# BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

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

NOVEMBER, 1941.

### I.—SUB-ATOMICS.

Spectra of Cd IV, In V, and Sn VI in the isoelectric sequence Rh I to Sn VI. M. Green (Physical Rev., 1941, [ii], 60, 117—121; cf. Gilbert, A., 1935, 1292).—The spectra were photographed in the region 270—1800 A. with a 3-m. normal-incidence vac. spectrograph, and a highly condensed high-voltage vac. spark light source. Data and classifications are tabulated for 185 lines of Cd IV, 43 of In V, and 39 of Sn VI, with assignment of 51 term vals. for Cd IV, 32 for In V, and 25 for Sn VI. The irregular doublet law and the law of const. second difference were applied in the classification of many of the lines. The separation of the  $4d^{9}$   $^{2}D$  multiplet of the ground state was found for each of the three ions. Most of the odd terms arising from the  $4d^{8}$ 5p electron configuration and some of the even terms arising from the  $4d^{8}$ 5p configuration were determined. N. M. B.

Hyperfine structure of osmium lines. T. Kawada (Proc. phys.-math. Soc. Japan, 1938, [iii], 20, 653—655; Chem. Zentr., 1938, ii, 3891).—Measurements with glass and quartz Lummer plates give the following displacement vals. (×  $10^{-3}$  cm.-1) and relative intensities, respectively, for components of the lines specified:  $4420\cdot64$  A.  $(d^6s^2D_4-d^8sp^7D_4)$ ; a, -98, 15; b, 0, 100; c, 66, 53; d, 128, 41; e, 189, weak; f, 258, 23:  $4261\cdot01$  A.  $(d^6s^2D_4-d^8sp^7D_5)$ ; a, -207, 16; b, 0, 100; c, 66, 52; d, 131, 32; f, 327, 22:  $4135\cdot95$  A.  $d^6s^2D_4-d^6sp^7P_4$ ); a, -126; b, 0; c, 59; d, 105; f, 218 (no intensities). The b, c, and d components are attributed to  $^{190}$ Os,  $^{190}$ Os, and  $^{188}$ Os, respectively; the displacements occur in the  $d^6s^2D_4$ , s level. The lighter isotopes give the deepest levels, as in Hg, Pt, and W. The a and f components are ascribed to  $^{180}$ Os (spin  $\frac{1}{2}$ ), and the e component of the  $^{4420}$ O A. line to  $^{186}$ Os.

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Recombination law for weak ionisation [in atmospheric air]. P. J. Nolan (Nature, 1941, 148, 26).—Experiments have been carried out on air free from nuclei to test the implications of a previously proposed equilibrium equation (cf. A., 1940, I, 425).

L. S. T.

"Shot effect" in temperature-limited diodes. M. Surdin (Nature, 1941, 148, 27).—The classical formula of the shot effect is derived by following Bernamont's method for the Johnson effect.

L. S. T.

Effect of light in gases under electrical discharge. S. S. Joshi and G. S. Deshmukh (Nature, 1941, 147, 806).—The instantaneous diminution of the discharge current in Cl<sub>2</sub> on irradiation reported previously (A., 1941, I, 151) has been extended to other gases subjected to ionisation by collision in electric fields due to alternating potentials in Siemens tubes. The photo-variation of the discharge current diminishes rapidly in the order Cl<sub>2</sub>, Br<sub>2</sub>, NCl, and I<sub>2</sub>. The effect has also been observed in O<sub>2</sub>, air, N<sub>2</sub>, and H<sub>2</sub>, but is \$\infty\$ in the halogens. The effects of changes in conditions are described.

L. S. T.

Nuclear magnetic moments of  $^{13}\mathrm{C},\,^{13}\mathrm{5Ba},\,\mathrm{and}\,^{137}\mathrm{Ba}.\,$  R. H. Hay (Physical Rev., 1941, [ii], 60, 75—86; cf. A., 1940, I, 382).—From measurements of g vals. by the mol. beam magnetic resonance method and determinations of the signs of the nuclear magnetic moments  $\mu,\,\mathrm{vals.}$  of  $\mu$  (in nuclear magnetons) were found with the help of nuclear spins  $I.\,$  For  $^{13}\mathrm{C}$  the g val. is  $1\cdot402\pm0\cdot004$  and the moment is positive. This, with the results of theoretical treatment of the  $^{13}\mathrm{C}$  nucleus, indicates  $I=\frac{1}{2},\,$  giving  $\mu=0\cdot701\pm0\cdot002.\,$  For  $^{13}\mathrm{FB}$  and  $^{137}\mathrm{Ba}$  the moments are positive, the g vals. are  $0\cdot5575\pm0\cdot0017$  and  $0\cdot6236\pm0\cdot0019,\,$  and with  $I=\frac{3}{2}$  for both nuclei, the vals. 303

of  $\mu$  are  $0.8363\pm0.0026$  and  $0.9354\pm0.0029$ , respectively, and the ratio of the moments is  $1.1174\pm0.0010$ . All g vals. are referred to the val. 2.1688 for Li. For Ba only two resonance min. were found.

Precision measurement of nuclear magnetic moments by the molecular beam magnetic resonance method. Moments of <sup>1</sup>H, <sup>7</sup>Li, <sup>1</sup>°F, and <sup>28</sup>Na. S. Millman and P. Kusch (*Physical Rev.*, 1941, [ii], 60, 91—100).—A direct comparison of nuclear magnetic moments with the electronic moment was made by the measurement of the Larmor precession frequency of the nucleus and the frequencies of some of the lines of the radiofrequency spectra of the alkali atoms in the same magnetic field. The magnetic moment of the proton is found to be 2.7896±0.0008 nuclear magnetons. The corr. vals. are <sup>7</sup>Li 3.2532, <sup>19</sup>F 2.625, and <sup>23</sup>Na 2.215, and the corr. g val. for <sup>7</sup>Li is 2.1688±0.0010. From these results re-calc. g vals. and magnetic moments for 18 other nuclei are tabulated.

Electronic g factors for alkali atoms. M. Phillips (*Physical Rev.*, 1941, [ii], 60, 100—101; cf. preceding abstract).—An investigation of possible theoretical deviations from  $g_J=2$  for the ground state of the alkalis indicates that none is large enough to affect measurably the experimental results.

Residual current of an ionisation chamber and the true conductivity of dielectric liquids. A. Rogozinski (Physical Rev., 1941, [ii], 60, 148—149).—A method is described for determining residual current due to phenomena inside an ionisation chamber which are essential for cosmic-ray intensity measurements. In a chamber containing a dielectric liquid the residual current can be practically identified with the true conductivity of the liquid; in the case of liquid hexane it is only 1/6 of the total current. The method described allows a decision as to whether the true conductivity of the liquid tends to zero with continued purification, or whether the liquid behaves, with respect to ionising radiations, as a high-pressure gas.

Isotopic constitution of lead and the measurement of geological time. III. A. O. Nier, R. W. Thompson, and B. F. Murphey (Physical Rev., 1941, [ii], 60, 112—116; cf. A., 1939, I, 169).—Mass-spectrographic measurement of the relative abundances of the isotopes Ra-G, Ac-D, and Th-D, in 13 samples of common Pb and in 8 samples of radiogenic Pb (from different localities), 5 of which originated from minerals containing U and Th, afforded three independent determinations of the age. The age of the oldest sample (from Manitoba monazite) appears to be nearly 2 × 10° years. Full data are tabulated.

N. M. B.

Production of electron pairs. J. C. Jaeger (Nature, 1941, 148, 86; cf. A., 1936, 400).—The vals. of the cross-section per atom for absorption by pair production by  $\gamma$ -rays of energy  $5mc^2$  for the at. nos. 82 and 54 are tabulated with the vals. calc. on the Born approximation. L. S. T.

 $\gamma$ -Ray transition of radio-bromine, R. E. Siday (*Proc. Roy. Soc.*, 1941, A, 178, 189—201).—The cloud chamber was used to investigate the  $\gamma$ -rays emitted in the disintegration of the metastable radio-Br,  $^{80}$ Br. The principal  $\gamma$ -ray has an energy of 47 kv. and a coeff. of internal conversion in the K shell of 0.43. A weaker component of 37 kv. energy was also observed.

Precise measurement of the energies of  $\beta$ -rays from radium (B+C). A. F. A. Harper and N. F. Roberts (*Proc. Roy. Soc.*, 1941, A, 178, 170—188).—Measurements were carried out on 11 lines of the  $\beta$ -ray spectrum of Ra-B and on one

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line of Ra-C, two different types of magnetic spectrograph being used. The results, accurate to 1 part in 104, confirm those of Rogers (cf. A., 1937, I, 275). A source of error, due to scattering of electrons in the photographic emulsion, which produces a change of shape of the line is thought to be the most important factor limiting the accuracy obtainable by the method.

G. D. P.

Helium repulsive potential from collision cross-section measurements. I. Amdur and H. Pearlman (J. Chem. Physics, 1941, 9, 503—506; cf. A., 1940, I, 89).—Total collision cross-sections for fast (300—1000 e.v.) He atoms, scattered in He at room temp., have been measured. The val. of the repulsive intermol. potential necessary to produce the observed variation of cross-section with voltage is discussed. J. W. S.

Induced radioactivity of krypton and xenon. E. P. Clancy (Physical Rev., 1941, [ii], 60, 87—90; cf. A., 1940, I, 340).— Irradiation of Kr with 11-Me.v. deuterons produces 102 min., 4·0 hr., and ~35 hr. activities. Se bombarded with 22-Me.v. α-particles gives Kr activities of 114 min. and ~33 hr. The 114-min. period coincides with that assigned to 83° Kr growing out of 83° Br (cf. Langsdorf, ibid., 141). The 102-min. period is similarly assigned and is probably formed by a (d, p) or (d, d) reaction. The 4-hr. activity is attributed to 87 Kr., and the weak 33—35-hr. activity to 79 Kr or 81 Kr. Irradiation of Xe with deuterons produces activities of 68 min. and 9·6 hr., assigned to 137 Xe and 135 Xe, respectively, and a 5·4-day activity which also appears in the irradiation of Te with α-particles and is due to 133 Xe. N. M. B.

Effect of temperature on the secondary electron emission of nickel. (Miss) M. Healea and (Miss) C. Houtermans (*Physical Rev.*, 1941, [ii], **60**, 154; cf. A., 1941, I, 1).—The effect was studied for Ni bombarded with 1000-e.v. He<sup>+</sup> ions from ~900° through the Curie point to ~ room temp. No change > random variations of ~1% was found. This accords with the results of Wooldridge (cf. A., 1940, I, 404) for 160-e.v. electrons as bombarding particles. N. M. B.

Artificial radioactivity of <sup>45</sup>Ti. J. S. V. Allen, M. L. Pool, J. D. Kurbatov, and L. L. Quill (*Physical Rev.*, 1941, [ii], **60**, 155).—A strong radioactive positron period of 3.08 hr. was produced by proton and by deuteron bombardment of Sc, and is assigned to <sup>45</sup>Ti according to the reactions <sup>45</sup>Sc (*p*, *n*) <sup>45</sup>Ti and <sup>45</sup>Sc (*d*, 2*n*) <sup>45</sup>Ti. N. M. B.

Fission yield by fast neutrons. M. Ageno, E. Amaldi, D. Bocciarelli, B. N. Cacciapuoti, and G. C. Trabacchi (Physical Rev., 1941, [ii], 60, 67—75; cf. Roberts et al., A., 1939, I, 234, Ladenburg et al., ibid., 504).—Measurements of the fission cross-section  $\sigma$  of U for neutrons from the D + D, D + Be, and D + B reactions indicate that  $\sigma$  has a nearly const. val.  $\sigma_t$  between 1 and 10 Me.v.; for neutrons from the Rn + Be and D + C reactions  $\sigma$  is  $\sim \frac{1}{6}\sigma_t$  and  $\frac{1}{6}\sigma_t$ , respectively, and for D + Li neutrons  $\sigma = 1.40\sigma_t$ . This last-named was attributed by Bohr (cf. A., 1941, I, 144) to successive transformations possible for energies of the impinging neutrons >10 Me.v. A similar increase of  $\sigma$  was observed for Th, in good agreement with theory.

N. M. B.

Total and scattering cross-sections for slow neutrons. M. D. Whitaker and W. C. Bright (*Physical Rev.*, 1941, [ii], 60, 155).

—Experiments are described and data reported for the total, scattering, and capture cross-sections of C, Pb, CS<sub>2</sub>, Fe, Ni, Cu, and Mn for slow neutrons.

N. M. B.

Uranium fission with Li-D neutrons: energy distribution of the fission fragments. K. Lark-Horovitz and R. E. Schreiber (Physical Rev., 1941, [ii], 60, 156).—Using U sputtered on Al foil and U<sub>2</sub>O<sub>3</sub> deposited on a brass disc, fission with slow neutrons gives results agreeing with available data; both types of targets show two peaks (with single particles) at 64 and 95 Me.v. On filtering out the slow neutrons, there appeared, in addition, a peak at 86 Me.v., assigned to symmetrical fission, and peaks at 52 and 110 Me.v. apparently corresponding with highly asymmetrical fission. About 5% of the total no. of tracks gave a peak at 130—135 Me.v. believed to be due to a new type of ternary or triple fission, and 0.5% at 145 Me.v. Results are confirmed by using the thin foil and observing the total ionisation. With slow neutrons the main peak is at 164, and with fast neutrons at 172 Me.v., with indications of fragments at 190—200 Me.v. The energy distribution confirms the process of symmetrical fission corresponding with chemical evidence (cf. Segrè, A., 1941, I., 314).

