S. T.

Centrifuge cooling unit. H. L. Wunderly and L. S. Smelo (*Ind. Eng. Chem. [Anal.]*, 1940, 12, 754).—A metal cooling unit filled with solid CO_2 is attached to the under side of the centrifuge lid, and maintains a temp. 8° or $9^\circ <$ room temp. (29°) during 10-min. periods. L. S. T.

Introduction of the thyatron into the regulatory system of thermostats. V. G. Sotschevanov (*J. Appl. Chem. Russ.*, 1940, 13, 793–795).—Applications of thyatron relays for thermoregulatory systems are illustrated. R. T.

Adjustable mercury-filled metal thermo-regulator. F. Pagitt (*Ind. Eng. Chem. [Anal.]*, 1941, 13, 60).—The regulator described is rugged, and provides rapid heat transfer, and a simple adjustment for changing temp. over wide ranges. Temp. can be maintained to $\pm 0.001^\circ$ for long periods of time. L. S. T.

Improved Cottrell b.p. apparatus. V. T. Jackson (*J. Chem. Educ.*, 1940, 17, 472).—The difficulty of keeping a const. flow of liquid over the bulb of the Beckmann thermometer is eliminated. L. S. T.

Self-heating hot-bottle. J. St. L. Philpot (*Chem. and Ind.*, 1941, 88).—The device consists of a bag containing ~ 1 lb. of Fe filings mixed with 1% of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$; the mixture should pass a mesh of ~ 150 per in. When 15 ml. of H_2O are added the temp. rises to $70\text{--}100^\circ$, owing to catalysis of rusting by Cu deposited on the Fe. The bag can be used several times without refilling. A. J. E. W.

Improved radiation pyrometer. T. R. Harrison and W. H. Wannamaker (*Rev. Sci. Instr.*, 1941, 12, 20–32).—The error

involved in the reading of a radiation pyrometer owing to ambient temp. effects is considered, and shown to be considerable. These effects can be compensated by using a Ni resistance shunt in conjunction with a pyrometer having a thermopile with a fairly high conduction factor. Such an instrument is described. It shows ambient temp. errors of $<3^\circ \text{F}$. in the furnace temp. being measured, for ambient temp. variations of $50\text{--}200^\circ \text{F}$. The response of the instrument is rapid. A. J. M.

Direct-reading measuring microscope. J. E. Sears and A. Turner (*J. Sci. Instr.*, 1941, 18, 17–19).—Measurements are made to within 0.01 mm. by direct reference to a 305-mm. glass scale and vernier, which can be traversed, together with the photographic film, beneath a low-power microscope in which the film and scale can be viewed together. D. F. R.

Adapting the polarising microscope for use as a polarimeter. A. Marion (*Ind. Eng. Chem. [Anal.]*, 1940, 12, 777).—The adaptation is made by adding to the microscope stage an analyser constructed from two sections of Polaroid cut so that their planes of polarisation include an angle of $\sim 5^\circ$ when semi-circular sections are mounted in place with a slight overlap. The Polaroid analyser is placed at the top of a glass cell of 150 cu.mm. capacity. Performance is illustrated by results obtained with aq. glucose, fructose, maltose, and sucrose. L. S. T.

Time-saving adaptation for photomicrography. J. A. Quense and W. M. Dehn (*Ind. Eng. Chem. [Anal.]*, 1941, 13, 68).—The device renders unnecessary the removal of the camera when the photomicrograph is to be taken without the nicol analyser and with either polarised or unpolarised illumination. L. S. T.

Accurate measurement of X-ray diffraction films. H. P. Klug (*Ind. Eng. Chem. [Anal.]*, 1940, 12, 753–754).—The measuring device is described and illustrated. L. S. T.

Colorimetric analysis of a two-component colour system. H. W. Knudson, V. M. Meloche, and C. Juday (*Ind. Eng. Chem. [Anal.]*, 1940, 12, 715–718).—It is shown experimentally and theoretically how photo-electric filter photometers can be used to resolve the intensity of one colour in presence of a second. Typical experimental results for synthetic mixtures of Fe^{+++} and Al^{+++} and hæmatoxylin are recorded. A method for determining small amounts of Al in natural waters containing only small amounts of Fe is given. L. S. T.

Camera for photographic demonstration. D. H. Gurinsky (*J. Chem. Educ.*, 1940, 17, 432).—A camera in which exposure, development, and fixing can be performed without removing the film is described for demonstrating the photographic process. L. S. T.

Collimated light beams in spectrophotometry. G. O. Langstroth, W. W. Brown, and K. B. Newbound (*Canad. J. Res.*, 1940, 18, A, 186–192).—It has been shown experimentally, in agreement with a theoretical prediction, that a considerable variation of the distance between the linear light source (slit) and the collimating lens is permissible. F. J. G.

Reflecting mirror optical system for the ultracentrifuge. W. G. France and E. R. Lang (*Rev. Sci. Instr.*, 1941, 12, 32–34).—An aluminised reflecting mirror optical system for use in place of the customary long-focus lens with air-driven ultracentrifuges is described. Typical sedimentation pictures taken with the apparatus are given. A. J. M.

Silica gauge for measuring thickness by means of interference colours. K. B. Blodgett (*Rev. Sci. Instr.*, 1941, 12, 10–14).—The construction of a gauge for measuring the thickness of unimol. films by interference of light is described. A SiO_2 film of the correct thickness is obtained on lead glass by treating the glass with HNO_3 . A unimol. layer of the substance to be examined is deposited on the SiO_2 film, and its thickness is determined by observing the change in intensity of reflected light owing to the increased thickness. Equations are given from which the thickness may be calc. A. J. M.

Simple method for refractive index determination. S. M. Cox (*J. Sci. Instr.*, 1941, 18, 20–21).—Measurements are made with $\sim 0.5\%$ accuracy on glass rods, which may be prepared by heating in the flame, without grinding or polishing. D. F. R.

Residual photometric errors in the commercial recording spectrophotometer.—See B., 1941, I, 83.

