

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

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

MARCH, 1942.

I.—SUB-ATOMICS.

Intensities of a triplet of Si III in early-type spectra. I. H. Abdel-Rahman (*Month. Not. Roy. Astron. Soc.*, 1941, **101**, 312—316).—The total intensities of the three lines of a Si III triplet, measured in 31 early-type stars, are nearly \propto the square roots of the theoretical emission intensities. Present theory indicates a discrepancy which may possibly be explained on the assumption of a large damping const. The relative intensities of the lines are discussed with regard to luminosity and total absorption. W. J.

Spectroscopy in the vacuum ultra-violet. J. C. Boyce (*Rev. Mod. Physics*, 1941, **13**, 1—57).—A review of spectrographic technique and recent data on at. and mol. spectra, spectra of solids, and astrophysical applications in the vac. ultra-violet. L. J. J.

Quantitative spectral analysis with composite electrodes.—See A., 1942, I, 74.

Absorption of light by sodium vapour. D. C. Stockbarger (*J. Opt. Soc. Amer.*, 1940, **30**, 362—364).—Apparatus suitable for class demonstration of the Na principal series is described. The absorption tube is of stainless steel, and the pressure used is atm., or a little above. A. J. M.

Spark spectrum of europium, Eu II. H. N. Russell, W. Albertson, and (Miss) D. N. Davis (*Physical Rev.*, 1941, [ii], **60**, 641—656).—An analysis and interpretation of available data (cf. King, A., 1939, I, 502). Identifications of 156 levels and data, and classifications of 467 lines, are reported; ~2000 lines remain unclassified. The strongest lines of Eu II arise from transitions based on the ground level f^7s^0 of Eu III. Series of three consecutive $^9S^0$ and $^7S^0$ terms give 11.21 v. for the ionisation potential. Zeeman patterns for 459 lines and g vals. for 118 levels are tabulated; those for the low levels agree with theory, but the higher levels are much perturbed. Patterns for a few lines of Eu I and Eu III are given; the latter confirm that the ground state is $^8S^0$. N. M. B.

Formula for the reduction of Lummer plate fringes.—See A., 1942, I, 75.

Zeeman effect in the rhodium arc spectrum at high fields. J. P. Molnar and W. J. Hitchcock (*J. Opt. Soc. Amer.*, 1940, **30**, 523—535).—The Zeeman effect for Rh I has been photographed in fields up to 94,000 gauss. Data are given for 446 lines and vals. are calc. for nearly all the known low and middle spectral terms of Rh I. For terms arising from the low, even configurations, the g vals. agree with those given by LS coupling formulæ. This holds for $J = 4\frac{1}{2}$ and $3\frac{1}{2}$, but for terms having $J = 2\frac{1}{2}$ or $1\frac{1}{2}$ there is considerable deviation due to a perturbation of the terms in the d^9s configuration by those in the d^9 configuration. The g sum rule is, however, valid when the terms from the two configurations are taken together. For the odd configurations the assignment of L and S quantum nos. to levels is difficult because the coupling is intermediate. The g sum rule does not hold satisfactorily, the vals. of g lying between those predicted by LS and JJ coupling formulæ. A list of 14 additional terms is given. Old term vals. have been recalcd. on the basis of new λ data. A. J. M.

Push-pull photo-electric photodensitometer for determining fine structure in ultra-violet absorption spectra.—See A., 1942, I, 74.

X-Ray photon efficiency of a multiplier tube.—See A., 1942, I, 75.

Mechanism of electrical discharges in gases of low pressure. M. J. Druyvesteyn and F. M. Penning (*Rev. Mod. Physics*, 1941, **13**, 72—73; cf. A., 1941, I, 357).—Corrections. L. J. J.

At. wt. of fluorine calculated from density and X-ray data. C. A. Hutchison and H. L. Johnston (*J. Amer. Chem. Soc.*, 1941, **63**, 1580—1582).—From available X-ray and ρ data on LiF and calcite the at. wt. of F is computed as 18.9935 ± 0.0015 in agreement with gas-density determinations on CF_4 and SiF_4 but not with the mass-spectrographic val. W. R. A.

Mol. wt. of potassium bromide and at. wt. of silver, bromine, and potassium. R. K. McAlpine and E. J. Bird (*J. Amer. Chem. Soc.*, 1941, **63**, 2960—2965).—The mean mol. wt. of KBr from the ratio $KBrO_3 : KBr$ is 119.01. The ratio $KBr : Ag$ is 1.103191 when the KBr is produced by thermal decomp. of $KBrO_3$ and 1.103195 when KBr is prepared by the action of Br on $K_2C_2O_4$. The at. wts. of Ag, Br, and K are, therefore, 107.879, 79.915, and 39.096, respectively. W. R. A.

Isotopic weights of sulphur and titanium. T. Okuda and K. Ogata (*Physical Rev.*, 1941, [ii], **60**, 690—691).—With a Bainbridge-Jordan mass-spectrograph measurements by the doublet method gave the following isotopic wts.; calc. packing fractions are shown in parentheses: ^{32}S $31.98089 \pm 0.7 \times 10^{-4}$ (-5.98 ± 0.02), ^{34}S $33.97711 \pm 3.3 \times 10^{-4}$ (-6.73 ± 0.10), ^{46}Ti $45.96612 \pm 9.5 \times 10^{-4}$ (-7.36 ± 0.21), ^{47}Ti $46.96473 \pm 9.5 \times 10^{-4}$ (-7.50 ± 0.20), ^{48}Ti $47.96332 \pm 4.8 \times 10^{-4}$ (-7.46 ± 0.10), ^{49}Ti $48.96479 \pm 5.3 \times 10^{-4}$ (-7.19 ± 0.11), ^{50}Ti $49.96229 \pm 3.8 \times 10^{-4}$ (-7.54 ± 0.08). The calc. chemical at. wt. of Ti is 47.88 ± 0.04 , in good agreement with the international val. 47.90. N. M. B.

Scattering of protons by protons from 200 to 300 ke.v. G. L. Ragan, W. R. Kanne, and R. F. Taschek (*Physical Rev.*, 1941, [ii], **60**, 628—640; cf. Hafstad, A., 1938, I, 168).—With special arrangements of scattering chamber and proportional counters, measurements as a function of energy and of angle give results in good agreement with Breit's calculations (cf. A., 1939, I, 395) based on a square-well proton-proton interaction potential of radius e^2/mc^2 and depth 10.500 Me.v. Full data are tabulated and plotted. N. M. B.

Action of fast hydrogen ions on lithium chloride. J. D. Craggs and J. F. Smee (*Nature*, 1941, **148**, 531).—Bombardment of targets of LiCl, prepared by fusion of $LiCl \cdot nH_2O$ on to a Mo surface, with H ions ($^1H^+$ and $^2H^+$ in the ratio of $\sim 1:1$) at 100 $\mu a.$ and 600 kv. changes the colour to purple in regions struck by the beam. With an increase in c.d. the colour intensity increases and the centre of the bombarded area is black. The effect is superficial, and exposure to air for 3—5 min. restores the white colour. LiOH targets turn grey on bombardment. The purple colour may be due to a subchloride. Bombardment of CaF_2 produces a purple colour stable for <4 days. L. S. T.

Chemical effects of the nuclear isomeric transition in bromine; evidence for atomic bromine and some of its properties. D. de Vault and W. F. Libby (*J. Amer. Chem. Soc.*, 1941, **63**, 3216—3224).—The nuclear isomeric transition of radio-Br of half-life 4.5 hr. (I) to radio-Br of half-life 18 min. (II) has been investigated by keeping compounds containing (I) under various conditions for ~ 2 hr. and then carrying out chemical separations on them. The transition usually induces a shower of electrons from the Br atom. Thus, if the mol. containing the Br is in the gaseous state it will be decomposed by the resulting large positive charge. (II) is ejected and quickly neutralised by electron transfer on collision with neutral mols., yielding HBr, Br_2 , or free Br atoms. The Br atoms are not very sol. in H_2O or conc.

H_2SO_4 and do not react readily with org. compounds such as EtBr. In liquid phases substitution reactions occur as a result of the cage effect keeping the highly-charged Br in contact with neighbouring mols. for a longer time so that they are broken up by the charge and the fragments may combine with the Br. ~25% of (II) ejected from org. compounds in the gas and in the liquid will interchange with Br_2 or react with reducing agents, but is not extracted by H_2O , whereas another portion is readily extracted by H_2O . The amount of (II) which goes into or remains in org. form is reduced to a min. in the gaseous phase or by adding EtOH or NH_3 Ph to liquids. Substitution into CS_2 has been observed and substitution into CCl_4 occurs from either Br_2 or alkyl bromides. The products from the gas phase at 21 mm. pressure show no preference for either negative or positive charged plates. The extraction from BrO_3 depends slightly on the presence of Br^- ions and this may indicate that an intermediate form is involved in this extraction. W. R. A.

Artificial radioactive isotopes of thallium, lead, and bismuth. K. Fajans and A. F. Voigt (*Physical Rev.*, 1941, [ii], 60, 619–625; cf. A., 1940, I, 384).—Deuteron bombardment of Tl gives a low-intensity 65-min. Pb isotope (unassigned) emitting γ -rays and 1.00-Me.v. electrons. Deuteron and neutron bombardment of Tl gives an activity of half-life 3.5 ± 0.5 years (provisionally ^{208}Tl) emitting β -particles of max. energy 0.87 Me.v. The 52-hr. Pb (unassigned) from the deuteron bombardment of Tl emits 450-ke.v. γ -rays, 370-ke.v. conversion electrons, and 95-ke.v. X-rays. The half-life of 3-hr. Pb (cf. Krishnan and Nahum, A., 1941, I, 3) is measured as 3.32 ± 0.03 hr. and its β -ray energy as 0.70 Me.v. The 6.4-day Bi emitted 1.1-Me.v. γ -rays and 0.86-Me.v. electrons. Excitation functions for 3-hr. Pb and 6.4-day Bi are measured; that for the latter indicates production by a (d, n) reaction (see following abstract). A 10-min. positron activity in Pb and 18-hr. Bi activity are not confirmed.

N. M. B.

Use of uranium lead in the assignment of artificial radioactive isotopes. K. Fajans and A. F. Voigt (*Physical Rev.*, 1941, [ii], 60, 626–627; cf. preceding abstract).—In order to establish the origin of the 3.3-hr. Pb and 6.4-day Bi, ordinary Pb and U-Pb were bombarded with deuterons and the intensities of the resulting activities were compared with the abundances of the isotopes. Results indicate that 3.3-hr. Pb is produced from ^{208}Pb by the reaction $^{208}\text{Pb}(d, p)^{209}\text{Pb}$, and 6.4-day Bi from ^{209}Pb , the assignment depending on the type of reaction, probably $^{209}\text{Pb}(d, n)^{210}\text{Bi}$.

N. M. B.

Momentum loss of heavy ions. J. H. M. Brunings, J. H. Knipp, and E. Teller (*Physical Rev.*, 1941, [ii], 60, 657–660; cf. A., 1941, I, 285).—The capture and loss of electrons in collisions is characterised by the velocity V_e within the ion of the participating electron or electrons having velocity V , and $V_e = \gamma V$. In order to calculate the momentum loss of a heavy ion in its passage through matter the charge of the ion as a function of its velocity is estimated on the assumption that V_e is that of the energetically most easily removable electron, and also that V_e is that of the outermost electron. Both estimates are based on the Fermi-Thomas model, and in the first case γ increases with at. no. and in the second case decreases. The probable val. of V_e is between these extremes.

N. M. B.

Resonance level of mercury at negative energy. M. Kimura (*Physical Rev.*, 1941, [ii], 60, 688–689).—Scattering cross-sections of Hg for C, D, and I neutrons were measured by the method of back scattering. Vals. are calc., with certain specified assumptions, for assumed resonance levels at -0.3, -0.1, and -0.05 e.v. The -0.1 e.v. val. best fits experimental results.

N. M. B.

Long-lived activity of rhodium. O. Minakawa (*Physical Rev.*, 1941, [ii], 60, 689–690).—Powdered Rh was bombarded with slow neutrons from Be + D and fast neutrons from Li + D. The slow neutrons gave the previously known 44-sec. and 4-min. activities; the fast neutrons gave a 210 ± 6-day activity emitting negative and positive electrons, with intensity ratio 1.2, and γ -rays. The upper energy limit of the mixed β -rays was 1.1 ± 0.1 Me.v. Results indicate that the long-lived activity is ^{102}Rh produced by $^{102}\text{Rh}(n, 2n)^{101}\text{Rh}$, and as it emits positive or negative electrons goes over to ^{102}Pd or ^{102}Ru , respectively.

N. M. B.

Tracks of nuclear particles in photographic emulsions. M. M. Shapiro (*Rev. Mod. Physics*, 1941, 13, 58–71).—A review of results obtained by the direct photographic method of recording nuclear tracks.

L. J. J.

Relativistic field theories of elementary particles. W. Pauli (*Rev. Mod. Physics*, 1941, 13, 203–232).—Mathematical. A review of field theories for particles with spin 0, $\frac{1}{2}$, and 1. The results are applied to the radiationless collision of charged particles, the Compton effect, "bremsstrahlung," and pair generation.

L. J. J.

II.—MOLECULAR STRUCTURE.

Afterglow in mercury vapour. (Miss) M. B. M'Ewen (*Nature*, 1941, 148, 532–533).—An explanation involving mol. rather than at. ions is discussed.

L. S. T.

Absorption spectrum of suspensions of carbon black.—See A., 1942, I, 56.

Transmission of infra-red radiation through fog. P. N. Smith and H. V. Hayes (*J. Opt. Soc. Amer.*, 1940, 30, 332–337).—Observations formerly made in connexion with fogs over inland waters have now been carried out at sea. It is found that it is possible to detect and measure the energy of infra-red radiation of λ 3 μ . or more through the worst conditions of fog and ambient illumination to distances considerably > the limit of visibility. Longer rays suffer less attenuation in passing through fog than the shorter visible or nearly visible rays.

A. J. M.

Improved computations on conjugation and hyperconjugation. R. S. Mulliken and C. A. Rieke (*J. Amer. Chem. Soc.*, 1941, 63, 1770–1771).—Mathematical. Observed hyperconjugation shifts in ultra-violet spectra have been calc. by a method which is discussed.

W. R. A.

Electronic spectra of polyatomic molecules. H. Sponer and E. Teller (*Rev. Mod. Physics*, 1941, 13, 75–170).—A comprehensive survey. The theory of electronic states is discussed with reference to selection rules, vibrations and the Franck-Condon principle, coupling between vibration and electronic motion, anharmonicity and predissociation, rotational structure, and isotopic effect. The theory is applied to typical examples: linear mols. (Hg halides, C_2N_2 , and N_2O), tetrahedral mols. (OsO_4 and RuO_4), CH_4 derivatives (MeI , CH_3O , and NH_3Me), and C_6H_6 and derivatives. In appendices are tabulated data and observations for all available investigations on the gaseous phase since 1936 and a complete bibliography of original papers.

N. M. B.

Metallic reflexion by compressed crystalline powders. J. A. Sanderson (*J. Opt. Soc. Amer.*, 1940, 30, 566–567).—Powdered marble, CaSO_4 , plaster of Paris, gypsum, talc, K_2CrO_4 , and AgNO_3 , when pressed into plates under a pressure of ~40,000 lb. per sq. in., reflect strongly in the infra-red at $\lambda\lambda$ characteristic of their functional groups. It is suggested that such plates could be used to investigate the optical properties of substances not available in the form of large crystals.

A. J. M.

Infra-red absorption and reflexion spectra of KHF₂ and KDF₂. J. A. A. Ketelaar (*J. Chem. Physics*, 1941, 9, 775–776).—Measurements made between 1 and 16 μ . are in accord with previous results for part of this range (A., 1940, I, 282). It is shown, however, that the max. at 1222 and 1450 cm^{-1} in absorption and 1238 and 1490 cm^{-1} in reflexion are both fundamentals, whilst the three other pairs of bands of decreasing intensity at <3500 cm^{-1} are combination frequencies of these with a frequency of 560–600 cm^{-1} . The bands above this limit are due to second harmonics of the 5099 and double 3730 cm^{-1} fundamentals and their combinations with the 560 cm^{-1} frequency. The spectrum of KDF₂ is similar, with a shift of the fundamentals to 891 and 1046 cm^{-1} in reflexion, but the 560 cm^{-1} frequency is unchanged, and is therefore the symmetrical frequency. As the spectra of KHF_2 and RbHF_2 are almost identical, the other frequencies are due to the HF_2 group, which resonates between the structures FH F and F HF .

J. W. S.

Molecular configurations in rotational isomerism. S. Mizushima, Y. Morino, and M. Takeda (*J. Chem. Physics*, 1941, 9, 826).—Priority in suggesting that the co-existence of the *trans* and *gauche* forms of $(\text{CH}_2\text{Cl})_2$ and similar mols. accounted

for the no. of depolarised lines in their spectra is claimed (cf. Edgell and Glocker, A., 1941, I, 242). W. R. A.

Ultra-violet absorption spectra of organic molecules. II. Effect of substituent groups on the absorption of diphenyl. (Miss) B. Williamson and W. H. Rodebush (*J. Amer. Chem. Soc.*, 1941, **63**, 3018—3025).—The effect of type and position of substituents in the diphenyls on the ultra-violet spectrum has been investigated using F, Cl, Br, I, OH, OMe, CO₂Me, NH₂, and NO₂ disubstituted derivatives. With increasing size of group in the *o*-positions the departure from coplanarity increases. Good agreement between possible resonance structures and vals. for extinction coeff. and λ of max. absorption has been obtained. W. R. A.

Absorption spectrum of diphenylene. (Miss) E. P. Carr, (Miss) L. W. Pickett, and (Miss) D. Voris (*J. Amer. Chem. Soc.*, 1941, **63**, 3231—3232).—Diphenylene in C₆H₁₄ gives well-defined bands from 25,000 to 32,000 cm.⁻¹ and a very intense band with max. at 40,250 cm.⁻¹. The spectrum has similarities to those of C₁₀H₈ and fluorene. W. R. A.

Ultra-violet absorption spectrum of pyrimidine. F. M. Ueber (*J. Chem. Physics*, 1941, **9**, 777—779).—Wave nos. of 112 absorption bands of pyrimidine vapour in the 2700—3300 Å. region have been measured and are classified into four categories according to intensity. Assignments of individual bands into a no. of series have been made and all prominent series show spacings of approx. 1014 cm.⁻¹. Other characteristic ν are 613, 669, and 680 cm.⁻¹. W. R. A.

Near ultra-violet absorption spectrum of monochlorobenzene. H. Spöner and S. H. Wollman (*J. Chem. Physics*, 1941, **63**, 816—825).—The absorption spectrum of PhCl (symmetry C_{2v}) has been studied in the first order of a 3-m. grating spectrograph at 2750—2400 Å. The band system corresponds with an electronic transition A₁ → B₁ with the transition moment lying on the mol. plane perpendicular to the C—Cl linking. The 0,0 band appears strongly. Several progressions involving totally symmetrical vibrations have been found. "Forbidden" bands appear owing to the excitation of the non-totally symmetrical vibration (ϵ_g^+ = 606 cm.⁻¹), the excitation of which is responsible for the appearance of the C₆H₆ spectrum. Comparison with the spectrum of solid PhCl at -259° supports the analysis. W. R. A.

Ultra-violet absorption spectra of amino-acids. A. D. Marezni and F. Villalonga (*Rev. Soc. argent. Biol.*, 1941, **17**, 232—243).—23 NH₂-acids have been examined with a Zeiss spectrograph and a W arc. The aliphatic and the cyclic acids without a C₆H₅ ring show total absorption between 2600 and 2000 Å.; those with C₆H₅ rings have selective absorption bands. It is not known where the absorption by aliphatic acids begins; position isomerides have the same absorption spectra. Substitution of H by OH or SH in the aliphatic acids shifts the absorption into the visible; this does not occur when OH is fixed on a pyrrolidine ring. NH₂-acids containing S show greater mol. extinction than other aliphatic acids; the characteristic curve of cystine is probably due to dissociation of the S-S group. Max. mol. extinction is produced by the cyclic NH₂-acids and it increases with increasing mol. wt. J. T. L.

Effects of hydrochloric acid and salts on the absorption of light by β -naphthaquinonesulphonic acid. B. Wingfield and S. F. Acree (*J. Res. Nat. Bur. Stand.*, 1941, **27**, 361—370).—The spectral absorption of 3×10^{-4} M- β -naphthaquinonesulphonic acid has been measured in the presence of HCl, KCl, Li₂SO₄, CaCl₂, and AlCl₃. There is an increase in absorption with salt concn. but no marked shift in the absorption band; the increase in absorption = k (molal activity of electrolyte)^{1/2}, where k varies from 0.144 to 0.353. The results suggest that the sp. effects of ions on the absorption of indicators should be taken into account for accurate p_H measurements. D. F. R.

Effect of molecular environment on the absorption spectra of organic compounds in solution. II. $\alpha\beta$ -Unsaturated ketones. K. L. Evans and A. E. Gillam (*J.C.S.*, 1941, 815—820).—The absorption spectra of a no. of $\alpha\beta$ -unsaturated ketones in EtOH have been determined. In the majority of cases Woodward's generalisation (A., 1941, II, 197) that the nature of the substitution of the chromophoric group in these compounds can be predicted from the location of the main absorption bands holds satisfactorily. An exception is isothujone. The effect on the absorption spectra of sub-

stituting simple $\alpha\beta$ -unsaturated ketones with Me groups has been studied. Substitution on the β -C produces a larger bathochromic effect than does substitution on the α -C. Examination of the absorption spectra of some ketophenanthrene derivatives enables conclusions to be drawn concerning their structure if Woodward's generalisation is used. The generalisation does not extend to the location of the band due to the CO-group. A. J. M.

Light absorption of cobalt thiocyanate solutions. II. Aqueous non-electrolytes as solvents. A. von Kiss and P. Csókán (*Z. physikal. Chem.*, 1941, **A**, 188, 27—40).—The extinction coeffs. of various solutions of Co(CNS)₂ in H₂O, org. liquids, and mixtures of H₂O and org. liquid have been measured at room temp. over the λ range 2000—7000 Å. The changes in the form of the absorption curve produced by addition of org. liquid or of excess of CNS' are attributed to the formation of complex mols. J. W. S.

Light absorption and constitution of chlorophyll derivatives. III. Absorption of the dihydroxy-compounds. F. Pruckner (*Z. physikal. Chem.*, 1941, **A**, 188, 41—59).—The absorption spectra of dioxan solutions of the (OH)₂-compounds derived from various porphyrins are shifted towards lower λ and towards higher λ relative to spectra of the corresponding chlorins and porphyrins, respectively, but are most closely related to the spectra of the chlorins. The absorption spectra of HCl solutions of these compounds and of dioxan solutions of their Cu complexes also indicate their intermediate position between chlorins and porphyrins. J. W. S.

Method of spectrophotometry for solutions in liquified gases. Absorption spectra (in the visible region) of solutions of nitro- and azo-compounds in liquid ammonia [and liquid sulphur dioxide]. A. I. Schattenstein and E. A. Izrailevitch (*Acta Physicochim. U.R.S.S.*, 1940, **12**, 73—98).—Apparatus for the investigation of absorption spectra of solutions in liquified gases at -70° to 70° is described. Absorption spectra in the visible are recorded for solutions in aq. alkali, liquid NH₃, and liquid NH₃ containing KNH₂, of a large no. of indicators, and also of one indicator in liquid SO₂. The results confirm that the acid-base equilibrium in a solution depends on the nature of the solvent, and that SO₂ is an acid-like solvent. F. J. G.

Electron energy levels in biochemistry.—See A., 1942, III, 57.

Spectroscopic determination of association equilibria.—See A., 1942, I, 62.

Quenching of fluorescence in solution. III. Nature of the quenching process. G. K. Rollefson and R. W. Stoughton (*J. Amer. Chem. Soc.*, 1941, **63**, 1517—1520).—Measurements of the activity of a fluorescent substance in the presence of a quencher indicate that the quenching action cannot be attributed to complex formation before photoactivation. The effect of temp. and changes in η on the quenching process supports this idea. The simple resonance transfer theory and the electron transfer theory are discussed and shown to be inadequate. W. R. A.

Polarisation of fluorescence of simple aromatic hydrocarbons in solution. D. C. Chakravarti and S. C. Ganguly (*Trans. Faraday Soc.*, 1941, **37**, 562—566).—Analysis of the fluorescence of glycerol solutions of anthracene, phenanthrene, naphthalene, chrysene, and perylene, excited by polarised light of λ 3650, 4047, and 4358 Å., shows that the polarisation is practically the same for all the fluorescence bands, and is independent of the frequency of the incident light. The results of measurements at 30° and -79° indicate that the polarisation in solutions of infinitely high viscosity, in which the mols. would be non-rotating but randomly oriented, must be ~50%. It is inferred that in the substances studied the mol. fluorescence is due either to a single linear oscillator or to a set of linear oscillators radiating independently. F. L. U.

Reversible photochemical processes in rigid media. Phosphorescent state. G. N. Lewis, D. Lipkin, and T. T. Magel (*J. Amer. Chem. Soc.*, 1941, **63**, 3005—3018).—The phosphorescence when a dye is illuminated in a homogeneous, rigid solvent has been examined theoretically and experimentally. With fluorescein in boric acid glass, a typical phosphor, two emission bands are found which are associated with two different unimol. processes (α and β) by which the phosphorescent state may return to the normal state. The

α -process obeys the Arrhenius equation and the heat of activation is 8 ± 1 kg.-cal. The rate of the β -process has been investigated down to 20° K. The β -process cannot be unequivocally explained by suggested mechanisms. With intense illumination the phosphorescence approaches a max. and a new absorption spectrum, belonging to the phosphorescent state, appears. The dye mol. does not turn appreciably in the glass. A new kind of dichroism has been recognised from which the degree of orientation in the phosphorescent and normal states has been calc. W. R. A.

Raman effect in seventeen optical glasses. R. Norris (*Proc. Indian Acad. Sci.*, 1941, 14, A, 178—186).—The Jena glasses examined all showed a continuum following the exciting line. The continuum is a genuine Raman effect, not due to fluorescence. Data are recorded for a no. of broad, diffuse bands in each glass examined. L. J. J.

Infra-red and Raman spectra of polyatomic molecules. XV. Diborane. F. Stitt (*J. Chem. Physics*, 1941, 9, 780—786).—The infra-red spectrum of B_2H_6 from 400 to 4000 cm^{-1} shows much absorption, and further work will be required before a complete analysis can be made. On the assumption that B_2H_6 has the same structure as C_2H_6 two tentative analyses, both in accord with C_p data from 100° to 300° K., have been proposed. One of these requires a singlet electronic state 412 cm^{-1} above the ground state and a potential barrier within the mol. of $\sim 15,000$ g.-cal. per mol., whilst the other postulates an electronic state $\leq 1600\text{ cm}^{-1}$ above the ground state and a potential barrier of ~ 5000 g.-cal. per mol. W. R. A.

Raman spectra of acetylenes. V. Alkylacetylenes. M. J. Murray and F. F. Cleveland (*J. Amer. Chem. Soc.*, 1941, 63, 1718—1721).—Raman displacements, estimated intensities, and depolarisation factors are given for 6 alkylacetylenes, but only ν_ν and intensities for Δ^0 -octadecene. W. R. A.

Raman spectra of halogenated ethylenes. E. N. Prileshaeva, J. K. Sirkin, and M. V. Volkenstein (*Acta Physicochim. U.R.S.S.*, 1940, 12, 176—180).—The Raman spectrum of C_2Cl_4 in CCl_4 and C_2H_2 solutions is recorded, and compared with published data for other halogen derivatives of C_2H_4 . A progressive decrease in the C:C frequency on halogenation is attributed to resonance with singly-bonded structures. F. J. G.