Mechanism of the sodium coulometer. J. Steigman (Physical Rev., 1941, [ii], 60, 157).—NaNO<sub>3</sub> was bombarded with slow neutrons, an electric light bulb was then dipped in the molten salt, and an electrolysis current run for 1 hr. With a Geiger-Müller counter the activity of the Na deposited inside the bulb was 0.2% of that of the NaNO<sub>3</sub>. This supports the mechanism proposed by Burt (cf. A., 1925, ii, 921) that the Na ions on the inside of the glass are neutralised and vaporised as metal and that Na ions from the fused salt replace those of the glass, the process being one of replacement rather than of diffusion (cf. Zworykin, A., 1926, 1032).

N. M. B.

Chemistry of atomic nuclei. F. Körösy (J. Hung. Chem. Soc., 1941, 2, No. 5, 1—8).—A summary of laws, rules, and experimental methods, and a description of the high-voltage apparatus used.

E. A.

Chemistry of energetic atoms produced by neutron capture. W. F. Libby (Science, 1941, 93, 283—285).—A discussion. Retention of induced radioactivity occurs mainly in the target substance. Dilution with a solvent no atoms of which are near the active atom in mass results in zero limiting retention. Retention in the gaseous state is 

in the liquid or solid state, but is not necessarily zero at zero pressure. L. S. T.

Photographic method of estimating the mass of the mesotron. D. M. Bose and (Miss) B. Choudhuri (Nature, 1941, 148, 259—260).—A statistical method of estimating the mass of the particles described previously (cf. A., 1941, I, 145) is detailed. The results confirm the previous view that the tracks are due to secondary mesotron showers produced chiefly by cosmicray neutrons.

L. S. T.

Effect of temperature on cosmic radiation. F. X. Roser (Ann. Acad. Brasil. Sci., 1941, 13, 145—158).—The variation of the intensity of cosmic radiation is due to the combined effect of the diurnal and the annual meteorological changes.

Thundercloud as a source of penetrating particles. E. C. Halliday (Physical Rev., 1941, [ii], 60, 101—106).—Observations of 65 thunderstorms and 5000 cloud-chamber photographs of electron tracks with 4500 control photographs were made. A statistical examination of the relative no. of penetrating electron tracks in the two sets of photographs indicates a strong possibility that penetrating electrons are ejected from thunderclouds and reach the earth at considerable distances from the clouds. The experiments indicate that the hypothesis that the ejected electrons travel in helical paths about the earth's magnetic field is untenable.

Azimuthal variations of cosmic radiation for 60° zenith angle at 22° latitude. P. S. Gill (Physical Rev., 1941, [ii], 60, 153; cf. Hutner, A., 1939, I, 296).—A preliminary report of experiments to find the predicted azimuthal variation at a fixed zenith angle. Directional asymmetries are shown by the curves for the no. of counts at various azimuthal angles. The asymmetry is  $9.1\pm0.8\%$  for true magnetic N. and S.

Proper lifetime of mesotrons. J. Barnóthy and M. Forró (Physical Rev., 1941, [ii], 60, 154).—Experiments with a two-fold coincidence counter to determine the average path length before decay, and thus the proper lifetime  $\tau_0$  of mesotrons, are described. Assuming that the mesotrons are generated mainly at a height corresponding with 8 cm. Hg pressure and have a rest energy  $E_0 = 7 \times 10^7$  e.v., calculations are given leading to the val.  $\tau_0 = 1.6 \times 10^{-6}$  sec., in good accord with available data.

N. M. B.

Interaction of mesotrons and nuclei. J. R. Oppenheimer and J. Schwinger (Physical Rev., 1941, [ii], 60, 150—152).— Difficulties arising from a development of the formalism of mesotron field theories in analogy with the method of classical electrodynamics or with the perturbation technique of quantum electrodynamics led to the Heisenberg-Bhabha treatment of the mesotron equations and the Bhabha-Heitler theory of proton isobars. In order to amplify the conclusions of Wentzel, based on the connexion of these two sets of ideas, an investigation is made of nuclear forces and the small scattering, zero spin, and highly multiple production of mesotrons in cosmic rays. Heisenberg's treatment is, in part, generalised, and the classical problem of the coupling of neutral and charged, scalar and pseudo-scalar mesotrons to an extended spatially fixed source is considered. Wentzel's quantum problem of the charged scalar field is treated, with

an extended source instead of a lattice space, in the limit where the coupling const. is large, and, analogously, for the neutral pseudo-scalar in the corresponding limit. N. M. B.

Finite self-energies in radiation theory. I. A. Landé (Physical Rev., 1941, [ii], 60, 121—127).—Mathematical. The Fourier terms in the expression for the energy in Fermi's classical radiation theory are modified by consideration of the energy reduction factor, due to radiative damping, of an electric particle vibrating in a field. Hence the Dirac finite radius  $r_0$  due to the damping term in the equation of motion of the electric particle now occurs in a modified Coulomb energy expression and the finite self-energy of a single particle becomes  $e^2/2r_0 = 0.75mc^2$ . N. M. B.

Bose-Einstein statistics and degeneracy. D. S. Kothari and B. N. Singh (*Proc. Roy. Soc.*, 1941, A, 178, 135—152).—The thermodynamic properties of degenerate and non-degenerate Bose-Einstein gas in the completely non-relativistic and relativistic cases are derived. The relativistic degenerate case corresponds with black body radiation. The possibility of the existence of non-degenerate radiation is discussed.

G. D. P.

#### II.—MOLECULAR STRUCTURE.

Properties of the free radical CS. V. Kondrateev and E. Magaziner (J. Phys. Chem. Russ., 1940, 14, 6—9).—CS was produced by discharge in vapour of CS<sub>2</sub> or of S and paraffin oil, and detected by its absorption bands. The absorption decayed within t min. CS<sub>2</sub> and O<sub>2</sub> up to 100° and 30 mm. Hg did not affect t. It strongly depended on the state of the walls of the vessel, and was, e.g., raised by rinsing the vessel with  $H_2O$  and lowered by rinsing with aq.  $H_3PO_4$ . At room temp. t was  $\sim 10$  min. and at  $100^\circ$  3 min. On the walls a brown powder (polymeric CS?) was deposited. J. J. B.

Absorption spectrum of gaseous azoimide. J. M. Tolmatschev (J. Phys. Chem. Russ., 1940, 14, 10—15).—HN $_3$  shows two series of diffuse bands. One consists of 8 bands between 3260 and 2812 A., each  $\sim \!\! 30$  A. wide. The other has 15 bands between 2304 and 2016 A., each  $\sim \!\! 12$  A. wide. There is also a continuous absorption. No conclusion as to the structure of HN $_3$  can be reached from these results.

Infra-red absorption spectrum of propane. (Miss) V. L. Wu and E. F. Barker (J. Chem. Physics, 1941, 9, 487—491). —The absorption spectrum of  $C_3H_8$  has been examined in the  $\lambda$  region  $1.35-35\,\mu$ . The bands fall into three symmetry classes, designated  $A_1$ ,  $B_1$ , and  $B_2$ , distinguishable by their characteristic contours. By analogy with the corresponding frequencies in  $C_2H_6$ ,  $C_2H_4$ , and cyclopropane probable assignments of the bands are made.

J. W. S.

Spectroscopic studies of the simpler porphyrins. III. Absorption spectra of ms-tetraphenylporphine and a series of its metal complex salts. V. M. Albers and H. V. Knorr (f. Chem. Physics, 1941, 9, 497—502; cf. A., 1936, 1048; 1941, 1, 238).—Absorption curves and mol. absorption coeffs. of ms-tetraphenylporphine and its Cu, Ag<sub>2</sub>, Mg, Zn, Cd, Hg, SnCl<sub>2</sub>, Pb, MnCl, FeCl, Co, and Ni complex salts are reported for the visible spectral range. Variations in the spectra of the salts are spectral for the salts are for other ms-tetrasubstituted porphines studied.

J. W. S.

Dispersion spectra of crystalline and amorphous benzophenone. M. Vuks (Acta Physicochim. U.R.S.S., 1940, 13, 31-42).—A method of obtaining single crystals of the labile modification (m.p.  $23\cdot5^\circ$ ) of COPh<sub>2</sub> is described. Raman spectra for the two cryst. modifications, for the liquid, and for vitreous COPh<sub>2</sub> at  $-52^\circ$  are recorded. In the region  $\Delta\nu < 150$  cm. the spectra of the two cryst. modifications are different, and the lines of the stable modification shift to lower  $\Delta\nu$  as the temp. rises to the m.p. (46°). Evidently the spectrum in this region depends on the lattice structure. The melts of the two modifications give the same Raman spectrum, and apart from a slight shift towards higher  $\Delta\nu$ , there is no change of this when the liquid is cooled into the vitreous state. F. J. G.

Spectral investigation of chemical processes in organic compounds at low temperatures. II. A. Terenin (Acta Physicochim. U.R.S.S., 1940, 13, 1—30).—The study of the behaviour of org. compounds in thin films at -180° under ultra-violet excitation (A., 1941, I, 72) has been continued.

NH<sub>2</sub>Ph in radiation of λ 3100-4000 A. gives a violet luminescence having a max. at 3300 A., i.e., slightly shifted towards longer  $\lambda$  as compared with the fluorescence of the vapour. This luminescence increases gradually to a max. during excitation, and afterwards persists for a time, decreasing in intensity according to a hyperbolic law. In radiation of shorter \(\lambda\) (2000-2200 A.) the violet glow soon changes to a green fluorescence, which is due to phenazine, formed by photocondensation of two adjacent mols, of NH<sub>3</sub>Ph, with liberation of H<sub>2</sub>. The violet afterglow extends beyond the original zone of excitation. As the absence of free electrons is shown by the absence of photoconductivity, there are two alternative explanations; either excitation by recombination of migrating H atoms, or direct migration of electronic excitation energy (an "exciton") in the lattice. In presence of  $\mathrm{NH_3}$  (which affords H atoms in light of  $\sim\!2000$  A.), an enhancement of the afterglow occurs, as would be expected on the former hypothesis, but NH<sub>3</sub> does not produce any after-glow in dibenzyl. MeCHO gives a blue luminescence having a continuous spectrum and decaying exponentially. C10H8 gives a deep violet fluorescence, i.e., its fluorescence spectrum is shifted towards the visible. In light of  $\lambda < 3000$  A. and in presence of CCl4 this fluorescence changes to an intense white fluorescence, and after evaporation of the CCl, a yellow-green fluorescence appears the spectrum of which is identical with the "hauptspektrum" of  $C_{10}H_8$ . Possible interpretations of this spectrum are discussed.

Spectral investigation of chemical processes in organic compounds at low temperatures. II. Correction. A. Terenin (Acta Physicochim. U.R.S.S., 1941, 14, 566—567).—With improved apparatus the spreading of the afterglow of NH<sub>2</sub>Ph previously reported (see preceding abstract) is not observed.

Spectrochemical researches on xanthates. I. Alkyl xanthates and ethylthioxanthate. II. By-products of xanthation and viscose. K. Atsuki and T. Takata (J. Soc. Chem. Ind. Japan, 1940, 43, 394—397B, 397—400B).—I. The first and second absorption bands  $(1/\lambda)$  of the compounds RO·CS·SNa are: R = Me 3350, 2650, Et 3350, 2600, Pr. Bu, and CH<sub>2</sub>Ph 3300, 2600, and amyl 3350, 2590. They show no third band, this being characteristic of RS·CS·SNa, the other bands of which are 2100—3150 and 2400; the former is considered to be due to the >CIS radical since RO·CS·SNa has the bands 3300—3350 and 2600—2650. Replacement of Na by K has little effect but Co, Bi, and VO''' produce considerable differences.

II. Vals. obtained for by-products of xanthation and viscose (I) indicate that (I) contains both >C.S and SNa·C.S, which are responsible for its first and second bands (3360 and 2600—2650), respectively, and that (I) is a pure compound in an alkaline medium and has the constitution (cellulose·O)CS·SNa, which is the result of replacing the alkyl radical of an alkylxanthate by cellulose. The second band disappears when (I) is hydrolysed.

J. G.

Absorption of light by chlorophyll solutions. G. Mackinney (J. Biol. Chem., 1941, 140, 315—322).—The absorption coeffs. ( $k_a$ ,  $k_b$ ) of chlorophyll a and b in MeOH (99.8%), Et<sub>2</sub>O (containing 2—3% of EtOH), and 80% aq. COMe<sub>2</sub> have been determined and compared with published vals. in anhyd. Et<sub>2</sub>O and COMe<sub>2</sub>. At 6600 A.  $k_a$  in the impure Et<sub>2</sub>O is  $\sim 4\%$  > and at 4720 A. is  $\sim 20\%$  <  $k_a$  in anhyd. Et<sub>2</sub>O. The determination of chlorophyll a and b in Avena and Malva extracts by the suitable application of simultaneous equations derived from absorption data in aq. COMe<sub>2</sub> of chlorophyll a and b separately is illustrated. C. R. H.

Absorption spectra of hæmoglobin in solution and in red blood corpuscles. D. Keilin and E. F. Hartree (Nature, 1941, 148, 75—77).—Experiments are recorded confirming and extending results of previous workers, viz., that the strong Soret or γ-band in the absorption spectrum of hæmoglobin and oxy-, CO-, and met-hæmoglobin in solutions is barely perceptible or completely invisible in these pigments within intact corpuscles. This failure to observe the γ-band is due to an optical effect brought into play by the properties of surfaces separating hæmoglobin from the surrounding medium.