Apparatus for the study of rapid chemical reactions. D. Dubois (*J. Biol. Chem.*, 1941, **137**, 123—137).—A modification of the Thiel and Logemann apparatus (cf. A., 1936, 433) is described. The observation tube (made of transparent plastic) is moved vertically through the light beam, and the changes in light absorption occurring during the reaction are recorded automatically as a curve on a time scale. The average half reduction time of oxyhemoglobin is found to be 0.028 sec. (temp. 20—27°, p_H 8.4—9.5), compared with Millikan's val. of 0.038 sec. at 22° and p_H 8.6 (A., 1936, 1224).
E. M. W.

Apparatus for plating hydrogen electrodes. V. A. Lamb (*J. Chem. Educ.*, 1940, **17**, 539).—Apparatus is described. Pd-black is preferred to Pt-black on account of easier removal of old deposits and less poisoning of the electrodes. L. S. T.

Silver chloride electrode in acid-base titrations. J. E. Vance (*Ind. Eng. Chem. [Anal.]*, 1941, **13**, 68).—Advantages over the HgCl electrode are that the possibility of plating-out Hg on the H electrode is eliminated, the liquid junction is avoided, and the experimental arrangement is simplified since the Ag—AgCl electrode is immersed directly in the acid being titrated. In titrating acids other than HCl, NaCl is added to provide Cl⁻. For HBr or HI the corresponding halide electrode is used. The quinhydrone can replace the H electrode, and during the titration p_H must then be kept ± 8.5 .
L. S. T.

Use of a condenser to reduce galvanometer oscillations in polarographic measurements, with particular application to compensation method of measuring small diffusion currents. J. J. Lingane and H. Kerlinger (*Ind. Eng. Chem. [Anal.]*, 1940, **12**, 750—752).—The galvanometer oscillations are damped, without affecting the diffusion current, by connecting an electrolytic condenser of high capacitance across the galvanometer shunts. Application of this principle extends greatly the practical applicability of the compensation method of measuring small diffusion currents. An improved compensation circuit is described.
L. S. T.

Electronic relay. C. E. Rudy, jun., and P. Fugassi (*Ind. Eng. Chem. [Anal.]*, 1940, **12**, 757).—A circuit utilising a cold-cathode, starter anode, gas-filled tube is described and illustrated. The many advantages of such a tube over a hot-cathode, high-vac. tube are described.
L. S. T.

Regulated filament emission for cyclotrons. E. Pollard (*Rev. Sci. Instr.*, 1941, **12**, 37).—Unsteadiness in cyclotron beams may be due to variation in filament emission. A method for keeping the emission current steady, thus avoiding variations in the cyclotron beam of $>2\%$ during a proton count, is described. The use of the regulator also results in considerably longer life of the filaments.
A. J. M.

Filament-bearing balance. J. de Ment (*J. Chem. Educ.*, 1940, **17**, 437).—Sensitive balances carrying loads of 20—40 g. can be constructed from a wooden beam suspended from a human hair or a steel wire. An ordinary knife-edge bearing balance can be converted into a semimicro-balance by the use of the filament-bearing principle.
L. S. T.

Determination of the centre of gravity of the beam of a chemical balance. H. V. Moyer (*J. Chem. Educ.*, 1940, **17**, 540).—A method is described.
L. S. T.

Gravimetric analysis by means of the thermo-balance. M. Kobayashi (*Sci. Rep. Tôhoku*, 1940, **29**, 391—411).—A bibliography of papers (1936—1940) giving data for the variation with temp. of heating in the wts. of compounds commonly used for the gravimetric determination of 62 chemical elements.
O. D. S.

Micro-burettes and -pipettes based on the principle of capillarity. M. P. Poljakov (*J. Appl. Chem. Russ.*, 1940, **13**, 638—640).—Capillary micro-burettes and -pipettes are described.
R. T.

Gasometer for micro-Dumas determinations. J. G. Sandza and J. F. Alicino (*Ind. Eng. Chem. [Anal.]*, 1940, **12**, 776—777).—The gasometer described is constructed from two test-tubes and delivers a measured vol. of CO₂ confined over H₂O in a system closed to the atm. The abs. blank is 0.014 \pm 0.001 ml.
L. S. T.

Micro-apparatus for fractional recrystallisation. L. C. Craig (*Ind. Eng. Chem. [Anal.]*, 1940, **12**, 773—774).—A filter stick suitable for filtration of the solution just before the final crystallisation, and two centrifuging vessels for crystallisation of small quantities of material from small vols. of conc. solutions, are described and illustrated.
L. S. T.

Distinguishing individual quantitative filter-papers. C. E. Otto (*J. Chem. Educ.*, 1940, **17**, 519).—Aq. solutions of different coloured dyes are streaked along the edges of a packet before it is broken. Suitable dyes are Water Blue, Nigrosine CPP, Erie Fast Scarlet 4BAP, and Auramine OP.
L. S. T.

Laboratory-size leaf-type pressure filter. T. F. Clark, N. Porges, and S. I. Aronovsky (*Ind. Eng. Chem. [Anal.]*, 1940, **12**, 755—757).—The filter described has an effective filtering surface of 54 sq. in., and a calc. wet-cake capacity of 0.69 l. Hydraulic pressures up to 30 lb. per sq. in. have been used. The filter leaves are adaptable to either top or bottom drainage.
L. S. T.

Supersonic oscillator. B. H. Porter (*Ind. Eng. Chem. [Anal.]*, 1940, **12**, 748—749).—The laboratory model described consists essentially of a high-voltage rectifier and an oscillator that motivates a quartz crystal in a dielectric fluid.
L. S. T.

Acetone-ether mixtures for drying glassware. A. E. Markham (*Ind. Eng. Chem. [Anal.]*, 1940, **12**, 748).—A mixture of COMe₂ (1 vol.) and Et₂O (1 vol.) is more efficient than pure COMe₂, and has a better solvent power for greases, especially the usual stopcock preps.
L. S. T.

Determination of chemical stability of glass.—See B., 1941, I, 101.