Raman effect. CXV. Rotation isomerism. VIII. Vinyl, acetyl, isopropenyl, and allyl derivatives. L. Kahovec and K. W. F. Kohlrausch (*Z. physikal. Chem.*, 1940, B, 46, 165—180).—The Raman spectra of $CH_2=CHI$, AcI , and $CH_2=CMeI$, and additional measurements on $CH_2=CMe_2$, $AcCl$, $AcBr$, $CH_2=CMeCl$, and $CH_2=CMeBr$, are recorded. These data are compared with recorded data for other vinyl, Ac , isopropenyl, and allyl derivatives, and the spectra analysed. The results indicate the co-existence of at least two stereoisomerides in liquid allyl derivatives. F. J. G.

Raman effect. CXVI. New crystal powder apparatus. A. W. Reitz (*Z. physikal. Chem.*, 1940, B, 46, 181—193).—Apparatus (of which the principle has been noted: A., 1937, I, 345) for determining Raman spectra of solid substances is described in detail. Results for $p\text{-OH}\cdot C_6H_4\cdot CHO$, pyrimidine, antipyrine, C_6Cl_6 , and C_6Me_6 are recorded and discussed. F. J. G.

Raman spectra evidence for hindrance of resonance by o -substitution. R. H. Saunders, M. J. Murray, and F. F. Cleveland (*J. Amer. Chem. Soc.*, 1941, 63, 3121—3123).—Raman shifts for the CO in $RCOMe$, $RCHO$, $RCOCl$, RCO_2Me , and RNO_2 are determined for $R = Ph$, CH_2Ph , $o\text{-tolyl}$ (except $o\text{-C}_6H_4Me\cdot COMe$), and mesityl, and for duryl Me ketone. Comparison of the series Ph and CH_2Ph shows that conjugation of the CO and Ph causes the frequency to decrease by $20\text{--}30\text{ cm}^{-1}$. This indicates a decrease in the amounts of resonating quinonoid forms present, due to coplanarity of the Ph nucleus and the COX . $o\text{-Me}$ lessens this decrease in the frequency, mesityl more so than $o\text{-tolyl}$; this is due to steric hindrance preventing coplanarity and thus stabilising the resonating quinonoid forms. However, the smaller CHO group is unaffected by steric hindrance and the decrease in frequency with mesitaldehyde is as great as with $PhCHO$. It is concluded that Raman spectra are of service in detecting steric hindrance. R. S. C.

Measurement of the radiation of hot flame gases with the photo-cell.—See A., 1942, I, 73.

Photo-electric cells for the visible spectral range.—See A., 1942, I, 74.

Relation between temperature radiation of white oxides and the photo-effect at sensitised metal surfaces. F. Skaupy (*Kolloid-Z.*, 1941, 94, 65).—From the linear relationship between the temp. radiation of white oxides (Al_2O_3 , ZrO_2) and temp. for specimens of different particle size it appears that the temp. corresponding with zero emission is the lower the smaller is the size. Further, the emission for a given temp. exhibits an upper limit of wave-length which increases with decrease of grain size. It is considered that the similarity between this behaviour and the photo-effect at metal surfaces indicates that the primary process in the latter effect is light absorption. F. L. U.

Conductivity and hardness of manganese-copper alloys.—See A., 1942, I, 53.

High-frequency energy losses in solutions containing macromolecules.—See A., 1942, I, 58.

Validity of the principle of superposition in solid dielectrics. H. Silva and B. Gross (*Physical Rev.*, 1941, [ii], 60, 684—687).—A.c. measurements in carnauba wax in the frequency range $20\text{--}20 \times 10^6$ cycles per sec. are reported and results are correlated in terms of the principle of superposition. N. M. B.

Dicyclopentadiene: preparation from the monomeride; dielectric constants of dimeride at several temperatures.—See A., 1942, II, 83.

Constancy of the valency angles of the carbon tetrahedron. Dipole moments of stereoisomeric $\beta\gamma$ -dichloro- Δ^2 -butenes. G. P. Michailov and D. V. Tischtschenko (*Acta Physicochim. U.R.S.S.*, 1940, 12, 129—138).—The dipole moments of the lower- and higher-boiling isomerides of $\beta\gamma$ -dichloro- Δ^2 -butene are 0.00 and 2.41 D., respectively, confirming that the latter is the *cis* isomeride. The val. 2.41 D. is in agreement with that calc. on the assumption that there is no deformation of the valency angle. Recorded data are compared to show that in aromatic and ethylenic derivatives the higher-boiling isomeride has the greater dipole moment. F. J. G.

Dispersion of silicate glasses as a function of composition. M. L. Huggins (*J. Opt. Soc. Amer.*, 1940, 30, 514—518).—The dispersion of silicate glasses in the visible range can be calc. from their compositions and d by the use of a small no. of consts. characteristic of each element. In cases where the best data are available the average discrepancy between experimental and calc. vals. of $n_F - n_C$ is $\sim 5\text{--}8 \times 10^{-5}$. A. J. M.

Brewsterian angle and refractive indices. A. H. Pfund (*J. Opt. Soc. Amer.*, 1941, 31, 679—682).—A method of determination of refractive index (n) by measurements of the Brewsterian angle is described. Reliable n vals. can be determined for black materials such as anthracite coal and amorphous Se. Surface films must be eliminated to obtain reliable results. L. J. J.

Partition functions of molecules with internal torsions. I. Single asymmetric top attached to rigid framework. (Miss) D. Price (*J. Chem. Physics*, 1941, 9, 807—815).—Mathematical. An extension of the method used by Crawford for "pseudo-rigid" mols. (A., 1941, I, 198) to the case involving mols. containing an asymmetric top. From the exact classical kinetic energy for a rigid framework with asymmetric tops a quantum-mechanical operator is derived for the case of one top with small moment of inertia and small asymmetry. From this operator the energy matrix of the mol. is obtained, and hence the partition function for translation and over-all and internal rotations, correct to second order. W. R. A.

Deduction of the concept "liquid with fixed structure" from a consideration of the expansion of thermodynamic functions of state for normal and highly-polymerised liquids. K. Ueberreiter (*Z. physikal. Chem.*, 1940, B, 46, 157—164).—The entropy of a monomeric liquid may be written $S = S_V + S_T + S_{P_0}$, where S_V refers to intramol. vibrations, S_T to thermal agitation, and S_{P_0} to position and orientation of the mols. S_{P_0} possesses a relaxation time, and if this becomes large the liquid is "congealed." The finite vals. of S at 0° K. for supercooled liquids are S_{P_0} . For a highly polymerised liquid S_{P_0} and S_T may each be subdivided into two terms, referring to the individual chain-members and to the chain as a whole. If the degree of polymerisation is sufficiently

great, the last terms may be neglected, so that $S = S_V + (S_T)_{\text{micro}} + (S_P)_{\text{micro}}$. The polymeride may thus be regarded as analogous to the monomeric liquid, but with the degree of mobility of the mols. arbitrarily limited: "liquid with fixed structure," and the fact that it congeals at higher temp., follow. Since the end members of a chain have greater mobility than those in the middle, increase of chain-length leads to decrease of total mobility and rise of temp. of congelation, but this tends towards a limit. The change of expansion coeff. on congelation is also due to the fixation of magnitudes dependent on orientation and position.

F. J. G.

Diamagnetic susceptibility of methane. C. A. Coulson (*Proc. Physical Soc.*, 1942, 54, 51—54).—Mathematical. Calculations based on the mol.-orbital and electron-pair approx. wave functions are compared with the self-consistent-field val. (cf. Buckingham, A., 1941, I, 400), and show that in the latter an error of ~25% is due to the preliminary averaging of the positive charges on the four protons. The new val. agree among themselves, but are \gg the experimental val.; reasons are discussed.

N. M. B.

Magnetic moments at high frequencies. L. Page (*Physical Rev.*, 1941, [ii], 60, 675—684).—Mathematical. The magnetic moments of conducting permeable spheres and cylinders in an oscillating magnetic field are calc. as functions of the conductivity, permeability, radius of cross-section, and λ . The electric moment of a conducting sphere in an oscillating electric field is also obtained. Results are applied to the determination of the effect of particle size on the effective permeability of magnetic powders.

N. M. B.

Electrostatic component of the force of sliding friction. R. Schnurmman and E. Warlow-Davies (*Proc. Physical Soc.*, 1942, 54, 14—27; cf. A., 1941, I, 367, 370).—An experimental study of jerky motion due to relaxation oscillation. It is suggested that, owing to contact electrification, the electrostatic component of the force of sliding friction assumes appreciable proportions when the boundary layer has dielectric properties; thus cycles of slow charging and rapid discharging occur, and cause relative motion to proceed by cycles of slow sliding and rapid slipping when the average velocity, determined by the rate of propulsion of one friction element, is $<$ the velocity for which the frictional force is a min.

N. M. B.

Laws of deformation of real materials. II. Deformation of highly polymerised materials. V. A. Kargin and G. L. Slonimski (*Acta Physicochim. U.R.S.S.*, 1940, 12, 931—945).—The basic principles of Boltzmann and Volterra's theory of deformation have been applied to the physical changes which occur during deformation of highly polymerised materials. (Cf. A., 1942, I, 90.)

C. R. H.

Calculation of the binding energy by the method of orthogonalisation. M. F. Mamotenko (*Acta Physicochim. U.R.S.S.*, 1940, 12, 946—947).—The exchange integrals and the binding energy of two like atoms with only one electron apiece outside the completed shells can be calc. from the integrals of non-orthogonalisation and the Coulomb integrals. The calc. binding energies of H_2 and Li_2 are 72 and 27 kg.-cal. per mol., respectively.

C. R. H.

Surface tension and molecular dimensions. A. E. Ridler and J. H. Smith (*Nature*, 1941, 148, 566—567).—Equations are presented showing that mols. of long-chain compounds tend to stand erect in their own liquid surfaces just as they do on substrates such as H_2O . ρ is independent of chainwise association in the surface layer. Data for MeOH, EtOH, PrOH, BuOH, *n*-octyl and myricyl alcohols are given; dy/dT is approx. the same for each alcohol, indicating that the mol. basal area is approx. equal for all the members of the series.

L. S. T.

Whirling arm for producing small differences of pressure, its calibration by aid of a smoke manometer, and its application to measurements of surface tension.—See A., 1942, I, 75.

III.—CRYSTAL STRUCTURE.

High-intensity X-ray monochromator.—See A., 1942, I, 74.

Quantum theory of X-ray reflexion. (a) Basic ideas. (b) Mathematical formulation. (Sir) C. V. Raman. (c) **Experimental confirmation.** (Sir) C. V. Raman and P. C 2 (A., I.)

Nilakantan (*Proc. Indian Acad. Sci.*, 1941, 14, A, 317—331, 332—355, 356—376).—A detailed account of work already noted (A., 1941, I, 402).

W. R. A.

Quantum-theoretical explanation of the appearance of forbidden X-ray reflexions in diamond. P. R. Pisharoty (*Proc. Indian Acad. Sci.*, 1941, 14, A, 377—386).—Structure amplitudes of the dynamic stratifications excited in the crystal lattice of diamond when monochromatic X-radiation passes through a thin crystal have been calc. on the assumption that the incident X-rays impart to each degree of freedom corresponding with an infra-red oscillation of the lattice an energy of $h\nu^*$, where ν^* is the frequency of oscillation. Some planes which have zero structure amplitude for the classical Bragg reflexions have finite dynamic structure amplitudes for the Raman or quantum reflexions. This accounts for the appearance of the so-called "forbidden" reflexions in diamond.

W. R. A.

Absolute intensity of the Raman X-ray reflexions in diamond. P. R. Pisharoty (*Proc. Indian Acad. Sci.*, 1941, 14, A, 434—438).—Lattice planes of diamond which are "allowed" and "forbidden" for the Raman reflexions by the lattice oscillation of 1332 cm^{-1} have been worked out. The intensities of the quantum reflexions from the (111) planes and of the incident monochromatised X-radiation at various settings are compared.

W. R. A.

Multiple spots and streamers exhibited by the (111) dynamic reflexions in diamond. P. R. Pisharoty and R. V. Subrahmanian (*Proc. Indian Acad. Sci.*, 1941, 14, A, 439—444).—The three sets of phase waves of the lattice oscillations in diamond give rise to three Raman reflexions from the (111) planes, two of which appear as streamers if the angle of incidence, θ , $<$ the Bragg angle θ_B and as spots when $\theta > \theta_B$. The intensity and orientation of these reflexions when the plane of incidence of the classical reflexion is parallel or inclined to a (110) symmetry plane are discussed. All oscillations of phase wave-lengths of <1000 lattice spacings are coherent, whilst those with $\lambda \sim 100$ lattice spacings are incoherent.

W. R. A.

Quantum reflexion and the quantum scattering of X-rays in rock-salt. C. S. Venkateswaran (*Proc. Indian Acad. Sci.*, 1941, 14, A, 395—401).—The diffuse max. in the Laue patterns of rock-salt are due mainly to quantum or Raman reflexions of the X-rays which excite monochromatic or infra-red vibrations in the crystal lattice.

W. R. A.

Lattice spectrum and the Raman X-ray reflexions by rock-salt. C. S. Venkateswaran (*Proc. Indian Acad. Sci.*, 1941, 14, A, 426—433).—Lattice vibrations of rock-salt and the intensities of the first and second orders of the Raman X-ray reflexions from the (111), (100), and (110) planes have been calc. for the three principal modes of vibration. The intensities of the (222), (200), and (220) Raman reflexions are \propto those of their corresponding Bragg reflexions. The intensity of the (111) Raman reflexion is only 1/40 of that due to (222), whereas the ratio of the corresponding Bragg reflexions is 9/33.

W. R. A.

X-Ray reflexions of the second kind in metallic crystals. B. Dayal (*Proc. Indian Acad. Sci.*, 1941, 14, A, 421—425).—The strong Raman reflexions from various lattice planes of Al are reported and discussed. The angle between the crystallographic planes and the phase waves is $\sim 90^\circ$.

W. R. A.

Quantum reflexion of X-rays in calcite. P. Nilakantan and P. G. N. Nayar (*Proc. Indian Acad. Sci.*, 1941, 14, A, 450—458).—Numerous planes in calcite exhibit quantum reflexions and the dynamic spacings do not vary much with the setting of the crystal. The sharpness of the reflexions, their intensities, and the influence of temp. have been investigated and interpreted by the quantum theory of X-ray reflexion.

W. R. A.

Low-temperature studies of the Raman X-ray reflexions in crystals. C. S. Venkateswaran (*Proc. Indian Acad. Sci.*, 1941, 14, A, 387—394).—Raman reflexions of X-rays by carborundum (I), NaCl, $NaNO_3$, and pentaerythritol (II) have been determined at liquid air temp. and their intensities are compared with those at room temp. From the relative intensities at various temp. the infra-red ν active in the particular reflexion has been ascertained and is $\sim 800\text{ cm}^{-1}$ for (I), 160 for NaCl, 200 for $NaNO_3$, and <100 for (II), in agreement with a low frequency observed in the Raman or

infra-red spectrum of the crystal. This X-ray effect, therefore, provides a means of evaluating infra-red ν of crystals.

W. R. A.

Raman X-ray reflexions in organic crystals. I. Naphthalene. II. Benzophenone. III. Hexamethylenetetramine. C. S. Venkateswaran. IV. Benzil. R. V. Subrahmanian (Proc. Indian Acad. Sci., 1941, 14, A, 402—408, 409—414, 415—420, 445—449).—I. Raman reflexions from 001, 011, 110, 111, 201, 200, 202, 120, 211, 222, and 222 planes of a crystal of $C_{10}H_8$ have been measured and the results are explained in relation to the crystal structure and lattice vibrations of $C_{10}H_8$ by the quantum theory of X-ray reflexion in crystals (see above).

II. Similar measurements on $COPH_2$ are recorded.

III. Reflexions from the (110), (200), (211), and (111) planes of $(CH_2)_3N_4$ have been measured and are discussed.

IV. The three alternate planes of the form (2201) in benzil give intense Raman reflexions when X-radiation falls along the trigonal axis or transverse to it. The three benzil mols. in the unit cell lie in equiv. positions along the three-fold screw axis with an inclination of 14° of the aromatic planes. This deduced inclination agrees well with the val. deduced from diamagnetic susceptibilities of the crystal. W. R. A.

X-Ray study of ternary solid solutions of magnesium and silicon in aluminium. X-Ray study of ageing of aluminium-magnesium-silicon alloys.—See A., 1942, I, 53.

Crystal structure of the carbamide-hydrogen peroxide additive compound, $CO(NH_2)_2 \cdot H_2O_2$. C. S. Lu, E. W. Hughes, and P. A. Giguère (*J. Amer. Chem. Soc.*, 1941, 63, 1507—1513).—The space-group is D_{2h}^{14} —*Pnca* and there are 4 mols. per unit cell of a_0 6.86, b_0 4.83, c_0 12.92 Å. The $CO(NH_2)_2$ mols. retain their configuration and H_2O_2 mols. have the configuration proposed by Penney and Sutherland (A., 1934, 1158) with the two OH linkings in planes making a dihedral angle of $\sim 106^\circ$. The O—O distance is 1.46 ± 0.03 Å. and the packing of mols. is effected by H bonds. W. R. A.

Crystal structure of melamine. E. W. Hughes (J. Amer. Chem. Soc., 1941, 63, 1737—1752).—Melamine (I) has a monoclinic unit with a 10.54, b 7.45, c 7.25 Å., β $112^\circ 2'$, space-group $P2_1/a$, 4 mols. per cell. Locations of atoms have been worked out and suggest resonance hybrid mols., the packing of which is effected by H bonds. The empirical resonance energies of (I) and other cyanuric derivatives have been calc. and compared with those calc. by quantum mechanics. The hemihydrated monohydrochloride of (I) is orthorhombic with a 16.75, b 12.29, c 6.93 Å., space-group *Cmcm*, *Cmc*, or *C2cm*. W. R. A.

Electron diffraction observations of the surface reaction of hydrogen selenide on zinc oxide.—See A., 1942, I, 70.

Limits of the Kossel-Stranski theory of crystal growth. W. Kleber (Kolloid-Z., 1941, 94, 39—42).—Criticism of a paper by Balarev (*Kolloid-Beih.*, 1940, 52, 45). F. L. U.

Anisotropy of the electronic work function of metals. R. Smoluchowski (Physical Rev., 1941, [ii], 60, 661—674).—Mathematical. Available explanations of the experimentally determined difference of the work function for different faces of a crystal are shown to be unsatisfactory. The Wigner-Bardeen theory is developed (cf. A., 1935, 1050). According to this theory the work function is a sum of a vol. contribution and one due to a double layer on the surface of the metal. The origin of the latter is described and general formulae for the double layers are derived and discussed more fully for a simple cubic and a body-centred cubic lattice. The min. problem of the surface energy is solved for four faces of a body-centred crystal and results are applied to the case of W. The differences of work function of the respective faces are in satisfactory agreement with experiment. Calc. surface energies agree with the observed stability of certain crystal faces. N. M. B.

Magnetisation of single crystals of iron and of iron-nickel alloys in very weak fields. Y. Shimizu (J. Inst. Metals Japan, 1941, 5, 176—188; Japan Nickel Rev., 1941, 9, 211—219).—The initial magnetic susceptibilities of single Fe crystals as determined by the method of demagnetisation by heating are 3—4 times the vals. obtained by demagnetisation by alternating fields. The difference, which is attributed to the agitating effect of magnetostriction due to the alternate fields, differs with the orientation of the crystal and decreases with rise of temp., vanishing at the crit. temp. For Fe-Ni alloys (18.5% Fe), of zero magnetostriction, the initial

susceptibility is almost independent of temp. and alternating fields have no effect on it. J. W. S.

Mechanical properties of solids. E. N. da C. Andrade (Nature, 1941, 148, 520—525).—A lecture. L. S. T.

ΔE effect of iron, nickel, and cobalt. M. Yamamoto (J. Inst. Metals Japan, 1941, 5, 167—174; Japan Nickel Rev., 1941, 9, 206—210; cf. B., 1938, 1425).—The change of Young's modulus with magnetisation (ΔE effect) of annealed specimens of electrolytic Fe, Ni, and Co and of decarburised 0.1% C steel has been measured at 0—900 oersteds. The modulus is increased in each case to a saturation val. but Fe and Ni show a secondary increase in the field range below saturation, whilst the modulus of Co shows a max. and a min. in the low magnetisation range. The results for the steel are in accord with the view that the effect decreases with increasing C content, whilst the results for both Fe and Ni are in accord with current theories. J. W. S.

IV.—PHYSICAL PROPERTIES OF PURE SUBSTANCES.

Electric and magnetic dimensions. G. D. Yarnold (Proc. Physical Soc., 1942, 54, 46—50; cf. Brown, A., 1941, I, 318; Duncanson, *ibid.*).—The distinction between the consts. having dimensions in the equation for an inverse-square law of force and the dimensionless consts. dielectric const. K and magnetic permeability μ is discussed. From the definitions given for K and μ the usual equations for the inverse-square laws of force are readily derived. N. M. B.

Magnetic behaviour of catalase.—See A., 1942, III, 171.

Dispersion by supersonics.—See A., 1942, I, 56.

Homologous series of α -substituted aliphatic acids.—See A., 1942, II, 74.

Heat content of silica, wollastonite, and thorium dioxide above 25° .—See A., 1942, I, 116.

Freezings and compressions to 50,000 kg. per sq. cm. P. W. Bridgman (J. Chem. Physics, 1941, 9, 794—797).—The variation in melting temp. with pressure up to 50,000 kg. per sq. cm., the change in vol. on freezing, in terms of the vol. of the liquid at atm. pressure and room temp. as a function of pressure on the melting curve, and the latent heat of melting against pressure along the melting curve have been investigated for H_2O , Bu^iOH , $EtOH$, CH_2Cl_2 , $PhCl$, $CHCl_3$, CS_2 , Pr^iBr , and $EtBr$. In lower pressure ranges the entropy difference between liquid and solid decreases, but for five of the nine substances studied it increases along the curve. In this pressure range, also, sub-cooling of the liquid occurs and great sluggishness of growth of crystals, some substances not crystallising at all. No cases of superheating, i.e., retarded liquefaction, were encountered. Compressibility of the solid phase is always $<$ that of the liquid at the same pressure, but by $>25\%$. Differences between the vols. of solid and liquid diminish with rising temp., as do abs. vols., but the internal energies appear to increase. W. R. A.

Latent heats of vaporisation. H. P. Meissner (Ind. Eng. Chem., 1941, 33, 1440—1443).—Theoretical. The Clapeyron equation can be rewritten as $d \log_e p_0 / d(1/T_0) = -\Delta H / R(p_g - p_l)$ from which ΔH can be evaluated solely from data for v.p. and crit. temp. and pressure. Assuming that v.p. data for pure substances conform rigidly to $\log_e p_0 = -A/T_0 + B$, the former equation can be integrated to give $\ln p_g = [\Delta H / RT_0(p_g - p_l)] [1 - T_0/T_g]$. A graphical solution of this equation is presented enabling vals. of $\Delta H / T_0$ to be obtained with max. and average errors of $\pm 9\%$ and $\pm 5\%$, respectively. (T_g = crit. temp., T_0 = saturation temp. at pressure p_0 , $T_g = T_0/T_c$, p_g = reduced v.p., ΔH = mol. heat of vaporisation, $p_g = p_0 v_g / RT_0$, and $p_l = p_0 v_l / RT_0$, where v_g and v_l are mol. vol. of saturated vapour and liquid respectively. A and B are consts.) C. R. H.

Thermal properties of crystalline and glassy boron trioxide. J. C. Southard (J. Amer. Chem. Soc., 1941, 63, 3147—3150).—The vals. of H for temp. $>298^\circ K$. have been determined for $cryst. B_2O_3$ (up to m.p.) and for glassy B_2O_3 (to $1777^\circ K$). The heat and free energy of the reaction $B_2O_3 (cryst.) \rightarrow B_2O_3 (glass)$ are, respectively, 4360 ± 20 and 2600 g.-cal. per g. formula wt. at $298.1^\circ K$. The calc. entropy of B_2O_3 glass

at 298.1°K , is 18.9 ± 0.3 g.-cal. per degree per g. formula wt. An equation has been derived for the free energy of formation of liquid B_2O_3 at $>1000^\circ \text{K}$. (Cf. A., 1942, I, 116.)

W. R. A.

Thermal expansion studies of boric oxide glass and of crystalline boric oxide. J. J. Donoghue and D. Hubbard (*J. Res. Nat. Bur. Stand.*, 1941, 27, 371—379).—Interferometric measurements of the expansion of cryst. B_2O_3 and B_2O_3 glass gave only qual. results, owing to the presence of H_2O . The sample of cryst. B_2O_3 melted at 450 – 451° and did not recrystallise on cooling.

D. F. R.

Maximum difference between densities of ordinary and heavy water. T. L. Chang and J. Y. Chien (*J. Amer. Chem. Soc.*, 1941, 63, 1709—1711).—From measurements of ρ of D_2O from its f.p. to 50° it has been shown that the max. difference between $\rho_{\text{D}_2\text{O}}$ and $\rho_{\text{H}_2\text{O}}$ is at 40° .

W. R. A.

Melting curves of the gases A. Kr, Xe, CH_4 , CH_3D , CD_4 , C_2H_4 , C_2H_6 , COS, and PH_3 , up to 200 atm. pressure. Volume change on melting. K. Clusius and K. Weigand (*Z. physikal. Chem.*, 1940, B, 46, 1—37).—The initial slopes of the m.p.-pressure curves have been determined for A, Kr, Xe, CH_4 , CH_3D , CD_4 , C_2H_4 , C_2H_6 , COS, and PH_3 . From the results the vol. differences between the solid and liquid phases have been calc. The relative vol. change on melting is approx. the same for the three inert gases, viz., ~ 1.15 , and for H_2 , HD, and D_2 ~ 1.12 . From a consideration of the free mobility of the mols. in a liquid it is deduced that for an ideal monat. liquid in the neighbourhood of its f.p. the ratio of the mol. vols. of liquid and solid would be 1.14, in agreement with the val. found for the inert gases. The effects of departures from spherical symmetry, of association, and of excitation of new degrees of freedom on the vol. ratio are considered. It is to be expected, and is found, that the entropy of melting is symbatic with the vol. ratio.

F. J. G.

Preparation and vapour pressures of cyclobutene and cyclobutane.—See A., 1942, II, 83.

Experimental verification of Thomson's equation. K. S. Lialikov (*Acta Physicochim. U.R.S.S.*, 1940, 12, 43—58).—The evaporation of a system of Hg drops has been studied statistically, and results in agreement with Thomson's equation are obtained for the range of radii 0.5 – 2.0μ .

F. J. G.

Complexity of phosphorus pentoxide. III. Appearance of two liquid phases. A. Smits [with E. P. S. Parvé, P. G. Meerman, and H. C. J. de Decker] (*Z. physikal. Chem.*, 1940, B, 46, 43—61).—When quickly heated in a sealed capillary, the metastable volatile modification (I) of P_2O_5 melts at $\sim 430^\circ$ to a colourless liquid which very rapidly changes into the stable form. Apparatus is described by means of which the v.p. of a short-lived liquid may be determined in <10 sec., and with this the v.p. curve of liquid (I) has been determined from 452° to 488° . The triple point of (I) is at 423° and 3800 mm. , its heat of fusion is 3.6 kg.-cal. , and the heat of vaporisation of liquid (I) is $17.5 \text{ kg.-cal. per g.-mol.}$ of P_4O_{10} . The two modifications are complex, and the relation between them is discussed in the light of this concept.

F. J. G.

Determination of Beattie-Bridgeman constants from critical data. F. W. Brown (*Ind. Eng. Chem.*, 1941, 33, 1536—1537).—The equations of Maron and Turnbull (cf. A., 1941, I, 200) for the determination of Beattie-Bridgeman consts. have been derived in a simple manner from the law of corresponding states. The consts. for H_2 have been recalcd. on the basis of the Lennard-Jones model of intermol. forces.