L. S. T.

Quenching and depolarisation of resonance radiation by collisions with molecules of a foreign gas. A. Ellett, L. O. Olsen, and R. Petersen (*Physical Rev.*, 1941, [ii], 60, 107—111).—A semi-classical theory is presented. The total de-

polarising probability is divided into two parts to allow for adiabatic and non-adiabatic depolarisation. The equations for polarisation are generalised to apply to observed polarisation results from several lines of a hyperfine group, and the effect of a magnetic field applied along the direction of observation is included in the treatment. Experimental results on the polarisation of the Hg line  $\lambda 2537$  A. as a function of pressures of  $H_2$ ,  $D_2$ ,  $N_2$ , and  $O_2$  and as a function of magnetic field at various const. gas pressures show good agreement with the theory. Calc. cross-sections for quenching and depolarisation are tabulated.

N. M. B.

Spectral character of reflexion by a regularly stratified medium. R. V. Subrahmanian (Proc. Indian Acad. Sci., 1941, 13, A, 467—482).—The intensity and spectral character of the light reflected from a regularly stratified medium are calc. by standard electromagnetic theory methods. For small vals. of the reflecting power, there is a sharply defined primary band of selectively reflected  $\lambda\lambda$ , accompanied by secondary bands of diminishing intensity on the longer- $\lambda$  side. The effect of variation in the reflecting power, thickness, and no. of laminæ is discussed.

L. J. J.

Luminescence, absorption, and scattering of light in diamonds. I. Fluorescence. II. Phosphorescence. P. G. N. Nayar (Proc. Indian Acad. Sci., 1941, 13, A, 483—497, 534—542).—I. All  $\lambda\lambda <$ 4156 A. excite a sharp band at 4156 A., discrete, rather diffuse bands at 4278, 4387, 4514, and 4643 A., and a feeble superimposed continuous spectrum to 6300 A., in all crystals of diamond. The intensity of the fluorescence in different crystals examined varied by a factor ~104. The fluorescence spectrum brightens and disappears as the exciting  $\lambda$  is made equal to and then >4156 A. The effect is ascribed to the degree of structural perfection of the crystal. Between —180° and 200°, the bands broaden unsymmetrically and shift towards longer  $\lambda\lambda$  with increasing temp. At higher temp, the fluorescence disappears.

II. After illumination is cut off, the same series of bands

II. After illumination is cut off, the same series of bands as that found in fluorescence is emitted, with a continuous region 5050-6300 A. The intensities in the discrete and continuous regions are of the same order. Only the discrete system is regarded as true fluorescence. The phosphorescence requires  $\sim 1$  min. for its full excitation and several min. for decay. At  $\sim -180^\circ$  the phosphorescence disappears in a few sec., but is again emitted when the temp. is raised. At high temp. phosphorescence is brighter and more persistent.  $\lambda\lambda > 4156$  A. excite a low-intensity spectrum identical with that of phosphorescence.  $\lambda\lambda$  slightly >4156 A. excite fluorescent 4156 A.

Raman effect in relation to crystal structure: lattice oscillations. S. Bhagavantam (Proc. Indian Acad. Sci., 1941, 13, A, 543—563).—Both low- and high-frequency Raman lines of crystals are representatives of the various optical series of normal oscillations of crystal lattices. Formulæ applying to internal, rotatory external, and translatory external oscillations are developed. Translatory oscillations especially in org. crystals and others of low m.p. are characterised by weak Raman lines of low frequency. Rotatory oscillations have large frequencies and give strong Raman lines if the rotating group is optically anisotropic.

L. J. J.

Intensities of the Raman lines in carbon dioxide. N. S. N. Nath and E. V. Chalam (*Proc. Indian Acad. Sci.*, 1941, 13, A, 339—351).—The polarisability of a mol. is assumed to consist of the bond polarisabilities as functions of the inter-nuclear distances. Certain normal co-ordinates can be quadratic functions of some of the variations in the inter-nuclear distances and this accounts for the appearance of overtone Raman lines. The ideas have been applied to CO<sub>2</sub>.

W. R. A.

W. R. A. Depolarisation of light scattered by liquids. K. S. Bai (Proc. Indian Acad. Sci., 1941, 13, A, 439—460).—The depolarisation (ρ) of scattered light, for different slit-widths of a spectrograph of high dispersion and resolving power, has been investigated for tetralin, HCO<sub>3</sub>H, AcOH, PrβCO<sub>2</sub>H, PhNO<sub>2</sub>, Et lactate, C<sub>6</sub>H<sub>6</sub>, C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>, CHBr<sub>3</sub>, (CH<sub>2</sub>·OH)<sub>2</sub>, cyclohexanol, CHCl<sub>3</sub>, Et<sub>2</sub>O, EtOH, MeOAc, COMe<sub>2</sub>, and CCl<sub>4</sub> at different temp. ρ for the unmodified line corresponding with the limiting slit-width is finite for all these liquids. The "wing" in liquids starts with max. intensity at the Rayleigh line and falls off exponentially with increasing wave-no. shift. A theoretical treatment is developed which explains the observed effect of temp. on the intensity distribution in the "wing." W. R. A.

Photo-electric efficiency of ferromagnetic metals at different temperatures in the soft X-ray region. S. R. Rao and K. S. S. Iyer (Proc. Indian Acad. Sci., 1941, 13, A, 411—438).—The photo-electric sensitivities of Fe, Co, Ni, and Cu for soft X-rays have been investigated from 30° to 950°. For Fe the sensitivity is const. up to 780° and thereafter decreases  $\sim 10\%$  up to 900°, beyond which it increases. It appears therefore that the transition from a-Fe to  $\beta$ -Fe is accompanied by a change in the photo-electric threshold. Vals. for Co and Ni are unaffected by temp. and no change in photo-electric threshold is evidenced in transitions from one crystal form to another or at the Curie point of Ni. The photo-electric effect due to soft X-rays more closely resembles the effect with ultra-violet radiation than the effect produced by hard X-rays.

W. R. A.

Rectification in discharge tubes. II. V. T. Chiplonkar (Proc. Indian Acad. Sci., 1941, 13, A, 323—338; cf. ibid., 1939, 10, 381).—The pressure variation of the rectification ratio in discharge tubes, with air,  $H_2$ , and  $N_2$ , has been studied as a function of the relative sizes of the electrodes and the interelectrode distance. The rectification ratio is dependent on the nature of the gas. The curves for air and  $N_2$  are similar but differ greatly from that for  $H_2$ . W. R. A.

Effect of admixture of silver on rectifying properties of Cu-Cu<sub>2</sub>O cells. K. R. Dixit (*Proc. Indian Acad. Sci.*, 1941, 13, A, 498—503).—Admixture of Ag with Cu in Cu-Cu<sub>2</sub>O barrier-layer rectifiers gives max. rectification with 7.5% Ag in the case of layers formed at 800°, and 6% Ag for layers formed at 850°.

L. J. J.

Effect of flow on the dielectric constant of liquids. S. P. Prasad, B. N. Singh, and B. D. Singh (Nature, 1941, 147, 712).—When flowing through condenser plates of small separation, xylene (a mixture of o-, m-, and p-), Et<sub>2</sub>O, EtOH, and C<sub>8</sub>H<sub>6</sub> show small, but distinct, decreases in the vals, of  $\epsilon$ . For a given separation, the charge increases in magnitude with increase of rate of flow. Polar as well as non-polar liquids show the effect, but a viscous liquid, e.g., C<sub>5</sub>H<sub>11</sub>OH, shows it to a much smaller extent.

L. S. T.

Dipole moments of some nitro- and amino-derivatives of benzene and naphthalene. V. Vassiliev and J. Sirkin (Acta Physicochim. U.R.S.S., 1941, 14, 414—416).—Vals. of  $\mu\times 10^{18}$ , in  $C_6H_6$  and dioxan, respectively, are recorded as follows: PhNO2, 4·01, 4·03; NH2ph, 1·54, 1·77; o-NO2·C<sub>6</sub>H<sub>4</sub>·NH2, 4·26, —; p-NO2·C<sub>6</sub>H<sub>4</sub>·NH2, 6·17, 6·81; 2·3·1-, —, 7·30, 2·4·1-, —, 6·48, 2·5·1-, —, 2·67, 2·6·1-, 1·88, —, 3·4·1, —, 8·90, and 3·5·1-(NO2)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·NH2, —, 5·91; 2·4·6·1-(NO2)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>·NH2, —, 3·25; 1·2·4-, —, 7·11, and 1·3·5·NO2·C<sub>6</sub>H<sub>3</sub>(NH2)<sub>2</sub>, —, 5·86; 3·1·4·NO2·C<sub>6</sub>H<sub>3</sub>Me·NH2, 4·37, —; 2·4·1-NO2·C<sub>6</sub>H<sub>3</sub>(NH2)<sub>2</sub>, —, 5·86; 3·1·4·NO2·C<sub>6</sub>H<sub>3</sub>Me·NH2, 4·37, —; 2·4·1-NO2·C<sub>6</sub>H<sub>3</sub>(NH2)<sub>2</sub>, —, 5·86; 3·1·4·NO2·C<sub>6</sub>H<sub>3</sub>Me·NH2, 4·37, —; 2·4·1-NO2·C<sub>6</sub>H<sub>3</sub>(NH2)<sub>2</sub>, 7·22, —; a-C<sub>10</sub>H<sub>7</sub>·NH2, 1·77, 2·10; 2·1-, 4·89 at 40°, —; 3·1-, 5·14, —, 4·1-, —, 6·97, 5·1-, 5·22, —, 8·1-, 3·12, —, 1·2·, 4·47 at 40°, —; 4·2-, 4·62, —, 5·2-, 5·03, —, 6·2-, —, 7·10, and 8·2-NO2·C<sub>10</sub>H<sub>6</sub>·NH2, 4·47, —; 2·4·1-, —, 5·05, and 1·6·2-NO2·C<sub>10</sub>H<sub>5</sub>Br·NH2, —, 5·13; 1-, 3·98, —, and 2-nitrotetralin, 4·81, — All vals. are at 25° unless otherwise indicated. Deviations from vector additivity of the moments of polar groups are attributed to the influence of resonance structures, and the sp. effect of dioxan on the moments of NH2-compounds to the formation of a complex (having a H-bond) with dioxan. F. J. G.

Statistical mechanics of fusion. J. G. Kirkwood and (Miss) E. Monroe (J. Chem. Physics, 1941, 9, 514—526).—Mathematical. The theory is based on the use of local free energies. The entropy and vol. changes of A during fusion are calc. from the theory and are considered to be in adequate agreement with experiment, especially at 1 atm. pressure.

Self-consistent field for methane and its applications. R. A. Buckingham, H. S. W. Massey, and S. R. Tibbs (*Proc. Roy. Soc.*, 1941, A, 178, 119—134).—An approximation is obtained by averaging the proton distribution over all orientations so as to get a spherically symmetrical nuclear field. The eightelectron problem is then solved. The wave functions are used to calculate the charge distribution, energy, diamagnetic susceptibility, and polarisability of the mol. and also the van der Waals force between two mols. The scattering of slow electrons by the field is also investigated, the observed

similarity in the behaviour of A and CH<sub>4</sub> being reproduced by the theory. Comparison with observation shows that the theory for CH<sub>4</sub> is not less satisfactory than similar calculations for atoms. G. D. P.

Force constants of carbon-carbon bonds. J. W. Linnett (Trans. Faraday Soc., 1941, 37, 469—473).—By the application of a force field analogous to that used for C<sub>2</sub>H<sub>6</sub>, Me halides, and MeCN (cf. A., 1940, I, 99) the fundamental frequencies of CH:CMe and CMe:CMe are calc. The length of the C-C single bond in CMe:CMe is ~1·47 A. or slightly larger. The vals. given by Crawford and Brinkley (A., 1941, I, 101) for the force consts. for these two compounds are too small; more satisfactory vals. are 5·5 and 5·3 × 10<sup>5</sup> dynes per cm., respectively.

Chemical bond in hard compounds. I. A. Brager (Acta Physicochim. U.R.S.S., 1941, 14, 297—306).—Published vals. of a for TiC, TiN, TiO, VC, VN, and VO are compared, and the most reliable vals. selected as follows: TiC, 4·320 A.; TiN, 4·235; TiO, 4·16; VC, 4·23; VN, 4·129; VO, 4·08 A. For each metal, a is a linear function of the at. radius of the non-metal, indicating covalent linkings, and moreover vals. of a for isoelectronic substances are closely similar, and decrease linearly with increase in the no. of electrons available per bond. On the other hand small differences between the experimental vals. of a and those calc. from the at. radii indicate some ionic character of the linkage, increasing from Ti to V and from C through N to O in analogous compounds, and from V to Ti in isoelectronic compounds. F. J. G.

Structure of boron hydrides. J. Sirkin and M. Diatkina (Acta Physicochim. U.R.S.S., 1941, 14, 547—561).—The proposed structure for  $B_2H_6$  contains a  $B^-$  ion bonded with 4 H atoms and a  $B^+$  ion bonded with 2 H atoms; in the actual mol. resonance occurs between this and a corresponding structure with the signs reversed. Somewhat similar structures are suggested for the remaining hydrides; all of them contain bivalent  $B^+$  and quadrivalent  $B^-$  ions. F. L. U.

Magnetism and molecular structure of sulphur compounds. S. S. Dharmatti (*Proc. Indian Acad. Sci.*, 1941, 13, A, 359—370).—The diamagnetic susceptibilities of S<sub>2</sub>Cl<sub>2</sub>, S<sub>2</sub>I<sub>2</sub>, SCl<sub>2</sub>, SOCl<sub>2</sub>, SO<sub>2</sub>Cl<sub>2</sub>, and CISO<sub>3</sub>H have been calc. according to the methods of Slater and Angus and compared with experimental vals. The vals. for various valency states of S have been calc.