Grinding and scratching crystalline surfaces. R. S. Rivlin (*Nature*, 1940, **146**, 806—807).—De Gramont's method of studying a surface broken into many small facets of various orientations can be applied to the ground surfaces of transparent materials. A ground, (0001) plane of quartz gives a refraction pattern which can be used to determine the *a* axes. Refraction patterns have also been obtained for ground surfaces of calcite, selenite, rock-salt, etc. Any marked cleavages possessed by a crystal are apparent in the refraction patterns of ground or scratched surfaces. The patterns also indicate zones of easy fracture.
L. S. T.

[Laboratory] hood. I. Lin (*J. Chem. Educ.*, 1940, **17**, 447).—A glass funnel is inverted over the vessel in which evaporation is taking place, and is connected through a wash bottle to a water pump.
L. S. T.

Automatic mercury valve. H. B. McGlade (*Science*, 1940, **92**, 464).—The arrangement described prevents the forcing or accidental spilling of Hg from an open tube without interfering with the flow or oscillation of the Hg.
L. S. T.

Vapour density apparatus. J. M. Hendel and O. Ochsreiter (*J. Chem. Educ.*, 1940, **17**, 533—535).—An improved form of the Victor Meyer apparatus, giving a precision of 2% in mol. wt. determinations, is described.
L. S. T.

High rotational speeds in vacuum. C. S. Smith (*Rev. Sci. Instr.*, 1941, **12**, 15—20).—Rotors freely suspended in a high vac. were rotated at high speed by electrostatic and electromagnetic forces. The highest speed attained was 3200 r.p.s.
A. J. M.

High-pressure valve. M. J. Moore (*J. Sci. Instr.*, 1941, **12**, 23).—The valve consists of a hard rubber tapered plug in a metal seating. Leakage past the spindle to which the plug is attached is prevented by a circular rubber diaphragm fixed between the spindle and valve seating. The valve has been used satisfactorily up to 50 atm. in a Wilson expansion chamber.
D. F. R.

Determination of average mol. wts. or particle sizes for polydispersed systems. E. O. Kraemer (*J. Franklin Inst.*, 1941, **231**, 1—21).—Mathematical. A consideration of the interrelation of several types of average vals. of significance in determinations by indirect methods, and of conditions under which different averages may be calc. from each other. The methods examined are Staudinger's viscosity rule for average mol. wt., average axial ratio and particle size from viscosity of ellipsoidal particles, and average particle size from light absorption.
N. M. B.

Effect of gravitational field on the thermal diffusion separation method. M. Farber and W. F. Libby (*J. Chem. Physics*,

1940, 8, 965—969).—The effect of a gravitational field on the thermal diffusion method of gas separation has been investigated by the use of a hollow spinning disc, with one hot surface. For He—CO₂ mixtures both the equilibrium separation and the rates of separation increase with increasing centrifugal force up to a max. val., after which both fall rapidly. The results indicate that the standard thermal diffusion column would be improved by placing it in a gravitational field of ~10 times the normal val. J. W. S.

Theory of separation of mixtures by the thermo-diffusion method. A. I. Brodski (*J. Appl. Chem. Russ.*, 1940, 13, 663—669).—The application of the Clusius—Dickel thermo-diffusion method (A., 1938, I, 539) to separation of gaseous mixtures is discussed, and its applications are illustrated for sp. cases. R. T.

Removal of stopcock grease from burette tips. C. B. White and R. C. McGlenn (*Ind. Eng. Chem. [Anal.]*, 1941, 13, 61).—CCl₄ is employed. L. S. T.

Vacuum still for purification of a single substance or recovery of a single fraction. F. C. Holmes (*Ind. Eng. Chem. [Anal.]*, 1941, 13, 61).—Two receiving vessels are connected to the lower end of the condenser by means of a T-shaped tube, and the distillate is directed into one or other of the receivers by tilting the whole apparatus. The apparatus is suitable for purification of a few ml. of oleic acid, in which a rapid change of receivers is essential. L. S. T.

Convenient method for conducting the Kjeldahl digestion. B. O. Heston and S. R. Wood (*J. Chem. Educ.*, 1940, 17, 475).—A Gooch crucible is fitted tightly into the mouth of the digestion flask by means of Pb or Sn foil. The crucible is filled two thirds full with loosely-placed asbestos moistened with conc. H₂SO₄. The acid fumes from the digestion are then absorbed completely. L. S. T.

Nomograph for correcting barometer readings for temperature. S. M. Troxel (*J. Chem. Educ.*, 1940, 17, 431). L. S. T.

Simple test for straight-line relationships. D. E. Babcock (*J. Chem. Educ.*, 1940, 17, 440).—The method illustrated for determining whether a linear relationship exists between physico-chemical data is based on the condition that the area of a triangle formed by three points in a straight line is zero. L. S. T.

XII.—LECTURE EXPERIMENTS AND HISTORICAL.

Lecture demonstrations in general chemistry. S. B. Arenson (*J. Chem. Educ.*, 1940, 17, 434—436, 469—472, 513—515).—Selected demonstrations of various types are described. L. S. T.

XIII.—GEOCHEMISTRY.

Measurement of the excess weight of air oxygen by exchange with inorganic salts. O. R. Alexander and N. F. Hall (*J. Amer. Chem. Soc.*, 1940, 62, 3462—3464).—The density difference due to O alone has been determined for two samples of H₂O (Madison tap and Lake Michigan). Lake Mendota H₂O, purified by refluxing with KMnO₄ and alkali for 12 hr. and then distilled, was used as standard. Purified air was caused to react with excess of H₂ to give another reference H₂O. The O exchange between H₂O and K₂Cr₂O₇ was measured by changes in ρ . If Lake Mendota H₂O is normal in O isotopic composition the atm. O₂ has an excess ρ of 7.1 ± 0.2 γ d. Madison tap H₂O is 0.88 γ d lighter than Lake Mendota H₂O and Lake Michigan is 0.15 γ d denser. W. R. A.