C. R. H.

Influence of constitution on the viscosity of liquids. R. Linke (*Z. physikal. Chem.*, 1941, A, 188, 11—16).—The vals. of the consts. A and B in the Andrade-Sheppard equation $\log \eta = A + B/4.57T$ are evaluated from the published vals. of η for various hydrocarbons. The effects of structural factors on the vals. of A and B in series of isomerides are deduced.

J. W. S.

Structural viscosity of pectin sols.—See A., 1942, I, 58.

Viscosity nomographs for organic liquids. D. S. Davis (*Ind. Eng. Chem.*, 1941, 33, 1537—1539).—Three nomographs have been constructed so as to permit solutions of Souders' η equation $\log(\log \eta) = Id/M - 2.9$, where $I = \eta$ -constitutive const., which may be evaluated by summation of general at. and structural consts., d = density, and M = mol. wt.

C. R. H.

Laws of deformation of real materials. I. G. L. Slonimski (*Acta Physicochim. U.R.S.S.*, 1940, 12, 99—128).—Mathematical. A no. of deductions from the Boltzmann-Volterra theory are made for important special cases. (Cf. A., 1942, I, 85.)

F. J. G.

Migration in crystal lattices. R. M. Barrer (*Trans. Faraday Soc.*, 1941, 37, 590—599).—The treatment of diffusion in solids is developed by combining the kinetic method with the statistical theory of disorder in crystal lattices. Equations for the diffusion coeff. derived by assuming four different mechanisms lead to vals. of D which cover the observed range. In an alloy AB zeolitic diffusion of A is likely when the ratio of at. radii A:B is <0.59 ; when the radii are more nearly equal diffusion should occur usually by migration of Schottky defects or by place exchange. In salt pairs the mechanism is usually migration of Schottky or Frenkel defects.

F. L. U.

V.—SOLUTIONS AND MIXTURES (INCLUDING COLLOIDS).

Compressibility of gas mixtures. I. p - V - T data for binary and ternary mixtures of hydrogen, nitrogen, and carbon dioxide. I. R. Kritschewski and V. P. Markov (*Acta Physicochim. U.R.S.S.*, 1940, 16, 59—66).—Data on the compressibility of binary and ternary mixtures of H_2 , N_2 , and CO_2 at 0 – 200° and at $>500 \text{ atm.}$ are recorded.

F. J. G.

Equation of state for gas mixtures. J. S. Kasarnovski (*J. Phys. Chem. Russ.*, 1940, 14, 1640—1652).—If all the pressures are given for the same mol. vol., the pressure of a mixture $p = p_1N_1 + p_2N_2 + aN_1N_2(p_1 - p_2)$, p_1 and N_1 being the pressure and mol. fraction of the first component, and a a const. In non-polar gas mixtures a is independent of temp.; in polar mixtures it depends on temp. but is independent of N_1 . The equation can also be applied to mixtures of a gas and a saturated vapour, e.g., to p of H_2 and NH_3 over liquid NH_3 . An analogous equation is valid for ternary mixtures.

J. J. B.

Regular solutions of gases in liquids. II. Concentrated solutions of hydrogen at high pressures. M. G. Gonikberg (*Acta Physicochim. U.R.S.S.*, 1940, 12, 921—930).—Equations for the equilibrium in gas-non-polar liquid systems at high concns. and pressures have been derived and tested with data for solutions of H_2 in liquid N_2 , CO , CH_4 , and C_2H_4 . (Cf. A., 1941, I, 80.)

C. R. H.

Densities of aqueous morpholine solutions. H. M. Trimble and (Miss) A. F. Buse (*J. Amer. Chem. Soc.*, 1941, 63, 3236).—Vals. of ρ at 25° , 30° , and 35° have been determined pyknometrically for aq. morpholine (I) solutions [14.2 – 100 wt.-% of (I)]. For (I) $n_{20}^{20} = 1.4542 \pm 0.0002$.

W. R. A.

Viscosities of binary liquid mixtures. R. Linke (*Z. physikal. Chem.*, 1941, 188, 17—26).—The η of binary mixtures containing C_6H_6 , PhMe, PhCl, and cyclohexane have been measured at various temp. and the consts. A and B of the Andrade-Sheppard equation are evaluated. In most cases A and B vary linearly with the mol. composition of the mixture, but with mixtures containing cyclohexane large deviations from linearity are observed, the effect being the greater the lower is the dipole moment of the second component.

J. W. S.

Vapour pressures of binary liquid mixtures. J. R. Lacher and R. E. Hunt (*J. Amer. Chem. Soc.*, 1941, 63, 1752—1756).—An apparatus for making vapour-liquid equilibrium measurements is described and its accuracy is discussed. The systems $\text{C}_2\text{H}_5\text{Br}$ -PhCl and $\text{-Pr}^n\text{NO}_2$ have been investigated. Both show positive vol. changes on mixing (i) and the excess entropy change (ii) is of the same sign. The qual. correlation between (i) and (ii) is discussed with reference to these and other systems and an explanation is tentatively offered.

W. R. A.

Theory of osmotic pressure. W. V. Metcalf (*Kolloid Z.*, 1941, 94, 157—161).—The objections raised by Thiel (*ibid.*, 1940, 91, 316) against the author's theory (A., 1940, I, 354) are discussed and considered to be invalid.

F. L. U.

Determination of diffusion coefficients. B. Serin and R. T. Ellickson (*J. Chem. Physics*, 1941, 9, 742—747).—Diffusion

equations derived from Fick's law are discussed and a graphic method to extend their applicability is developed. The law is shown to be in accord with experimental data for the diffusion of O_2 in Cu (A., 1940, I, 19), for which the activation energy is 50.5 kg.-cal. per g.-mol. The law is also in accord with literature data for the rates of interaction of SiO_2 and $BaCO_3$ at 800–890° and of $CaCO_3$ and MoO_3 at 487–550°.

J. W. S.

Diffusion coefficients in solution. Improved method for calculating D as a function of concentration. W. G. Eversole, J. D. Peterson, and H. M. Kindsater (*J. Physical Chem.*, 1941, 45, 1398–1403).—A new equation expressing diffusion coeff. as a function of concn. corrects inaccuracies in an earlier derivation (cf. A., 1935, 702; 1937, I, 459). C. R. H.

Solutions. Relationship between surface tension, internal pressure, vapour pressure, and osmotic pressure. A. Giacalone (*Z. physikal. Chem.*, 1941, A, 188, 1–10; cf. A., 1940, I, 203; 1941, I, 80).—Substances which lower or raise the γ of H_2O also produce corresponding departures from the theoretical v.p. depression and properties associated with it. Thus aliphatic alcohols, acids, amides, and ketones decrease, and inorg. salts increase, the f.p. depression relative to the theoretical val. The effect of salts is the greater the higher is the valency of the cation, and is ascribed to electrostatic dipole interaction between the ions and H_2O mols.

J. W. S.

Surface tension, liquid density, and vapour density of sulphur dioxide solutions of potassium thiocyanate at 10°, 15°, 20°, and 25°. W. G. Eversole, G. H. Wagner, and G. C. Bailey (*J. Physical Chem.*, 1941, 45, 1388–1397).—Experimental vals. covering the range 0–0.8M KCNS are recorded. The increase in relative surface tension (σ/σ_0) with molarity is much more pronounced than in aq. solutions. In the dil. range the large positive slope of the σ/σ_0 -molarity curve agrees with the Onsager-Samaras theory. An apparatus for measuring v.d., d , and σ on the same solution in a closed system is described. C. R. H.

Solutions with anomalous viscosity. K. Boedeker (*Kolloid-Z.*, 1941, 94, 161–163).—Polyglycol ethers of the composition $R-C_6H_4-(O-CH_2-CH_2)_n-OH$ (R = alkyl) are insol. in H_2O when n is < 6 , beyond which the solubility increases with increasing n . Aq. solutions in which $n = 10$ –12 become turbid when the temp. is raised and separate into two liquid phases, one being nearly pure H_2O , the other ether containing an amount of H_2O that decreases with rising temp. For a given concn. η first decreases slightly with rising temp. over a short range, and then increases rapidly, reaching a max. just before demixing occurs. At const. temp. η exhibits a max. at ~60 vol.-% of the ether; this max. may reach very high vals. (1370 at 20°, $H_2O = 1$) and the system may solidify at the room temp. These effects are attributed to a combination of solvation and immobilisation of solvent by the formation of a network. F. L. U.

Electric polarisation and association in solution. III. Dipole moments of alcohols in very dilute benzene solutions. A. A. Maryott (*J. Amer. Chem. Soc.*, 1941, 63, 3079–3083). The polarisations and dipole moments (μ) of MeOH, EtOH, Pr^i OH, and Bu^i OH have been determined in C_6H_6 at 30°. Vals. of μ are: MeOH 1.62; EtOH, Pr^i OH, Bu^i OH 1.66. The concns. of alcohol were 10^{-4} – 10^{-2} mol. fraction. No change of polarisation with concn. was observed. Since ascertainment vals. are $<$ recorded vals. there is a slight negative solvent effect. W. R. A.

Magnitude of the solvent effect in dipole moment measurements. IV. Determination of distortion polarisation and its additivity in the alkyl and aryl halides. A. Audsley and F. R. Goss (*J.C.S.*, 1941, 864–873; cf. A., 1940, I, 354, 358).—Methods for determining the distribution of the polarisation of binary liquid mixtures between their components are discussed. By combining data for liquid and vapour states it is possible to determine the distortion potential, $P_{\Sigma+A}$, with accuracy. Within certain limits $P_{\Sigma+A}$ can be treated as an additive property, so it is possible to determine it for the volatile members of an homologous series and thence, by adding definite increments, to calculate $P_{\Sigma+A}$ for the higher non-volatile members. The vals. of $P_{\Sigma+A}$ for C, H, and the halogens in compounds of the type RX are calc., and it is shown that whereas the electron polarisation P_{Σ} increases, P_A tends to decrease through the series F, Cl, Br, I. A. J. M.

Dispersion of the dielectric constants of solutions of strong electrolytes. M. V. Belikov and B. N. Finkelstein (*Acta Physicochim. U.R.S.S.*, 1940, 12, 303–308).—The effects of variations of the frictional and electrophoretic forces with frequency on the frequency-variation of the dielectric const. and hence on the conductivity of strong electrolytic solutions are deduced mathematically. J. W. S.

Incorporation and diffusion of foreign atoms in the zinc sulphide lattice. N. Riehl and H. Ortmann (*Z. physikal. Chem.*, 1941, A, 188, 109–126).—The diffusion of foreign atoms (Cu, Ag, Mn, Fe) in ZnS phosphors has been studied. The initial temp. and velocity of diffusion are independent of the anion with which the diffusing atom is originally combined, and of the presence or absence of a flux. The initial temp. for diffusion are: Cu, ~300°; Ag, ~400°. ZnS-Cu phosphors can be prepared in the ordinary way at 450°. ZnS-Ag phosphors at $< 580^\circ$, and the former are always the more coarsely cryst. These results indicate that the diffusion occurs through the vacant lattice spaces, and more easily with Cu on account of its smaller size, and also that the presence of the foreign atom hinders recrystallisation, again less so in the case of the smaller Cu atom. When present together, Cu and Ag atoms diffuse simultaneously, but the diffusion of the latter soon ceases, Ag can diffuse into a ZnS-Cu phosphor containing 0.01% of Cu, but not into one containing 0.2%. No displacement of Cu by Ag occurs. On the other hand Cu diffuses readily into ZnS-Ag phosphors, displacing Ag, which wanders to the surface of the crystal and may be chemically detected there. The phosphorescence of ZnS-Cu and ZnS-Ag phosphors is "killed" by heating at 950°, but not at 600°, with FeS. On the other hand Fe can be chemically detected in the phosphors after heating at 270°. This indicates that at the lower temp. Fe diffuses into vacant spaces, but at the higher temp. displaces Cu or Ag atoms. The diffusion of Mn is slow at 800°, rapid at 950°, indicating that it occurs not in vacant spaces but by displacement of Zn, and, correspondingly, the diffusion of Mn is not hindered by the presence of Ag and causes no displacement of Ag from ZnS-Ag phosphors. When cryst. ZnS is heated with FeS and MnS at 800°, the blue luminescence of the ZnS is at first "killed" by the Fe, but on continued heating the luminescence of Mn appears, confirming that the Mn displaces Zn and does not occupy vacant spaces. F. J. G.

Thermodynamic properties of binary solid solutions on the basis of the nearest neighbour approximation. E. N. Lassetre and J. P. Howe (*J. Chem. Physics*, 1941, 9, 747–754).—Mathematical. A method for calculating the approx. partition function for a binary solid solution is developed on the assumption that the mols. of the two components are distributed at the lattice points of a given lattice and that the energy of a configuration is determined by the interaction of nearest neighbours. J. W. S.

Thermodynamic properties of binary solid solutions. Phase separation. E. N. Lassetre and J. P. Howe (*J. Chem. Physics*, 1941, 9, 801–806).—Mathematical. By an extension of a method previously developed (cf. preceding abstract) it is shown that for a lattice which is large in at least two dimensions the largest eigenval. of the fundamental matrix is doubly degenerate over a finite temp. range, and in this range a separation into phases occurs. W. R. A.

Refraction and dispersion of glasses. J. C. Young and A. N. Finn (*J. Opt. Soc. Amer.*, 1941, 31, 383–384).—The results of Huggins (A., 1941, I, 163, 408) are in agreement with those of the authors (B., 1941, I, 226). L. J. J.

Anomalous changes in the α phase of the nickel-antimony system. N. Shibata (*J. Inst. Metals Japan*, 1941, 5, 41–45; *Japan Nickel Rev.*, 1941, 9, 226–227).—Thermo-magnetic, dilatometric, and electrical resistance measurements confirm that the anomalous changes in the α phase of the Ni-Sb system are due to the formation of an ordered α' phase. It is formed at ~460° and its range of existence at room temp. is ~88–90% of Ni. It is paramagnetic, so the Curie point of Ni is lowered by adding Sb and vanishes suddenly over the composition range 88–90% Ni. J. W. S.

Longitudinal magneto-resistance effect at various temperatures in nickel-cobalt alloys. Y. Shirakawa (*J. Inst. Metals Japan*, 1941, 5, 35–41; *Japan Nickel Rev.*, 1941, 9, 229–231).—The resistance of various Ni-Co alloys has been

measured at -195° to 1150° and in longitudinal magnetic fields of 0–1600 oersteds. The changes in the resistance of the face-centred cubic and hexagonal close-packed solid solutions are similar to the changes observed with pure Ni and Co, respectively. The change is high for the face-centred cubic alloys, particularly at low temp. J. W. S.

New type of δ transformation of iron-nickel alloy due to supercooling and the mechanism of the formation of an intermediate phase during the quenching of the eutectoid alloy. K. Iwase and S. Takeuchi (*J. Inst. Metals Japan*, 1941, 5, 68–76; *Japan Nickel Rev.*, 1941, 9, 205–206).—The δ transformation of Fe-Ni alloy in which a phase containing less Ni than austenite is pptd. from the austenite proceeds so slowly that it can easily be stopped and the austenite supercooled. If the austenite is kept at a temp. at which α and γ phases can coexist it remains supercooled, but if kept in the temp. range of the homogeneous α phase the $\gamma \rightarrow \alpha$ lattice change occurs with change of d . Hence with alloys of low [Ni] the α phase is formed regardless of the speed of quenching, but with high [Ni] austenite persists at room temp. even after slow cooling. This, however, changes to the α phase on cooling below room temp. When slight pptn. occurs during cooling, however, the residual austenite becomes richer in Ni and the lattice transformation point is lowered, leading in some cases to the persistence of "remnant austenite" at room temp. The intermediate phase sometimes occurring in eutectoid alloys is a supersaturated α -solid solution. J. W. S.

Equilibrium diagram of the complete ternary system copper-antimony-nickel. II. Equilibria in the solid state of the whole ternary alloy system. N. Shibata (*J. Inst. Metals Japan*, 1941, 5, 12–25; *Japan Nickel Rev.*, 1941, 9, 223–226).—The system has been studied by dilatometric and microscopic methods and the results are recorded in tables and graphs. J. W. S.

Magnetic investigation of ternary alloys of the copper-antimony-nickel system. N. Shibata (*J. Inst. Metals Japan*, 1941, 5, 46–49; *Japan Nickel Rev.*, 1941, 9, 227–228).—The magnetic crit. points of Ni-Cu alloys are higher than those recorded previously. The Curie point of Ni (380°) is lowered by the addition of Cu and with $\sim 40\%$ Cu is at room temp. The effect of Sb on the crit. point of Ni is \gg that of Cu. Annealing decreases the magnetic field of the ternary alloys in the as-cast condition, this effect being greater for alloys in the composition range in which the susceptibility to dendrite formation is more pronounced. J. W. S.

Transformations and mass effect in nickel-chromium and nickel-chromium-molybdenum steels. H. Shimoda (*J. Iron and Steel Inst. Japan*, 1941, 27, 1–8; *Japan Nickel Rev.*, 1941, 9, 229).—By cooling at different rates in a Sato quenching test machine the change of transformation point with cooling rate and the velocity of transformation of open-hearth Ni-Cr and Ni-Cr-Mo steels have been determined. The effect of cooling rate on the mechanical properties of Charpy and tensile specimens tempered at various temp. has also been investigated. J. W. S.

X-Ray investigation of iron-nickel-chromium alloys. A. J. Bradley and H. J. Goldschmidt (*Iron and Steel Inst.*, 1941, *Advance copy*, 11 pp.).—From X-ray powder photographs of slowly cooled Fe-Ni-Cr alloys the relative amounts of the different constituents present were determined and the phase boundaries delineated in a ternary diagram. The four single-phase fields correspond with a body-centred cubic Fe-rich solid solution, α' body-centred cubic Cr-rich solid solution, γ face-centred Ni-rich solid solution, and σ -FeCr; the two-phase fields are $\alpha + \gamma$, $\alpha' + \gamma$, $\alpha + \sigma$, $\alpha' + \sigma$, and $\gamma + \sigma$ and the three-phase fields $\alpha + \gamma + \sigma$ and $\alpha' + \gamma + \sigma$. The no. and structure of the phase fields confirm the results of earlier work but the boundaries are different, showing that many alloys are very susceptible to heat-treatment at low temp. The range of σ is considerably broadened by addition of Ni, for whilst it is practically confined to the theoretical composition FeCr in the binary system it extends to $\sim 6\%$ of Ni and from 45 to 60% of Cr in the ternary and the solubility limits vary greatly with change in temp.; it is suggested that a large part of the α' may transform to σ on very prolonged low-temp. annealing. A. R. P.

Solubility of macromolecular substances.—See A., 1942, I, 97.

Entrainment of cobalt by stannic sulphide. J. F. Flagg (*J. Amer. Chem. Soc.*, 1941, 63, 3150–3153).—The entrainment of radio-Co⁺⁺ by SnS₂ has been investigated at different temp., p_H , time of keeping, and radio-Co⁺⁺ concn. The entrainment decreases with rising temp. and with acidity and the log of amount entrained per g. SnS₂ \propto the log of radio-Co⁺⁺ concn. Addition of acetaldehyde prevents entrainment. W. R. A.

Sorption of hydrogen by metals. Temperature variation experiments. C. W. Griffin (*J. Amer. Chem. Soc.*, 1941, 63, 2957–2960; cf. A., 1939, I, 195).—The sorption of H₂ on Pt and Co in the massive state and supported on brick has been investigated over the temp. cycle -78.5° to 0° to -78.5° and the pressure range 0 to 760 mm. Adsorption and dissolution occur. The sorptive process is mainly adsorption on the supported metal, little dissolution taking place. In the massive state the dissolution is 5–10 times that in the supported condition. W. R. A.

Adsorption of electrolytes on charcoal. E. Kutschinski, R. Burstein, and A. Frumkin (*Acta Physicochim. U.R.S.S.*, 1940, 12, 795–830).—Over a wide range of electrode potentials (ϕ) there is a linear relation between ϕ of an activated C electrode in H₂SO₄, KOH, and Na₂SO₄ solutions and the amount of adsorbed electrolyte, except when ϕ approaches zero. The variations of the zero-point charge between $\phi = -0.05$ and 0.15 are explained by the influence of adsorbed O on the mechanism of the origination of the interfacial potential. The magnitude of this variation \propto the quantity of electricity necessary to displace ϕ by a definite amount. The relation between ϕ and the amount adsorbed by a C electrode oxidised at 400° has been investigated and shown to be explainable in terms of the electrochemical theory. C. R. H.

Adsorption at crystal-solution interfaces. XII. Adsorption of isomeric dyes by crystals of cupric acetate during their growth from solution. W. G. France and (Miss) K. M. Wolfe (*J. Amer. Chem. Soc.*, 1941, 63, 1505–1507).—Dyes, prepared by coupling diazotised NH₂Ph (A) and *o*-(O), *m*-(M), and *p*-(P)-sulphonated NH₂Ph with mono- and di-sulphonic acids of α - and β -C₁₀H₇OH and -C₁₀H₇NH₂, were adsorbed by Cu(OAc)₂ crystals during their growth from solution. M and P dyes predominate in the formation of orthodome faces on Cu(OAc)₂, whilst A and O dyes predominate in the stair-step formation. Most of the adsorbed dyes possess PhN₂C₁₀H₇-1 nucleus. Nine pairs of dyes with NH₂ replacing OH on the C₁₀H₇ ring have the same effect on the crystal habit of Cu(OAc)₂. The orthodome faces of Cu(OAc)₂ appear to have alternate layers of positive and negative ions and the C atoms of the OAc groups appear to lie along the two-fold axis of symmetry. The possibility of a layer lattice in Cu(OAc)₂ is also indicated by the b.p. and lack of hardness. W. R. A.

Effect of the solubility of silver salts on their adsorption by composite gels of silica and sesquioxides. V. A. Kargin, P. S. Vassiliev, and O. I. Dmitrenko (*J. Phys. Chem. Russ.*, 1940, 14, 1628–1639).—The magnitude of adsorption of Ag⁺ from salt mixtures by gels of Fe₂O₃, Fe₂O₃ + 2SiO₂, and Al₂O₃ + SiO₂ usually is large when a slightly sol. Ag salt can be formed. Thus, Na₂SO₄ raises the adsorption of Ag⁺ from AgNO₃ more than NaOAc or NaNO₃ do, since Ag₂SO₄ is less sol. than AgOAc or AgNO₃. This effect can be masked by competition between Na⁺ and Ag⁺ for the adsorption space. From a solution of AgSO₄ alone Ag⁺ is adsorbed more than from AgNO₃ alone, and the adsorption isotherm often rises at high concns. like those of nearly saturated vapours. J. J. B.

Electro-capillary curves in liquid ammonia. II. Inorganic electrolytes. A. M. Murtazaev (*Acta Physicochim. U.R.S.S.*, 1940, 12, 225–230; cf. A., 1939, I, 520).—A method for determining electro-capillary curves in liquid NH₃ at room temp. is described. From the electro-capillary curve of N-NH₄NO₃ in NH₃ in contact with Hg the capacity of the electric double layer on the Hg is calc. to be 11 μ F. per sq. cm. Addition of NaCl, NaBr, and KI causes a shift of the electro-capillary curve similar to that shown in aq. solution. J. W. S.

Spreading of oils on water. II. Non-ionised molecules having only one polar group. W. A. Zisman (*J. Chem. Physics*, 1941, 9, 729–741; cf. A., 1941, I, 411).—Alcohols, esters, ketones, phenols, and non-ionised acids and amines cause spreading of a mineral oil on H₂O only when their mol. concn.

in the oil is $>$ a certain val., dependent on the nature of the polar group, the chain length, the possible geometrical configurations of the mol., and its solubility in the oil. Spreading is shown to be due to reversible adsorption at the oil-H₂O interface associated with the osmotic pressure of the polar mols. dissolved in the oil. The average life of the adsorbed mols. is \ll that of ionisable mols. The area per mol. at film pressure 11.3 dynes per cm. has been calc. for a no. of compounds and its changes with the chain length and the nature of the polar group are discussed. The occurrence of anomalous spreading due to the formation of cryst. ppts. of the polar compounds has been used to measure the solubility in oils of various straight-chain saturated acids and alcohols.

J. W. S.

Spreading of oils on water. III. Spreading pressures and the Gibbs adsorption relation. W. A. Zisman (*J. Chem. Physics*, 1941, 9, 789-793).—When spreading pressure is plotted against concn. of long-chain alcohols the curves are hyperbolas. Empirical formulae have been fitted to each alcohol and an equation of state of the polar mols. adsorbed at the oil-H₂O interface has been derived. The interfacial monolayer consists of a stable mixed film of polar and non-polar mols. Applications to the interpretation of phenomena involved in stabilisation of emulsions and the structure of cell membranes are noted.

W. R. A.

Spreading coefficients of Nekal BX solutions. M. R. B. Rao and K. S. G. Doss (*Proc. Indian Acad. Sci.*, 1941, 14, A, 170-177).—Langmuir's floating lens method has been used to determine the spreading coeff. of paraffin oil on aq. Nekal BX (I) solutions. Small ($\sim 0.005\%$) concns. of (I) increase the spreading of the oil on H₂O very markedly, whilst higher concns. produce little further effect. Spreading coeffs. of (I) solutions on oil surfaces become less negative with increasing concn. of (I), but remain negative up to 0.2%. It is concluded that wetting by such solutions takes place by penetration rather than by spreading. Adhesion tensions of aq. solutions against oil give a better measure of the wetting power.

L. J. J.

Repulsive forces between surfaces divided by liquid films. B. Derjaguin (*Acta Physicochim. U.R.S.S.*, 1940, 12, 314-316).—An error in Langmuir's theory (A., 1939, I, 140) of the repulsive forces in wetting films of aq. electrolytes is pointed out. Correction of this error increases the discrepancies between the calc. and observed decrease of the γ of H₂O produced by small additions of electrolyte. It is inferred that Jones and Ray's experiments do not permit the calculation of the thicknesses of wetting films, which have been measured directly (A., 1938, I, 194).

J. W. S.

Unstable interfacial solutions. H. Dunken (*Z. physikal. Chem.*, 1940, B, 46, 38-42).—The conditions for formation of an interfacial solution are discussed. It is shown experimentally that by addition of stearic acid (I) to a H₂O-C₆H₁₄ interface an unstable interfacial solution is realised, (I) forming at first a unimol. layer in the interface before passing completely into the C₆H₁₄.

F. J. G.

Viscosity and relaxation in unimolecular layers. A. E. Bresler and S. E. Bresler (*J. Phys. Chem. Russ.*, 1940, 14, 1604-1619).—A paraffin wax dish carries in the middle a paraffin disc on a stem; when the dish is filled the H₂O level is 1 cm. above the disc. Into the H₂O is lowered a paraffin ring the radius of which is $>$ that of the disc. The film is deposited on the surface bounded by the ring; it rotates when the dish and disc are rotated. The speed of paraffin particles embedded in the film depends on the distance from the centre of the ring; it increases with the no. of revolutions of the dish and the area per mol. of the film. The speed t sec. after the rotation of the dish has started is $v_0[1 - \exp(-t/\tau)]$, $v_0 = \text{const.}$, $\tau = \text{relaxation time}$; this equation is analogous to those obtaining in gels. The val. of τ is, e.g., 10.2 sec. for myristic acid at 32.6 A.² per mol., 12.6 sec. for cetyl alcohol at 30.7 A.², 11.0 sec. for Et stearate at 29.9 A.², and 12.1 sec. for Et 1:16-dimethyltetradecandicarboxylate. CaCl₂ and Al(NO₃)₃ do not affect the viscosity of the films when the solution is in contact with paraffin wax only. If a glass ring is used, CaCl₂ (10⁻³M.) and Al(NO₃)₃ (10⁻³M.) increase the τ of dil. myristic acid films by 50-100%. Conc. films on these salt solutions are rigid and move as a whole. Since films on salt solutions possess shear elasticity they cannot consist of perfectly oriented mols. Probably mols. in the monolayers are entangled; this picture

accounts also for the area per mol. being higher in films (20.5 A.²) than in crystals (18 A.²).