W. R. A.

Effect of dislocations on magnetisation near saturation. W. F. Brown, jun. (Physical Rev., 1941, [ii], 60, 139—147; cf. A., 1941, I., 29).—Mathematical. The effect of dislocations is calc. by direct use of dislocation theory. The deviation from saturation is assumed to be due to magnetostrictive forces localised in the stress field about, rather than at, the dislocation. Pairs of dislocations of opposite sign, separated by a short distance, contribute a term a/H to the deviation from saturation. Pairs separated by a long distance and surplus dislocations of one sign contribute a term  $b/H^2$ . From data for the variation of the empirical a and b with plastic strain, and assuming a val. for the distance Y between the members of a dislocation pair, the density of dislocations and the "block" length can be calc. The orders of magnitude agree with those obtained in the theory of hardening if Y is taken  $\approx 2 \times 10^{-6}$  cm. All but  $\approx 1\%$  of the dislocations appear to be members of such pairs.

Magneto-acoustic effect. M. R. Rao (Physical Rev., 1941, [ii], 60, 156—157).—The magnetic anisotropy of the mols. of a liquid in a strong magnetic field results in a tendency to orient themselves relatively to the lines of force. The change to be expected in the velocity of sound is calc. from the thermodynamic equations. In PhNO₂, which is strongly anisotropic, it is expected to be ∼3—4% at room temp.

Calculation of the energy of repulsion. II. M. F. Mamotenko (Acta Physicochim. U.R.S.S., 1940, 13, 43—48; cf. A., 1940, I, 12).—The author's method is used to compute the energy of repulsion between Li<sup>+</sup> and H<sup>-</sup> ions, and between two H<sub>2</sub> mols.

F. J. G.

Thermal repulsion. L. A. Ramdas and S. Y. Joglekar (*Proc. Indian Acad. Sci.*, 1941, 13, A, 374—385).—Thermal repulsion of particles or objects in a convectionless thermal field has been investigated. The pressure is ~1000 times as large as the radiation pressure. The application to a thermal filter and a dust counter is described.

W. R. A.

Forces between neutral molecules and metallic surfaces. H. Margenau and W. G. Pollard (*Physical Rev.*, 1941, [ii], **60**, 128—134).—Mathematical. A general formula for the interaction between a neutral mol. and a metal is developed, and its relation to the image force law is shown. The latter is found to be valid only for mols. containing slowly moving charges, such as rigid permanent dipoles. An evaluation of the general formula involving empirical polarisabilities, f vals., and resonance frequencies is made, and numerical data for various gases and metals are tabulated.

N. M. B.

#### III.—CRYSTAL STRUCTURE.

Diffuse reflexion of X-rays. M. Born (Nature, 1941, 147, 674; cf. A., 1941, I, 245).—Suggestions put forward by Raman, Bragg, and Preston are not accepted. The effect is a consequence of Debye's theory of the influence of thermal vibrations on the scattering of X-rays. The position of the spots is closely connected with the vibrational spectrum of the crystal, and the new interference effects are due, not to the geometry, but to the dynamics, of the lattice. L. S. T.

Quantum theory of X-ray reflexion. (Sir) C. V. Raman and P. Nilakantan (Current Sci., 1941, 10, 241—245).—Irrespective of the crystal setting employed the modified reflexions by the planes in diamond appear with practically unaltered intensity when the crystal is cooled to liquid air temp. The reflexions are due to optical and not to acoustic vibrations of the lattice and are a quantum-mechanical effect. The Faxén formula is irrelevant and the modified reflexions arise from the fact that the phase-waves of the optical vibrations have a precisely determined orientation and azimuth with reference to the crystal planes.

W. R. A.

Quantum theory of X-ray reflexion. (Sir) C. V. Raman, P. Nilakantan, and P. R. Pisharoty (Nature, 1941, 147, 805).— The view that the second kind of specular reflexion given by the lattice planes in a crystal is due to the scattering of X-rays by elastic waves of thermal origin (cf. A., 1941, I, 102) is criticised. Optical vibrations of the lattice are held to be responsible, and the intensity of the reflexions is determined, not by classical mechanics, but by quantum dynamics.

Diffuse spots in X-ray crystal photographs. (Sir) W. H. Bragg (Nature, 1941, 148, 112; cf. preceding abstract).—The pattern of diffuse spots in X-ray crystal photographs can be calc. from the first principles of wave interference. It is the true diffraction pattern of the crystal lattice considered as a three-dimensional grating. Neither thermal conditions nor elastic properties enter into the calculations. Up to the present, the agreement between this true diffraction pattern and the observed effects is within the errors of experiment, and the correlation extends to those details described by Lonsdale (see following abstract) for the diamond. L. S. T.

Diffuse X-ray diffraction from the two types of diamond. (Mrs.) K. Lonsdale and H. Smith (Nature, 1941, 148, 112—113).—Details of diffuse scattering in the two types of diamond are described and illustrated. In the normal type, the diffuse spots often show horn-like extensions, and division into groups of smaller spots. These secondary effects are absent in the scattering shown by the rarer and more transparent type of diamond. This disappearance eliminates the possibility that these secondary effects are due to thermally excited lattice vibrations.

L. S. T.

Temperature study of the diffuse X-ray diffraction by diamonds. (Mrs.) K. Lonsdale and H. Smith (Nature, 1941, 148, 257—258).—Evidence that the two types of diffraction (see preceding abstract) shown by diamonds may have different origins is presented. In contrast to the primary diffuse spots, the secondary effects vary considerably in intensity for diamonds of similar shape and size. Type-I diamonds always show some effect, whereas type-II show none. Secondary diffraction is affected in intensity only slightly by a temp. change of >800°, but the primary diffraction is more sensitive to temp. changes. Photographs illustrating temp. effect are reproduced. The primary diffuse spots, observed and temp.-sensitive for both types of diamond, appear to correspond with the diffuse spots observed for all other crystals under suitable conditions. The secondary spots and streaks of type-I diamonds are not typical of diffuse diffraction in general.

L. S. T.

Presentation of crystal chemistry. A. F. Wells (Phil. Mag., 1941, [vii], 32, 106—136).—A geometrical classification, based on interat. distances, is proposed for cryst. structures. Four main classes, involving finite, one-dimensional (chain), two-dimensional (layer), and three-dimensional complexes in the structure, are distinguished. These classes are subdivided according to the nature of the bonds between such complexes (van der Waals, H, or ionic bonds). Classifications according to bond type and according to bond strength for ionic crystals are discussed.

Determination of the orientation of aluminium single crystals by electron microscopy. H. Mahl (Metallwirts., 1940. 19, 1082—1085).—By the deep etching of Al in a mixture of HF and HCl the cryst. structure is shown up by minute steps on the surface. These cannot usually be seen in an ordinary microscope, but are clearly shown by the electron microscope. Examples at magnifications of 3000—11,000 are shown. The orientation can be determined approx. by inspection of a photograph of the specimen, and a method is given for determining it more exactly by measurement of the difference in brightness of the different surfaces. C. E. H

Study of the growth of chemical compounds on a copper single crystal by electron diffraction. I. H. Usmani (Phil. Mag., 1941, [vii], 32, 89—105).—Electron diffraction from the surface of thin films of Cu<sub>2</sub>l<sub>2</sub>, Cu<sub>2</sub>Br<sub>2</sub>, Cu<sub>2</sub>S, and Cu<sub>2</sub>O, deposited electrolytically at low c.d. on an etched Cu single-cryst. surface, shows definite orientation relationships to the Cu base. The most densely packed (111) plane is in each case parallel to the (111) plane of the Cu. Cu<sub>2</sub>I<sub>2</sub>, Cu<sub>2</sub>Br<sub>2</sub>, and Cu<sub>2</sub>S show spinel twinning about the (111) plane. Electrolytic Cu sulphide does not agree with the X-ray structure of either Cu<sub>2</sub>S or CuS, but shows cubic symmetry with a unit cell of edge 4·058 A. Direct action of H<sub>2</sub>S gas on Cu gives a single crystal overlaid by a polycryst. structure. The single crystal structure has hexagonal symmetry, different from that obtained electrolytically and from that shown by X-rays.

L. J. J.

X-Ray studies of compounds in the systems PbO-B<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>O-PbO-SiO<sub>2</sub>. H. F. McMurdie (J. Res. Nat. Bur. Stand., 1941, 26, 489—494).—Interplanar spacings and estimated relative intensities are recorded for a- and  $\beta$ -4PbO,B<sub>2</sub>O<sub>3</sub>, a-and  $\beta$ -2PbO,B<sub>2</sub>O<sub>3</sub>, 5PbO,4B<sub>2</sub>O<sub>3</sub>, PbO,2B<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O,4PbO,8SiO<sub>2</sub>, K<sub>2</sub>O,PbO,4SiO<sub>2</sub>, K<sub>2</sub>O,2PbO,2SiO<sub>2</sub> (I), and another K<sub>2</sub>O-PbO-SiO<sub>2</sub> compound of unknown composition. (I) is hexagonal with  $a \cdot 5 \cdot 62 \pm 0 \cdot 02$  and  $c \cdot 7 \cdot 57 \pm 0 \cdot 02$  A. J. W. S.

X-Ray study of the orientation of artificial fibres. I. V. A. Kargin and N. V. Michailov. II. N. V. Michailov, V. A. Kargin, and V. M. Buchman (J. Phys. Chem. Russ., 1940, 14, 195—204, 205—207).—I. From X-ray patterns of rayon fibres the quant. angle distribution of cellulose chains is calc. It is a pure random distribution only for viscose rayon kept for 2 hr. in boiling H<sub>2</sub>O; all other samples show some preferred orientation. The degree of orientation is raised by stretching wet fibre and drying it under load; this treatment increases also the tensile strength of fibres both wet and dry, and reduces the total elongation of dry fibres. The orientation of stretched fibres is destroyed by boiling H<sub>2</sub>O; the fibres obtained have a high tensile strength when dry, and a very high total elongation both when wet and when dry. The disappearance of orientation in hot H<sub>2</sub>O shows that the crystal-like state is not that of max, stability.

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II. When a fibre of cellulose xanthate (I) is transformed into hydratocellulose (II), and the resulting fibre stretched, it shows an orientation. When the stretched fibre is kept for 2 hr. in boiling H<sub>2</sub>O, however, this orientation disappears and the X-ray pattern becomes identical with that before stretching. When a fibre of (I) is first stretched and then transformed into (II), its orientation is not affected by boiling H<sub>2</sub>O. The orientation obtaining during the formation of (II) is stable, probably due to links between cellulose chains, whereas an orientation produced by later deformations is "elastic."

Structure and properties of cellulose and its esters. XI. Nature of surface reactions in the course of esterification of cellulose. Z. Rogovin, N. Michailov, and M. Sverdlin (J. Phys. Chem. Russ., 1940, 14, 208—210).—The X-ray pattern of Cu-NH<sub>3</sub> rayon changes when 42% of the OH radicals present are coupled with AcOH. This percentage is lower

than for ramie cellulose and shows that calculations of the micelle size from acetylation experiments are unconvincing.

Structure of black carbon. A. H. White and L. H. Germer (J. Chem. Physics, 1941, 9, 492—497).—Electron diffraction patterns of C films produced on SiO<sub>2</sub> by the thermal decompose CH<sub>4</sub> indicate that the C crystallites are strongly oriented. The films are made up of pseudo-crystals, in each of which the C atoms are arranged hexagonally in planes, as in graphite, but successive parallel at layers are displaced so that no regularities exist other than the uniform separation of the planes and regular arrangement of the atoms in each plane.

J. W. S.

Magnetisation in crystalline media. W. Peddie (*Phil. Mag.*, 1941, [vii], 32, 225—238).—Weber's theory of magnetisation is developed in application to a cubic cryst. medium. The theory accounts for all the normal phenomena of magnetisation.

O. D. S.

Further investigations of solid n-paraffins. Repulsion potential and compressibility. A. Müller ( $Proc.\ Roy.\ Soc.$ , 1941, A, 178, 227—241).—The substances investigated were n-C<sub>1</sub>,H<sub>36</sub>, m.p. 22°, n-C<sub>23</sub>H<sub>48</sub>, m.p. 47°, commercial wax, m.p. 58°, and n-C<sub>29</sub>H<sub>60</sub>, m.p. 64·5°. Compressibilities were measured by X-ray methods in the pressure range 700—1500 atm. Linear compressibilities in a plane normal to the chain axes are 3 to  $12 \times 10^{-12}$  cm.² per dyne; in the direction of the chain the figure is < one tenth of this. The repulsive forces between mols. are shown to have their origin in the H shells which surround the C chains. The forces are of the same order as those between He atoms.

Internal friction of single crystals of copper and zinc. T. A. Read (Amer. Inst. Min. Met. Eng., 1941, Tech. Publ. 1309, 12 pp.; Met. Tech., 1941, 8, No. 3; cf. A., 1940, I, 405).—
The fraction of energy lost per ½-cycle when single-crystal rods of Cu and Zn are set in longitudinal vibration at 33·5 and 39 kilocycles per sec. by piezo-electric oscillations may be as low as 1 × 10<sup>-5</sup> when the crystals are carefully annealed but is greatly increased by very small amounts of cold-work. The damping properties of Cu crystals do not change with time at room temp. and are not affected by the vibration stresses employed, but Zn crystals show recovery at room temp. and their damping is increased by oscillation stresses and depends on their orientation. The results are explained on the basis that internal friction is caused by slip and are discussed in terms of the dislocation theory.