Radium content of mineral springs in Japan. T. Nakai (*Bull. Chem. Soc. Japan*, 1940, 15, Suppl., 333—426).—477 determinations by the Rn emanation method of the Ra content of thermal springs and brines from oil fields from different parts of Japan are tabulated. The geographical distribution of Ra is shown, and a comparison of mineral waters in other countries is made; those of Japan are comparatively poor in Ra. The highest concns. vary from 1 to 11×10^{-11} g. per l. The mineral springs of Masutomi, Yamana Prefecture, have the highest Ra content of the Japanese cold springs. The hot springs of Misasa, Tottori Prefecture, are the most radioactive in Japan and rank second to Ischia in Italy. Data for these and other springs are recorded, and relationships between Ra and Rn contents, and

orifice temp., and p_H are discussed. Chemical classifications of mineral springs and their Ra contents are also discussed. Data for the extraction of Ra from mineral waters by means of various pptns. are given. The best results are obtained by using Ba, Ca, and Sr sulphates and carbonates as carriers. The % amount of Ba pptd. with or adsorbed by MnO₂ or MnO₂ + Fe₂O₃·nH₂O is also large. L. S. T.

Ecological aspects of the intertidal area of the Estuary of the Aberdeenshire Dee. A. Milne (*Trans. Roy. Soc. Edin.*, 1940, 60, 107—139).—Data concerning temp., [H⁺], and salinity are recorded, and the intertidal fauna and their different distributions are described. The estuary has only $\frac{1}{5}$ to $\frac{1}{10}$ of the species (macrofauna) common to long estuaries. This is due apparently to the high fluctuation in salinity and the absence of mudflats. Salinity is responsible chiefly for distribution in this estuary. *Mytilus* is sensitive to salinity even when apparently tightly closed, and the salinity of the retained H₂O of both *Mytilus* and *Patella*, when uncovered at low tide, is never < a min. val. L. S. T.

Geology and ground-water resources of the "Equus Beds" area in south central Kansas. S. W. Lohman and J. C. Frye (*Econ. Geol.*, 1940, 35, 839—866).—The H₂O-bearing formations, the results of test drillings, the shape of the H₂O table and movement of H₂O, and H₂O-level fluctuations are described and illustrated. L. S. T.

Radioactivity of ocean sediments. III. Radioactive relations in ocean water and bottom sediment. C. S. Piggot and W. D. Urry (*Amer. J. Sci.*, 1941, 239, 81—91; cf. A., 1940, I, 44).—The highest concns. of Ra ($3—22 \times 10^{-12}$ g. per g.) occur in a so-called red clay, a fine-grained material found underlying very deep H₂O. The U content of bottom sediments is insufficient to maintain the high [Ra] found in and near the surface of these sediments. The high Ra contents in the surface material often appear to be due to deposition of an excess of Io. They are superficial and of no great geophysical significance, and at greater depths in the sediments the Ra content reaches a val. in equilibrium with the U. This Ra content is comparable with that of sedimentary rocks (0.05—0.5 $\times 10^{-12}$ g. per g.). Various mechanisms for the mode of distribution of the radio-elements between the ocean and its sediments are discussed. L. S. T.

Synthesis and X-ray analysis of gehlenite and anorthite. K. Akiyama (*J. Soc. Chem. Ind. Japan*, 1940, 43, 341B).—Gehlenite and anorthite have been synthesised from CaO, Al₂O₃, and SiO₂, at 1450°, and their X-ray diffraction patterns recorded. Each is a single compound. F. J. G.

Zoning in spherulites. A. D. Howard (*Amer. Min.*, 1940, 25, 614—618).—The origin of zoning in natural and artificial spherulites is discussed. L. S. T.

Crystallography of dolerophanite. W. E. Richmond and C. W. Wolfe (*Amer. Min.*, 1940, 25, 606—610).—Rotation and Weissenberg photographs give a_0 9.39, b_0 6.30, c_0 7.62 Å., β 122° 41 $\frac{1}{2}$ '; space-group C_{2h}—C2/m. ρ is 4.17 and the unit cell contains 4[Cu₂SO₅]. n_x is 1.715, n_y 1.820, and n_z 1.880 [H. Berman]. L. S. T.

Unusual occurrence of gypsum at Kalgoorlie, W. Australia. R. T. Prider (*Amer. Min.*, 1940, 25, 591—605).—Selenite encrustations have developed on the walls and roof above the apparent H₂O level of certain parts of the mine which appear to have existed as airlocks during flooding. The occurrences and crystallography are described, and the genesis of the encrustations is discussed. The deposits developed probably during a short period of several months while the mines were being unwatered and pressures in the airlocks decreasing. L. S. T.

Cristobalite in bentonite. J. W. Gruner (*Amer. Min.*, 1940, 25, 587—590).—X-Ray examination of two bentonites from Wyoming establishes the presence of cristobalite (I). A chemical analysis [R. B. Ellestad] indicates 30% of (I). The origin of the (I) is volcanic. L. S. T.

Optical evidence of polysynthetic twinning in arsenopyrite. J. S. Lukesh (*Amer. Min.*, 1940, 25, 619—621).—Determination of crystal structure shows that arsenopyrite is monoclinic and not orthorhombic. Twinning has been observed on polished sections of arsenopyrite under polarised light. L. S. T.

Cuprobismutite. C. Palache (*Amer. Min.*, 1940, 25, 611—613).—Cuprobismutite consists of a mixture of emplectite and bismuthinite. The name should be discarded.

L. S. T.

Nature of the ore-forming fluid. C. N. Fenner (*Econ. Geol.*, 1940, 35, 883—904).—A discussion of Graton's views (A., 1940, I, 379), and a reply to his objections to the author's conception of the nature of the ore-forming fluid (cf. also *ibid.*, 161).

L. S. T.

Width of albite-twinning lamellæ. J. D. H. Donnay (*Amer. Min.*, 1940, 25, 578—586).—The width of albite-twinning lamellæ depends on the obliquity of the twin; the smaller is the obliquity, the higher is the frequency of the twin and the thinner are the lamellæ. The curve of obliquity plotted against composition shows that the lamellæ should be thinnest in oligoclase and increase in width slowly towards anorthite (I) and rapidly towards albite (II). Pure (I) and (II) should show disappearance of polysynthetic twinning. The results support the French theory of twinning.