J. J. B.

Mechanical (elastico-viscous) properties of thin gliadin layers. Formation and collapse of their structure. A. S. Achmatov (*Acta Physicochim. U.R.S.S.*, 1940, 12, 253-268).—Using the methods described previously (A., 1939, I, 73) it has been shown that when a grain of gliadin is deposited on a clean surface of 0.1N-HCl a surface layer is gradually formed, the two-dimensional pressure and phase-boundary potential varying regularly with time but attaining const. vals. in 5-10 min. The phase-boundary potential isotherm is in satisfactory agreement with that obtained by Hughes and Rideal (A., 1932, 909). Studies of the logarithmic decrement of oscillations with time carried out by the oscillating disc method show a considerable increase in the decrement with increasing period, suggesting the existence of a structure in the films. The mechanical energy absorbed by the film was ~ 1.87 erg per period (14 sec.). Irradiation with ultra-violet light ($\lambda < 2800$ A.) causes irreversible collapse of the film followed by the production of sol. decomp. products.

J. W. S.

Change of concentration in electrolyte solutions during filtration through collodion membranes. W. Hacker (*Kolloid-Z.*, 1941, 94, 11-29).—Aq. solutions of HCl, LiCl, NaCl, KCl, RbCl, NH₄Cl, MgCl₂, and BaCl₂ were filtered through collodion membranes, and any changes in concn. were determined by measuring the conductivity of the liquid on the membrane and of the filtrate. No measurable change occurred with LiCl, MgCl₂, and BaCl₂; in the others the filtrate was less concn. than the original liquid, the concn. of which in all cases was ~ 0.001 N. The sieve action always increases with increase in the rate of stirring of the liquid being filtered, and with HCl it increases also with dilution.

F. L. U.

Shear-elasticity in the surface of suspensions and sols, particularly of fibrinogen solutions. W. Grüning (*Kolloid-Z.*, 1941, 94, 164-169).—Surface elasticity is shown by suspensions of kaolin, talc, animal C, etc. in H₂O, and by sols of V₂O₅ and of benzopurpurin. Defibrinated blood (ox, pig, horse) normally shows the same effect, but, except with horses' blood, the effect is abolished when the blood is concn. by centrifuging and the removal of some plasma. The surface elasticity of fibrinogen solutions is destroyed by denaturation and by the addition of thrombin, trypsin, or albumin (albumin from some sources is ineffective), but is not notably affected by variation of p_H or of the concn. of NaCl.

F. L. U.

Modified theory of the electrical double layer. R. B. Whitney and D. C. Grahame (*J. Chem. Physics*, 1941, 9, 827-828).—A preliminary note presenting a picture of the double layer at a metal-solution interface. Adjacent to the metal there is a partly filled layer of specifically adsorbed negative ions, not separated from the surface by H₂O mols. A diffuse layer of positive and negative ions extends from the metal into the interior of the solution. Since a hydrated cation is usually larger than an unhydrated anion the anion approaches the metal more closely.

W. R. A.

Determination of viscosity at high stresses and defined rates of shear. II. F. Wachholtz and W. K. Asbeck (*Kolloid-Z.*, 1941, 94, 66-81).—Linseed oil containing 10 vol.-% of TiO₂ pigment exhibits anomalous flow even at the high rates of shear (s) obtained with the band viscometer previously described (*ibid.*, 1940, 93, 280). The force-flow relations for this suspension are represented equally well by Bingham's and Ostwald's formulae, but for a 45 vol.-% suspension in mineral oil only by Bingham's. In order to compare the viscous behaviour of different suspensions the val. of η at an infinitely high rate of shear must be calc. This may be done by plotting $\log \eta$ against $1/\sqrt{s}$, when the straight lines obtained can be extrapolated to cut the $\log \eta$ axis at $s = \infty$. The vals. of η_{∞} obtained in this way can be used to characterise the suspensions. Thus, the shape of the curves $\log \eta_{\infty}$ -vol.-% solid is independent of the η of the liquid used provided no chemical action occurs; it depends, however, on the shape of the suspended particles. There is a linear relation between $\log \eta_{\infty}$ of the suspension and $\log \eta_{\infty}$ of the oil; if chemical action occurs (e.g., between Zn-white and α -crotonic acid present in the oil) the slope of the curves is altered, but they remain linear. The curves give no

information about the behaviour of the suspensions at low s vals. F. L. U.

Congo-rubin. R. Haller (*Kolloid-Z.*, 1941, **94**, 199—203).—When a 0.1% solution of Congo-rubin is filtered through a column of finely divided CaCO_3 at 70–80° the greater part is adsorbed and forms a blue layer from which the dye can be extracted with boiling H_2O . The filtrate is a red solution which shows no colour change on the addition of electrolytes. Congo-rubin solutions therefore contain two disperse phases of different dispersities. F. L. U.

Constitution of dilute soap solutions.—See A., 1942, I, 99.

High mol. wt. aliphatic amines and their salts. I. Behaviour of the hydrochlorides of dodecylamine and octadecylamine in water. A. W. Ralston, E. J. Hoffman, C. W. Hoerr, and W. M. Selby (*J. Amer. Chem. Soc.*, 1941, **63**, 1598—1601).—The systems $\text{C}_{12}\text{H}_{25}\text{NH}_2\cdot\text{HCl}\cdot\text{H}_2\text{O}$ and $\text{C}_{18}\text{H}_{37}\text{NH}_2\cdot\text{HCl}\cdot\text{H}_2\text{O}$ have been investigated. Except when very dil., all solutions yield foams which are stable for several hr. Certain concn. ranges exhibit thixotropy and many samples have stringy, curd-like fibres. These and other properties indicate the colloidal properties in these systems. The phase rule diagrams resemble those obtained with compounds in which the aliphatic group is part of the anion. W. R. A.

Solubility of macromolecular substances. IX. Separation of multimolecular mixtures by fractional precipitation. G. V. Schulz (*Z. physikal. Chem.*, 1940, **B**, **46**, 137—156).—Theoretical. It is shown that in the partition of a mixture of polymerides between two immiscible liquids, the higher polymerides are conc. preferentially in the liquid in which the potential energy is lower, and the more so, the smaller is the relative vol. of this liquid. The influence of different variables on the effectiveness of the separation is illustrated by means of curves, and it is shown that there is no limiting mol. wt. above which separation becomes impracticable. These conclusions may be extended to the analogous case of fractional pptn. The effect of repeated fractionation on the distribution of mol. wts. is considered and illustrated graphically. With repeated fractionation the heterogeneity of the fractions decreases rapidly at first, and then much more slowly, so that a completely uniform fraction could be obtained only by an infinite no. of fractionations. F. J. G.

Molecular size distribution in three-dimensional polymerides. I. Gelation. II. Trifunctional branching units. III. Tetrafunctional branching units. P. J. Flory (*J. Amer. Chem. Soc.*, 1941, **63**, 3083—3090, 3091—3096, 3096—3100).—I. A diagrammatical scheme which facilitates statistical analysis of three-dimensional polymerides is presented. The condition for formation of infinitely large mols. is $\alpha > 1/(f-1)$ where f is the functionality of the branch units and α is the probability of chain branching as opposed to chain termination. Methods of calculating α from the no. of chain units, the ratio of the two types of reactants (e.g., $\cdot\text{OH}$ and $\cdot\text{CO}_2\text{H}$), and the extent of reaction are given. The no.-average mol. wt. need not be very large when the statistical conditions for incipient formation of infinitely large three-dimensional networks are fulfilled. Many smaller mols. are interspersed with giant networks. Observed gel points for polymerides of tricarballic acid with diethylene glycol, adipic and succinic acids are compared with the theoretical crit. points for the formation of infinite networks, and discrepancies are attributed to the formation of some intramol. linkings, no account of which is taken in the theoretical treatment. The results support the hypothesis that gelation is the result of the formation of infinitely large mols. and occurs at $\alpha > 0.5$.

II. The distribution of mol. species of various complexities in three-dimensional polymerides in which the chain-branching units are trifunctional has been investigated by statistical methods. Simple single chains (containing no branching units) are always present even at the gel point. A rapid rise in no.-average mol. wt. occurs as the gel point is approached and reaches infinity at $\alpha = 0.5$. The simultaneous presence of sol and gel after gelation results from random distribution of branch units in the polymeride. Gelation occurs at $\alpha > 0.5$ and the wt. fraction of the sol is given by $(1-\alpha)^2/\alpha^2$. Highly branched species are preferentially converted into gel beyond the gel point, and consequently the average complexity of the sol fraction decreases.

III. The distribution of species in three-dimensional polymerides composed of randomly cross-linked chains of uniform

length in which the branching units are tetrafunctional has been investigated statistically. Results are similar to those for trifunctionally branched polymerides. Gelation occurs when the cross-linking index γ (no. of structural units cross-linked per chain) is 1, and the no.-average mol. wt. is twice that of the chains. The effect of non-uniformity in length of chain is discussed. When the chains are randomly distributed in length $\gamma = 0.5$ at the gel point. The theoretical application to vinyl-divinyl copolymerides is briefly discussed. W. R. A.

Double refraction of flow studies with methyl methacrylate polymerides in solution. A. J. de Rosset (*J. Chem. Physics*, 1942, **9**, 766—774).—An apparatus for the measurement of double refraction of flow is described. The vortical angle, double refraction of flow, and viscosity (η) of dioxan solutions (1—50 g. per l.) of a series of $\text{CH}_2\text{CMe}\cdot\text{CO}_2\text{Me}$ polymerides have been measured at 25°. In all cases the birefringence (S) is \propto the velocity gradient (v). For dil. solutions S per unit of v per unit η varies linearly with concn. From the vortical angle measured in dil. solution the rotary diffusion const. for each polymeride is deduced and the lengths of the polymeride mols. are calc. as 890—1880 Å. The shape and structure of the polymeride mols. are discussed and tentative vals. of the mol. wts. and length/width ratios (r) are assigned. The sp. η increment at infinite dilution varies linearly with r^2 , in accord with theory. J. W. S.

Coagulation of hydrophobic sols by electrolyte mixtures. IV. Electrophoretic mobility of the negative silver iodide sol in electrolyte mixtures. L. Lepin and A. Bromberg (*Acta Physicochim. U.R.S.S.*, 1940, **16**, 139—158).—The cataphoretic mobility (U) of a dil. negative AgI sol in solutions of K_2SO_4 , KNO_3 , MgSO_4 , $\text{Mg}(\text{NO}_3)_2$, $\text{Ce}_2(\text{SO}_4)_3$, and $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$, and their mixtures, has been studied. With increasing concn. of any one salt, U decreases smoothly, and more rapidly the greater is the valency of the cation. On the other hand, with a given cation the decrease of U is less rapid the greater is the valency of the anion. In mixtures, increasing concn. of a multivalent electrolyte in presence of a fixed concn. of K_2SO_4 causes a decrease of U which is less rapid the greater is $[\text{K}_2\text{SO}_4]$. These effects are parallel to those found in the coagulation of AgI sols by electrolytes (A., 1939, I, 563) and depend in the same way on the valency of the cation and on the ionic strength, except where [as with $\text{K}_2\text{SO}_4 + \text{Ce}_2(\text{SO}_4)_3$] complex formation occurs. F. J. G.

Activity-coefficient theory of coagulation of weakly solvated sols. W. Ostwald (*Kolloid-Z.*, 1941, **94**, 169—184).—Several objections to the author's theory (cf., e.g., A., 1939, I, 470) are discussed and replied to, in particular those of Weiser and Milligan (A., 1940, I, 411). F. L. U.

Effect of electrostatic forces on electrokinetic potentials. W. G. Eversole and W. W. Boardman (*J. Chem. Physics*, 1941, **9**, 798—801).—The explanation of electrokinetic phenomena on the basis of the thermal and electrical energy of the ions in a solution near a charged wall and the assumption of an immobilised layer attached to the solid wall are discussed. Vals. of the surface potential of the solid and the thickness of the immobilised layer have been calc. from electrokinetic potentials for 16 solutions. W. R. A.

VI.—KINETIC THEORY. THERMODYNAMICS.

Energy of isomerisation of *cis*- and *trans*-dichloroethylene. R. E. Wood and D. P. Stevenson (*J. Amer. Chem. Soc.*, 1941, **63**, 1650—1653).—The gaseous equilibrium between *cis*- and *trans*-(CHCl_2)₂ has been studied between 185° and 275° with I as catalyst and the val. of ΔH° for the isomerisation of *cis*-(CHCl_2)₂ has been calc. as 723 g.-cal. per mol. At 0° K. the *cis*-form is more stable than the *trans*- by ~530 g.-cal. per mol. The sum of two unknown $\nu\nu$ of *trans*-(CHCl_2)₂ has been computed by combining equilibrium with spectroscopic and electron diffraction data. W. R. A.

Iodination. I. Equilibrium in systems of iodine and various unsaturated organic compounds in the dark in different non-polar solvents. J. C. Ghosh, S. K. Bhattacharyya, M. M. Dutt, and M. J. Rao (*J. Indian Chem. Soc.*, 1941, **18**, 171—176).—The equilibrium consts. for the reactions $\text{I}_2 + \beta\text{-amylenes} \rightleftharpoons \beta\text{-C}_8\text{H}_{16}\text{I}_2$ (at 0° and 30°) and $\text{I}_2 + \alpha\text{-pinene} \rightleftharpoons \text{C}_{10}\text{H}_{16}\text{I}_2$ (at 0° and 27°) in CCl_4 , C_6H_6 , and CS_2 have been determined. They are independent of initial concn. but

depend on the temp. and the solvent. The heats of reaction are -4000 to -6000 and -3000 to -5000 g.-cal., respectively.

F. J. G.

Association of benzoic acid in benzene. F. T. Wall and P. E. Rouse, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 3002—3005).—The association of BzOH in C_6H_6 has been investigated by a v.p.-lowering method and the dissociation const. for the dimeride is given by $\log K = 3.790 - 1977/T$. The heat of dissociation of the dimeride is computed as 9000 ± 400 g.-cal.

W. R. A.

Electron-sharing ability of organic radicals. XII. Effect of the radicals on the degree of association of polar molecules. XIII. Effect of the radicals in the solvent molecule. F. A. Landee and I. B. Johns (*J. Amer. Chem. Soc.*, 1941, **63**, 2891—2895, 2895—2900).—XII. The ionisation of the dimeric form of carboxylic acids to $2R\cdot C(O^-)O \rightarrow H^+$ with rearrangement to $R\cdot C(O)OH$ will occur less with weak than with strong acids. The association of AcOH, Pr^iCO_2H , BzOH, $CH_2Cl\cdot CO_2H$, $CHCl_2\cdot CO_2H$, and $CCl_3\cdot CO_2H$ in the vapour state and in Et₂O has been investigated; it decreases as the electron-sharing ability of the radical increases.

XIII. The normalising effect of a solvent is due to the association of the solvent with the solute. The electron-sharing ability of the radicals in a series of ketones determines their normalising power on BzOH and EtOH but their dielectric consts. have little, if any, effect on association by H-bonding.

W. R. A.

Ionisation constant of HCO_3^+ from 0° to 50° . H. S. Harned and S. R. Scholes, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 1706—1709).—The e.m.f. of the cell $H_2|Na_2CO_3(m_1), NaHCO_3(m_2), NaCl(m_3)|AgCl-Ag$ has been measured from 0° to 50° at 5° intervals and ionisation consts. of HCO_3^+ have been evaluated. Equations for thermodynamic functions are derived and the vals. of these functions at 25° are: ΔH 3600 g.-cal.; ΔC_p -65 g.-cal. per degree; ΔS -35.16 g.-cal. per degree. The expression for ΔG° is $13278.55 - 29.7286T + 0.10884T^2$.

W. R. A.

Constitution of dilute soap solutions. IV. Hydroxyl ion activity of sodium laurate solutions at 20° . P. Ekwall and L. G. Lindblad (*Kolloid-Z.*, 1941, **94**, 42—57).—The OH⁻ activity of Na laurate (NaL) solutions was determined with a glass electrode in the concn. range 0.001—0.18N. The hydrolysis const. (K_h)—concn. curve consists of several sections representing various equilibria. Below 0.006N. hydrolysis leads to the formation of free HL; at the lowest concns. K_h decreases normally with increasing c , but becomes const. when the liquid is saturated with HL. Immediately above 0.006N. K_h reaches a min., and the separated HL vanishes over a short range of concn. corresponding with the formation of dissolved NaL.HL. At 0.0075N. the latter substance separates and K_h increases, the process being represented as $2L' + H_2O \rightarrow LHL' + OH'$. At 0.021—0.022N. the curve becomes steeper, corresponding probably with $4L' + H_2O \rightarrow LHL_3''' + OH'$. A still steeper rise beyond 0.03N. indicates hydrolysis of medium aggregates, e.g., $(L')_6$. K_h increases less rapidly at 0.035—0.037N. and becomes const. at 0.05—0.06N. These observations are in full agreement with the hydrolysis theory previously put forward (*ibid.*, 1940, **92**, 141), which enables the degree of aggregation to be deduced from measurements of the OH⁻ activity. Only below 0.006N. is NaL a normal 1—1 electrolyte. Above 0.037N. large aggregates are formed, but association reaches a limit at 0.05N.

F. L. U.

Reduction equilibria of zinc oxide and carbon monoxide. E. C. Truesdale and R. K. Waring (*J. Amer. Chem. Soc.*, 1941, **63**, 1610—1621).—Equilibrium data have been calc. from a revised free energy equation, $ZnO(s) + CO(g) = Zn(g) + CO_2(g)$; $\Delta G^\circ = 47557 + 6.194T \log T - 0.045 \times 10^{-3}T^2 + 0.0655 \times 10^5T^{-1} - 49.747T$ and compared with existing experimental data.

W. R. A.

Hydration of the ethylenic linkage. I. Equilibrium between isobutene, *tert*-butyl alcohol, and water. C. W. Smart, H. Burrows, (Miss) K. Owen, and O. R. Quayle (*J. Amer. Chem. Soc.*, 1941, **63**, 3000—3002).—Measurements of the equilibrium const. (k) for the hydration of isobutene (I) at 100° have been made in mixtures of (I) and BuOH, respectively, with aq. dioxan containing HgCl₂ as catalyst. Vals. of k are in agreement but the error due to free space in the reaction vessel is indeterminate. The average val. of k at 100° is 38. Preliminary measurements with CET_3OH and

CPr_3OH indicate that the % dehydration of CPr_3OH lies between those of BuOH and CET_3OH .

W. R. A.

Thermodynamic properties of binary solid solutions.—See A., 1942, I, 92.

Heat of combustion of *cis*- and *trans*-decahydronaphthalene. G. F. Davies and E. C. Gilbert (*J. Amer. Chem. Soc.*, 1941, **63**, 1585—1586).—The isothermal heats of combustion of *cis*- and *trans*-decahydronaphthalene at 25° are, respectively, 10851.3 ± 1.1 and 10836.0 ± 1.0 g.-cal. per g. The standard heat of formation and the heat of isomerisation of the two forms have been calc.

W. R. A.

Heats of combustion. I. Heat of combustion of acetone. C. B. Miles and H. Hunt (*J. Physical-Chem.*, 1941, **45**, 1346—1359).—An accurate redetermination of the heat of combustion of $COMe_2$ to CO_2 and liquid H_2O has given the vals. 435.32 ± 0.20 and 427.77 ± 0.26 kg.-cal.¹⁵ for gaseous and liquid $COMe_2$ respectively at 25° and 1 atm. const. total pressure.

C. R. H.

Heat contents of bivalent sulphates in extremely dilute aqueous solutions. A. L. Robinson and W. E. Wallace (*J. Amer. Chem. Soc.*, 1941, **63**, 1582—1584).—By a modification of the method of Young et al. (A., 1938, I, 616) applied to the heats of dilution of $CaSO_4$, $MgSO_4$, $CdSO_4$, $CuSO_4$, and $ZnSO_4$ it is shown that s , the limiting derivative of the apparent mol. heat content with respect to $\sqrt{\text{concn.}}$ (c), has max. val. between $\sqrt{c} = 0.02$ and 0.03. The modified method appears to give better agreement with the Debye-Hückel limiting law than previously.

W. R. A.

Entropy of mixing and heat of dilution of cellulose triacetate in dioxan. F. Kunze (*Z. physikal. Chem.*, 1940, **A**, 188, 90—98).—The temp.-dependence of the osmotic pressure of dil. solutions of cellulose triacetate in dioxan has been studied, and from the results the entropy of mixing and the heat of dilution have been calc. The entropy of mixing in the more dil. range has the "ideal" val., but increases more rapidly than this with increasing concn. It is suggested that this corresponds with an increased no. of configurations resulting from change of place between solvent mols. and individual chain-members of the long-chain solute mols. The heat of dilution is positive at concn. < 6.22 g. per l., but becomes negative at higher concn. This and the abnormally high temp.-dependence of the osmotic pressure indicate association.

F. J. G.

Anhydrous sodium soaps. Heats of transition and classification of phases. R. D. Vold (*J. Amer. Chem. Soc.*, 1941, **63**, 2915—2924).—The transition temp. and heats of transition of the series of soap phases, curd-fibre, subwaxy, waxy, superwaxy, neat, and isotropic liquid of Na laurate (I), myristate (II), palmitate (III), stearate (IV), and oleate (V) have been investigated using a new differential calorimeter capable of measurements up to 340° . For (II), (III), and (IV) similar heat effects are observed and indicate that similar changes in structure are involved. The behaviour of (IV) and (V) suggests that the structural changes do not occur in the same order as for (I), (II), and (III). At the transitions from curd \rightarrow subwaxy and subwaxy \rightarrow waxy the heat effect is large and varies with chain length. At high transition temp. the heat effect is small and relatively independent of chain length. The low-temp. transitions are probably due to rearrangement of the C chains whilst the high-temp. changes are attributed to rearrangement of the polar heads of the mols.

W. R. A.

Kinetics and rapid thermochemistry of carbonic acid.—See A., 1942, I, 104.

VII.—ELECTROCHEMISTRY.

Elimination of liquid junction potentials. III. Comparison of the silver-silver chloride and silver-silver bromide electrodes at 25° . B. B. Owen and E. J. King (*J. Amer. Chem. Soc.*, 1941, **63**, 1711—1712).—The standard potentials of the Ag-AgCl and Ag-AgBr electrodes have been compared by means of the cell $Ag-AgBr|KBr(x)m, KNO_3(1-x)m|KNO_3(1-x)m, KCl(x)m|AgCl-Ag$ at 25° . The difference between these potentials is 0.15100 v. in good agreement with vals. for cells without liquid junctions. The method employed (cf. A., 1938, I, 624) is fundamentally sound provided that the ionic strength is not too high.

W. R. A.

Overvoltage of hydrogen on lead in the presence of surface-active organic compounds. L. Vaniukova and B. Kabanov (*J. Phys. Chem. Russ.*, 1940, 14, 1620—1625).—The H overvoltage on spongy Pb in 2—8N-H₂SO₄ is raised by org. additions. The increase is independent of the c.d. Substituted NH₄ compounds cause the highest increase, e.g., iso-C₄H₉, 0.46 v. in 0.002M. solution, Bu 0.26 v. in 0.001 M., and Pr 0.15 v. in 0.01M. solution. Sulphates of (NMe₂CH₂)₂, NPhMe₂, benzylpyridine, β-naphthaquinoline, and acridine cause an increase of 0.01—0.35 v. Hexoic acid, C₇H₁₅OH, and other aliphatic substances are less active. No definite mechanism of the effect is suggested. J. J. B.

Europium and ytterbium in rare earth mixtures. Polarographic determination.—See A., 1942, I, 114.

Polarographic reduction of osmium tetroxide. W. R. Crowell, J. Heyrovsky, and D. W. Engelkeir (*J. Amer. Chem. Soc.*, 1941, 63, 2888—2890).—The polarographic reduction of OsO₄ in saturated solutions of Ba(OH)₂ and Ca(OH)₂ at 25° has been investigated using the dropping Hg electrode, and compared with K₂OsO₄ in a saturated solution of Ca(OH)₂. The current-voltage curves for OsO₄ show three waves and the three steps in the reduction are considered to correspond, respectively, with HO₂OsO₄ → OsO₄'' + OH', OsO₄'' + 2H₂O → OsO₂ + 4OH' (I), and 2OsO₄ + H₂O → Os₂O₃ + 2OH' (II). The half-wave potentials of (I) and (II) are -0.44 v. and -1.20 v. (against the normal calomel electrode), respectively. The current-voltage curve of K₂OsO₄ shows waves corresponding with the last two found with OsO₄. W. R. A.

VIII.—REACTIONS.

Unsensitised slow combination of hydrogen and oxygen between the second and third explosion limits in the temperature range 500—560°. F. S. Dainton (*J. Chem. Physics*, 1941, 9, 826—827).—Polemical against Oldenburg and Sommers (A., 1941, I, 302). W. R. A.

Theory of displacements of mixtures giving maximum flame velocities. A. R. T. Denues (*J. Amer. Chem. Soc.*, 1941, 63, 1757—1758; cf. A., 1941, I, 270).—Relations have been derived between the displacements of mixtures giving max. flame velocities for H₂ and for CO and the composition of the atm. used for combustion. W. R. A.

Carbon monoxide-oxygen flame. VII. OH radical in flames of moist carbon monoxide. H. Kondratieva and V. Kondratiev (*Acta Physicochim. U.R.S.S.*, 1940, 12, 1—8).—The presence of OH has been detected in flames of moist CO and O₂ at 10—62.5 mm., the partial pressure of OH being ~4 × 10⁻³ mm., i.e., ~100 times the equilibrium concn. The rate of production of OH is approx. the reaction rate, confirming that it plays an essential part in the reaction. F. J. G.

Radiation of the flame of carbon monoxide and ozone, and the mechanism of this reactions. M. Zatzorski, V. Kondratiev, and S. Solnischkova (*J. Phys. Chem. Russ.*, 1940, 14, 1521—1527).—When a mixture of CO and O₂ containing 3.5% of O₃ passes through a quartz tube at atm. pressure, the decomp. of O₃ becomes noticeable at 120—130° and quant. at 250°, but the % of CO oxidised is low (0.2—1%) and decreases when the temp. rises; this negative temp. coeff. is probably due to the low average [O₃] at higher temp. The spectrum of the CO + O₃ flame at 150—250° is identical with that of the CO-air flame except that the former shows no OH bands. The luminosity of the flame increases with temp.; if the mol. collisions extinguishing the luminescence are taken into account, it is calc. that at 150° 1 in 10³ of the CO₂ mols. formed is excited, and at 250° 1 in 20—30. Excited CO₂ mols. can be produced only in the reaction CO + O → CO₂, but ordinary CO₂ is formed also directly from CO and O₂ in a reaction the activation energy of which seems to be ~20 kg.-cal. J. J. B.

Propagation of the cool flame in combustible mixtures containing 0.03% of carbon disulphide. N. Semenov and V. Voronkov (*Acta Physicochim. U.R.S.S.*, 1940, 12, 831—878).—Cool-flame propagation in O₂-N₂ mixtures containing 0.03% of CS₂ has been investigated. As [O₂] decreases, the region of propagation extends to lower temp. The rate of flame propagation increases with temp. and increases rapidly with increase in pressure to a max. at ~50 mm. Hg, following which the rate gradually decreases. Equations for the

influence of pressure and temp. on the rate of propagation and for the limits of self-ignition and flame propagation have been derived and satisfactorily applied to the experimental data. C. R. H.