J. C. C.

#### IV.—PHYSICAL PROPERTIES OF PURE SUBSTANCES.

Ionic diamagnetic susceptibility and diamagnetic correcting constants. (Miss) V. C. G. Trew (Trans. Faraday Soc., 1941, 37, 476—492).—The methods available for calculating ionic susceptibility are surveyed and critically discussed. A table of proposed vals. for univalent ions and for CO<sub>3</sub>" and SO<sub>4</sub>" is given. There is a systematic deviation between calc. and theoretical vals. The effect due to the homopolar bond, indicated by the difference between ionic vals. and those for the corresponding atoms in covalent combination, is not const., but rises regularly with increase in the effective at no.

F. L. U.

Adiabatic demagnetisation of paramagnetic salts. W. J. de
Haas and E. C. Wiersma (Act. VII Congr. int. Froid, 1937, 2,
267—278; Chem. Zentr., 1938, ii, 3896—3897; cf. A., 1940,
I, 388).—Magnetic balance and ballistic methods for the
determination of  $\chi$  at <4° K. are described. Temp. reached
by adiabatic demagnetisation are calc. from  $\chi$ , using the
Curie law.

A. J. E. W.

Influence of changes of structure and particle size on magnetic susceptibility. K. E. Zimens and J. A. Hedvall (Svensk Kem. Tidskr., 1941, 53, 12—23).— $\chi$  is unaffected by changes in particle size (measurements with TiO<sub>2</sub> and Se), but small differences in  $\chi$  for different cryst. forms of the same substance occur (rutile, anatase, and amorphous TiO<sub>2</sub>; blende and wurtzite; hexagonal, monoclinic, and amorphous Se; rhombic and monoclinic S). "Active" forms of S and TiO<sub>2</sub> of intermediate structure gave intermediate vals. of  $\chi$ . Irradiation of Se and of ZnS phosphors had no effect on  $\chi$ , probably because comparatively massive samples were used and thus only a small proportion of the atoms were activated. Vals. of  $\chi$  for Na<sub>2</sub>CO<sub>3</sub>, 10H<sub>2</sub>O, Na<sub>2</sub>CO<sub>3</sub>, 43H<sub>2</sub>O, KAl(SO<sub>4</sub>)<sub>2</sub>, and alum show that the contribution of the H<sub>2</sub>O mols, to the

vals. is additive; the  $H_2O$  mols. are thus not chemically combined. Changes of  $\chi$  during the thermal dehydration of kaolin (pholerite) indicate that its  $H_2O$  is chemically combined, but that the  $H_2O$  in metakaolin is not.

Magnetic studies of solid solutions. II. Properties of quenched copper-iron alloys. F. Bitter, A. R. Kaufmann, C. Starr, and S. T. Pan (*Physical Rev.*, 1941, [ii], 60, 134—138; cf. A., 1940, I, 67).—Susceptibility and magnetisation measurements are reported. The alloys studied show unusual magnetic properties both in the saturation effects at low temp. and in the apparent change in the magnetic moment of the dissolved Fe atoms over the temp. range 14—1300° K.

Ferromagnetic properties of hæmatite. E. T. Hayes (U.S. Bur. Mines, 1941, Rept. Invest. 3570, 29 pp.).—The use of the Gouy-type magnetic balance has been extended to measure susceptibilities over a large range of field strength, and to permit the determination of the hysteresis consts. of weakly ferromagnetic substances. The application of the method to hæmatite (I) shows the latter to be weakly ferromagnetic, with a max. susceptibility  $\sim 3500$  oersted. Small amounts of impurities cause a rapid displacement of this max. to weaker fields. Hysteresis curves drawn between H and  $4\pi I$  are unique for (I), since a ferromagnetic substance is being dealt with in a susceptibility range usually assigned to paramagnetic substances. Saturation occurs in fields of 8000-10,000 oersted. The residual magnetism of (I) after magnetisation in fields of this strength is 2-12 gauss. The vals. of the coercive force exceed those of any other natural mineral, and approach that of the best alloys for the construction of permanent magnets. The Curie point of (I) is  $\sim 685^{\circ}$ .

Velocity of sound in binary alloys. G. E. Allan (*Phil. Mag.*, 1941, [vii], 32, 165—170).—Observations are recorded for series of Sn-Pb, Sn-Zn, Cu-Zn, and Fe-Ni alloys. The relation between percentage composition and velocity of sound is roughly linear in the case of the Sn-Pb and Sn-Zn alloys, and shows a min. at ~50% in the Cu-Zn series, and at ~60% Fe in the Fe-Ni series, with inflexions in both cases at ~75% Cu and Fe, respectively. L. J. J.

Cytochrome-c. II. Optical properties. IV. Magnetic properties of ferrous and ferric cytochrome-c.—See A., 1941, III, 793.

Data on theoretical metallurgy. IX. Entropies of inorganic substances. Revision (1940) of data and methods of calculation. K. K. Kelley (U.S. Bur. Mines, 1941, Bull. 434, 115 pp.; cf. A., 1937, I, 123).—Available data of the entropies at 298·1° K. of the elements and inorg. compounds are presented, with tables summarising sp. heat and entropy data and data concerning changes in state over the range 0—298·1° K., and explanations of the methods used in calculating entropies. A bibliography of 419 references is appended.

C. R. H.

Specific heat of β-brass. R. Eisenschitz (Nature, 1941, 147, 778; cf. A., 1939, I, 559).—Theoretical. A rigorous evaluation of the partition function at const. vol. is given for the two-dimensional quadratic lattice.

L. S. T.

Heat capacity of certain halomethanes. G. Glockler and W. F. Edgell (J. Chem. Physics, 1941, 9, 527—529).—A semi-empirical method of calculating C3 for the halogen derivatives of CH<sub>4</sub>, based on additive contributions of the bonds and angles present, is developed. The mean deviation from the vals. calc. statistically is 0.9%.

J. W. S.

Restricted rotation potential and frequency assignment in propylene. D. Telfair and W. H. Pielemeier (J. Chem. Physics, 1941, 9, 571).—The vals. of C? for propylene at 360—500° K., as determined by supersonic methods are in accord with Wilson and Wells' frequency assignment (A., 1941, I, 241) and a rotation-restricting potential of ~2000 g.-cal. per g.-mol., but are in accord with Pitzer's assignment (A., 1937, I, 398) only if there is an entropy of mixing, which is regarded as improbable.

J. W. S.

Slopes of pv isotherms of helium, neon, argon, hydrogen, nitrogen, and oxygen at  $0^{\circ}$ . C. S. Cragoe (J. Res. Nat. Bur. Stand., 1941, 26, 495—536).—The methods of determining the variation of pv with p or d at const. temp. and low pressure from available data are discussed with particular reference to the reliability of the vals. at  $0^{\circ}$ . These vals.

are of importance in at. wt. determination, gas thermometry, gas analysis, etc.

J. W. S.

Solid helium. T. Nagamiya (Proc. Phys.-Math. Soc. Japan, 1940, III, 22, 492—503; Rev. Phys. Chem. Japan, 1941, 15, 55).—On the assumption that the mean positions of the atoms in solid He form a cubic close-packed lattice and that each atom is in the lowest energy state in a mean field of force which is exerted on it by its neighbours, the energy-vol. curve of solid He at 0° K. has been calc. Agreement with experiment is good but this does not necessarily confirm the original assumptions.

J. W. S.

Equation of state of solid helium. G. Kane (J. Chem. Physics, 1941, 9, 568—570).—From Margenau's vals. of the potential energy of interaction between two He atoms (A., 1940, I, 59) and a consideration of the He crystal to be hexagonal and close-packed with an ideal axial ratio, the equation of state for solid He is derived. Agreement with experiment is rather poor. Nagamiya's calculation of the equation of state (preceding abstract) is invalidated by a mathematical error.

J. W. S.

Production of waves by the sudden release of a spherical distribution of compressed air in the atmosphere. J. J. Unwin (Proc. Roy. Soc., 1941, A, 178, 153—170).—A theoretical method is devised for the solution of problems connected with the production of waves by spherical concns. of compressed air. A solution is worked out for a not very intense initial pressure, the results showing some features of interest in the differences to be expected from those predicted by sound-wave theory. The method is applicable to any spherically symmetrical motion up to such a time as the formation of a shock wave occurs and then it fails owing to the assumption of const. entropy.

G. D. P.

Viscosity and structure of molten quartz glass. N. V. Solomin (J. Phys. Chem. Russ., 1940, 14, 235—243).—The coaxial-cylinder method was used, the outer cylinder being of graphite, and the inner one of W. The furnace was lined inside with C. At 1720°, 1800°, 1880°, 1940°, and 2000°  $\eta$  of SiO<sub>2</sub> (containing 0.01% of Al<sub>2</sub>O<sub>3</sub>) is 2.94  $\times$  106, 5.74  $\times$  105, 1.47  $\times$  105, 5.60  $\times$  104, and 2.825  $\times$  104 poises, respectively. Molten SiO<sub>2</sub> presumably contains aggregates of some hundred mols.; the size of the aggregates is reduced by heating and by addition of metal oxides. J. J. B.

# 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. Kritschevski and V. P. Markov (J. Phys. Chem. Russ., 1940, 14, 101—104).—Vals. are recorded for the mol. vol. of the mixtures  $H_2$  49·5,  $N_2$  50·5;  $H_2$  73·6,  $CO_2$  26·4;  $N_2$  75·8,  $CO_2$  24·2;  $H_2$  31·5,  $N_2$  35·2,  $CO_2$  33·3;  $H_2$  54·4,  $N_2$  23·5,  $CO_2$  22·1, and  $H_2$  27·1,  $N_2$  54·7,  $CO_2$  18·1 between 50 and 500 atm. and 0° and 200°, and of the mixtures  $H_2$  47·3,  $CO_2$  52·7 and  $N_2$  52·7,  $CO_2$  47·3 between 50 and 500 atm. and 50° and 200°. The vals. are correct within 0·5%.

Compressibility of hydrogen-nitrogen-methane mixtures at high pressures. P. Bolschakov and A. Etherman (Acta Physicochim. U.R.S.S., 1941, 14, 365—370).—Data on the compressibilities of  $\rm H_2-N_2-CH_4$  mixtures are recorded. The compositions of the mixtures and the experimental conditions were as follows:  $64\cdot4\%$   $\rm H_2+25\cdot0\%$   $\rm N_2+10\cdot6\%$   $\rm CH_4$ , at 50-800 atm. and  $-30^\circ$  to  $250^\circ$ ;  $70\cdot37\%$   $\rm H_2+25\cdot2\%$   $\rm N_2+4\cdot5\%$  CH<sub>4</sub> at 300-800 atm. and  $-30^\circ$  to  $50^\circ$ . F. J. G.

Determination of the azeotropic mixture of ethyl alcohol and m-xylene. P. Lebed (J. Phys. Chem. Russ., 1940, 14, 277).—
This contains EtOH 85 and xylene 15 wt.-%. Its heat of evaporation is 196 g.-cal. per g.

J. J. B.

Theory of azeotropic mixtures. V. A. Kireev (Acta Physicochim. U.R.S.S., 1941, 14, 371—386).—The excess,  $F_m^E$ , of the observed over the ideal free energy of mixing for a binary mixture in which the mol. fraction of one component is m, is in the great majority of cases of the form  $F_m^E = m(1-m)K$ , where K may be either positive or negative and is a measure of the degree of deviation from linearity of the v.p.—composition curve. This leads to an equation  $(1-2m)\log p_m = (1-m)^2\log p_1 - m^2\log p_2$ , where  $p_1, p_2$ , and  $p_m$  are the v.p.

of the pure components and the azeotropic mixture, which gives good agreement with observation in all but the most abnormal cases. Further, on the assumption (which is true in many cases) that  $KT=\mathrm{const.}$ , the dependence of the composition of the azeotropic mixture on the temp. is given by  $-m/T^2+1/2T^2+(L_1-L_2)/2KT^2+C=0$ , where C is an integration const. and  $L_1$  and  $L_2$  are the heats of vaporisation of the pure components. This also gives good agreement with observation. F. J. G.

Viscosity in the systems acetic acid-dimethylaniline and diethylaniline. V. V. Udovenko (J. Gen. Chem. Russ., 1940, 10, 1923—1925).—The  $\eta$ - and d-composition curves at 25°, 45°, and 65° exhibit max. at 80—85 mol.-% of AcOH.

Relation between viscosity and density of liquids and liquid mixtures. M. K. Srinivasan (Phil. Mag., 1941, [vii], 32, 253—258).—The variation of viscosity ( $\eta$ ) of liquids and binary liquid mixtures with temp. can be represented by the empirical equation:  $\log \eta = \alpha + \beta/(\rho_0 - \rho)$ , where  $\rho$  is the density of the liquid and  $\alpha$ ,  $\beta$ , and  $\rho_0$  are consts. The equation agrees with published data for org. liquids, including the associated test. alcohols, for org. binary mixtures, and for metals, but does not agree with data for  $H_2O$ . The equation also represents the variation of  $\eta$  with composition of binary mixtures at const. temp.

O. D. S.

Influence of pressures up to 1000 kg, per sq. cm. on the viscosity of highly viscous liquids (lubricating oils etc.). M. P. Volarovitsch (Acta Physicochim, U.R.S.S., 1940, 13, 69—82, 564—565).—Data on the influence of high pressures on  $\eta$  for a no. of highly viscous liquids (lubricating oils, colophony, solutions of sugar in glycerol) are given. With increase of pressure,  $\eta$  increases markedly, approx. according to  $\log \eta = a + bP$ , and the temp. coeff. of  $\eta$  also increases. F. J. G.