L. S. T.

Rammelsbergite and parammelsbergite: distinct forms of nickel diarsenite. M. A. Peacock and A. S. Dadson (*Amer. Min.*, 1940, 25, 561—577).—Rammelsbergite (I) from Eisleben and Schneeberg is orthorhombic with a_0 3.53, b_0 4.78, c_0 5.78 Å.; space-group D_{2h}^{12} — $Pmnn$, ρ_{obs} 6.95, ρ_{calc} 7.05, and unit cell $2[\text{NiAs}_2]$. Structural data are similar to those of marcasite and not loellingite. A new chemical analysis of (I), and its behaviour towards etching agents, are recorded. In air saturated with H_2O , (I) is etched almost completely in 12 hr. Parammelsbergite (II) from three localities in Ontario is orthorhombic or pseudo-orthorhombic, apparent space-group D_{2h}^{11} — $Pbma$ or C_{2v}^5 — $Pb2a$, with a_0 5.74 ± 0.01, b_0 5.81 ± 0.01, c_0 11.405 ± 0.03 Å., ρ_{obs} 7.12, ρ_{calc} 7.24, and unit cell $8[\text{NiAs}_2]$. Chemical analyses and behaviour towards etching reagents are recorded. (II) appears to decompose more rapidly than (I) in moist air. (I) and (II) are readily and best distinguished by their X-ray powder diagrams, which are reproduced.

L. S. T.

Geochemistry of quicksilver mineralisation. R. M. Dreyer (*Econ. Geol.*, 1940, 35, 905—909).—A reply to criticism (cf. A., 1941, I, 62).

L. S. T.

Geology of the Highland Border from Glen Almond to Glen Artny. D. A. Allan (*Trans. Roy. Soc. Edin.*, 1940, 60, 171—193).

L. S. T.

Morphological analysis of danburite. J. D. H. Donnay (*Trans. Roy. Soc. Canada*, 1940, [iii], 34, IV, 33—43).—The method described previously (A., 1940, I, 150) is applied to danburite, and gives results in agreement with those obtained by X-ray analysis. Vals. predicted for a_0 , b_0 , and c_0 are 8.03, 8.74, and 7.71 Å., respectively.

L. S. T.

Certain biotite gneisses of the Grenville series near Kingston, Ontario. W. T. Love (*Trans. Roy. Soc. Canada*, 1940, [iii], 34, IV, 53—62).—Biotite gneisses and conditions of metamorphism are described. Four chemical analyses of the gneisses and one of biotite conc. from Grenville gneiss are presented.

L. S. T.

Ultrabasic rocks of the Fort Fraser map-area (west half), northern B.C. J. E. Armstrong (*Trans. Roy. Soc. Canada*, 1940, [iii], 34, IV, 21—32).—Two large areas of ultrabasic rocks are described. The rocks have been partly to completely serpentinised, and in many places have undergone later hydrothermal alteration to carbonate-quartz-mariposite and carbonate-talc rocks. Existing theories of origin, mode of emplacement, serpentinisation, and steatitisation of ultrabasic rocks are discussed.

L. S. T.

Oxide ores from the auriferous and argentiferous lead mine at Bolkardağ, Turkey. G. C. Ladame (*Schweiz. min. petr. Mitt.*, 1938, 18, 404—428; *Chem. Zentr.*, 1938, ii, 3670).—The deposits contain Pb 7—22% (as galena, cerussite, anglesite, mimetite, pyromorphite, and Pb-jarosite), Zn 1—7.8% (as blende, calamine, smithsonite, and aurichalcite), Cu 0.2, Fe_2O_3 30—54, MnO 1.5—2.5, SiO_2 5—23, As traces—1.3%, Ag 392—704, Au 2—13.6 g. per m. ton (in chalcocite and pyrites). Concentrates are obtained containing Pb 51—63%, Ag 1890—3200, Au 7—96 g. per m. ton.

A. J. E. W.

Mineralisations in the Guedmoua region. F. von der Weid (*Arch. Sci. phys. nat.*, 1940, [v], 22, Suppl., 133—136).—Five different deposits are described.

L. S. T.

Rare copper-cobalt mineral from the Meskani (Iran) deposit. M. Gysin and P. Kovaliv (*Arch. Sci. phys. nat.*, 1940, [v], 22, Suppl., 126—130).—The mineral is grey, and a fractured surface tarnishes rapidly in air until it is black. The blackening is accompanied by an increase in wt. The mineral, hardness 4, ρ 6.862—7.097 (powder), is readily fused by the blowpipe, giving off As fumes. Heated in an open tube it gives a mirror of As. It is sol. in HNO_3 , and contains Cu 59.43, Co 3.95, As 33.72, S 0.25, insol. 0.78, gangue (carbonates) 1.87%. Spectrographic examination confirms the absence of Sb, but shows the presence of traces of Fe, Ni, and Ti, also Sr, probably from the gangue. The mineral is a mixture of three anisotropic constituents, viz., hexagonal domeykite, Cu_2As , safflorite, CoAs_2 , and a small amount of cobaltite, CoAsS .

L. S. T.

Quartz monzonites from the valley of the Ak-Su, Anatolia. M. Gysin (*Arch. Sci. phys. nat.*, 1940, [v], 22, Suppl., 108—112).—Mineral analyses of 10 samples are recorded.

L. S. T.

Syenite-monzonite rocks from the north of Shéhine-Kara-Hissar, Anatolia. M. Gysin and H. N. Pamir (*Arch. Sci. phys. nat.*, [v], 22, Suppl., 105—108).—Mineral compositions of 6 samples are recorded. The rocks are similar in character to those from Divrik (Gysin, *Compt. rend. Soc. Phys. Hist. nat. Genève*, 1939, 56, 126).

L. S. T.

Mineralogical analysis of some marine sands of Anatolia. M. Gysin and P. Kovaliv (*Arch. Sci. phys. nat.*, 1940, [v], 22, Suppl., 84—89).—Magnetic and density separations of sands from the Ordu region, and the microscopical examination of the fractions obtained, are described, and the mineralogical compositions recorded. The average composition is magnetite 34.70, oligist (martite) 4.40, ilmenite 1.76, limonite 0.16, green pyroxene (I) 29.04, alkaline-earth carbonates 2.65, basic plagioclase (II) 14.13, miscellaneous 13.16%. The abundance of (I), (II), and lava debris, the scarcity of quartz, and the absence of tourmaline and F minerals show that these sands arise from the disintegration of basic volcanic rocks, principally andesites.