Inflammability of ether-oxygen-helium mixtures. Their application in anaesthesia. G. W. Jones, R. E. Kennedy, and G. J. Thomas (*U.S. Bur. Mines*, 1941, *Rept. Invest.* 3589, 15 pp.).—The [O₂] in Et₂O-O₂-He mixtures must be kept < ~16% in the range of mixtures usually employed in anaesthesia if explosion hazards are to be eliminated. The addition of He to Et₂O-O₂ mixtures therefore offers some difficulty if strictly non-inflammable mixtures are demanded. There is, however, a considerable range of mixtures in which, although flame was propagated slowly upward through the test apparatus, no explosive violence was produced. The range and composition of these mixtures are shown graphically, and their use under certain conditions is recommended. Preliminary experiments on the inflammability and clinical use of cyclopropane-O₂-He mixtures indicate that the addition of 5% or more of Et₂O to non-inflammable mixtures of cyclopropane-O₂-He in the upper limit range does not bring the mixtures back again into the inflammable range. H. C. M.

Ignition conditions of gas mixtures. XVI. Effect of peracetic acid on the cold-flame oxidation of acetaldehyde. B. V. Aivazov, N. P. Keir, and M. B. Neiman (*J. Phys. Chem. Russ.*, 1940, 14, 1535—1549).—Mixtures of MeCHO and O₂ can burn with a red flame when [O₂] : [MeCHO] is > 0.25 or with a cold flame when [O₂] : [MeCHO] is > 0.085. For a mixture [O₂] : [MeCHO] = 0.75 the zone of a slow oxidation lies below the line 180 mm. Hg at 205°, 60 mm. at 235°, and 50 mm. at 280°, and the zone of red flame above 140—150 mm. at 210—220° and 260 mm. at 250—300°. Between these zones three regions of cold flame are situated. In the first (220—250° at 100 mm.), after the induction period τ, an ignition takes place, and the pressure p after ignition is > before. In the second (250—280° at 100 mm.) after a short induction period and ignition p is < before. In the third, at higher temp., two ignitions occur. In the zone of slow oxidation the rate of reaction is ∝ p^{0.66}exp.(-15,600/Rt); it is raised by AcO₂H, e.g., five times when 2.3 mm. of AcO₂H are added to 83 mm. of MeCHO + 0.75 O₂. During the induction period of the cold flame oxidation [AcO₂H] in the reaction mixture increases. τ is the smaller the higher are p and the ratio [MeCHO] : [O₂]. It is reduced by an addition of AcO₂H, e.g., from 3.5 sec. to 1 sec. when 4 mm. of AcO₂H are added to 56 mm. of MeCHO + 0.75 O₂. AcO₂H explodes above 275° at 8 mm. and above 340° at 2 mm.; addition of 1.67 CO₂ per 1 mol. of AcO₂H reduces the explosion temp. at these pressures to 240° and 290°, respectively. The strong influence of an inert gas shows that the explosion of AcO₂H is a chain reaction and has no thermal character. The oxidation of MeCHO gives first AcO₂H; [AcO₂H] increases exponentially with time until the concn. at which AcO₂H explodes is reached. This explosion is the cold flame of MeCHO. This theory accounts for the magnitude of τ and its variation with the amount of AcO₂H added. J. J. B.

Carbon dioxide reduction. A. F. Semetschkova and D. A. Frank-Kamenetzki (*Acta Physicochim. U.R.S.S.*, 1940, 12, 879—898).—The primary step in the reaction CO₂ + C → 2CO over the range 600—900° and for pressures 50—200 mm. Hg is CO₂ + C → CO + (CO), where (CO) denotes chemisorbed CO. This step occurs on the free C surface and requires activation in the gas phase, the energy of activation being 26—27 kg.-cal. Its independence of surface conditions leads to the assumption that it is really the energy possessed by a mol. in the gas phase. The reaction is inhibited by (CO). The binding energy of (CO) is strongly affected by surface conditions and especially by the presence of mineral admixtures. C. R. H.

Thermal decomposition of methyl n-butyl ether. S. J. Magram and H. A. Taylor (*J. Chem. Physics*, 1941, 9, 755—761).—The thermal decomp. of MeOBuⁿ at 480—560° is analogous to that of other ethers, and there is no evidence of the formation of MeOH and C₂H₄ by ring-closure through a H-bond. In the primary decomp. 58—63% yields CH₄ and PrⁿCHO and the remainder CH₂O, C₂H₄, and C₂H₆. The decomp. of the PrⁿCHO and CH₂O is rapid compared with the primary reaction, suggesting that it is induced by radicals from the ether. The energy of activation of the primary

reaction is 54.0 and 56.6 kg.-cal. per g.-mol. at 200 and 100 mm. pressure, respectively, but is increased to ~60 kg.-cal. per g.-mol. for the NO-inhibited reaction. The constancy of the activation energies of both normal and inhibited reactions for a series of ethers suggests that the mechanism is similar in each case.

J. W. S.

Dissociation of tetraphenylhydrazine and its derivatives. G. N. Lewis and D. Lipkin (*J. Amer. Chem. Soc.*, 1941, **63**, 3232—3233).—Polemical against Cain and Wiselogle (A., 1940, I, 325).

W. R. A.

Exchange reaction between hydrogen and deuterium in heterogeneous systems. L. V. Kortschagin and M. I. Urizko (*J. Phys. Chem. Russ.*, 1940, **14**, 1566—1568).—Alizarin, *o*-anisidine, and *o*-toluidine (I) when shaken with H₂O containing D₂O exchange 2 H per mol.; dimethylglyoxime exchanges 8 H showing tautomerism involving the Me groups. Kinetic experiments on the exchange between D₂O and (I) gave no definite results.

J. J. B.

Coulombic energy of activation. E. S. Amis (*J. Amer. Chem. Soc.*, 1941, **63**, 1606—1609).—The two ways of measuring the energy of activation of a reaction depend on whether the temp. coeff. of the reaction rate is measured (a) in a solvent of const. composition or (b) in isodielectric solvents. With (a) ϵ varies and the temp. coeff. includes not only the increased energy of the reactants due to pure thermal effect but the changed effect of the solvent on the reactants. The conditions for ionic reactions are discussed on the assumption that the effect of the solvent is due mainly to an influence on the coulombic forces between the electrically charged particles. Influences of electrostatic forces on reaction rates as a function of ϵ of the solvent can be interpreted by measurement of the energies of activation in isodielectric media, and the part of the energy of activation which changes in isodielectric media is assumed to be the coulombic energy. The change of energy of activation between the different ionic type reactants in various solvents is a change in the coulombic energies of the ions down to ϵ 40. At ϵ > 40 the calc. changes of coulombic energies are progressively > observed changes in energies of activation as ϵ is lowered.

W. R. A.

Effect of solvation on the kinetics of bimolecular reactions in solution. V. A. Holzschmidt (*Acta Physicochim. U.R.S.S.*, 1940, **16**, 25—42).—The effect of solvation on the rate of a bimol. reaction in solution is considered in the light of the theory of the transition state. It is concluded that normal vals. of the non-exponential factor will be obtained if the mols. react in that form in which they are present in the largest amount: i.e., as solvates if strongly solvated or as unsolvated mols. if only slightly solvated. An increased val. of *B* results if normal mols. of a strongly solvated substance react, and a decreased val. of *B* if solvated mols. of a slightly solvated substance react.

F. J. G.

Rate of oxidation of sulphite ions by oxygen. E. C. Fuller and R. H. Crist (*J. Amer. Chem. Soc.*, 1941, **63**, 1644—1650).—Factors affecting the rate of reaction of Na₂SO₃ solutions saturated with O₂ at 1 atm. have been investigated. The rate depends directly on [Cu⁺⁺] when this is > 10⁻⁶M., the Cu⁺⁺ ions acting as a positive catalyst. Mannitol (I) acts as a negative catalyst and its inhibitory effect is uniform over a 10⁵-fold change in the concn. of (I). Without catalysts the reaction is of first order with respect to [SO₃²⁻] and the sp. reaction rate is 0.013 sec.⁻¹ at 25°. The effect of *p*_H depends on the *p*_H range; at *p*_H 8.2—8.8 the rate is independent of *p*_H. It decreases between 5.9 and 3.2 in a complicated way suggesting that it depends on [SO₃²⁻] and on [H⁺]² but not on [HSO₃⁻]. The data are discussed in terms of chain mechanisms resulting from reduction of O₂ and oxidation of SO₃²⁻ ions but no mechanism which will account for all the observed data has been found.

W. R. A.

Dielectric and solvent effects on the iodide-persulphate reaction. E. S. Amis and J. E. Potts, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 2883—2888; cf. A., 1941, I, 475).—Rate coeffs. (*k*), activation energies (*E*), and frequency factors (*B* of the Arrhenius equation) have been determined for the reaction between I⁻ and S₂O₈²⁻ in isodielectric (I) and iso-composition (II) EtOH-H₂O media at 20°, 30°, and 40°. The salt effect of KNO₃ in (I), ϵ = 69.00, agreed with predictions of the Debye-Hückel limiting law for $\mu^{1/2}$ < 0.212; *E* and *B* increase with rise in temp., and decrease with increasing $\mu^{1/2}$. An equation is derived for calculating differences of *E* and *B*

in (I) of specified ϵ , and in (II) of const. ϵ , and indicates that electrostatic influences predominate in this reaction.

W. R. A.

Kinetics and rapid thermochemistry of carbonic acid. F. J. W. Roughton (*J. Amer. Chem. Soc.*, 1941, **63**, 2930—2934).—The rate of heat evolution when HCl is mixed with NaHCO₃ has been studied by the thermal method of measuring the velocity of rapid chemical reactions. The heat is evolved in two stages, the first almost instantaneously owing to combination of H⁺ and HCO₃⁻ and the slower second stage owing to decomp. of H₂CO₃ to CO₂ and H₂O. The velocity coeff. of the reaction H₂CO₃ → CO₂ + H₂O has been evaluated for 4 temp. and increases markedly with rise in temp. Vals. of the heats of the reactions H⁺ + HCO₃⁻ → H₂CO₃ and H₂CO₃ → CO₂ + H₂O, the equilibrium const. of the reaction CO₂ + H₂O ⇌ H₂CO₃, and the true first ionisation const. of H₂CO₃ have been deduced. Preliminary measurements have also been made on the rate of dissociation of free NH₂CO₂H and the ionisation of its CO₂H group.

W. R. A.

Hydrolysis of dichloroacetic acid. F. Kunze (*Z. physikal. Chem.*, 1941, A, **188**, 99—108).—The velocity of hydrolysis of CHCl₂CO₂H (I) at 75—125° and in presence of various electrolytes has been studied. Practically only the anion reacts, and the reaction is unimol. when referred to it. The energy of activation is 31,400 g.-cal., and this rather high val. is the cause of the greater stability of (I) as compared with CH₂ClCO₂H and CCl₃CO₂H.

F. J. G.

Rate of inversion of sucrose as a function of the dielectric constant of the solvent. C. J. Plank and H. Hunt (*J. Physical Chem.*, 1941, **45**, 1403—1415).—Data for the inversion of sucrose by HCl in dioxan-H₂O mixtures show that the reaction coeff. (*k*) increases with increase in concn. of dioxan, the change closely corresponding with log *k*/*k*₀ = 11.6(1/*D* - 1/*D*₀) where *D* is the dielectric const. and the subscript 0 refers to vals. in H₂O. If *k*₀ = *k* calc. with reference to the concn. of sucrose in the H₂O contained in the dioxan-H₂O mixtures, then *k*₀ passes through a min. with increase in *D*. The change in *k* with [HCl] is > that expected if reaction rate ∝ [HCl]. The sp. rotation of invert sugar decreases sharply in proportion to the wt.-% of dioxan in the solvent, the val. in 80% dioxan being < 0.33 of the val. in H₂O.

C. R. H.

Polymerisation of styrene in thymol solution. J. K. Moore, R. E. Burk, and H. P. Lankelma (*J. Amer. Chem. Soc.*, 1941, **63**, 2954—2957).—The rate of polymerisation (*k*) of purified styrene in the antioxidant, thymol, has been investigated at 100° and 140°. *k* follows a third-order law which is attributed to a second-order chain-initiating action and a first-order chain-terminating mechanism. The energy of activation is 21,800 g.-cal., and the average mol. wt. of the polymeride is ~1000. No period of induction was observed. Thymol acted as a mild catalyst. No evidence for a free radical mechanism for the polymerisation was found.

W. R. A.

Reaction velocities at low temperatures. IV. Ionisation of nitroethane at temperatures between -32° and 20°. R. P. Bell and A. D. Norris (*J.C.S.*, 1942, 854—856).—The velocity coeffs. for the reaction between NaOH and EtNO₂ in 80% aq. MeOH over the temp. range studied can be expressed by the simple Arrhenius equation. The data give no indication of the "tunnel effect," but data at even lower temp. would probably provide a crucial test for this effect.

C. R. H.

Rate and equilibrium studies of carbinol formation in triphenylmethane and sulphonephthalein dyes. S. Hochberg and V. K. LaMer (*J. Amer. Chem. Soc.*, 1941, **63**, 3110—3120).—The rate (*k*) and equilibrium (*K*) consts. for the formation of the carbinols of the sulphonephthalein dyes, bromophenol-red, bromocresol-purple, and bromocresol-green, have been determined colorimetrically in H₂O and in isodielectric H₂O-MeOH media at 25°, 35°, and 45° and compared with existent data for bromophenol-blue. The bimol. mechanism of carbinol formation has been verified at 25° for crystal-violet by conductance measurements. The decomp. of the carbinol to regenerate the coloured form of the dye involves a mol. of H₂O. Energies of activation (*E*) and frequency factors are const. over the range of temp. studied. *k* for *m*-substituted sulphonephthaleins is in the same order as for the "substituent const." as applied to C₆H₄, and *k* is affected only by changes in *E*, the entropy of activation (*S*) remaining const. *o*-Substitution involves changes in *E* and *S*. At const. temp. (*T*), log *k* ∝ 1/ ϵ on the mol. fraction scale. The dependence

of K on T and ϵ in isocomposition media of const. ϵ is discussed on the electrostatic theory. Vals. of k are compared with predictions from the collision theory and it is thought that substituents in the o -position affect S through vibrational and rotation partition functions rather than through the translational partition functions. W. R. A.

Diffusion and kinetics of heterogeneous reactions. D. A. Frank-Kamenetzki (*Acta Physicochim. U.R.S.S.*, 1940, 16, 9—12).—Mathematical. Expressions for the net rate of reaction between a gas or a solute and a solid are derived for the region in which neither diffusion nor the true reaction rate may be neglected. These take specially simple forms when the reciprocals of the rates of the observed reaction, the true surface reaction, and the diffusion process are introduced. F. J. G.

Reactivity of amalgams. H. A. Liebhafsky and A. F. Winslow (*J. Amer. Chem. Soc.*, 1941, 63, 3137—3142).—With violent agitation the rate of oxidation (k) of Zn amalgams is practically independent of $[Zn]$ and is limited by the rate at which fresh amalgam surface is exposed. If this rate is kept const. k is approx. \propto the concn. of oxidising agent and is almost independent of temp. That two elementary processes, electron capture by the oxidising agent and expulsion of the resultant positive charges as Zn ions, are involved is borne out by the oxidation of Pb, Tl, Cd, Sn, and Cu amalgams. Qual. results for Na, Mg, and Al amalgams support these conclusions. Thus, removal of dissolved base metals from Hg by oxidation becomes progressively easier as their concn. decreases. The increment in $\log k$ for oxidation by O_2 is \propto increment in the standard electrode potential of the dissolved base metal and, hence, k appears to be \propto decrease in free energy for the reaction. This is similar to the relationship in overvoltage studies between current and applied voltage, and the inertness of the amalgams to H^+ ions is another similarity to overvoltage. The penetration of a potential barrier by electrons, postulated to explain overvoltage, appears to occur in the oxidation of amalgams. No relationship between k and electrode potential was found although it is believed that such a relationship exists. W. R. A.

Surface conditions of precipitates and rate of reaction. IV. Reduction of mercurous chloride by hydroxylamine. T. H. James (*J. Amer. Chem. Soc.*, 1941, 63, 1601—1605).—Although it would appear improbable from the mol. type structure and low electrical conductivity of Hg_2Cl_2 that interstitial Hg_2^{2+} could pass through the crystals or that the Gurney-Mott mechanism could operate in the reduction of the compound, it has been shown that Hg_2Cl_2 is reduced by NH_2OH in a manner similar to the reduction of $AgCl$. The influences on the rate of reduction of pptd. Hg_2Cl_2 of (i) the age of the ppt., (ii) adsorbed dyes and gelatin, (iii) $[NH_2OH]$, and (iv) variation in the concn. of excess of Cl^- have been studied. W. R. A.

Effects of heat on dry proteins. I. Kinetics of formation of insoluble ovalbumin. F. W. Bernhart (*J. Physical Chem.*, 1941, 45, 1382—1387).—The kinetics of the reaction which results in formation of insol. ovalbumin (I) from dry sol. (I) are essentially the same as those which describe autocatalytic reactions. The calc. activation energy for the reaction is 33 kg.-cal. per mol., a val. of the same order of magnitude as that (35 kg.-cal. per mol.) calc. for the heat-denaturation of (I) in solution after consideration of the influence of heats of ionisation on the observed vals. for the activation energy of denaturation. C. R. H.

Theoretical calculations for explosives. Temperatures, gaseous products, and effects of changes in carbonaceous material.—See B., 1942, I, 56.

Pyrolysis of formaldoxime. H. A. Taylor and H. Bender (*J. Chem. Physics*, 1941, 9, 761—765).—The thermal decomp. of $CH_2=N\cdot OH$ at 350—415° to yield HCN and H_2O is of the first order and has activation energy 39 kg.-cal. per g.-mol. The products react more slowly to yield mainly CO and NH_3 , with some N_2 , H_2 , C_2H_2 , and unsaturated compounds. The reaction is probably heterogeneous on a clean glass surface. It is accelerated by traces of air or NO. It is suggested that in the NO-inhibited decomp. of org. compounds, Me radicals form MeNO complexes, which by isomerisation yield $CH_2=N\cdot OH$. J. W. S.

Thermal reactions promoted by diacetyl. F. O. Rice and W. D. Walters (*J. Amer. Chem. Soc.*, 1941, 63, 1701—1706).—

A small amount of Ac_2 accelerates the decomp. of $COMe_2$ at 526°, presumably because Ac_2 acts as a source of free radicals near 500°. This acceleration causes more rapid formation of keten but is dependent on pressure. A chain mechanism is proposed: $Ac_2 \rightarrow 2Me + 2CO$; $COMe_2 \rightarrow 2Me + CO$; $Me + COMe_2 \rightarrow CH_3 + CH_2\cdot COMe$; $MeCO\cdot CH_2 \rightarrow Me + CH_2\cdot CO$; $Me + CH_2\cdot COMe \rightarrow COMeEt$. Small amounts of Ac_2 accelerate the decomp. of Et_2O , $MeCHO$, and $EtOH$ and, also, the polymerisation of C_2H_4 . W. R. A.

Joint action of tetralin hydroperoxide and nitro-compounds on the polymerisation of chloroprene. E. Tschilkina and S. Medvedev (*Acta Physicochim. U.R.S.S.*, 1940, 12, 293—302).— o -, m -, and p - $C_6H_4(NO_2)_2$, and p - $NO_2\cdot C_6H_4\cdot NH_2$ increase the rate of polymerisation of chloroprene in presence of tetralin hydroperoxide (I). The effect is not simply related to the dipole moment of the NO_2 -compound. By determination of the % of insol. material at various stages of the polymerisation it has been shown that the activation by $NO_2\cdot C_6H_4\cdot NH_2$ occurs through an increase in the rate of the primary linear polymerisation process, the rate of the secondary branching process remaining const. It is suggested that the true initiator of the process may be a mol. of the form $R\cdot N(OH)(OOR) \rightarrow O$, produced by interaction of the NO_2 -compound and (I). J. W. S.

Transition stages in catalysis. IV. Kinetics and thermodynamics of the transition stages of the homogeneous catalytic decomposition of hydrogen peroxide. N. I. Kobozov and E. E. Galbreich (*J. Phys. Chem. Russ.*, 1940, 14, 1550—1565).—The rate v of decomp. of H_2O_2 in presence of $K_2Cr_2O_7$, $\propto [K_2Cr_2O_7]$ between 0.002 and 0.009M. At 25° it changes during one experiment according to the first order, but at 0° the unimol. coeff. increases, and at 56° (vapour of $COMe_2$) decreases in the course of an experiment; at 56° the reaction appears to be of the second order. This behaviour can be accounted for if $Cr_2O_9^{2-}$ is the intermediate product, and $v \propto [Cr_2O_9^{2-}]$; then $v = kK[Cr_2O_7^{2-}][H_2O_2]^2/(1 + K[H_2O_2]^2)$, K being the equilibrium const. of $2H_2O + Cr_2O_9^{2-} \rightleftharpoons Cr_2O_7^{2-} + 2H_2O_2$. From the temp. coeff. of K the heat of the reaction $Cr_2O_7 \rightarrow Cr_2O_9$ is calc. as 2700 g.-cal. HNO_3 (0.001—0.005N.) reduces v at first, and strongly increases it near the end of the decomp. of H_2O_2 , so that a max. val. of v is reached. When v begins to rise, the conductivity of the solution rises also. The max. val. of v occurs at a higher degree of decomp. when the temp. is lower. In acid solution the ion $HCrO_4^-$ is the catalyst; its heat of formation from H^+ , $Cr_2O_7^{2-}$, and $2H_2O_2$ is calc. to be 17,600 g.-cal. $HCrO_4^-$ is ~ 5 times as efficient as a catalyst as is $Cr_2O_9^{2-}$. Contrary to an assumption by Eyring, the entropies of the intermediate products are very different from those of the final products. J. J. B.

Persulphate-iodide reaction. II. Critical increment, and catalysed reaction in presence of neutral salts. W. J. Howells (*J. C.S.S.*, 1941, 641—645).— E for the reaction is 12,840 g.-cal., and the probability factor is $\sim 10^{-4}$. E increases appreciably with increase of ionic strength, but is unaffected by interchange of cations. The catalytic effects of Fe^{3+} and Cu^{2+} ions are in qual. agreement with Brönsted's theory. F. J. G.

Catalytic effect of water on aminolysis of ethyl phenylacetate in n -butylamine. P. K. Glasoe, L. D. Scott, and L. F. Audrieth (*J. Amer. Chem. Soc.*, 1941, 63, 2965—2967).—The catalytic effect of H_2O on the aminolysis of $CH_2Ph\cdot CO_2Et$ in aq. NH_4Bu^a at 25° has been demonstrated and is attributed to the formation of $Bu^aNH_3^+$ and OH^- ions by interaction of H_2O with NH_2Bu^a . The prep. of phenylacet- n -butylamide, m.p. 57°, from $CH_2Ph\cdot CO_2Et$ and NH_2Bu^a is described. W. R. A.

Oxidation of phospholipins in presence of ascorbic acid and carcinogenic chemicals.—See A., 1942, III, 255.

Kinetics of para-ortho hydrogen conversion on charcoal. R. Burstein (*Acta Physicochim. U.R.S.S.*, 1940, 12, 201—208; cf. A., 1939, I, 87).—The rate (v) of the para-ortho conversion of H_2 at a charcoal (I) surface at 90° K. has been studied by the thermal conductivity method. On pure (I), outgassed at 950°, v is almost independent of $[H_2]$, indicating that the reaction proceeds primarily on active centres of the first kind. On (I) poisoned by adsorption of a definite amount of H_2 at 500°, v is almost independent of $[H_2]$ at low $[H_2]$ but at high $[H_2]$ $v \propto [H_2]$. The results permit explanation of the apparent discrepancies previously observed between the

activation energies as determined by the static and dynamic methods.

J. W. S.

Alkali and alkaline-earth metals as catalysts in the hydrogenation of organic compounds. F. W. Bergstrom and J. F. Carson (*J. Amer. Chem. Soc.*, 1941, **63**, 2934—2936).—Org. compounds which form additive compounds with alkali or alkaline-earth metals can be catalytically hydrogenated by high-pressure H_2 using the metal as catalyst. With Na as catalyst hydrogenation occurred at 170–250° except with C_6H_5N which was reduced at 130–150°. Ca behaves similarly to Na but less tar and resin are formed. H_2 in presence of Ca does not reduce C_6H_6 . Some of the hydrogenation using Na appears to be due to hydrogenolysis of the additive compound formed with Na since NaH was detected and must exhibit sp. catalytic activity in hydrogenation (cf. Hugel *et al.*, A., 1932, 819). The mechanism of hydrogenation is discussed.

W. R. A.

Mechanism of the catalytic dehydration and dehydrogenation of alcohols of the homologous series $C_nH_{2n+1}OH$. XII. A. Bork (*Acta Physicochim. U.R.S.S.*, 1940, **12**, 899—920).—From an examination of published data it is shown that Dohse's observation that the activation energy of the catalytic dehydration of alcohols is reduced as Me groups are introduced also holds for dehydrogenation reactions. The velocity of dehydration of alcohols of the series follows Arrhenius' exponential law. The pre-exponential term in the Arrhenius equation depends on the catalytic surface, the life period of the reacting mol., and steric factors. The reaction mechanism at the surface of the catalyst is discussed.

C. R. H.

Restricted and accelerated autoxidation of (a) ethers and unsaturated hydrocarbons, (b) benzaldehyde in presence of didiphenylene-ethylene.—See A., 1942, II, 49, 54.

Inhomogeneity in co-precipitated copper hydroxide-magnesium hydroxide catalysts and its effect on their activity. E. H. Taylor (*J. Amer. Chem. Soc.*, 1941, **63**, 2906—2911).—Co-pptd. (i) and reverse co-pptd. (ii) catalysts of the hydroxides of Cu and Mg have been prepared from $Cu(NO_3)_2$ and $Mg(NO_3)_2$ with NaOH and the catalytic activity has been studied by measuring the rate of decomp. of H_2O_2 . The activity of (ii) is > that of (i). Centrifuge experiments showed that (i) was inhomogeneous whilst (ii) was homogeneous. Applications of the methods of co-pptn. and reverse co-pptn. for preparing highly efficient promoted catalysts are briefly discussed.

W. R. A.

Effect of method of preparation on activity of co-precipitated copper hydroxide-magnesium hydroxide catalysts. J. W. Holmes and E. H. Taylor (*J. Amer. Chem. Soc.*, 1941, **63**, 2911—2915; cf. preceding abstract).—The effects of washing and rate of pptn. of co-pptd. (i) and reverse co-pptd. (ii) catalysts of Cu and Mg hydroxides prepared from $Cu(NO_3)_2$ and $Mg(NO_3)_2$ with NaOH have been studied by measuring their catalytic activity on the rate of decomp. of H_2O_2 . Changes in the activity of (i) are comparable with those caused with wide variations in composition. The activity of (ii) is only slightly affected. The results are interpreted in terms of the inhomogeneity of (i).

W. R. A.

Catalytic incomplete oxidation of methane with free oxygen.—See B., 1942, I, 19.

[Catalytic] pyrolysis of lower hydrocarbons in presence of methyl chloride.—See B., 1942, I, 72.

Synthetic corrosion pits and the analysis of their contents. E. D. Parsons, H. H. Cudd, and H. L. Lochte (*J. Physical Chem.*, 1941, **45**, 1339—1345).—Synthetic corrosion pits have been prepared by using as anode or pit bottom the exposed end of an Fe wire passing through a cork at the bottom of a vertical glass tube, and as cathode a flat coil of Cu wire above the glass tube. The portion of the Fe wire outside the glass tube is insulated with paraffin wax. The assembly is immersed in an electrolyte bath, the two wires being connected at a point above the liquid level. Alkaline NaCl was used as electrolyte and the contents of the glass tube were removed and titrated by a micro-potentiometric method. The results show that ion concn. in the glass tube is governed by both diffusion and electric transport, equilibrium existing between the two methods of ionic movement.