Unmixing effect of sound waves on liquid mixtures. K. F. Herzfeld (J. Chem. Physics, 1941, 9, 513—514).—Mathematical. The amount of unmixing and increase in sound absorption produced when sound waves are passed through liquid mixtures are calc. and found to be too small to be observed.

J. W. S.

Physical reflexions in a chemical mirror. R. E. Gibson (J. Washington Acad. Sci., 1941, 31, 325—348).—A historical survey of the theory of solutions.

F. L. U.

Density-composition tables for (A) nitric acid, (B) aqueous solutions of hydrochloric acid (Brit. Stand. Inst., B.S. 975, 976, 1941; 58 pp., 31 pp.).

Diffusion of electrolytes and of the ions in their mixtures. J. R. Vinograd and J. W. McBain (J. Amer. Chem. Soc., 1941, 63, 2008—2015).—The diffusion into H<sub>2</sub>O at 25° through a sintered glass membrane of KCl, LiCl, NaCl, NaI, NaCNS, NaHCO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub> and Na H tartrates, Na citrate, and tartaric acid has been measured. The diffusion of ions in mixed electrolytes diffusing in the same and opposite directions or of ions diffusing through salts or buffers originally present in uniform concn. is considered theoretically, and the effects due to concn. gradient and to electrical factors produced by the diffusion potential are assessed separately. W. R. A.

Electric conductivity and viscosity of the systems pyridine hydrochloride-pyridine and pyridine hydrochloride-water. S. Z. Schtamova (J. Phys. Chem. Russ., 1940, 14, 225—234). —The  $\eta$  of  $C_8H_8N,HCl-C_5H_8N$  mixtures between 95° and 135° and of  $C_8H_8N,HCl-H_2O$  mixtures between 55° and 135° increases regularly with  $[C_5H_5N,HCl]$ , showing that no compounds are formed in these systems. Electric conductivity  $\kappa$  increases with  $[C_5H_5N,HCl]$  in  $C_5H_8N$  and has a max. in  $H_2O$ ; after correcting for  $\eta$  it increases with  $[C_8H_8N,HCl]$  in  $H_2O$  as well. The mol. conductivity corr. for  $\eta$  has in the  $C_5H_5N$  solution a min. at 16 l. per mol. at 115°, and in aq. solution a min. at 0·18 l. per mol. at 95°. The temp. coeff. of  $\kappa$  in  $C_5H_5N$  between 95° and 115° is 1·1% per degree independently of temp.; in  $H_2O$  the temp. coeff. increases with  $[C_8H_8N,HCl]$ . The results show that an anomalous behaviour of mol. conductivity is also observed in systems involving no interaction between solute and solvent.

Mixed crystals. III. M. M. Popov, S. M. Skuratov, and I. N. Nikonova. IV. M. M. Popov, S. M. Skuratov, and M. M. Streltzova. V. M. M. Popov, J. P. Simonov, S. M. Skuratov, and M. N. Suzdaltzeva (J. Gen. Chem. Russ., 1940, 10, 2017—2022, 2023—2027, 2028—2040).—III. The mean

sp. heat (20—610°) of 1:1 KCl-KBr mixed crystals is 0.4% > that of a 1:1 KCl-KBr mixture, and that of 1:1 NaCl-KCl mixed crystals 0.6% > that of 1:1 NaCl-KCl mixture. IV. Mixed KCl-KBr or NaCl-KCl crystals, prepared by

fusion of the salt mixtures, are stable in absence of H<sub>2</sub>O. The heat of dissolution of the mixed crystals is < that of the corresponding mixtures.

V. Mixed crystals prepared as above present numerous X-ray spectrum lines not given by the constituent salts, unless these have previously been subjected to the same thermal treatment. Metastable forms of Ag, Au, and Pt may be obtained similarly.

R. T.

Densities of silicate glasses as a function of composition. M. L. Huggins (J. Opt. Soc. Amer., 1940, 30, 420—430).—The vol.  $V_0$  per g. of O is calc. for a series of well annealed glasses from published data of their densities. Results can be expressed accurately by  $V_0 = k + b_{\rm Si} + c_{\rm Si}N_{\rm Si} + \Sigma c_{\rm M}N_{\rm M}$ , where k is a very small const. depending on the annealing technique,  $N_{\rm Si}$  and  $N_{\rm M}$  are nos. of Si or other "metal" atoms per O atom respectively,  $b_{\rm Si}$  and  $c_{\rm M}$  is a const. valid for all vals. of  $N_{\rm M}$ . For glasses containing B allowance must be made for the presence of both tetrahedrally surrounded and triangularly surrounded B atoms. Densities can be calc. for glasses of known composition with an accuracy of 0·1%. The physical significance of the empirical formula is discussed.

Speed of crystallisation of some silicate glasses as a function of viscosity. A. Leonteeva (Acta Physicochim. U.R.S.S., 1940, 13, 423—428).—The trend of the curve of max. linear speed of crystallisation (v) against temp. (T) observed by Dietzel (B., 1930, 460) is in the opposite sense to the  $\eta$ -T curve measured on similar glasses by Washburn (Univ. III. Eng. Exp. Sta. Bull., 1924, 140) and it is shown that for temp. below the temp. of max.  $v, v = k/\eta + k_0 \log_\theta \eta$ , where k and  $k_0$  are consts., the vals. of which differ for different glasses.

I. W. S.

Platinum-mercury system. I. N. Plaksin and N. A. Suvarovskaja (Acta Physicochim. U.R.S.S., 1940, 13, 83—96). —Methods for the prep. and analysis of Pt amalgams are described, and the results of a study of the system Pt-Hg by means of X-rays and cooling curves are recorded. The following phases exist: a, a solid solution of Hg in Pt having  $\geqslant 23$  at.-% of Hg, and  $\beta$ ,  $\gamma$ , and  $\delta$ , three compounds of approx. compositions Pt<sub>3</sub>Hg, Pt<sub>2</sub>Hg, and PtHg. a decomposes at 486·1° to solid solution and liquid, and  $\beta$  and  $\gamma$  decompose at 236·5° and 159·1° respectively to the compound poorer in Hg and liquid. The solubility of Pt in Hg is 0·02% at 16° and 1·2% at 172°. F. J. G.

Solubility of gases in liquids at low temperatures and high pressures. II. Solubility of helium in liquid nitrogen at 78·0—109·0° K. and pressures up to 295 atm. M. G. Gonikberg and V. G. Fastovski (J. Phys. Chem. Russ., 1940, 14, 257—260).—The ratio of the mol. fractions of He in gas and liquid corr. for the activity coeff. is 4290, 2450, and 770 at 78·0°, 90·1°, and 109·0° K. respectively for low [He]. When the liquid contains 4% of He the gas contains at 78° 98·3%, at 90·1° 91%, and at 109·0° 60% of He. J. J. B.

Solubility of gases in liquids at low temperatures and high pressures. IV. Solubility of helium in liquid methane at 90.3° and 106.0° K. and pressures up to 160 atmospheres. M. G. Gonikberg and V. G. Fastovski (Acta Physicochim. U.R.S.S., 1940, 13, 399—404; cf. A., 1941, I, 80).—The distribution of He between liquid CH<sub>4</sub> and the vapour phase has been studied at 90.3° and 106.0° K. and at 26—160 atm., under which conditions it behaves in accordance with the dil. solution law. Henry's coeff. is 26,350 and 13,700 and the partial mol. vol. of the dissolved He is 18.4 and 20.2 c.c., at 90.3° and 106.0° K., respectively.

J. W. S.

Solubility of hydrogen in liquid hydrocarbons. H. Sattler (Angew. Chem., 1940, 53, 513).—The solubility of  $\rm H_2$  in  $\rm C_6H_{44}$ , cyclohexane,  $\rm C_6H_{6}$ , and m-xylene at  $\rm H_2$  pressures of 50, 100, and 150 atm. and at 35° and 72° was studied. The liquids were in thermodynamic equilibrium with the  $\rm H_2$ , and the quantity of  $\rm H_2$  evolved from a known quantity of the liquid at its own v.p. was determined volumetrically. Apparatus and procedure are described. At the pressures used, Henry's law is still applicable. The solubilities in c.c. of gas at n.t.p. per g. of solvent, at a  $\rm H_2$  pressure of 10 atm., are:

 $C_6H_{14}$  16·7, cyclobexane 10·9,  $C_6H_6$  7·8, and m-xylene 7·4 at 35°. Inaccuracy in measurement was <1%. At 72° the solubility of  $H_2$  in  $C_6H_6$  under the above conditions is 10·2. The theoretical significance of the variation of the solubility of a gas in chemically similar solvents is discussed.

Solubility of sulphur dioxide in molten copper. C. F. Floe and J. Chipman (Amer. Inst. Min. Met. Eng., 1941, Tech. Publ. 1308, 10 pp.; Met. Tech., 1941, 8, No. 3).—The solubility at 1100—1500° under pressures of 20—900 mm. of Hg was determined by a modified Sieverts method, using induction heating to melt the Cu which was contained in a fused SiO<sub>2</sub> tube. The results cannot be simply interpreted on the basis that chemical combination (6Cu + SO<sub>2</sub> = Cu<sub>2</sub>S + 2Cu<sub>2</sub>O) occurs, the deviation being most marked at low pressures, apparently owing to irregular behaviour of the dil. solutions. At 1100°, the solubility is 8:3 c.c. per 100 g. at 13:9 mm. and 165.5 c.c. per 100 g. at 893 mm.; at 1300° it is 251 c.c. per 100 g. at 752 mm. of Hg.

Physical studies of non-aqueous solvates. IV. Solubility of zinc bromide in diethyl ether. H. H. Rowley and R. B. Anderson (J. Amer. Chem. Soc., 1941, 63, 1908—1910; cf. A., 1939, I, 523).—The existence of ZnBr<sub>2</sub>,2Et<sub>2</sub>O (stable below 4°) and ZnBr<sub>2</sub>,Et<sub>2</sub>O (stable below 16—17°) has been demonstrated by measuring the solubility of ZnBr<sub>2</sub> in Et<sub>2</sub>O from -20° to 35°. The differential heats of dissolution have been calc. for the whole range of temp.

W. R. A.

High mol. wt. aliphatic amines and their salts. II. Solubilities of primary aliphatic amine hydrochlorides and acetates in ethyl alcohol and benzene. H. J. Harwood, A. W. Ralston, and W. M. Selby (J. Amer. Chem. Soc., 1941, 63, 1916—1920).— The solubilities of the hydrochlorides of the amines from  $C_{10}$  to  $C_{18}$  in 95% EtOH and of the acetates of the same amines in 95% EtOH and in  $C_6H_6$  have been determined in the range  $\sim 8-82^\circ$ . The solubility curves of the hydrochlorides are paired with the "even" derivative and the next homologue almost superposed and sometimes intersecting. The relationship between the solubility curves for the acetates is much more complicated. Polymorphic forms of octa- and hexa-decylamine acetates separate from EtOH but not from  $C_6H_6$ . W. R. A.

Fractional partition of the rare earths. D. B. Appleton and P. W. Selwood  $(J.\ Amer.\ Chem.\ Soc.,\ 1941,\ 63,\ 2029).$ —A mixture of  $\text{La}_2\text{O}_3$  and  $\text{Nd}_2\text{O}_3$ , containing  $38\cdot1\%$  of  $\text{La}_2\text{O}_3$ , was converted into the thiocyanates and an aq. solution shaken with an equal vol. of Bu°OH. After separation into two layers each layer was analysed by conversion into oxides. The  $\text{H}_2\text{O}$  layer contained  $38\cdot7\%$   $\text{La}_2\text{O}_3$  and the alcoholic layer  $37\cdot4\%$   $\text{La}_2\text{O}_3$ . The process can be carried on continuously and a comparatively rapid separation effected. W. R. A.

Quantitative expression for the extractability of metals in the form of dithizonates from aqueous solutions. Equilibrium constant of zinc dithizonate. I. M. Kolthoff and E. B. Sandell (J. Amer. Chem. Soc., 1941, 63, 1906—1908).—A quant expression for the extractability of metals as dithizonates has been derived from mass action and distribution laws and is tested for the Zn-dithizone equilibrium. W. R. A.

Kinetics of sorption and desorption. J. L. Zabeshinski (J.Phys. Chem. Russ., 1940, 14, 139-141).—The slowness of desorption as compared with sorption can be accounted for if the rate of sorption  $\alpha$   $(C_0 - C)$  and the rate of desorption  $\alpha$   $(C_0 - C)$  being the actual concn. of the vapour and (C) the concn. which would have been in equilibrium with the amount absorbed at a particular time.

Rate of sorption of sulphur dioxide by vanadium pentoxide. G. K. Boreskov and E. E. Ruderman (J. Phys. Chem. Russ., 1940, 14, 161—170).—The V<sub>2</sub>O<sub>5</sub> was in crystals of 10<sup>-4</sup> cm. The initial pressure of SO<sub>2</sub> was 750 mm. Hg. Between 273° and 418° the rate v of sorption gradually decreases and becomes negligible when the sorbed amount reaches ~0·2 c.c. per 1 g. of V<sub>2</sub>O<sub>5</sub>. Between 443° and 494° v is high and almost independent of the amount adsorbed; at 490°, e.g., it is 3 c.c. per 1 g. of V<sub>2</sub>O<sub>5</sub> per hr. V<sub>2</sub>O<sub>5</sub> heated several times with O<sub>2</sub> at 494° and evacuated takes up SO<sub>2</sub> more rapidly, both at 494° and at 393°, but an analogous treatment at 393° does not affect v. After sorption at 494° the sorbent contains the whole adsorbed amount as SO<sub>3</sub>, and an equiv. amount of V<sub>2</sub>O<sub>4</sub>. This reduction of V<sub>2</sub>O<sub>5</sub> cannot be a part of the cata-

lytic oxidation of  $SO_2$  in the presence of  $V_2O_5$  since the rate of sorption is about 100 times as small as the rate of oxidation. Below 418° only adsorption on the crystal surface takes place.