L. S. T.

Development of pseudo-stratification by metamorphic differentiation in the schists of Otago, New Zealand. F. J. Turner (*Amer. J. Sci.*, 1941, 239, 1—16).—The banded or laminated structure in the Palæozoic schists of the South Island, New Zealand, is a pseudo-stratification, and is mainly the result of metamorphic differentiation brought about by chemical mobilisation of the more readily sol. constituents of the rocks. Ten chemical analyses are discussed.

L. S. T.

American coal balls. W. C. Darrah (*Amer. J. Sci.*, 1941, 239, 33—53).—A large upper Pennsylvanian flora, containing >60 species, has been found in the coal balls in the Des Moines rocks of Iowa, Missouri, and Kansas. Species occurring in various mines and districts are tabulated. A chemical analysis [F. A. Gonyer] of a typical American coal ball is recorded. Pyrite (60%) and calcite (34%) are the main constituents; no dolomite is present. Org. matter (3.10%) is unexpectedly high.

L. S. T.

Radioactivity of sedimentary rocks and associated petroleum. K. G. Bell, C. Goodman, and W. L. Whitehead (*Bull. Amer. Assoc. Petroleum Geol.*, 1940, 24, 1529—1547).—Determinations of the radioactivity of 21 sedimentary rocks and 7 associated crude oils were made. The results corroborate the inferences of previous investigators that Rn tends to concentrate in crude oils. The amounts of radioactivity found in the oils examined are quantitatively sufficient to cause appreciable cracking by α -radiation during geologic time. These reactions, together with subsequent hydrogenation, may account for important changes in petroleum. This hypothesis would explain the presence of H_2 in some natural gases.

R. B. C.

Factors controlling pressure in petroleum reservoirs. J. S. Stewart (*Trans. Roy. Soc. Canada*, 1940, [iii], 34, IV, 123—134).—The origin and accumulation of petroleum, the development of reservoir pressure from hydrostatic causes, or wt. of overburden, or chemical action in the generation of petroleum from org. matter, and the control of pressure by seepage are discussed.

L. S. T.

INDEX OF AUTHORS' NAMES, A., I.

APRIL, 1941.