C. R. H.

Reduction of sulphurous acid at the dropping mercury electrode.—See A., 1942, I, 65.

Electrolytic deposition of copper and silver.—See B., 1942, I, 96.

Synthesis of silver hydrosols by electrolysis.—See A., 1942, I, 56.

Silver plating.—See B., 1942, I, 55.

Copper-lead alloys [electrodeposited] from ethylenediamine solution.—See B., 1942, I, 54.

Cyanide zinc-plating baths.—See B., 1942, I, 55.

Cadmium plating.—See B., 1942, I, 55.

Cobalt plating.—See B., 1942, I, 55.

Electrodeposition of tin from acid solutions.—See B., 1942, I, 55.

Alkaline tin plating.—See B., 1942, I, 55.

Electrolysis of magnesium aryl bromides in ethyl ether: behaviour of short-lived aryl free radicals.—See A., 1942, II, 84.

Electrolytic reduction of acetone. Factors influencing pinacol formation in alkaline solution.—See A., 1942, II, 76.

Electrolytic reduction of sorbic acid.—See A., 1942, II, 73.

Electrolytic reduction of benzophenone.—See A., 1942, II, 56.

Corona discharge on liquid dielectrics. Materials responsible for increases in power factor. J. Sticher and J. D. Piper (*Ind. Eng. Chem.*, 1941, **33**, 1567—1574).—A 4-hr. corona discharge on decahydronaphthalene (I) yielded ~1% of gas (mainly H_2), 5% of unsaturated hydrocarbons similar in mol. wt. to (I), and 12% of polymerised hydrocarbons of average mol. wt. 1200. ~82% of (I) remained unchanged. The substance which causes the increase in power factor is an unsaturated, coloured, and insol. constituent of the polymerised hydrocarbons which is formed in very small amounts. It is not necessarily exclusively hydrocarbon and it appears to be held in colloidal suspension. Two possible explanations of why such substances have high power factors are offered but neither is complete.

C. R. H.

Decomposition of potassium nitrate in sunlight. T. V. S. Rao and C. Gopal Rao (*J. Indian Chem. Soc.*, 1941, **18**, 228—232).—The decomp. of aq. KNO_3 to KNO_2 and O_2 occurs in light of $\lambda > 2900 \text{ \AA}$, and is favoured by increasing pH.

F. J. G.

Photo-activity of solids. IX. J. A. Hedvall, G. Borgström, and G. Cohn (*Kolloid-Z.*, 1941, **94**, 57—64; cf. A., 1940, I, 312).—Certain specimens of CdS adsorb phthalins in darkness from dil. solution to an extent that is considerably reduced when the substrate is illuminated with white light. The effect is due to the nature of the surface of the CdS and can be abolished by previously shaking the CdS with C_6H_5N , which extracts a small amount (e.g., 0.5%) of S. CdS that does not contain extractable S does not adsorb phthalins in darkness, nor are the latter adsorbed by finely divided S. The effect therefore depends on a loose combination of S in the surface of the CdS; this view is confirmed by the observation that inactive CdS can be rendered active by treatment with $(NH_4)_2S_x$, the product deactivated by extraction with C_6H_5N , and so on indefinitely. Adsorption experiments with various xanthen dyes show that whilst all are adsorbed in darkness only those containing at least one NAlk₂ group give decreased adsorption during illumination. The photo-effect is partly reversible, increased adsorption occurring when previously illuminated CdS is placed in darkness, and desorption occurring when the adsorption complex formed in darkness is afterwards illuminated.

F. L. U.

Photolysis of simple alkyl esters. J. K. Royal and G. K. Rollefson (*J. Amer. Chem. Soc.*, 1941, **63**, 1521—1525).—No H atoms are produced by photolysis of HCO_2Me or $MeOAc$. The rate of removal of Bi mirrors by free radicals produced by photolysis of HCO_2Me yields a val. of $6-8 \times 10^{-3}$ sec. for their half-life period compared with $2-3 \times 10^{-3}$ sec. for the free radicals from $COMe_2$. The photolysis of HCO_2Me in a static system yields principally CO , H_2 , CH_4 , C_2H_6 , $MeOH$, and a very small amount of CH_3O . The total reaction can be represented by a combination of the following: (a) $HCO_2Me \rightarrow MeOH + CO$; (b) $HCO_2Me \rightarrow 2CO + H_2$; (c) $HCO_2Me \rightarrow CO_2 + CH_4$; (d) $2HCO_2Me \rightarrow C_2H_6 + H_2 + 2CO_2$. At 50% decomp. the products indicate that the total reaction is 61% of (a), 16% of (b), 15% of (c), and 8% of (d). When

NO is added no H_2 , CH_4 , or C_2H_6 is found among the reaction products. Mechanisms for the four contributory reactions are discussed. W. R. A.

Thermal and photochemical decomposition of oxalyl bromide. J. E. Tuttle and G. K. Rollefson (*J. Amer. Chem. Soc.*, 1941, **63**, 1525—1530).—In both the thermal and the photochemical decomp. of $(COBr)_2$, the products are CO and Br. Throughout the range λ 4358—2652 Å. no variation in the nature of the reaction was observed and the quantum yield was slightly <1 . Br atoms were present during the course of the reaction. The thermal decomp. is a two-stage process, (i) $(COBr)_2 \rightarrow COBr + CO$, (ii) $COBr \rightarrow CO + Br$. Reaction (i) proceeds at $\sim 200^\circ$ as a homogeneous first-order reaction with an activation energy of 32 kg.-cal. Reaction (ii) is a heterogeneous reaction. W. R. A.

Photolysis of azomethane. C. V. Cannon and O. K. Rice (*J. Amer. Chem. Soc.*, 1941, **63**, 2900—2905).—The quantum yield in the photodecomp. of $(NMe)_2$ (I) at 3660 Å. is unity and remains unchanged (a) at pressures up to 63 cm., (b) by a 4-fold variation in light intensity, and (c) by excess of CO_2 . The increase in total pressure does not give a measure of the amount of decomp. because (I) appears to decompose by other reactions than those yielding directly N_2 and alkanes. Possible reactions are discussed. W. R. A.

Effect of ultra-violet light on methylcellulose in solution. L. Spitze, A. Mooradian, R. H. Hartigan, and L. A. Hansen (*J. Amer. Chem. Soc.*, 1941, **63**, 1576—1580).—Measurements of η , osmotic pressure, and Cu no. show that the methylcellulose (I) mol. is degraded when aq. solutions are irradiated with ultra-violet radiation from a quartz Hg arc lamp. The mean mol. wt. of (I) is $\sim 50,000$. W. R. A.

Photochemical studies. XXXIV. Photochemical decomposition of benzene. J. E. Wilson and W. A. Noyes, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 3025—3028).—On irradiation with $\lambda < 2000$ Å. C_6H_6 is decomposed to C_6H_4 , H_2 , and a solid resembling cuprene. C_6H_6 and D_2 do not combine photochemically. Definite conclusions regarding the mechanism of decomp. are not possible but tentative suggestions are advanced. W. R. A.

Mercury-photosensitised reactions involving benzene and hydrogen. G. S. Forbes and J. E. Cline (*J. Amer. Chem. Soc.*, 1941, **63**, 1713—1716).— C_6H_6 vapour is decomposed by Hg vapour excited by resonance radiation of λ 1849 Å. or by unsensitised radiation of <2000 Å., but not by Hg excited by resonance radiation of 2537 Å. PhOH vapour is, however, decomposed by 2537 Å. and the reaction is accelerated by H_2 , which seems to be added to aromatic rings because very little H_2O is formed. When mixtures of C_6H_6 and H_2 , both at 75 mm. and saturated with Hg vapour at 55° , are exposed to resonance radiation, principally 2537 Å., a fairly volatile product was obtained which appears to be a cyclohexadiene yielding, on bromination, 1:2:4:5-tetrabromocyclohexane. Less volatile products contain H and C in the ratio 0.107, b.p. 233° , and average mol. wt. 160. Dehydrogenation by chloranil gives Ph_2 and hydrogenation in the presence of Adams catalyst showed that 3.4 mols. of H_2 were taken up. The formation of three hydrogenated diphenyls, formed by combinations between the free radicals C_6H_5 and C_6H_7 , is postulated and supported by measurements of n and ρ . The following reaction mechanism is tentatively put forward: (i) $Hg + h\nu \rightarrow Hg^*$; (ii) $Hg^* + H_2 \rightarrow 2H + Hg$; (iii) $H + C_6H_6 \rightarrow C_6H_7$; (iv) $C_6H_7 + H \rightarrow$ cyclohexadiene (C_6H_8); (v) $C_6H_7 + C_6H_7 \rightarrow C_6H_8 + C_6H_8$; (vi) $C_6H_8 + H \rightarrow C_6H_9$; (vii) $C_6H_9 + C_6H_9 \rightarrow C_6H_{10} + C_6H_{10}$; (viii) $C_6H_9 + C_6H_7 \rightarrow C_6H_{10} + C_6H_8$. Since very little, if any, phenylcyclohexadiene is found among the reaction products the reaction $C_6H_8 + C_6H_7 \rightarrow C_6H_9 + C_6H_8$ + H is considered to be unimportant. W. R. A.

Photochemical decomposition of rotenone. L. S. Ts'ai and T. S. Ke (*J. Amer. Chem. Soc.*, 1941, **63**, 1717—1718).—From a study of the absorption spectra of solutions of rotenone (I) in EtOH saturated with CO_2 and with O_2 exposed to sunlight, it is concluded that O_2 does not decompose (I) in the dark but in light there is considerable decomp. Since the absorption curves for the solutions treated with CO_2 are only very slightly different from those treated with O_2 , O_2 can have little effect on the photo-decomp. of (I). W. R. A.

Behaviour of visual purple at low temperature.—See A., 1942, III, 23.

IX.—METHODS OF PREPARATION.

Polyhydric alcohol- and tartaric acid-copper-alkali complexes.—See A., 1942, I, 40.

Stability and activity coefficients of the silver-ammonia complex ion.—See A., 1942, I, 62.

Reaction between hydrogen and Pyrex glass. L. E. Roberts and C. Bittner (*J. Amer. Chem. Soc.*, 1941, **63**, 1513—1516).—When H_2 is heated with Pyrex glass at an initial pressure of 700 mm. and at 500 – 580° , the pressure drops steadily owing to diffusion. The rate of pressure drop increases rapidly with temp. Vols. of H_2 required at different temp. to restore the initial pressure and the efficiency of recovery of H_2 after heating in contact with Pyrex have been measured. ~ 45 – 75% of H_2 disappeared and ~ 0.1 of it as H_2O . The glass darkened even below the surface. No equilibrium was attained and it is concluded that the process is an irreversible reaction and that the amount of H_2 removed is sufficiently large to upset pyrolyses in Pyrex in which H_2 is a product. W. R. A.

Ion exchange between solids and solutions. H. F. Walton (*J. Franklin Inst.*, 1941, **232**, 305—337).—Minerals, synthetic inorg. and org. compounds, and colloids which show ionic exchange are enumerated and their structures discussed. The distribution of ions between the exchanger and solution and other physical chemical aspects of the process are also discussed and its applications in H_2O treatment and other uses are enumerated. J. W. S.

Water softening.—See B., 1942, I, 59.

Reactions between acidoids and substances sparingly soluble in water. O. Samuelson (*Svensk Kem. Tidskr.*, 1941, **53**, 60—66).—The reaction between 10 year-old ZnS and an org. sulphonic acid zeolite has been studied. The reagents were ground to <0.01 in. and suspended in H_2O , and the results compared with those obtained with HCl and ZnS. The zeolite liberated H_2S at the same rate as $2N-HCl$; it is concluded that the material is a strong acid and that reaction takes place by the action of H^+ in solution on solid ZnS. Similar results were obtained with H bentonite and $CaCO_3$. M. H. M. A.

Electrometric study of precipitation of hydrous indium hydroxide.—See A., 1942, I, 66.

Europium and ytterbium amalgams. H. N. McCoy (*J. Amer. Chem. Soc.*, 1941, **63**, 1622—1624).—Amalgams are formed when $M(OAc)_3$ ($M = Eu, Yb$) in K citrate is electrolysed between a Hg cathode and Pt anode at low voltage with good current efficiency or by the direct action of K amalgam. The solid amalgams $Hg_{10}Eu$ and $Hg_{10}Yb$ have been prepared. W. R. A.

Cyanogen halides. P. Kailasam (*Proc. Indian Acad. Sci.*, 1941, **14**, A, 165—169).—Dry Cl_2 has no action on CNI at temp. $>40^\circ$. Br_2 and dry $CNCl$ interact at room temp. forming a *cryst. compound*, $C_3N_3Cl_3Br$, m.p. 160 – 161° , subliming at $>100^\circ$; sol. in Et_2O , CS_2 , CCl_4 , and light petroleum, very sol. in $CHCl_3$, C_6H_6 , and $COMe$, insol. in cold, sol. in hot H_2O ; decomposed by EtOH and by H_2O at 100 – 120° , forming cyanuric acid; mol. wt. 206 in C_6H_6 . The substance behaves as a mol. compound $2C_3N_3Cl_3Br$, dissociating in C_6H_6 solution. Cyanuric chloride interacts with 47% aq. HBr at room temp., forming the *compound* $C_3N_3Cl_3Br$, m.p. 210° with volatilisation; sol. in org. solvents, insol. in cold H_2O , decomposed by EtOH and by H_2O at 120° , giving cyanuric acid. L. J. J.

Geochemical data on Saratoga mineral waters.—See A., 1942, I, 120.

Exchange reaction between gaseous and combined nitrogen. G. G. Joris (*J. Chem. Physics*, 1941, **9**, 775).—No isotope exchange between gaseous $^{15}N_2$ and $^{15}N^{14}N$ and aq. $NaNO_3$, $NaNO_2$, or $NH_4OH.HCl$ could be detected after 360 hr. contact. The results obtained with radioactive N_2 (A., 1941, I, 420) are attributed to difficulties arising in operation with the radioactive isotope. J. W. S.

Formation of [metal] nitrosyls, nitrosocarbonyls, nitrosocyanides, and nitrosohalides. B. Ormont (*Acta Physicochim. U.R.S.S.*, 1940, **16**, 159—175).—The stability and properties of metallic nitrosyl and carbonyl compounds are compared and discussed. It is concluded that the NO mol. donates three electrons to the central atom if by so doing the effective

at. no. of the latter is not increased above the val. for an inert gas, and in these cases the NO compound is more stable than the corresponding CO compound. Otherwise the NO mol. donates only two electrons, and is then less firmly held than CO.

F. J. G.

Ammonium salts of aliphatic carboxylic acids. S. Zuffanti (*J. Amer. Chem. Soc.*, 1941, **63**, 3123—3124).—An apparatus for the prep. of anhyd. NH_4 salts of aliphatic carboxylic acids is described. NH_4 salts of the following have been prepared (m.p. in parentheses): EtCO_2H (107°), $\text{Pr}^i\text{CO}_2\text{H}$ (108°), $\text{Pr}^n\text{CO}_2\text{H}$ (118°), $\text{Bu}^i\text{CO}_2\text{H}$ (108°), $\text{Bu}^n\text{CO}_2\text{H}$ (91°), n - (108°), and *iso*-hexoic (102°), *n*-heptoic (112°), *n*-octoic (114°), *n*-nonoic (115°).

W. R. A.

Sulphur monoxide. E. Kondratieva and V. Kondratieff (*J. Phys. Chem. Russ.*, 1940, **14**, 1528—1534).—The composition (SO) $_n$ of the gas giving rise to the characteristic absorption spectrum between 3400 and 2500 Å. is proved by analysis; d agrees with S_2O_2 . From the emission spectrum of the real SO its absorption spectrum can be approx. calc.; it is different from that observed. The coeff. of absorption of S_2O_2 is independent of temp. between -70° and 20°, showing that no measurable dissociation to SO takes place. The spectrum of S_2O_2 appears under conditions which make formation of SO energetically impossible. This spectrum cannot be due to S_2 mols. since it is too complicated for a diat. mol.

J. J. B.

Mechanism of polymerisation of thiocyanogen from the magnetic viewpoint.—See A., 1942, I, 48.

Dehydration of some pure and mixed chromi-selenic alums and formation of corresponding complex chromi-selenates. P. C. Raychoudhury (*J. Indian Chem. Soc.*, 1941, **18**, 277—280).— $\text{NH}_4\text{Cr}(\text{SeO}_4)_3 \cdot 12\text{H}_2\text{O}$ on dehydration at 80—110° yields $(\text{NH}_4)_2[\text{Cr}(\text{SeO}_4)_2] \cdot 2.5\text{H}_2\text{O}$. $\text{Cr}_2(\text{SeO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ yields $(\text{NH}_4)_2[\text{Cr}_2(\text{SeO}_4)_3(\text{SO}_4)] \cdot 3$ (90—105°) and 1.5 (110°) H_2O . $\text{Cr}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SeO}_4 \cdot 24\text{H}_2\text{O}$ yields $(\text{NH}_4)_2[\text{Cr}_2(\text{SO}_4)_3(\text{SeO}_4)] \cdot 4$, 3.5 , 3 , and $2.5\text{H}_2\text{O}$ at 80—100°, 110—120°, 130—150°, and 150—180°, respectively. $\text{NaCr}(\text{SeO}_4)_2 \cdot 12\text{H}_2\text{O}$ yields $\text{Na}_2[\text{Cr}_2(\text{SeO}_4)_3] \cdot 2$, 1 , and $0.5\text{H}_2\text{O}$ at 90—100°, 110—120°, and 140—150°. $\text{Cr}_2(\text{SO}_4)_3 \cdot \text{Na}_2\text{SeO}_4 \cdot 24\text{H}_2\text{O}$ yields $\text{Na}_2[\text{Cr}_2(\text{SO}_4)_3(\text{SeO}_4)] \cdot 4$, 3 , and $2\text{H}_2\text{O}$ at 80—85°, 90—100°, and 120—160°. All these products form green solutions which, when cold and freshly prepared, give no reactions for Cr^{+++} , SO_4^{--} , or SeO_4^{--} . They are decomposed when the solutions are heated.

F. L. U.

Reactions in mixtures of chromite, magnesite, and alumina.—See B., 1942, I, 88.

Formation of ammonium phosphomolybdate in presence of certain organic acids. W. C. Davies (*Analyst*, 1942, **67**, 1—4).—Preformed NH_4 phosphomolybdate is sol. in neutral solutions of citric, oxalic, and malic acids. It is suggested that sol. complexes are formed and that their formation accounts for the interference of certain org. acids with the gravimetric and colorimetric determination of H_3PO_4 . Excess of phosphomolybdate and higher temp. tend to reduce the interference.

S. B.

Ferric thiocyanate. H. I. Schlesinger (*J. Amer. Chem. Soc.*, 1941, **63**, 1765—1767).—Polemical against Bent and French (A., 1941, I, 210).

W. R. A.

Complex compounds of diguanide with trivalent metals. VIII, IX.—See A., 1942, II, 78.

Complex compounds of diguanide with bivalent metals. II. Nickel diguanidines. P. Rây and B. C. Purakayastha (*J. Indian Chem. Soc.*, 1941, **18**, 217—224).—The following complex salts are described: $\text{RCl}_2 \cdot 2\text{H}_2\text{O}$; $\text{RBr}_2 \cdot 2\text{H}_2\text{O}$; RI_2 ; $\text{RF}_2 \cdot 4\text{H}_2\text{O}$; $\text{RF}_2 \cdot \text{HF} \cdot (\text{NH}_4)_2\text{HF} \cdot 3.5\text{H}_2\text{O}$; $\text{R}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$; $\text{R}(\text{BrO}_3)_2 \cdot 1.5\text{H}_2\text{O}$; $\text{R}(\text{IO}_3)_2 \cdot 0.5\text{H}_2\text{O}$; $\text{R}_2(\text{IO}_3)_2 \cdot 7.5\text{H}_2\text{O}$; $\text{R}(\text{ClO}_4)_2$; $\text{R}(\text{MnO}_4)_2$; $\text{R}(\text{BF}_4)_2$; $\text{R}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$; $\text{R}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$; $\text{RSO}_4 \cdot 3\text{H}_2\text{O}$; $\text{RFSO}_4 \cdot 3\text{H}_2\text{O}$; $\text{RS}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$; $\text{RS}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$; $\text{R}(\text{CNS})_2$; $\text{RSeO}_4 \cdot 3\text{H}_2\text{O}$; $\text{RCrO}_4 \cdot 3\text{H}_2\text{O}$; $\text{RCO}_3 \cdot 2\text{H}_2\text{O}$; $\text{R}_2\text{Fe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$; $\text{R}_2[\text{Fe}(\text{CN})_6] \cdot 6\text{H}_2\text{O}$; $\text{R}[\text{Fe}(\text{CN})_6](\text{NO}) \cdot \text{H}_2\text{O}$; $\text{R}_2[\text{Co}(\text{CN})_6] \cdot 6\text{H}_2\text{O}$; $\text{R}_2[\text{Co}(\text{NO}_2)_6] \cdot 18\text{H}_2\text{O}$; RHgI_4 ; $\text{RI}(\text{I}_2) \cdot 1.5\text{H}_2\text{O}$; $\text{RCl}(\text{I}_2) \cdot 3\text{H}_2\text{O}$; $\text{R} = \text{Ni}(\text{C}_2\text{H}_7\text{N}_5)_2$. The solubility relations and isomorphism of these salts are discussed.

F. J. G.

X.—ANALYSIS.

Principles of quantitative spectrochemical analysis. N. S. Bayliss (*J. Proc. Austral. Chem. Inst.*, 1941, **8**, 250—260).—

The C or graphite arc, the relation of spectrum intensity to concn., the photographic image, quant. analysis by means of the spectrograph, and errors due to background and stray light are discussed. Spectrochemical analysis is specially suitable for routine work, is widely applicable, and, for concns. of 1 to 0.001%, is often superior to chemical analysis.

L. S. T.

Micro-method of chromatographic analysis. M. O'L. Crowe (*Ind. Eng. Chem. [Anal.]*, 1941, **13**, 845—846).—The method is suitable for a rapid preliminary selection of solvents, adsorbents, and elutriants. Adsorbents are placed in the cups of a porcelain spot plate and moistened with various solvents. A drop of the solution under investigation is allowed to flow from the rim of the cup into the adsorbent. Larger separations can be effected in Petri dishes. The method is useful in the analysis of small quantities of biological materials.

L. S. T.

Karl Fischer reagent. VIII. Determination of water of hydration in salts. W. M. D. Bryant, J. Mitchell, jun., D. M. Smith, and E. C. Ashby. IX. Reactions with inorganic oxides and related compounds. Oxidation and reduction reactions. J. Mitchell, jun., D. M. Smith, E. C. Ashby, and W. M. D. Bryant (*J. Amer. Chem. Soc.*, 1941, **63**, 2924—2927, 2927—2930; cf. A., 1941, II, 180).—VIII. The titrimetric determination of H_2O in 25 hydrates which include the hydrated sulphates of the metals extending from Mn to Zn and in the desiccants, activated Al_2O_3 , SiO_2 gel, CaCl_2 , and partly dehydrated CaSO_4 ("Drierite"), has been investigated using the Karl Fischer reagent. The titration was rapid and complete except for "Drierite," which gave a low val. attributed to the H_2O being zeolitic in nature.

IX. The nature and stoichiometry of reactions of the Karl Fischer reagent with inorg. substances other than H_2O , e.g., oxides and salts of the alkali and alkaline-earth metals, have been investigated. Two types of reactions are described, (i) involving the O of metal oxides and salts of oxygen acids and (ii) oxidation and reduction of cations and anions by a modified I_2 - I' couple.

W. R. A.

[Determination of] fluorine in water.—See B., 1942, III, 39.

Determination of nitrates in water by a modification of the phenoldisulphonic acid method.—See B., 1942, III, 39.

Molybdenum-blue reaction. Spectrophotometric study. J. T. Woods and M. G. Mellon (*Ind. Eng. Chem. [Anal.]*, 1941, **13**, 760—764).—The application of the Mo-blue reaction to the colorimetric determination of PO_4^{--} , AsO_4^{--} , and SiO_3^{--} has been investigated spectrophotometrically. Ranges of the methods, conformity of the blue system to Beer's law, and the effects of variables such as time, temp., acidity, and amounts of reactants on the colour developed have been examined. For PO_4^{--} , the relative merits of H_2SnCl_4 , quinal, aminonaphtholsulphonic acid, and a reduced molybdate solution as reductants are compared. The inadequacy of certain proposed permanent standards is shown, and the effects of 63 ions, many of which interfere, are tabulated.

L. S. T.

Rapid determination of phosphorus in ferromolybdenum and in calcium molybdate.—See B., 1942, I, 50.

Colorimetric determination of phosphorus in steel and cast iron.—See B., 1942, I, 94.

Use of granulated zinc alloyed with 0.3% of copper for the Gutzeit test for arsenic. G. Taylor and J. H. Hamence (*Analyst*, 1942, **67**, 12—13).—Cu-Zn alloy used in the Gutzeit test (cf. B., 1941, III, 211) does not give a heavier stain on HgCl_2 papers than that produced by the ordinary granulated Zn with the same quantity of As. Less erratic results are obtained and there is no need to employ a preliminary reduction with SO_2 . HgBr_2 papers may be used with the Cu-Zn alloy and give stains which are more intense and more easily assessed than those given with HgCl_2 papers.

S. B.

"Partition method" for determination of boron [in glass].—See B., 1942, I, 36.

Hydrofluosilicic acid method for determination of quartz. F. H. Goldman (*Ind. Eng. Chem. [Anal.]*, 1941, **13**, 789—791).—Procedure for determining the quartz (I) content of "settled dusts" is described. Mechanical losses, and losses due to dissolution of (I) by the H_2SiF_6 have been reduced greatly by using a const. temp. of 10°, a Munroe crucible

instead of filter-paper, the addition of SiO_2 gel to the H_2SiF_6 , and HNO_3 instead of HCl for dissolution of sol. material.

L. S. T.

Rapid procedure for determination of carbonate. A. C. Kuyper and L. M. Jones (*Ind. Eng. Chem. [Anal.]*, 1941, 13, 801—802).—The total CO_2 is pptd. quantitatively by adding aq. NaOH followed by aq. SrCl_2 to the sample. The reaction mixtures are neutralised (pink to phenolphthalein), a known excess of HCl is added, and CO_2 is removed by aerating, and heating at 80° if necessary. The remaining acid is titrated with alkali. Large amounts of NH_3 interfere with the phenolphthalein end-point, and Mg^{++} interferes in so far as $\text{Mg}(\text{OH})_2$ is not redissolved during neutralisation. CO_2 -free NaOH is most easily prepared by adding saturated aq. NaOH to slightly acid, boiling distilled H_2O .

L. S. T.

[Semimicro-]detection of carbon dioxide and sulphur dioxide from mixtures of carbonates and sulphites. G. B. Heisig and A. Lerner (*Ind. Eng. Chem. [Anal.]*, 1941, 13, 843).—1 mg. of the solid (or neutral solution) is heated with 5 drops of 5N- AcOH for 2 min. in a small test-tube. The evolved gases are passed through a capillary of special shape fixed in the upper half of the tube, and containing acid $\text{Fe}[\text{Fe}(\text{CN})_6]$, and above this, aq. $\text{Ba}(\text{OH})_2$. In presence of 0.005 mg. of SO_2 the brown solution of $\text{Fe}[\text{Fe}(\text{CN})_6]$ turns blue in 1 min., and the CO_2 passes on to the $\text{Ba}(\text{OH})_2$, which becomes turbid with <0.025 mg. of CO_2 . In absence of CO_2 , 3 mg. of SO_2 fail to give a ppt. with the $\text{Ba}(\text{OH})_2$. In presence of NO_3^- , $\text{S}_2\text{O}_3^{--}$, and S^{--} , the CO_2 and SO_2 must be pptd. first with aq. $\text{Sr}(\text{OAc})_2$.