J. J. B.

Adsorption of vapours under pressures. I. R. Kritschevski and R. S. Kalvarskaja ( $Acta\ Physicochim.\ U.R.S.S.$ , 1940, 13, 49—68).—The influence of hydrostatic pressure on the adsorption of a vapour has been studied theoretically and experimentally. It is shown thermodynamically that at const. chemical potential the adsorption decreases with increasing hydrostatic pressure. Experimentally, the adsorption of  $C_6H_6$  and of  $CCl_4$  on activated charcoal at  $50^\circ$  under pressures of 1—600 atm. of  $N_2$  or  $H_2$  was determined. The theoretical prediction was confirmed, the effect being > that calc. from Polanyi's theory, showing that the mol. vol. in the adsorbed is > in the liquid state. At const. mol. fraction in the gas phase, with increasing pressure, the adsorption passes through a max. when the partial mol. vols. in the gas and in the adsorbed state are equal. Data on the saturation concn. of  $CCl_4$  and  $C_6H_6$  vapours in compressed  $N_2$  are also given.

F. J. G.

Synthetic resins as exchange adsorbents.—See B., 1941, II, 352.

Theory of capillary condensation and other capillary phenomena taking into consideration the disjointing effect of multimolecular liquid films. B. Derjaguin (J. Phys. Chem. Russ., 1940, 14, 137—147).—Because of the disjointing effect of thin films (cf. A., 1940, I, 111) capillary condensation may cause swelling of the sorbent. This effect is also involved in the capillary rise in slits and cylindrical capillaries.

Electrocapillary curves of mercury in liquid ammonia. III. Surface-active organic substances. A. Murtazaev and I. Igamberdiev (J. Phys. Chem. Russ., 1940, 14, 217—219).— The curves in  $0\cdot1\text{N-NH}_4\text{NO}_3$  are depressed by hydrocarbons between  $+0\cdot2$  and  $-0\cdot4$  v.; no measurements were possible at higher positive potentials. The depression at the max. of the electrocapillary curve in  $0\cdot5\text{M}$ . solutions rises from  $1\cdot9$  dynes per cm. for  $C_6H_6$  to  $14\cdot6$  dynes per cm. for mesitylene, Hydrocarbons do not shift the max. of the curve.

Adhesion of mineral particles to air bubbles. O. S. Bogdanov and M. S. Filanovski (J. Phys. Chem. Russ., 1940, 14, 244—247).—Motion pictures are made of air bubbles and PbS particles meeting each other and moving together in H<sub>2</sub>O containing Bu xanthate and pine oil. The speed of small particles sliding along the interface bubble/H<sub>2</sub>O is calc.

Structure of surface layers of ordinary solutions. B. M. Gouguell ( $Acta\ Physicochim.\ U.R.S.S.$ , 1941, 14, 433–450).— For binary solutions the mixture rule  $a_1\gamma_1+a_2\gamma_2=\gamma$  is obtained, where  $\gamma$  denotes surface tensions and  $\alpha$  mol. area fractions, defined by  $a_1=s_1A_1/(s_1A_1+s_2A_2)...s_1$  and  $s_2$  being the surface mol. fractions, and  $A_1$  and  $A_2$  the mol. areas; the subscripts refer to the two components. In the resulting expression  $(\gamma_1-\gamma)/(\gamma-\gamma_2)=s_2A_2/s_1A_1$ , which gives a relation between the individual  $\gamma$  vals. and the composition of the surface layer, A represents an apparent mol. area, which is not necessarily const. but may vary with the orientation of the surface mols. The expression is checked by assuming parachor additivity according to the equation  $s_1[P]_1+s_2[P]_2=(\gamma^4/\rho)(s_1M_1+s_2M_2)$ , where M is the mol. wt. of the components and  $\rho$  the density of a solution of the composition  $s_1$  (or  $s_2$ ). Very good agreement is found between observed vals. of  $\gamma$  and those calc. by the mixture rule after obtaining s and A vals. by applying the parachor expression for the systems  $H_2O$ -AcOH,  $H_2O$ -MeOH,  $H_2O$ -EtOH,  $H_2O$ -PraOH, and  $H_2O$ -COMe2. The compositions of the surface layers obtained are used to calculate adsorption and mol. areas of the components. A vals. for the alcohols exhibit a sharp min. in fairly dil. solution corresponding with vertical orientation, and then increase with increasing concn., presumably as a result of changed orientation. The composition at min. A is the same as that at which foam stability is a max., and it is suggested that at such a composition the alcohol and  $H_2O$  mols. form a condensed film. In AcOH solutions A shows a min. followed by a max, and the val. for pure AcOH is exactly half that for vertically oriented AcOH mols., indicating that the surface layer in pure AcOH is bimol. as in the solid fatty acids.

Effect of surface films on the rate of evaporation of water and aqueous solutions. A. S. Cheinman (J. Phys. Chem. Russ., 1940, 14, 118—123).—The rate K of evaporation of  $\mathrm{H}_2\mathrm{O}$  from 0.5—0.75% gelatin solution is < that from  $\mathrm{H}_2\mathrm{O}$ ; the difference increases with the speed v of the air blowing away the vapour and reaches 3% when v is 1.44 m. per sec. This effect is due to the gelatin reducing the stirring of the surface by the air blast. A saturated film of cetyl alcohol reduces K of  $\mathrm{H}_2\mathrm{O}$  by 20% at v=0 and by 67% at v=1.36; this reduction is intensified by NaCl in the underlying  $\mathrm{H}_2\mathrm{O}$ . A solid film of Na oleate does, and a liquid film of oleic acid does not, lower K. Solid paraffin films are ineffective.

Thermodynamic theory of the spreading of liquids to form duplex films and of liquids or solids to form monolayers. W. D. Harkins (J. Chem. Physics, 1941, 9, 552—568).—A thermodynamic theory of the spreading of any liquid or solid over the surface of a liquid is developed. It is considered that both duplex and monolayer spreading can occur, and conditions under which the two forms of spreading occur are deduced. The passage of the unstable duplex layers into monolayers and lenses is discussed. The action of a spreading oil in inducing the spreading as a duplex film of a non-spreading oil is also discussed.

J. W. S.

Spreading of oils on water. I. Ionised molecules having only one polar group. W. A. Zisman (J. Chem. Physics, 1941, 9, 534—551).—The spreading on  $\mathrm{H_2O}$  of drops of mineral oil containing various org. acids and amines with one polar group has been studied under conditions favouring dissociation at the oil- $\mathrm{H_2O}$  interface. Max. spreading is induced by a substratum of  $p_{\mathrm{H}}$  9·0—10·5. Only acids containing  $\stackrel{<}{\leftarrow}14$  C atoms and having one straight saturated chain form rigid interfacial films on substrata containing  $\mathrm{Ca}^{**}$ ,  $\mathrm{Cu}^{**}$ ,  $\mathrm{Pb}^{**}$ ,  $\mathrm{Fe}^{**}$ ,  $\mathrm{Al}^{***}$ ,  $\mathrm{I}^{**}$ ,  $\mathrm{I}^{**}$ , or  $\mathrm{Th}^{***}$ . The ions of higher valency have the greatest effect. The areas of some OH-acid films are unaffected by  $p_{\mathrm{H}}$  or by the presence of metallic ions. The effect of  $\mathrm{Ca}^{**}$  on the spreading of oleic acid-stearic acid mixtures has been studied in detail.

Surface films of polar crystals. (Sir) J. Larmor (Nature, 1941, 148, 26).

L. S. T.

Damping of waves by surface-active substances. I, II. V. Levitsch (Acta Physicochim. U.R.S.S., 1941, 14, 307—320, 321—328).—I. Mathematical. It is shown that the presence of a surface film, independently of its nature, will always have a damping effect on surface waves.

II. Mathematical. A solute which is strongly adsorbed at

II. Mathematical. A solute which is strongly adsorbed at the surface will have a damping effect analogous to that of a surface film.

F. J. G.

Internal phase and emulsifier as factors determining the viscosity of oil-in-water emulsions. B. A. Toms (J.C.S., 1941, 542—547).—The viscosity  $\eta$  of 50 vol.-% emulsions of 11 different org. liquids in  $H_2O$  was measured at  $20^\circ$ , the Na and K salts of do-, tetra-, hexa-, and octa-decoic and oleic acids being used as emulsifiers. If the vol. fraction of the internal phase is calc. by Hatschek's equation, the ratio (h) of the calc. to the actual val. is not appreciably affected by substituting K for Na, but may be changed by 10-20% by altering the fatty acid radical; for the saturated acids  $h=\sim1\cdot3$ , whilst for oleic  $h=\sim1\cdot2$ . Alteration of the org. liquid, other factors remaining const., can lead to considerable variations in h. The observed variations are attributed to interactions between oil, soap, and  $H_2O$ . F. L. U.

Particle size and shape of colloidal carbon.—See B., 1941, I, 431.

Calculation of particle size and mol. wt. from current centrifugal methods. J. W. McBain and F. A. Leyda (Acta Physicochim. U.R.S.S., 1941, 14, 421—432).—Formulæ applicable to various forms of centrifugal and ultracentrifugal equipment are given. Numerical data for hæmoglobin and for sucrose are recorded.

F. L. U.

Sedimentometric study of coarse disperse systems. Influence of the concentration of the disperse phase on the particle size distribution of aqueous suspensions of barium sulphate in the presence of electrolytes. N. A. Figurovski and V. N. Rozanova (J. Phys. Chem. Russ., 1940, 14, 73—81).—A sedimentometric balance was used. In suspensions of well washed BaSO<sub>4</sub> the relative no. of small particles  $(1-2 \mu)$  slightly increases, and that of large particles  $(7-10 \mu)$  slightly decreases, with increase of dilution d (50—2000 g. of

 $\rm H_2O$  per g. of BaSO<sub>4</sub>). In the presence of  $7\times 10^{-6}$  or  $18\times 10^{-6}$  g. of NaOH per c.c. a min. of the degree of dispersity is observed at d=200 or 100. At d=200 small concns. of NaOH increase, and large concns. reduce, the dispersity,  $\rm H_2SO_4~(9\times 10^{-6}~to~2\times 10^{-4}~g.~per~c.c.)$  and NaCl (2  $\times~10^{-5}$  to 5  $\times~10^{-5}~g.~per~c.c.) lower the dispersity.$ 

Preparation of colloidal suspensions of metals and their alloys. E. Andronikaschvili and I. Tzabadze (Acta Physicochim. U.R.S.S., 1940, 13, 369—378).—Conc. colloidal suspensions of Pb, Sn, and Pb-Sb and Sn-Pb alloys in EtOH, xylene, or Et<sub>2</sub>O have been obtained by agitating the finely divided metal with the solvent. With Pb in EtOH the concn. reached 10%. The  $\eta$  of the conc. sols is > that of the pure liquids. The degree of dispersion, concn., and  $\eta$  are dependent on the initial particle size and the conditions of agitation. In spite of precautions to exclude O<sub>2</sub> considerable oxidation of the particles occurs. Coagulation occurs after 2—3 days, the process being accelerated by the presence of air. The production of the dispersions is attributed to the mechanical disintegration brought about by collision between the particles in the earlier stages and rubbing together of the particles in the later stages of the agitation.

Nature of lyophilic sols. S. A. Glückmann (Acta Physicochim. U.R.S.S., 1940, 13, 379—392).—It is suggested that very dil. solutions of highly polymerised compounds are analogous to true solutions, but that at a definite concan association begins and increases with increasing concn. The aggregates should be regarded as suspended in the liquid and in mobile equilibrium with mols. in solution. Thus very dil. solutions are bivariant, but more conc. solutions univariant. The stability of the sols is attributed to the predominance of the attractive force to the solvent over the attraction to the aggregate. Coagulation is caused by shifting of the adsorption equilibrium on the solvated part of the aggregate. The theory is supported by observations of the  $\eta$  and vol. changes during addition of coagulant liquids to lyophilic sols (cf. A., 1936, 1066).

Rheology of clay. H. H. Macey (J. Sci. Instr., 1941, 18, 159—165).—Theoretical and experimental investigations of the rheological properties of liquid and solid clay—H<sub>2</sub>O mixtures are reviewed critically. The properties of the solid mixtures can be explained on the theory that the surfaces of the particles are mutually repulsive and so appear to be separated by H<sub>2</sub>O films.

J. W. S.

Electron microscope study of curd fibres of sodium laurate. L. Marton, J. W. McBain, and R. D. Vold (J. Amer. Chem. Soc., 1941, 63, 1990—1993).—The structure of Na laurate (I) curd has been investigated photographically, using an electron microscope. The curd consists of a mass of fibres which are thin ribbons, the widths of which tend to integral multiples of twice the length of mols. of (I). The rigidity of the curd is attributed to the fibres branching to form a felt. Capillary spaces of variable diameter, in which H<sub>2</sub>O is retained at low R.H., are formed at the fibre junctions. Part of (I) is present in the curd as granules 100 to 200 A. in diameter irregularly spaced along the fibres. The structure of the curd is in accord with previous deductions from microscopic and ultramicroscopic data for curd fibres. W. R. A.