- ADKINS, H., 117.
 Akiyama, K., 134.
 Alexander, O. R., 123, 133.
 Alexandrov, A. P., 112.
 Alexandrovitch, V. A., 123.
 Alicino, J. F., 131.
 Alimarin, I. P., 128.
 Allan, D. A., 135.
 Allport, N. L., 128.
 Amdur, E., 127.
 Anderson, H. L., 95.
 Aoki, H., 93.
 Arbuzov, K. N., 111.
 Arenson, S. B., 133.
 Arimori, T., 114.
 Armstrong, J. E., 135.
 Arnell, J. C., 118.
 Aronovsky, S. I., 132.
 Atanasoff, J. V., 105.
 Avila, W., 115.
- BABCOCK, D. E., 133.
 Baibaev, A. I., 123.
 Baker, R. H., 117.
 Baker, W. O., 103.
 Bamford, C. H., 122.
 Bamford, D. A., 122.
 Band, W., 110.
 Barve, P. M., 113.
 Baudisch, O., 125.
 Bauer, S. H., 104.
 Beach, J. Y., 104.
 Beatty, H. A., 106.
 Bell, K. G., 136.
 Belousov, A. M., 126.
 Belousova, A. G., 126.
 Bennett, W. H., 121.
 Berg, J. N., 112.
 Bergo, G., 118.
 Bhabha, H. J., 96.
 Blacet, F. E., 121.
 Blaedel, W. J., 121.
 Bloch, E., 110.
 Blodgett, K. B., 130.
 Blum, I. A., 110.
 Borezkov, G. K., 120.
 Bound, M., 95.
 Bowden, F. P., 104.
 Bowman, D. W., 93.
 Boyd, E., 109, 110.
 Bray, W. C., 118.
 Bresler, S., 108.
 Brickwedde, F. G., 96.
 Brinkley, S. R., jun., 123.
 Brodski, A. I., 123, 133.
 Brown, H. C., 123.
 Brown, W. G., 100.
 Brown, W. W., 130.
 Bruce, W. F., 98.
 Buckingham, R. A., 94.
 Burawoy, A., 97.
 Burbo, P. Z., 108.
 Burcik, E. J., 97.
 Burg, A. B., 123.
 Burrows, M. G. T., 120.
 Burton, M., 122.
 Buzagh, A., 108.
- CALINGAERT, G., 106.
 Carlisle, C. H., 103.
 Carreró, J. G., 129.
 Cartledge, G. H., 128.
 Celsi, S. A., 128.
 Chapman, S., 102.
 Charin, A., 111.
 Chazina, J. G., 125.
 Cherry, G. W., 115.
 Clark, T. F., 132.
 Coffin, C. C., 118.
 Cohen, K., 125.
 Conn, G. K. T., 97.
 Copeland, L. C., 115.
 Copley, M. J., 108.
 Copulsky, W., 96.
 Cornog, J., 115.
 Coulson, C. A., 100.
 Cox, S. M., 130.
 Craig, L. C., 132.
 Creutz, E. C., 94.
 Critchfield, C. L., 96.
 Crowfoot, (Miss) D., 103.
- DABHOLKAR, V. D., 95.
 Dacey, J. R., 118.
 Dadson, A. S., 135.
 D (A., I.)
- DARRAH, W. C., 136.
 Datar, D. S., 111.
 David, W. T., 117.
 Davis, F. J., 99.
 Debye, P., 105.
 Dehn, W. M., 130.
 Delasso, L. A., 94.
 Demers, P., 114.
 De Ment, J., 131.
 Denisov, E. N., 128.
 Derendjaev, S., 121.
 Der Weid, F. von, 135.
 Desai, B. N., 113.
 Deshpande, P. Y., 99.
 Dixon, J. K., 120.
 Dole, K. K., 119.
 Donnay, J. D. H., 135.
 Douglas, A. E., 96.
 Dow, W. A., 113.
 Dreyer, R. M., 135.
 Dubois, D., 131.
 Duncanson, W. E., 100.
- EHRENHAFT, F., 93.
 Elder, A. E., 111.
 Epik, P. A., 115.
 Epstein, L. F., 98.
 Essin, O., 121.
 Evans, F., 95.
 Evans, R. R., 106.
 Eyring, H., 99.
 Eyster, E. H., 97.
- FALL, P. H., 93.
 Farber, M., 132.
 Feng, L. S. K., 110.
 Fenner, C. N., 135.
 Fermi, E., 95.
 Flagg, J. F., 126.
 Focke, A. B., 104.
 Fontana, B. J., 114.
 Fordham, S., 104.
 Foster, L. M., 120.
 Fowkes, F. M., 109.
 Fox, S. W., 106.
 France, W. G., 130.
 Frank, H. S., 116.
 Frazer, D., 95.
 Frizzell, L. D., 109.
 Frost, A. A., 108.
 Frye, J. C., 134.
 Fünfer, E., 105.
 Fürth, R., 106.
 Fugassi, P., 131.
 Fuller, C. S., 103.
 Furman, N. H., 126.
- GARDNER, J. H., 107.
 Gaydon, A. G., 97.
 Giauque, W. F., 105.
 Ginsberg, E., 108.
 Goldhaber, M., 94.
 Golovati, R. N., 115.
 Goodman, C., 136.
 Gotó, H., 127.
 Granskaja, T. A., 112.
 Gratschev, K. J., 121.
 Green, J. B., 93.
 Grosse, A. V., 95.
 Gruner, J. W., 134.
 Guggenheim, E. A., 113.
 Gurinsky, D. H., 130.
 Guzmán, J., 128.
 Gysin, M., 136.
- HADEN, W. L., jun., 122.
 Hall, N. F., 123, 133.
 Harkins, W. D., 109, 110.
 Harrison, T. R., 129.
 Hart, D., 119.
 Hart, P. J., 105.
 Haugaard, G., 117.
 Hauser, E. A., 112.
 Haxby, R. O., 95.
 Hazelhurst, T. H., 123.
 Helmholz, L., 104.
 Hendel, J. M., 132.
 Herman, R. C., 93.
 Hersberg, G., 96.
 Heston, B. O., 133.
 Hill, R. D., 94.
 Hirschelwood, C. N., 118.
 Hirschfelder, J. O., 96.
 Hoard, J. L., 103.
 Hofstadter, R., 93.
 Hofstadter, R., 93.
 Holley, C. E., jun., 124.
- HOLMES, F. C., 133.
 Holst, G., 114.
 Howard, A. D., 134.
 Hoyt, C. S., 116.
 Hufford, R. W., 129.
 Huffman, H. M., 106.
 Huggins, M. L., 99, 103.
 Hurlburt, H. M., 96.
 Hurka, V. R., 108.
 Hurlburt, E. H., 93.
- INNES, W. B., 109.
 Inoue, S., 107.
 Irving, H., 115.
 Isakov, E. N., 127.
 Ischkin, I. P., 108.
 Ivanov-Emin, B. N., 128.
- JACKSON, V. T., 129.
 Jahn, H. A., 102.
 James, T. H., 121.
 Jánossy, L., 95.
 Jauncey, G. E. M., 102.
 Johnson, C. R., 119, 126.
 Johnson, T. H., 95.
 Jones, F. W., 107.
 Jones, G., 109.
 Jones, J. L., 118.
 Jones, R. N., 98.
 Juday, C., 130.
- KALITEVSKAJA, A. I., 112.
 Kallemann, S., 129.
 Kammer, E., 105.
 Kasbekar, G. S., 107.
 Kerlinger, H., 131.
 Kikuchi, S., 93.
 King, J. F., 93.
 Kirkwood, J. G., 101.
 Klug, H. P., 130.
 Knott, G., 110.
 Knudson, H. W., 130.
 Kobayashi, M., 131.
 Kolthoff, I. M., 126.
 Kondratev, V., 117.
 Kosheurova, V. A., 110.