L. S. T.

Modified electrometric determination of silver by a dead-stop end-point procedure. R. H. Lambert and R. D. Walker (*Ind. Eng. Chem. [Anal.]*, 1941, 13, 846—848).—The volumetric method described for determining $1 \cdot 10 \times 10^{-9}$ g.-mol. of Ag makes use of the polarised-electrode method of Foulk and Bawden (A., 1926, 927). Metallic Ag only is determined, and the method is unaffected by Ag^+ . The reactions involved are $2\text{Ag} + \text{I}_2 \rightarrow 2\text{AgI}$ and $\text{I}_2 + \text{Na}_2\text{AsO}_3 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{AsO}_4 + 2\text{HI}$. The AgI is dissolved by the 30% KI present during the titration, and the HI neutralised by 0.02N- NaHCO_3 . Special precautions for reducing the errors involved with such low $[\text{Ag}]$ are discussed. 0.0001N. solutions are generally used, but the end-point is still definite and reproducible with 0.00001N. solutions. 5 $\mu\text{g.}$ of Ag can be determined to $\pm 1\%$, and 0.5 $\mu\text{g.}$ to $\pm 10\%$.

L. S. T.

Determination of radium in some igneous rocks. E. Föyn, E. Gleditsch, and I. T. Rosenqvist (*Amer. J. Sci.*, 1941, 239, 805—808).—Granitic rocks are disintegrated by heating with NH_4F , HF , and the Rn evolved with the SiF_4 and NH_3 is transferred eventually to the ionisation chamber of an electrometer and its activity measured. The method is rapid and gives results as good as those given by fusion with Na and K carbonates. Gneiss granite from Höl, Drivdalen, and augen gneiss from Rüse, Drivdalen, contain 1.11×10^{-12} and 0.77×10^{-12} g. Ra per g., respectively. Chemical analyses of these two rocks are recorded.

L. S. T.

Fluorescence tests for beryllium and thorium. C. E. White and C. S. Lowe (*Ind. Eng. Chem. [Anal.]*, 1941, 13, 809—810).—1-Amino-4-hydroxyanthraquinone (I) gives a red fluorescence (ultra-violet light) with Be^{++} in alkaline solution, and with Th^{+++} in acid solution. In ordinary light, the Be solution has the same purple colour as the alkaline solution of (I). 1 part of Be^{++} in 10^8 of H_2O can be detected in a dilution of 1 in 4×10^7 . $[\text{NaOH}] > 0.3\text{N.}$ diminishes the fluorescence. Be^{++} can be detected easily in presence of Al^{+++} by dissolving the $\text{Be}(\text{OH})_2 + \text{Al}(\text{OH})_3$ ppt. in NaOH and adding (I). $\text{Li}^+ < 0.007$ g. per 10 ml. gives a similar fluorescence. CrO_4^{--} oxidises the reagent, but moderate concns. of other common ions are without effect. Tartrate decreases the intensity of fluorescence slightly, but nullifies the effect of ions such as PO_4^{--} , AsO_4^{--} , MoO_4^{--} , WO_4^{--} , and uranate, which ppt. Be^{++} in alkaline solution. The Th^{+++} solution must be adjusted to $p_{\text{H}} \sim 2$ (thymol-blue), and the test is sensitive to 40 $\mu\text{g.}$ of Th^{+++} in a dilution of 1 to 250,000. Ce^{+++} , Au^{+++} , and ions of the Pt metals destroy the reagent, and many anions interfere.

L. S. T.

Polarographic analysis. W. C. Davies (*Chem. and Ind.*, 1941, 883—884).—A criticism (cf. B., 1941, I, 557). Complete chemical separation of an element before polarographing is not always essential. The essence of inorg. polarographic

analysis is avoidance by the use of proper ground solutions of as many chemical separations as possible.

L. S. T.

Polarographic analysis. A. C. Coates and R. Smart (*Chem. and Ind.*, 1942, 41—42).—A reply to criticism (cf. preceding abstract). 0.01—0.5% of Zn in Al or its alloys can be determined polarographically with a speed and accuracy unobtainable by other methods. The presence of Fe as a major impurity in Al renders the determination of the minor impurities inaccurate unless preliminary separations are made. In the polarographic analysis of metals, chemical separations, which can be relatively crude, are usually necessary when max. accuracy is required.

L. S. T.

Spectrochemical analysis of trace elements in [mixed] fertilisers. Zinc.—See B., 1942, III, 5.

Simultaneous determination of zinc and sulphur in zinc sulphide concentrates by combustion of sulphur in oxygen.—See B., 1942, I, 52.

Rapid method for the micro-analysis of lead. L. T. Fairhall and R. G. Keenan (*J. Amer. Chem. Soc.*, 1941, 63, 3076—3079).—The content of Pb in normal urine as determined by dithizone is $>$ that measured by chemical separation. A rapid micro-method for the determination of Pb is described. Aq. NH_3 is added to urine in a glass-stoppered mixing cylinder until the froth is coloured blue with thymolphthalein indicator (p_{H} 10) and the ppt. is allowed to settle, collected, and dissolved in dil. HNO_3 . The solution is boiled gently; 30 c.c. of 50% citric acid are added and the solution is neutralised by aq. NH_3 . The solution is extracted with a solution of dithizone in CHCl_3 (100 mg. per l.), and washed three times with H_2O to remove citric acid. The Pb is removed from the CHCl_3 layer by 10 c.c. of 2% HNO_3 and pptd. as PbCrO_4 , boiled, filtered, dissolved in a few drops of HCl , and washed into a 5-c.c. glass-stoppered flask. KI is added and the solution titrated with 0.002N- $\text{Na}_2\text{S}_2\text{O}_3$ using CS_2 to indicate the end-point. The procedure may be used for the determination of Pb in drinking water.

W. R. A.

Separation and determination of lead with salicylaldoxime. W. B. Ligett and L. P. Biefeld (*Ind. Eng. Chem. [Anal.]*, 1941, 13, 813—815).—Pptn. of Pb^{++} from nitrate solution by means of salicylaldoxime (I) commences at $p_{\text{H}} \sim 4.8$, and is complete at p_{H} 6.9, but in order to obtain a compound to which the theoretical factor of 0.6053 for $\text{PbC}_2\text{H}_3\text{O}_2\text{N}$ (II) can be applied, pptn. must be carried out at $p_{\text{H}} \sim 8.9$. The ppt. can then be dried at 105° for 1 hr. before weighing. Pb^{++} can be separated as the (I) compound from Ag^+ , Cd^{++} , and Zn^{++} , but not Cu^{++} , Ni^{++} , Co^{++} , Bi^{+++} , Fe^{++} , Mg^{++} , Mn^{++} , and Hg^{++} , in strongly ammoniacal solution. 0.05M- OAc^- increases the p_{H} necessary for commencement of pptn., completeness of pptn., and complete pptn. as (II), by ~ 0.5 unit.

L. S. T.

Use of titanous chloride in determination of lead in lead salts and in certain metal-copper alloys.—See B., 1942, I, 84.

Absorption spectrum as a quantitative test for mercury vapour in air. K. C. Clark and O. Oldenburg (*J. Chem. Physics*, 1941, 9, 786—788).— Hg vapour at v.p. \ll the toxic limit can be determined by comparing the spectrum of a suspected or contaminated atm. with standard calibration spectra.

W. R. A.

Separation and determination of mercury, bismuth, and zinc in "skin bleaches."—See B., 1942, III, 36.

Europium and ytterbium in rare earth mixtures. Polarographic determination. H. A. Laitinen and W. A. Taebel (*Ind. Eng. Chem. [Anal.]*, 1941, 13, 825—829).—Current-voltage curves for Eu and Yb in 0.1N- NH_4Cl are recorded and discussed, and applied to the polarographic determination of these elements. In 0.1N- NH_4Cl , the half-wave potentials of Eu and Yb , referred to the saturated Hg_2Cl_2 electrode, are -0.671 and -1.415 v., respectively. The polarographic method described for Eu gives results agreeing to within 3% with those obtained by means of the Jones reductor. Conditions favouring the polarographic determination of Yb are discussed, and satisfactory results have been obtained with ores containing $\sim 5\%$ Yb . In the simultaneous determination of Eu and Yb , correction must be made for the effect of decreasing drop time with an increase in negative potential.

L. S. T.

Fluorescence method for [determining] aluminium. C. E. White and C. S. Lowe (*Ind. Eng. Chem. [Anal.]*, 1941, 13, 810).—The test described previously (A., 1937, I, 580) is

improved by dissolving the Pontachrome Blue Black R in 95% EtOH, and by heating the test solution to $\sim 80^\circ$ before adding the reagent.

Analysis of aluminium and its alloys.—See B., 1942, I, 98.

Detection of gallium by a fluorescence reaction with 8-hydroxyquinoline. E. B. Sandell (*Ind. Eng. Chem. [Anal.]*, 1941, 13, 844–845).—Ga can be detected by adding 8-hydroxyquinoline to a solution having p_H 2.6–3, and shaking with $CHCl_3$. In presence of Ga, the $CHCl_3$ layer gives, in ultra-violet light, a yellowish fluorescence tinged with green. In reacts slightly at p_H 3, but not at p_H 2.6, whilst Li, Be, and Sc, in relatively large amounts, give faint fluorescences. Fe^{+++} and VO_3^{+++} must be reduced by means of $NH_2OH \cdot HCl$; Cu^{++} pptd. as $CuCNS$, and MoO_4^{+} as $PbMoO_4$ with $Pb(NO_3)_2$. Sn, Sb, Bi, Ti, Nb, Ta, and Te also are best removed before testing for Ga. Zn^{++} and F^- reduce sensitivity, and citrate inhibits the reaction. Most other ions have no effect. At p_H 3.0, 0.1 $\mu g.$ of Ga in 5–10 ml. of solution is detectable. Sensitivity is $>$ this at p_H 4, and $<$ this at p_H 2.6. Details of procedure are given.

L. S. T.

Auto-radiography of ores. C. Goodman and D. C. Picton (*Physical Rev.*, 1941, [ii], 60, 688).—Lapped surfaces of Mn minerals, after activation by slow neutrons, were placed in contact with photographic film. The relative brightness of the prints prepared from the auto-radiographs gives a qual. indication of the content and uniformity of distribution of Mn in the ores.

N. M. B.

Analysis of manganese minerals.—See B., 1942, I, 53.

Analysis of iron and manganese minerals and determination of phosphorus, aluminium, and titanate acid.—See B., 1942, I, 45.

Determination of ferrous iron in resistant silicates. M. H. Hey (*Min. Mag.*, 1941, 26, 116–118).—Rowledge's method of fusion with $2NaF + B_2O_3$ in a sealed glass tube (B., 1935, 949) is adapted on a micro-scale (10 mg.). The fusion cake is dissolved in ICl solution in HCl , and the liberated I titrated with KIO_3 .

L. J. S.

Silver reductor in analytical chemistry. E. E. Halls (*Ind. Chem.*, 1941, 17, 230).—The merits of the Ag reductor- $Ce(SO_4)_2$ method for Fe are compared with those of the $Ti_2(SO_4)_3$ method.

A. R. P.

Micro-analytical testing of iron and steel.—See B., 1942, I, 47.

Spectrographic analysis of tin-lead solders.—See B., 1942, I, 53.

Rapid colorimetric determination of zirconium in steel.—See B., 1942, I, 50.

Assaying cyanide solutions for gold.—See B., 1942, I, 97.

Colorimetric detection and determination of palladium with compounds containing the *p*-nitrosoanilino-group. L. G. Overholser and J. H. Yoe (*J. Amer. Chem. Soc.*, 1941, 63, 3224–3229).—Compounds containing the $p\text{-NO-C}_6\text{H}_4\text{-N}<$ group form highly coloured complexes with Pd^{++} salts similar to that formed with $NHPh \cdot C_6H_4 \cdot NO$ -*p*. Complexes of $PdCl_2$ and $Pd(NO_3)_2$ with the following have been prepared and have the general formula $Pd[NO \cdot C_6H_4 \cdot NX_2]_2$: *p*-nitroso-aniline, -dimethyl- (I) and -diethyl-aniline (II). They can be used for the detection of small amounts of Pd^{++} ions. (I) and (II) are better colorimetric reagents because they have (a) faster reaction rate, (b) greater stability, and (c) smaller temp. effect, and (d) are more suitable for spectrophotometric studies. Absorption curves for reagents and complexes are given and discussed. A procedure is given for the colorimetric determination of Pd in presence of Ag.

W. R. A.

XI.—APPARATUS ETC.

Adjustable vapour thermoregulator. J. Y. Yee (*Ind. Eng. Chem. [Anal.]*, 1941, 13, 839).—The Et_2O vapour thermoregulator described operates to $\pm 0.02^\circ$ between 20° and 40° .

L. S. T.

Thermostats employing external surface control. V. D. Hopper (*Proc. Physical Soc.*, 1942, 54, 55–62).—The principles involved in the production of const. temp. are discussed. They have been applied to the design of thermostats using an external resistance thermometer to control the heat

supply, which may be radiant heat or heated air. Sensitivity is $> 0.01^\circ$.

N. M. B.

Measurement of flame temperatures.—See B., 1942, I, 21.

Method of installing tube-wall thermocouples. E. L. Patton and R. A. Feagan, jun. (*Ind. Eng. Chem. [Anal.]*, 1941, 13, 823–824).—The method described can be used to locate a thermocouple junction at any point in the wall of the tube, and to carry the leads to any desired point through a substantially isothermal zone.

L. S. T.

Modified calorimeter for high temperatures. Heat content of silica, wollastonite, and thorium dioxide above 25° . J. C. Southard (*J. Amer. Chem. Soc.*, 1941, 63, 3142–3146).—A calorimeter for high-temp. sp. heats is described. The vals. of H above room temp. have been measured for wollastonite (up to $1433^\circ K.$), ThO_2 (up to $1780^\circ K.$), and SiO_2 glass (up to $1522^\circ K.$). Equations for the data have been constructed and hence vals. of C_p have been derived.

W. R. A.

Simple refractometer. F. Benford (*J. Opt. Soc. Amer.*, 1939, 29, 352–354).—A brass plate carrying a prism-shaped holder for the glass being tested is mounted on the table of a comparator used for measurement of λ in spectrum plates. The holder has a polished mirror vertical face and a polished face at an angle of 45° . The thickness of the plane-parallel glass plate and the apparent displacement of an object viewed through it are measured, and n is read from a curve. The average error is ± 0.006 .

A. A. E.

Counting of particles in the slit ultramicroscope. O. Spengler and H. Hirschmüller (*Kolloid-Z.*, 1941, 94, 29–30).—As a substitute for the short-lived high-pressure Hg lamp a C arc can be used to illuminate the slit for photographic exposures of 0.05 sec. if thin (~ 5 mm. diameter) electrodes are used and loaded with 100–120 amp.; the brightness of this source is approx. equal to that of the sun. Exposures are made on 16-mm. cine-film at the rate of 16 per sec. An automatic interruptor for visual counting is described.

F. L. U.

Film-contraction errors in lattice-spacing measurements. W. Hume-Rothery, G. V. Raynor, and A. T. Little (*J. Sci. Instr.*, 1941, 18, 239–240).—The assumption that a film expands and contracts uniformly during development and drying, and that no changes in length occur during exposure, is discussed. Changes which occur during exposure and drying are described. Films are preferably kept under conditions of const. temp. and humidity, and a current of filtered air of approx. the same humidity is passed through the camera before and during exposure.

A. A. E.

Supersonic cell fluorometer. H. B. Briggs (*J. Opt. Soc. Amer.*, 1941, 31, 543–549).—A method by means of which luminescence changes excited in phosphors by cathode-ray beams and extending over periods of a few μ -sec. is measured is described. A rectangular voltage-wave of known frequency is used to produce simultaneous excitation of the phosphor and a pulse of high-frequency supersonic waves from a quartz crystal. By varying the distance travelled through a liquid by the pulse before passing through a collimated light beam from the phosphor, it is arranged that a known time interval elapses between the luminescence change and the formation of a Debye-Sears diffraction pattern which is received by a photo-electric cell.

L. J. J.

Photographing sugar and other crystals. W. V. Morton (*News Edn. Amer. Chem. Soc.*, 1941, 19, 1194).—An inverted camera for photographing crystals under oblique illumination is described with reference to a sketch. The crystals are placed at the bottom of a glass cylinder in a non-aq. liquid, e.g., glycerol, saturated with sugar and the illumination is provided by four 40-w. lamps regularly disposed around the cylinder. The lens of the camera is placed below the cylinder and a ground-glass film plane with viewing mirror below is provided at the bottom of the plywood camera body carrying the whole of the apparatus.

A. R. P.

Lundegårdh apparatus [for spectrographic analysis of solutions]: its construction and use. J. A. C. McClelland and H. K. Whalley (*J.S.C.I.*, 1941, 60, 288–291).—A detailed description is given of the Lundegårdh apparatus in which the solution to be analysed is sprayed into a flame, and the light from the flame analysed by means of a quartz spectrograph. The use of the apparatus is described, and data on

the accuracy and sensitivity are given. Some analyses for which the method is regularly used are briefly described.

C. E. H.

Absorption spectrum as a quantitative test for mercury vapour in air.—See A., 1942, I, 114.

Photon counters for spectral investigations in the ultra-violet.—See A., 1942, I, 2.

Photometry in spectrochemical analysis. W. C. Pierce and N. H. Nachtrieb (*Ind. Eng. Chem. [Anal.]*, 1941, **13**, 774—781).—Methods for plate calibration, variations in plate gamma with λ , the effect of background and methods for its correction, accuracy obtained in photometric measurements of intensity ratios, and working curves and the factors governing the selection of an internal standard are discussed. Graphical computation methods are described. Criteria for evaluation of a photometer are given, and the construction of a satisfactory instrument is described. L. S. T.

Spectrographic analysis of briquetted tablets. H. W. Dietert (*J. Opt. Soc. Amer.*, 1941, **31**, 693—696).—Electrical excitation of specimens for spectrographic analysis is facilitated by pressing the specimen, mixed with a good electrical conductor such as sucrose, C, or metals, and in some cases with a binder such as sucrose, into firm tablets. An element, e.g., Fe, may be added as an internal standard. Details of briquetting and spectrographic procedure are given.

L. J. J.

Quartz photo-electric spectrophotometer. H. H. Cary and A. O. Beckman (*J. Opt. Soc. Amer.*, 1941, **31**, 682—689).—The photo-electric spectrophotometer described, for measurements in the ultra-violet and visible regions, incorporates a mirror-collimated quartz prism monochromator on the principle of the Littrow spectrograph, photo-cell with electronic amplifier, and direct-reading potentiometer. Performance data are recorded.

L. J. J.

Automatic recorder of spectral sensitivity of photo-electric surfaces. J. T. Tykociner and L. R. Bloom (*J. Opt. Soc. Amer.*, 1941, **31**, 689—692).—The method described employs a Hardy spectrophotometer with two glow discharge lamps, modulated at 60 cycles, one of which is controlled photo-electrically so that its light intensity \propto the relative spectral sensitivity of the photo-electrical surface investigated. The other lamp serves as a light intensity reference source, and its intensity is controlled mechanically. A detector phototube, controlling the recording mechanism by means of thyatron, receives the light emitted by both lamps.

L. J. J.

Raman effect. CXVI. New crystal powder apparatus.—See A., 1942, I, 83.

Magnetic device for control of the arc in spectrochemical analysis. R. Taylor (*J. Sci. Instr.*, 1942, **19**, 11).—The position of the arc is stabilised by rotating the lower electrode (25 r.p.m.) and deflecting the arc magnetically to its near edge.

A. A. E.

Mass spectrometer for isotope analysis. H. S. Brown, J. J. Mitchell, and R. D. Fowler (*Rev. Sci. Instr.*, 1941, **12**, 556; cf. A., 1941, I, 485).—Corrigenda.

D. F. R.

Calculation of the error due to the absence of guard electrodes in X-ray ionisation chambers. N. L. Walbridge (*Rev. Sci. Instr.*, 1941, **12**, 546—548).—An equation is given expressing the fraction of the incident X-ray power which escapes as kinetic energy of electrons; it can be used to eliminate the necessity of guard electrodes.

D. F. R.

Electrostatic generator for nuclear research at the Massachusetts Institute of Technology. L. C. Van Atta, D. L. Northrup, R. J. Van de Graaf, and C. M. Van Atta (*Rev. Sci. Instr.*, 1941, **12**, 534—545).—The construction of the generator and of the high-voltage accelerating tube mounted vertically in one of the columns is described. Currents up to 4×10^{-3} amp. and voltages up to 2.7×10^6 v. may be obtained. An account is given of experience with the acceleration of positive ion and electron beams and with the X-ray bombardment of In, Be, and D. Yield curves, showing the variation of initial counting rate with voltage of 5-min. bombardments, are given for Be and D.

D. F. R.

Continuous-reading electronic voltmeter for use with glass and other high-resistance electrode systems. C. J. Penner, F. B. Rolfsen, and L. Lykken (*Ind. Eng. Chem. [Anal.]*, 1941, **13**, 831—834).—The meter described has a range of

± 2.11 v., and a sensitivity of ± 0.001 v. It is designed for the accurate determination of potentials of electrode systems that have a resistance of > 5000 M Ω .

L. S. T.

Constant mercury level for the dropping mercury electrode. A. Langer (*Ind. Eng. Chem. [Anal.]*, 1941, **13**, 794).—A floating bulb valve device is described.

L. S. T.

Pyrex all-glass micro-electrophoresis cell. D. R. Briggs (*Ind. Eng. Chem. [Anal.]*, 1940, **12**, 703—705).—A cell and electrical circuit for measuring the migration velocities of particles suspended in org. or aq. liquids is described.

L. S. T.

Platinised porous graphite as a hydrogen electrode.—See A., 1942, I, 64.

Silicon carbide electrode.—See A., 1942, I, 65.

Treatment of platinum electrodes used for determining the redox potential of soil.—See B., 1942, III, 3.

Absolute measurement of electrical resistance by a method using the average electromotive force of a commutating generator. H. R. Nettleton and E. G. Balls (*Proc. Physical Soc.*, 1942, **54**, 27—46; cf. A., 1940, I, 41).—The e.m.f. across the resistance ($\sim 1 \Omega$) when conveying d.c. is balanced against the average e.m.f. of a commutating generator, the field coils of which convey the same current. The method allows the two main errors associated with break and self-inductance to be set against one another.

N. M. B.

Semi-conductor photocells and rectifiers.—See B., 1942, I, 61.

Rectifiers.—See B., 1942, I, 6.

Signer method for determining mol. wts. E. P. Clark (*Ind. Eng. Chem. [Anal.]*, 1941, **13**, 820—821).—Apparatus and procedure for determining mol. wts. by Signer's isothermal distillation method (A., 1930, 531) are described. Azobenzene furnishes a good standard where org. solvents are used. Typical mol. wts. for certain org. compounds are recorded.

L. S. T.

Determination of molecular and ionic weights of dissolved substances by the methods of dialysis and free diffusion. III. G. Jander and H. Spandau (*Z. physikal. Chem.*, 1941, **A**, 188, 65—89).—A reply to Brintzinger (*ibid.*, 1940, **187**, 317).

F. J. G.

[Apparatus for determining] densities of molten rocks and minerals.—See A., 1942, I, 123.

Attempted isotopic separation by fractional crystallisation. W. J. C. Orr (*Trans. Faraday Soc.*, 1941, **37**, 587—590).—A continuous counter-flow arrangement to deal with a crystalline phase and its saturated solution is described. No detectable separation of Cl isotopes was observed when the apparatus was operated continuously for 1 month with NaCl.

F. L. U.

Laboratory-size continuous distillation unit. R. W. Hufferd and H. A. Krantz (*Ind. Eng. Chem.*, 1941, **33**, 1455—1459).—A detailed description of the unit, which consists of an air-pressure feed system, a single column packed with Ni helices, a reboiler, a splash chamber, a total condenser with overhead product take-off, and the usual heating (electric) and cooling arrangements, is given. The efficiency corresponds with 52—56 theoretical plates. The unit can cope with a throughput of one quart per hr. at a reflux rate of 3:1.

C. R. H.

Analytical separation of sugars by distillation of their propionates.—See A., 1942, II, 79.

Distillation of sugar propionates at low pressure.—See A., 1942, II, 79.

Action of light on cellulose. VI. Measurement of the osmotic pressure of colloidal solutions. R. E. Montonna and L. T. Jilk (*J. Physical Chem.*, 1941, **45**, 1374—1381).—An apparatus for measuring with $< 5\%$ error the osmotic pressure of colloidal solutions using a denitrated collodion membrane is described. Data obtained with COME₂ solutions of cellulose nitrate illustrate the application of the method.

C. R. H.

Laboratory agitator. G. H. Botham (*Chem. and Ind.*, 1942, 10—11).—A simple mechanical agitator, suitable for use in a m.p. apparatus and working on slight suction or compression, is described.

H. G. R.

Small-scale centrifuge accessories for use with corrosive materials. G. F. Smith (*Ind. Eng. Chem. [Anal.]*, 1941, 13, 824).—Porcelain centrifuge cups with perforated bases are described. 1 lb. of crystals of average ρ can be centrifuged at 2000 r.p.m. and 10 lb. can be filtered, centrifuged, and washed in 1 hr. by means of the equipment described.

L. S. T.

Controlling apparatus to eliminate waste of water in using the ordinary filter pump. F. E. Holmes (*Ind. Eng. Chem. [Anal.]*, 1941, 13, 759–760).—A closed suction system with automatic control of the supply of H_2O to the aspirator is described. It is trustworthy, and operates continuously with little or no attention.

L. S. T.

Stability of the permanganate-periodate colour system. J. P. Mehlig (*Ind. Eng. Chem. [Anal.]*, 1941, 13, 819).—The exceptional stability of this colour system is re-emphasised (cf. A., 1939, I, 431).

L. S. T.

Nitric and sulphuric acids, a colourless cleaning mixture for glassware. W. C. Tobie (*J. Lab. clin. Med.*, 1941, 26, 1797–1798).—A 9:1 (vol.) mixture of conc. H_2SO_4 and HNO_3 is recommended.

C. J. C. B.

Modified Jones reductor. J. E. Edwards (*Ind. Eng. Chem. [Anal.]*, 1940, 12, 673).—The apparatus described permits reduction of warm solutions. The exit tube of a Jones reductor is connected by means of a 3-way tap and vertical glass tubing to the tap of a coil surrounded by cooling H_2O . The reduced solution is collected in a beaker contained in a Witt filtering apparatus.

L. S. T.

Capillary flowmeter. H. N. Alyea (*Ind. Eng. Chem. [Anal.]*, 1940, 12, 686).—The all-glass instrument described measures continuously the rate of flow of a liquid (a few ml. per hr.) immediately before it is vaporised in a catalyst chamber. It is insensitive to momentary fluctuations in room temp.

L. S. T.

Laboratory-scale flow regulator. V. H. Cheldelin and B. E. Christensen (*Ind. Eng. Chem. [Anal.]*, 1941, 13, 805).—Apparatus for regulating the slow flow of gases is described.

L. S. T.

Portable low-pressure gas tanks. G. R. Robertson (*Ind. Eng. Chem. [Anal.]*, 1940, 12, 686).—The tank described is suitable for distributing from a central supply 10–200 l. of O_2 for combustions, N_2 for experiments requiring an inert atm., and gaseous mixtures of special composition.

L. S. T.

Precision feed device for catalytic experiments. R. L. Burwell, jun. (*Ind. Eng. Chem. [Anal.]*, 1940, 12, 681–682).—In the apparatus described Hg is displaced by the gas evolved by the electrolysis of 30% aq. KOH. The displaced Hg forces the feed liquid into a pre-heater. The feed rate can be set or changed quickly to a predetermined val., and the apparatus can be used at pressures from 1 atm. to ~50 mm.

L. S. T.

Micro-hydrogenation apparatus. A. N. Prater and A. J. Haagen-Smit (*Ind. Eng. Chem. [Anal.]*, 1940, 12, 705–707).—In the apparatus described the reaction and measuring system is shaken as a unit, thus eliminating ground joints which must be able to rotate freely and yet remain gas-tight. Data for cinnamic and maleic acids with PtO_2 as catalyst and glacial AcOH as solvent illustrate the trustworthiness of the apparatus.

L. S. T.

Generator for production of pure carbon dioxide. W. H. Rauscher (*Ind. Eng. Chem. [Anal.]*, 1940, 12, 694–695).—An improved modification of the Poth type of generator is described.

L. S. T.

Removal of static charges from glassware by ultra-violet light. C. J. Rodden (*Ind. Eng. Chem. [Anal.]*, 1940, 12, 693).—Charges produced on glassware after wiping with chamois leather are dissipated readily by exposure for 10 min. to the light from a Hanovia Alpine sun lamp or General Electric Lab-Arc 60 cm. distant.

L. S. T.

High-vacuum valve. D. B. Cowie and G. K. Green (*Rev. Sci. Instr.*, 1941, 12, 556).—A high-vac. modification of the ordinary steam valve is described.

D. F. R.

Apparatus for sampling and testing explosion gases from blasting.—See B., 1942, I, 104.

[Apparatus for determining] rate of formation of nuclei in supersaturated solutions.—See A., 1942, I, 16.

Durability of glass containers.—See B., 1942, I, 37.

Nomograph for the solubility of sulphur dioxide in water.—See A., 1942, I, 54.

Nomographs for the solubilities of hydrogen and nitrogen in liquid ammonia.—See A., 1942, I, 54.

XIII.—GEOCHEMISTRY.

Temperature of the ionosphere.—See A., 1942, I, 3.

Optics of atmospheric haze.—See A., 1942, I, 44.

Fluctuations of atmospheric sulphur dioxide. W. J. Youden (*Contr. Boyce Thompson Inst.*, 1941, 11, 473–484).—Daily, weekly, and annual cycles in the atm. $[SO_2]$ are established by means of continuous records. Data are discussed in relation to weather conditions.

A. G. P.

Experiments on condensation nuclei. P. J. Nolan (*Proc. Roy. Irish Acad.*, 1941, 47, A, 25–38).—The initial val. of the ratio of concn. of total nuclei to concn. of uncharged nuclei, Z/N_0 , is independent of humidity and concn., but increases on storage from 1.9 to a final val., attained in 7–17 hr., of 2.5–3.5, depending on the initial concn. of the nuclei. The decay of atm. nuclei in a closed vessel follows the equation $dZ/dt = -\gamma Z^2 - \lambda Z$, the val. of γ agreeing with that of Kennedy's flame nuclei. The exponential loss is mainly due to diffusion taking place in a boundary layer of thickness \propto (linear dimensions of vessel)^{1/2}.

D. F. R.

Analysis of mineral water at Kinkei in Totigi province. K. Kuroda (*Bull. Chem. Soc. Japan*, 1941, 16, 234–237).—Spectroscopical and chemical examination has indicated the presence of 24 elements. The principal constituents are H_2SO_4 , $FeSO_4$, $Al_2(SO_4)_3$, and H_2SiO_3 . The H_2O , which has pH 2.4, contains ~0.05 Mache unit of Rn per l.

C. R. H.

Mineral spring at Surangudi, Tinnivelly District, South India. T. N. Muthuswami (*Quart. J. Geol. Soc. India*, 1941, 13, 95–101).—A more detailed account of work already noted (A., 1941, I, 308).

Ansh-Bulat mirabilite lake. A. V. Zdanovski and D. I. Riabtschikov (*Ann. Sect. Anal. Phys.-Chim.*, 1940, 13, 363–375).—Analytical data are recorded. The brine is of the sulphate type. During the winter months mirabilite is deposited in very large amount from the lake H_2O . Methods of utilising the residual brine for prep. of $MgCl_2$ and bromides are discussed.

R. T.

Geochemical data on Saratoga mineral waters, applied in deducing a new theory of their origin. L. W. Strock (*Amer. J. Sci.*, 1941, 239, 857–898).—Spectrochemical determinations of Zr, Sn, Be, Ti, V, Mn, and Ni in Saratoga H_2O show that Zr, Sn, and Be are enriched considerably compared with their average amounts in the lithosphere, whilst the other elements are depleted. The ratio Zr:Ti is > in the earth's crust by a factor 4700. The geochemical process responsible for this characteristic trace element distribution involves dissolution of Zr and Ti from their minerals by $Ca(HCO_3)_2$ solutions containing an excess of CO_2 , and the formation of $ZrO(CO_3)_2$, which is stable and sol. in aq. $Ca(HCO_3)_2$. The corresponding Ti ion is not stable under the same conditions, and the Ti is pptd. near its source and thus separated completely from the Zr by the mineral waters. Sn and Be are enriched by this process. Aq. $Ca(HCO_3)_2$ dissolves much Zr from pptd. ZrO_2 and from eudialite. Deposition of travertine from the Orenda spring shows that Ca is deposited from the waters much earlier than Mg and Zr. An attempt to trace the origin of the more abundant constituents in Saratoga H_2O to known geological formations of the region has been made, and a theory of origin that accounts for the amounts and ratios of the characteristic constituents is presented.

L. S. T.

Distribution and types of coliform bacteria in lakes and streams.—See A., 1942, III, 269.

Radioactivity of ocean sediments. IV. Radium content of sediments of the Cayman Trough [between Cuba and Jamaica]. C. S. Piggot and W. D. Urry. **V. Concentrations of the radioelements and their significance in Red Clay.** W. D. Urry and C. S. Piggot (*Amer. J. Sci.*, 1942, 240, 1–12, 93–103; cf. A., 1941, I, 134).—IV. The Ra contents of ocean-bottom cores from this trough are tabulated and discussed.

The radio-elements are not in equilibrium in the uppermost layers of the sediments at the bottom of the ocean. A history of U, Io, and Ra is reflected in the variation of the Ra content of ocean sediments with the depth below the ocean floor. Measurements of this variation show that the [U], [Io], and [Ra] at any given time are established by the usual growth and decay laws of radioactivity in a system that is not in radioactive equilibrium.

V. The relationship between U, Io, and Ra in the deep-sea deposits known as Red Clay is similar to that described previously for calcareous sediments of the ocean. The Red clay (246 cm. core) differs from the sediments by a very rapid decrease in the Ra content ($10.79 \pm 0.13 \times 10^{-12}$ g. per g.) just below the surface of the ocean bottom, and the attainment of the final equilibrium between U, Io, and Ra in the bottom quarter of the core, which indicates a slow deposition compared with that of the calcareous deposits. The Ra content at equilibrium with the U is only 7% of that near the surface of the deposit. The high surface concns. of Ra and Io are only transient phenomena produced by an unknown mechanism that concentrates these elements, relative to U, during deposition.

L. S. T.

Witsand meteorite, South-West Africa. S. J. Shand (*Amer. J. Sci.*, 1942, 240, 67–71).—The stone belongs to the class of "friable white chondrites." In addition to metallic Fe and some Ni-Fe, only olivine and hypersthene have been recognised.

L. S. T.

Luminescence of meteorites. J. D. Buddhue (*Amer. J. Sci.*, 1941, 239, 839–844).—Certain meteorites luminesce to different extents when exposed to an electric discharge in a vac., but not in X-rays or ultra-violet light. Enstatite is the most active mineral, but not all of it is active. Olivine is not active. The usual colour of the glow is bluish, but two howardites give a yellow glow, and two other stones a red luminescence. Roasting of the Holbrook, Arizona, meteorite in air changed the glow from blue to green. Inactive meteorites are all dark brown or black, whilst the most active are light in colour.

L. S. T.

Thermal state of the earth. H. Jeffreys (*Amer. J. Sci.*, 1941, 239, 825–835).—A review of data related to the internal heat of the earth indicates that (i) the average radioactivities of surface rocks show a steady decrease with increase of p , although there is much scatter within a given type, (ii) heat generated at depths up to ~300 km. has had sufficient time to be conducted out as rapidly as it is produced, (iii) fusion temp. are not a normal feature at any depth within the crust, and (iv) the thermal contraction available for mountain formation remains essentially unchanged.

L. S. T.

Distribution of helium and radioactivity in rocks. II. Mineral separates from the Cape Ann granite. N. B. Keevil (*Amer. J. Sci.*, 1942, 240, 13–21; cf. A., 1939, I, 106).—Data obtained by the He age method are recorded for the Essex Co. granite at Cape Ann, Mass., and its common mineral constituents. The granite is more radioactive than usual, probably owing to active accessories associated with the femic minerals. Relative radioactivities of the femics, quartz, and feldspar are ~23:2:1. In spite of the relatively high rate of He production, the femics gave the highest He index, 189. The quartz (94) and feldspar (59) showed evidence of losing He during geological time and after exposure at the surface. Further experiments on minerals are required before He index can be used in geological correlation.

L. S. T.

Alteration of radioactive minerals. T. C. Sarkar (*Proc. Indian Acad. Sci.*, 1941, 14, B, 261–270).—Four possible methods of alteration of radioactive minerals by solutions are discussed in explanation of the discordant Pb ratios of U and Th minerals. The most important of these is that Pb in radioactive minerals is present partly as plumbate and U partly as uranate, and that SiO_2 as silicate in percolating waters may displace plumbate and uranate ions. Age indications given by slightly-altered monazites may be trustworthy. No common Pb is present in radioactive minerals derived from pegmatites.

L. S. T.

Ore deposits of Captain's Flat, New South Wales. E. S. Kenny and C. St. J. Mulholland (*Proc. Austral. Inst. Min. Met.*, 1941, No. 122, 45–62).—The geology of the country surrounding Captain's Flat in the Federal Territory near Canberra, N.S.W., is described in detail. The ore consists

of galena, blende, and Cu pyrites in a gangue of quartz-sericite schist (altered porphyry) and is estimated to exceed 2,000,000 tons assaying Pb 7.9, Zn 13.11, Cu 0.7%; Au 1.2, Ag 48 dwt. per ton.

A. R. P.

Some tantalum-niobium minerals from W. Australia. A. B. Edwards (*Proc. Austral. Inst. Min. Met.*, 1940, No. 120, 731–744).—Tantalorutile (I) from Globe Hill, W. Australia, is a greyish-brown, anisotropic, homogeneous mineral, d 4.83, containing TiO_2 66.28, Ta_2O_5 15.44, Nb_2O_5 8.64, FeO 8.00, SnO_2 1.24, SiO_2 0.32, H_2O 0.18%. Analysis of a specimen from Melville showed TiO_2 43.2, Nb_2O_5 33.3, Ta_2O_5 7.6, FeO 10.8, MnO 3.6, SnO_2 0.4, SiO_2 0.6, H_2O 0.16%, d 4.9; microscopic examination of etched polished specimens showed it to consist of finely intergrown crystals of moscovite, rutile, and ilmenite. It is suggested that the Melville specimen is the result of unmixing of a solid solution of (I). Polished sections of ferrotantalite from Greenbushes showed no cassiterite (II), although the specimen contained 1.5% of SnO_2 ; the SnO_2 therefore appears to be in solid solution, as also does the 1.76% of Ta_2O_5 found in some specimens of (II) from the same locality. W. Australian ainalite, however, consists of crystals of (II) separated by crystals of a Ta_2O_5 -rich mineral. Analyses are given of three specimens of stibio-tantalite.

A. R. P.

Coated gold from Cobar, New South Wales. F. L. Stillwell and A. B. Edwards (*Proc. Austral. Inst. Min. Met.*, 1941, No. 121, 1–10).—Table concentrates obtained from the New Cobar mine contain a large no. of particles of "black Au"; this consists of native Au particles coated with native Bi (I), galena, galenobismutite (II), or maldonite (Au_2Bi), or with dark AgCl. Many of the particles of (I) and (II), which are also present in the concentrate, contain inclusions of Au, generally between crystal boundaries or in small cavities.

A. R. P.

Mineral composition of the Mount Oxide copper ore, Queensland. A. B. Edwards (*Proc. Austral. Inst. Min. Met.*, 1940, No. 118, 83–95).—The ore consists essentially of chalcocite (I) with minor amounts of pyrite; in the more oxidised parts the (I) is replaced by cuprite, tenorite, malachite, brochantite, and occasionally by azurite. The (I) appears to be of supergene origin, and its Cu content is probably derived from primary Cu sulphide minerals that once existed in the higher levels of the ore-body; the Cu dissolved from these latter was reprecipitated on the pyrite which existed in the lower zone, and the resulting (I) was then slowly oxidised locally to give the oxidised Cu minerals mentioned above.

A. R. P.

Barytes deposit at Pembroke, Hants County, Nova Scotia. A. E. Cameron (*Proc. Nova Scotian Inst. Sci.*, 1940–41, 20, 57–63).—The deposit described consists of >10⁶ tons of high-grade, light red barytes in Palaeozoic sediments. It appears to be a replacement deposit formed by descending supergene solutions percolating down through an Fe-rich calcareous series of sediments, and replacing the CaO -rich portions by BaSO_4 . The analysis is BaSO_4 97.1, CaO 0.1, Fe_2O_3 0.8, and SiO_2 1.1%.

L. S. T.

A crystal of augelite from California. M. A. Peacock and D. A. Moddle (*Min. Mag.*, 1941, 26, 105–115).—A detailed crystallographic description is given of a large ($15 \times 8 \times 6$ mm.) crystal of gem quality from White Mountain, Mono County (A., 1936, 50). Several new crystal-forms are referred to the axial ratio $a:b:c = 1.6419:1:0.6354$, $\beta = 67^\circ 33'$, adopting the val. of Prior and Spencer (A., 1895, ii, 507), but halving the c -axis. From a consideration of the morphology, as given by the distribution of the crystal-forms, and from the X-ray powder photograph, the space-group is $C_{2h}^2 = C_{2/m}$. The unit cell, of dimensions a 13.10, b 7.96, c 5.06 Å., contains $4[\text{Al}_2\text{PO}_4(\text{OH})_3]$. The optical data agree with those of Prior and Spencer.

L. J. S.

Anorthite-epidote-garnet-hornfels from Namaqualand, South Africa. C. B. Coetzee (*Min. Mag.*, 1941, 26, 134–139).—The hornfels composed of this unusual assemblage of minerals (for which optical data are given) occurs as bands in pyroxene-bearing gneisses. Chemical analysis (SiO_2 41.63, Al_2O_3 25.32, Fe_2O_3 6.33, CaO 22.06%, etc.) suggests that it has been derived from a marl. Analyses are also given of the associated migmatized amphibole-pyroxene-gneiss and of the younger granite-gneiss which induced the metamorphism.

L. J. S.

Identity of "eggonite" with sterrettite. F. A. Bannister (*Min. Mag.*, 1941, 26, 131–133).—"Eggonite" was originally

described by A. Schrauf (1879) as a Cd silicate from Altenberg, Belgium, but it was later found that the crystals had been fraudulently gummed on the specimens of Zn ore. Similar crystals described by J. Krenner (1929) as hydrous Al phosphate were associated with Ag ore from Felsőbánya, Hungary. X-Ray examination of old specimens of "eggonite from Altenberg" gave a 8.90, b 10.24, c 5.40 Å, d 2.44, which, together with earlier crystallographic and optical data, are in agreement with those for sterrettite, $\text{Al}_6(\text{PO}_4)_4(\text{OH})_6 \cdot 5\text{H}_2\text{O}$, from Fairfield, Utah (cf. A., 1941, I, 352). L. J. S.

Kornerupine and its chemistry. M. H. Hey, B. W. Anderson, and C. J. Payne (*Min. Mag.*, 1941, 26, 119–130).—Four micro-analyses of kornerupine of gem quality from Ceylon (A., 1940, I, 238) and of the "prismatic" variety from Waldheim, Saxony, show SiO_2 29.3–30.5, B_2O_3 2.5–3.6, Al_2O_3 35.8–42.9, Fe_2O_3 0–3.3, FeO 4.8–9.1, MgO 16.4–21.0, Na_2O trace–1.6, K_2O trace–0.6%. New determinations of FeO on the original materials previously analysed from Port Shephstone, Natal (A., 1940, I, 333), and Itronagay, Madagascar, gave 12.22 and 2.55%, respectively, with no Fe_2O_3 . Details of the method of analysis, especially for B_2O_3 and FeO, are given. The contents of the unit cell (a 13.68, b 15.95, c 6.68 Å) are given by the general formula $(\text{Al}, \text{Mg}, \text{Fe}^{\text{II}}, \text{Fe}^{\text{III}}, \text{Na})_{10}(\text{Si}, \text{B})_{18}\text{O}_{86}$; with a small replacement of Si by Al this is expanded to $\{(\text{Al}, \text{Fe}^{\text{III}})_{20+z+y+z}(\text{Mg}, \text{Fe}^{\text{II}})_{20-x-2y-z}\text{Na}_y\}\{\text{Si}_{18-x-z}\text{Al}_z\text{B}_z\text{O}_{86}\}$. Optical data are given for the materials analysed and for several other gem specimens from Ceylon. Two types are distinguished: those with $2V$ 20° – 25° , and a pseudo-uniaxial type with $2V$ 3° – 8° . Refractive indices are: α 1.665–1.682, β 1.6766–1.696, γ 1.677–1.699; d 3.290–3.449. L. J. S.

Microgranular uraninite from Isaka [Japan] and its absolute age. T. Iimori (*Amer. J. Sci.*, 1941, 239, 819–821).—Uraninite (I) in the Isaka pegmatite is finely dispersed throughout the whole rock body, and is intimately associated with fergusonite. (I) contains UO_2 22.23, UO_3 55.40, ThO_2 3.86, Y earths 14.60, Ce earths 0.41, PbO 1.01, Bi_2O_3 0.00, Fe_2O_3 0.17, Al_2O_3 0.44, SiO_2 0.11, $(\text{Nb}, \text{Ta})_2\text{O}_5$ 0.74, CO_2 0.28, H_2O 0.50, total 99.75%. The solution of the mineral in dil. HNO_3 gave 2.31×10^{-7} g. Ra per g., and the aq. solution obtained from the fused Nb-Ta fraction, 0.7×10^{-10} g. Ra per g., giving a Ra:U ratio of 3.43×10^{-7} and indicating equilibrium of the Ra and U. The approx. age calc. from the Holmes-Lawson formula is 103×10^6 years. L. S. T.

Densities of molten rocks and minerals. E. B. Dane, jun. (*Amer. J. Sci.*, 1941, 239, 809–818).— ρ and thermal expansion have been determined for synthetic diopside and synthetic akermanite and for diabase from Vinal Haven and bytownite from Norway by measuring the apparent loss in wt. of a Pt ball suspended in the molten material. Data for NaCl and B_2O_3 at temp. $>1200^\circ$ are also recorded. The results for diabase are compared with those of other observers. Chemical analyses of the diabases are recorded. Apparatus is described. L. S. T.

Royite, a new variety of quartz, from the Jharia coal-field. N. L. Sharma (*Proc. Indian Acad. Sci.*, 1940, 12, B, 215–220).—Royite (I) occurs as long, prismatic, brownish-black or black crystals in the sandstones and shales of the eastern portion of the Jharia coal-field. Chemical analysis [S. C. Niyogy] shows SiO_2 95.78, MgO 2.04, Al_2O_3 1.80, Fe_2O_3 0.14, CaO 0.37, MnO 0.03, TiO_2 trace, total 100.16%, with spectroscopic traces of Co, Ba, and Sr. (I) is regarded as a variety of quartz (II), which it resembles in ρ , hardness, and optical properties. In its paragenesis and crystal habit it resembles low-temp. (II), but its well-developed cleavage and association with biotite indicate that it is high-temp. (II). It differs from all varieties of (II) in showing a characteristic schiller, metallic lustre, and bladed structure. L. S. T.

Potassium salt deposits of the Taimir-Lena area. N. I. Bujalov (*Ann. Sect. Anal. Phys.-Chim.*, 1940, 13, 377–385).—Certain of the NaCl deposits contain up to 1% of KCl. R. T.

Isotopy of berlinite and quartz. H. Strunz (*Z. Krist.*, 1941, 103, 228–229).—Berlinite (I) has a_D 1.523, γ_D 1.529; from Debye-Scherrer photographs, the lattice is hexagonal, with a_0 4.92, c_0 10.91 Å, c_0/a_0 2.217; 3 mols. per unit cell. The properties of (I) correspond closely with those of synthetic AlPO_4 (cf. Huttenlocher, A., 1935, 1194), showing that (I) and quartz are isotypal. A. J. E. W.

Synthesis of durangite, $\text{NaAlF(AsO}_4\text{)}$. F. Machatschki (*Z. Krist.*, 1941, 103, 221–227; cf. A., 1938, I, 440).—A thick paste of syrupy aq. H_3AsO_4 and finely-powdered cryolite is heated in an autoclave at 200° for 36 hr. Durangite (I) is formed as small green monoclinic crystals, frequently giving crossed twins, or occasionally as plates; the crystals are optically negative and have high n and double refraction and weak pleochroism, with $a:b:c$ (goniometric) = 0.787:1:0.856, β $115^\circ 46'$. Rotation and powder X-radiograms give a 6.69, b 8.66, c 7.27 Å. ($a:b:c$ = 0.773:1:840), ρ_{calc} : 3.62. The smaller parameters of natural (I) may be due to replacement of AsO_4^{3-} by PO_4^{3-} . The colour of the synthetic (I) is attributed to V or Cr from the autoclave. The distinction between isomorphism and isotopy is discussed; according to Strunz (cf. A., 1937, I, 432) (I) and titanite should be regarded as isotypal and not isomorphous. A. J. E. W.

Gorceixite in Southern Rhodesia. A. M. Macgregor (*Bull. Imp. Inst.*, 1942, 39, 399–401).—Gorceixite, ρ 3.185, from the Triassic gravels of Somabula has [E. Golding] SiO_2 1.25, Al_2O_3 37.96, Fe_2O_3 3.76, MgO 1.28, BaO 11.88, CeO_2 7.00, P_2O_5 22.39, H_2O 15.05, total 100.57%. The high % of CeO_2 and the absence of CaO are noteworthy. L. S. T.

Spherosiderite [clay ironstone] deposits of the Lichtenstein Mountain at St. Stefan-Krauthaus. K. B. Matz (*Berg- u. Hüttenm. Monatsh.*, 1940, 88, 102–105).—The geology of the deposits is discussed and typical analyses are given. R. B. C.

Laboratory study of London Clay. L. F. Cooling and A. W. Skempton (*J. Inst. Civil Eng.*, 1941–42, 251–276).—Samples of London Clay taken from an extensive site in the region 40–90 ft. above the bottom of the stratum have been investigated. The clay is of the stiff-fissured type and appears to have been pre-consolidated under a pressure <20 tons per sq. ft. Mean vals. and total range of vals. of the most important physical properties are tabulated, and mechanical properties are correlated with H_2O content, liquid and plastic limits, and the unconfined compression test. L. S. T.

Spectroscopic studies of base-exchange materials. A. M. Buswell and B. F. Dudenbostel (*J. Amer. Chem. Soc.*, 1941, 63, 2554–2558).—From an examination of their infra-red spectra montmorillonites saturated with various cations can be classified into the four types: (i) extreme absorption with Ca^{++} and Mg^{++} , (ii) appreciable absorption with Li^+ , K^+ , and Ba^{++} , (iii) slight absorption with H^+ and Na^+ , and (iv) no change on attempted hydration with NH_4^+ montmorillonite. Clays of low base-exchange capacity contain less bonded (2.92μ) and unbonded (2.75μ) OH than the higher base-exchange montmorillonites. Clays allowing replacement of structural OH by phosphate absorb 25% < unphosphated clays. NH_4^+ montmorillonite exhibits a doublet at 3.13 and 3.27 μ characteristic of NH_4^+ halides. X-Ray data show that (i) the increased base-exchange capacity of greensand on heat-treatment is due to the formation of new particles, (ii) artificial zeolites are amorphous, and (iii) glauconite or greensand is crystalline. W. R. A.

Origin of the electric charge of clay particles.—See A., 1942, I, 57.

Sedimentation of clays.—See A., 1942, I, 57.

Isolation of components of North Dakota lignite. L. Zechmeister and W. T. Stewart (*J. Amer. Chem. Soc.*, 1941, 63, 2851–2852).—Extraction of N. Dakota lignite (30 kg.) with COMe_2 and then chromatography [$\text{Ca}(\text{OH})_2$] gives a substance (12 mg.), $(\text{C}_{16}\text{H}_{16}\text{O})_n$ (probably $n=3$), m.p. 328–330° (slight decomp.; corr.), and substances (1–3 mg. each), m.p. 261–264°, 273–274°, 238–240°, 297–298°, and 249–251°, respectively. R. S. C.

Stratigraphical results of pollen analysis of brown coal from Wackersdorf [Germany]. F. Thiergart (*Braunkohle*, 1941, 40, 407–408).—In two of the brown coal samples pollen and spores were preserved. A list is given of the pollen and spore genera together with the % composition. The pollen composition is discerned in relation to the age of the beds. The Wackersdorf brown coal is correlated with the Upper Miocene brown coal of Grünberg in Silesia. R. B. C.

Microspores in some coals of the productive coal measures in Fife. E. M. Knox (*Trans. Inst. Min. Eng.*, 1942, 101, 98–107).

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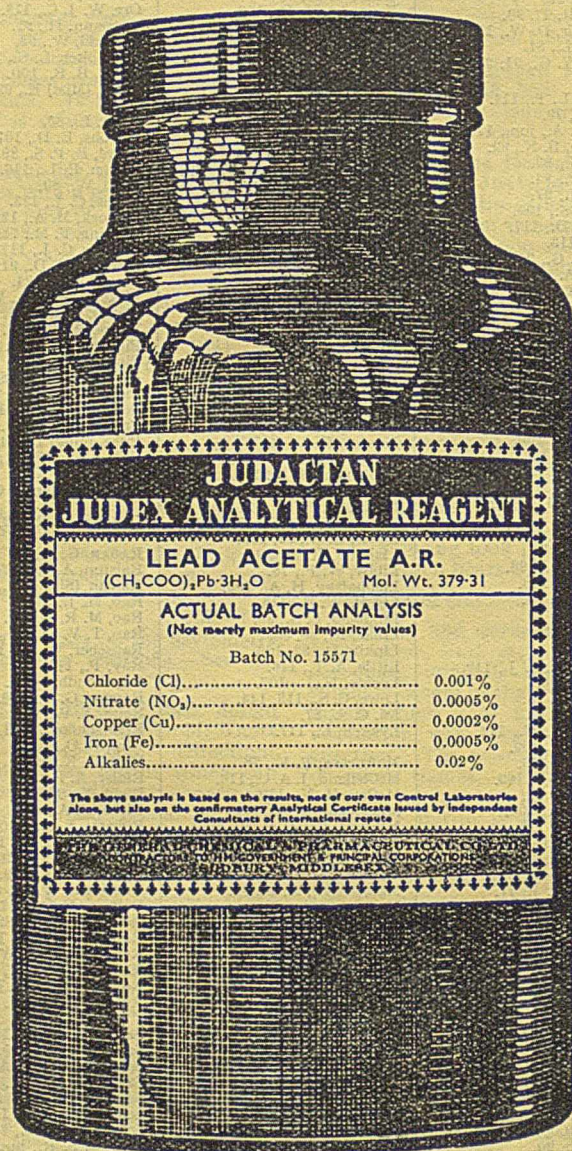
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