 Kovaliv, P., 136.
 Kraemer, E. O., 132.
 Krantz, H. A., 129.
 Krauzmann, W., 99.
 Krishnan, K. S., 105.
 Kuder, R. C., 106.
 Kuliev, A., 108.
 Kumlur, W. D., 99.
 Kuroda, H., 93.
 Kuznetsov, V. I., 128.
- LADAME, G. C., 135.
 Ladigin, N., 121.
 Lamb, V. A., 131.
 Landé, A., 96.
 Lajami, S. S., 96.
 Lang, E. R., 130.
 Langstroth, G. O., 130.
 Lazurkin, J. S., 112.
 Leah, A. S., 117.
 Le Beau, D. S., 112.
 Lee, E., 97.
 Leech, P., 107.
 Leibusch, A., 118.
 Libby, W. F., 132.
 Lin, I., 132.
 Lingane, J. J., 131.
 Lipson, H., 107.
 Lohman, S. W., 134.
 London, H., 105.
 Lonsdale, K., 102.
 Lortie, L., 114.
 Love, W. T., 135.
 Ludloff, H. F., 106.
 Lukesh, J. S., 134.
- McGLADE, H. B., 132.
 McGlenn, R. C., 133.
 McReynolds, J. P., 128.
 Maekawa, G., 114.
 Malpica, J. T. M., 126.
 Mamedaliev, J. G., 108.
 Margenau, H., 94.
 Marion, A., 130.
 Markham, A. E., 132.
 Martin, W. J., 103.
 Marvel, C. S., 108.
 Massey, H. S. W., 94.
 May, L., 122.
 Meibohm, E. P. H., 122.
- Meloche, V. M., 130.
 Meyer, M., 121.
 Meyrowitz, R., 119.
 Miller, A. R., 108.
 Millett, M. A., 109.
 Milligan, W. O., 104.
 Milne, A., 134.
 Moeller, T., 96, 113.
 Mokruschin, S. G., 110.
 Moore, M. J., 132.
 Morán, F., 107.
 Movshovitsch, F. L., 113.
 Moyer, H. V., 131.
 Mulliken, R. S., 100.
- NAKAI, T., 133.
 Nekrassov, N. I., 118.
 Newbound, K. B., 130.
 Nichols, P. M., 128.
 Nilakatan, P., 102.
 Nizami, S. B., 109.
 Norrish, R. G. W., 118.
 Nunn, L. G., jun., 119, 126.
- OCHSENREITER, O., 132.
 Ogata, K., 93.
 Okudo, T., 93.
 Olson, L. E., 115.
 O'Neal, R. D., 94.
 Ormout, B., 125.
 Otto, C. E., 127, 132.
 Otto, E. B., 127.
 Otto, W. H., 121.
- PAGGITT, F., 129.
 Palache, C., 135.
 Palmer, G. D., 105.
 Pamir, H. N., 136.
 Pan, Y. D., 126.
 Pape, N. R., 103.
 Paranjape, G. R., 96, 99.
 Patankar, V. S., 97.
 Payne, J. H., 120.
 Peacock, M. A., 135.
 Pearce, D. W., 116.
 Peters, C. A., 126.
 Philpot, J. St. L., 129.
 Piggot, C. S., 134.
 Plaksin, I. N., 107.
 Pligunov, V. P., 120.
 Poljakov, M. P., 131.
 Pollard, E., 131.
 Porges, N., 132.
 Porth, B. H., 132.
 Preis, E. M., 112.
 Price, W. C., 97.
 Prider, R. T., 134.
 Pristera, F., 129.
 Pugh, B., 117.
- QUENSE, J. A., 130.
 Qureshi, M., 111.
- RABINOWITZ, E., 98.
 Ralls, J. O., 119.
 Raman, C. V., Sir, 102.
 Ramml, N., 109.
 Randall, M., 115.
 Rao, I. D. S., 122.
 Rao, M. R., 107.
 Rao, M. R. A. N., 125.
 Raynor, G. V., 104.
 Reagh, J. D., 118.
 Redmon, B. C., 126.
 Rice, O. K., 106, 122.
 Richmond, W. E., 134.
 Rieke, C. A., 100.
 Rittner, E. S., 122.
 Rivlin, R. S., 132.
 Roberts, J. K., 108.
 Robinson, A. L., 116.
 Robinson, R. A., 114.
 Rochester, G. D., 95.
 Rogers, M. T., 104.
 Rosenblum, C., 96.
 Rowley, H. H., 109.
 Rudy, C. E., jun., 131.
- SACHAROV, B. A., 121.
 Sachs, G., 125.
 Sakai, W., 116.
 Saltshinkin, A. P., 113.
 Sandell, E. B., 127.
 Sanderson, R. T., 123.
 Sandza, J. G., 131.
- Sasaki, T., 111.
 Sawai, I., 107.
 Schaeffer, H. F., 105.
 Scharov, V. S., 112.
 Scheintzis, O. G., 127.
 Scheludko, M. K., 123.
 Schlesinger, H. I., 123.
 Schomaker, V., 100.
 Schulman, J. H., 110.
 Schumb, W. C., 122.
 Sears, J. E., 130.
 Seely, S., 93.
 Shima, S., 93.
 Shindo, S., 93.
 Shinn, M. B., 126.
 Short, O. A., 115.
 Shoupp, W. E., 95.
 Simpson, (Miss) D. M., 97.
 Skerrett, N. P., 122.
 Skljarenko, S. I., 121.
 Slater, J. C., 101.
 Smelo, L. S., 129.
 Smirnov, V. A., 127.
 Smith, C. S., 132.
 Smith, R. E., 118.
 Smyth, C. P., 98.
 Sobotka, H., 110.
 Sokolov, I. I., 113.
 Sotschevanov, V. G., 129.
 Stamm, A. J., 109.
 Steiner, K., 105.
 Stephens, W. E., 95.
 Stevenson, D. P., 100.
 Stewart, D. W., 125.
 Stewart, J. S., 136.
 Stewart, T. D., 114.
 Stockmayer, W. H., 120.
 Stone, M. H., 96.
 Stout, J. W., 105.
 Straus, H. A., 93.
 Sturtevant, J. M., 116.
 Sutherland, G. B. B. M., 97.
 Suvorovskaja, N. A., 107.
 Szasz, G. J., 114.
- TAPEROVA, A. I., 115.
 Tartakovskaja, V. E., 125.
 Taub, H., 118.
 Tawde, N. R., 97.
 Taylor, H. A., 122.
 Taylor, H. J., 95.
 Taylor, R. L., 118.
 Thomas, L. H., 96.
 Thompson, N. W., 122.
 Thomson, G. W., 106.
 Tokarev, N. V., 118.
 Troxel, S. M., 133.
 Turner, A., 130.
 Turner, F. J., 136.
- UBER, F. M., 98.
 Urry, W. D., 134.
- VANCE, J. E., 120, 131.
 Van Vleck, J. H., 102.
 Vischniakov, M. N., 112.
 Vora, V. C., 113.
- WAGNER, E. C., 126.
 Wall, F. T., 124.
 Walters, G. C., 116.
 Wannamaker, W. H., 129.
 Wells, A. F., 110.
 Wells, W. H., 95.
 Welo, L. A., 125.
 Wheeler, J. A., 94.
 White, C. B., 132.
 White, M. G., 94.
 Whitehead, W. L., 136.
 Williams, G., 104.
 Wilson, A. J. C., 107.
 Wilson, E. B., jun., 102.
 Wilson, R. R., 104.
 Winters, R., 98.
 Wolfe, C. W., 134.
 Wood, R. G., 104.
 Wood, S. R., 133.
 Wu, C.-K., 97.
 Wunderly, H. L., 129.
- YOST, D. M., 97.
 Young, T. F., 110.
- ZELLHOEFER, G. F., 108.
 Zuffanti, S., 115.