Process of viscous flow in highly-polymeric materials. V. Kargin and G. Slonimski (Acta Physicochim. U.R.S.S., 1941, 14, 329—336).—The relationships of viscous flow in plastic materials to the classical conceptions of the deformation of an elastic solid and the flow of a viscous liquid are discussed. In substances having long-chain mols., the first effect of a stress will be to produce a deformation of the individual mols., which is not equally distributed along the chain. Subsequently a relaxation process will equalise this deformation along the chain. At the same time a shift of the chain as a whole with respect to its neighbours may also occur, and the relative speeds of these processes will depend on the relative binding forces within a chain and between different chains, and on the mutual orientation of the chains. F. J. G.

Intraglobular absorption of organic substances by protein solutions. D. L. Talmud (Acta Physicochim. U.R.S.S., 1941, 14, 562—563).—Solutions of globular proteins can absorb the vapours of org. substances insol. in H<sub>2</sub>O in considerable amount; e.g., edestin in 2% solution in 10% aq. NaCl absorbs up to half its wt. of C<sub>5</sub>H<sub>12</sub>. This behaviour is compared

with that of soap solutions, and its further study is considered likely to throw light on the structure of protein mols.

Physical-chemical investigation of certain nucleoproteins. III. Molecular-kinetic studies with calf thymus nucleohistone. R. O. Carter (J. Amer. Chem. Soc., 1941, 63, 1960—1964; cf. A., 1941, I, 261).—The sedimentation velocities at 20° over the  $p_{\rm H}$  range 5—12 and the diffusion and sedimentation equilibria at 25° and  $p_{\rm H}$  6·4 of the nucleohistone (I) of the calf thymus gland have been measured. (I) is essentially monodisperse and shows the same mol. behaviour over the  $p_{\rm H}$  range 5·3 to 9. The mol. wt. of (I) computed from the sedimentation and diffusion data is 2,150,000. The ratio of the long to the short axis is 36.

Effect of organic dye ions on electrokinetic potential at the glass-water interface. D. O. Jordan (Trans. Faraday Soc., 1941, 37, 441—450).—Streaming potentials at sintered glass plates were measured with solutions of new-fuchsine, orange II, Congo-red, benzopurpurine 4 B, and sky-blue FF, the last two also in presence of dil. NaCl. The variation of the electric moment of the double layer (thickness of double layer × surface density of charge) with time and concn. is shown in diagrams. The dyes that form colloidal micelles in solution separate in a solid form at the interface.

Evidence for a rigid multilayer at a solid-liquid interface. W. G. Eversole and P. H. Lahr (J. Chem. Physics, 1941, 9, 530—534).—Assuming the presence of an immobile layer of electrolyte solution in contact with a wall of fixed potential, equations are derived interrelating the wall potential,  $\zeta$ -potential, and concn. (c) of the univalent salt solution. Introduction of literature data for the relationship between  $\zeta$ -potential and c leads to vals. of 8—63 A. for the thickness of the immobile layer, this being considered to support the hypothesis of the immobile layer and to indicate that the assumption of large sp. adsorption potentials (A., 1933, 1304) is unnecessary.

Electrokinetic behaviour of carbon. N. Bach (Acta Physicochim. U.R.S.S., 1941, 14, 463—482; cf. A., 1938, I, 244).—Sugar C, de-ashed, activated in CO<sub>2</sub> at 950°, and heated in H<sub>2</sub> to remove surface oxides, acquires a positive charge when placed in H<sub>2</sub>O in presence of O<sub>2</sub>. Under these conditions the C behaves as an O electrode and adsorbs anions but not cations. When such C is heated in  $O_2$  at  $350-450^\circ$  acid-forming surface oxides are produced and the C then becomes negatively charged in H2O and adsorbs cations to an extent increasing with the degree of oxidation. The sign of the charge deduced from the adsorption of anions and/or cations from 0.004n-KCl agrees in every case with that determined electrokinetically. The failure of Bennister and King (A., 1938, I, 450) to obtain positively charged C is attributed to surface oxidation consequent on allowing the C to cool in air after activation; C prepared by their method and afterwards cleaned in  $H_2$  is positive in  $H_2$ O and dil. electrolytes in presence of  $O_2$ . Graphite, when treated as described above, is also positively charged in presence of  $O_2$ , but differs from the sugar C in being sensitive to  $O_2$  at room temp.; the mobility of a specimen of graphite in  $H_2O$  was  $+5.6~\mu$ . per cm. when freshly prepared,  $+4~\mu$ . after keeping 1 month in  $O_2$ , and  $-3.6~\mu$ . after 3 months. Both graphite and sugar C are negative in 0.004 N-AOH even when freshly prepared. Sugar C containing 0.2% of Pt is negatively charged in aq. solutions in presence of H<sub>2</sub> as a result of its then functioning as a H electrode. The z-potential vals, for such negative H<sub>2</sub>-charcoal and for the positive O2-charcoal, calc. from mobility measurements at different  $p_{\rm H}$ , are consistent with the Gouy-Stern theory if the double layer is assumed to be either less diffuse than is provided by the theory, or more viscous than F. L. U. the bulk liquid.

Coagulation of colloids by exposure to high-frequency oscillations. S. S. Joshi and A. Purushottam (J. Indian Chem. Soc., 1941, 18, 138—140).—High-frequency oscillations from a condensed spark discharge produce rapid coagulation of many (but not all) colloids.

F. J. G.

## VI.-KINETIC THEORY. THERMODYNAMICS.

Equilibrium in chloride formation from mono-, di-, and triarylearbinols. J. O. Halford and E. B. Reid (J. Amer. Chem. Soc., 1941, 63, 1873—1878).—The equilibria in the liquid

phase  $(C_0H_6$  solution) at 60° of the reaction ROH + HCl = RCl +  $H_2O$  [R =  $CH_2Ph$  (I), p-xylyl (II),  $CHPh_2$  (III), o-, m-, and p-methylbenzhydryl, di-p- (IV) and di-o-tolylmethyl, o- and p-chlorobenzhydryl, di-p-tolylmethyl] have been investigated. The v.p. at 60° of ROH and RCl [R = (I), (II), (III), and (IV)] and the partial pressures of the solvent over their solutions in  $C_0H_0$  have been measured. From these data the vapour-phase equilibrium consts. have been calc. For the other eight reactions estimates of the vapour-phase consts. have been made. W. R. A.

Calculations of  $p_{\rm H}$  in buffer solutions on basis of Debye and Hückel's theory. H. Nukada (J. Pharm. Soc. Japan, 1940, 60, 242—246).—The Debye–Hückel equation for the calculation of  $p_{\rm H}$  cannot be applied in highly conc. solutions of strong electrolytes; for these the empirical equations of Bjerrum or of Brönsted must be used. Most of the buffer solutions in practical use are within the limits of applicability of the Debye–Hückel equation. Even within this concn., however, the activity coeff. is different according to the concn. of the solution, particularly when the latter is largely diluted. For this reason the correct val. of a to be used in the equation differs according to the concn. of the solution. If the difference in dissociation const. between steps of dissociation in polybasic acids is not great, the calculation becomes highly complex owing to the influence of various ions on one another. Calculations are given for the following: M./15 KH<sub>2</sub>PO<sub>4</sub> + M./15 K<sub>2</sub>HPO<sub>4</sub>; 0·1M-AcOH + 0·1M-NaOAc; 0·1M-NaOH + 0·1M-K H phthalate. H. W.

Influence of solvent on relative strengths of monocarboxylic acids. J. F. J. Dippy (J.C.S., 1941, 550—552).—The results obtained by Elliott and Kilpatrick (A., 1941, I, 210) for the strengths of substituted benzoic acids give general support to the author's contention that the order of strengths is not affected by the nature of the solvent. The exceptions, e.g., salicylic and o-toluic acids, are due to the operation of special factors such as H bond formation, which may reasonably be expected to vary with the solvent. Measurements of the dissociation const. K of CHPh<sub>2</sub>·CO<sub>2</sub>H, BzOH, CH<sub>2</sub>Ph·CO<sub>2</sub>H, CHPh:CH-CO<sub>2</sub>H, Ph·[CH<sub>2</sub>]·CO<sub>2</sub>H, and EtCO<sub>2</sub>H in H<sub>2</sub>O, 25% aq. COMe<sub>2</sub>, and 20% aq. sucrose show that K decreases in the order given in all three solvents.

Relative strengths of acids and bases. E. C. Lingafelter (J. Amer. Chem. Soc., 1941, 63, 1999—2000).—The strength of an acid or base is measured by the equilibrium const. K = [neutralisation compound]/[acid][base] and varies with the reference acid used. Thus, using H',  $\text{CN}' \sim \text{NH}_3 > \text{SO}_3''$  whilst, using Ag',  $\text{CN}' > \text{SO}_3'' > \text{NH}_3$ . Further, using H', CN' > Cl' > Br' > I'; using Cu',  $\text{CN}' > \text{I}' > \text{Br}' \sim \text{Cl}'$ ; and, using Hg'', CN' > I' > Br' > Cl'. Therefore, in agreement with Lewis (A., 1938, I, 574) but contrary to Luder (Chem. Rev., 1940, 27, 547), neither acids nor bases can be arranged in a monotonic series. W. R. A.

Local dielectric constant and solute activity. Hydrationassociation model for strong electrolytes. H. S. Frank (J. Amer. Chem. Soc., 1941, 63, 1789—1799).—The Debye—Pauling expression for the effect of local dielectric const. ( $\epsilon$ ) on the electrostatic free energy of a central ion due to its ionic cloud is derived by a new method. If  $\epsilon$  is <25 and if the ions can approach each other to distances equal to the sum of their crystal radii, the Debye—Pauling expression predicts, in disagreement with experiment, large negative deviations from the Debye—Hückel limiting law for activity coeffs. even in very dil. solutions. By assuming that the ions in aq. solution are hydrated and take part in an association equilibrium agreement is obtained. The assumption is in harmony with modern views on the structure of liquids. Vals. of the correct order have been obtained for the dissociation consts. of alkali halides. W. R. A.

Thermodynamic study of bivalent metal halides in aqueous solution. II. Activity coefficients of calcium, strontium, and barium chlorides at 25°. J. R. I. Hepburn and J. E. Garside (Trans. Faraday Soc., 1941, 37, 473—476).—The paper by Robinson (A., 1940, I, 359) bearing this title contains no reference to an earlier paper by Hepburn (A., 1932, 573) in which the same ground is covered and the same general conclusions are reached. Reasons are given in favour of using the experimental data of Lovelace et al. (A., 1921, ii,

239) for aq. KCl as a basis for calculating the abs. v.p. of other solutions from results of isopiestic measurements.

Heterogeneous equilibria in the ammonia—nitrogen system at high pressure. I. Kritschevski and P. Bolschakov (Acta Physicochim. U.R.S.S., 1941, 14, 353—364).—In the system NH<sub>3</sub>-N<sub>2</sub> there is a two-phase region at temp. >90° and at pressures >1500 kg, per sq. cm. The crit. point is at 53—57 vol.-% NH<sub>3</sub>, and is 1500 kg. per sq. cm. at 90° and 5500 kg. per sq. cm. at 125°. The crit. curve, starting from the val. for pure NH<sub>3</sub>, tends towards lower temp. at first but reaches a min. at 85—90° and subsequently rises. The system shows a barotropic phenomenon; e.g., at 90° and <1800 kg. per sq. cm. the phase rich in NH<sub>3</sub> is the denser, but at >1800 kg. per sq. cm. it is the lighter. The possibility of limited mutual solubility in gases is discussed thermodynamically.

Equilibrium of co-existing liquid and gas phases in the binary system methane-ethylene. L. M. Volova (J. Phys. Chem. Russ., 1940, 14, 268—276).—Vals. are recorded for the distribution of CH<sub>4</sub> between liquid and gas phases between 127° and 253° K. Above 190° K. only mixtures containing much C<sub>2</sub>H<sub>4</sub> were examined. Hildebrand's equation for regular solutions of two substances having different mol. vols. can be applied to the system.

J. J. B.

Composition of the vapours of equimolecular mixtures. V. Kireev (Acta Physicochim. U.R.S.S., 1940, 13, 454—466).— On the assumption that the max, or min, heat of mixing of liquids occurs when approx. equimol, quantities are used, it is shown that in binary mixtures in which no electrolytic dissociation occurs and under conditions such that the vapours obey approx. the ideal laws, the mol. fraction of one compound in the vapour of an equimol, mixture follows closely the ideal law  $m'' = p_b/(p_a + p_b)$ . The variation of the vapour composition in an equimol, mixture with change in temp. is given by  $dm''/m''(1-m'') = (L_b - L_a)dT/RT^2$ , where  $L_a$  and  $L_b$  are the mol. latent heats of the components in the free state. The rules are confirmed by experimental data.

J. W. S.

Vapour pressure of solutions of fluorosilieic acid. V. S. Jatlov and E. N. Pinaevskaja (J. Appl. Chem. Russ., 1941, 14, 11—13).—The v.p. of SiF<sub>4</sub> is > that of HF over solutions of H<sub>2</sub>SiF<sub>4</sub> at temp. < the b.p., to a degree diminishing with increasing [H<sub>2</sub>SiF<sub>4</sub>]. The partial pressures of HF, SiF<sub>4</sub>, and H<sub>2</sub>O are recorded, for conens. of H<sub>2</sub>SiF<sub>4</sub> >0.23%, at 50°, 75°, and 100°.

Dissociation pressure of monocalcium orthophosphate crystal hydrate. A. M. Sorokin (J. Appl. Chem. Russ., 1941, 14, 14—18).—The v.p. P of  $H_2O$  over  $Ca(H_2PO_4)_2$ ,  $H_2O$  at  $40-90^\circ$  is expressed by  $\log P=k/\theta$ . The heat of hydration of  $Ca(H_2PO_4)_2$  is 1.824 kg.-cal. R. T.

Stratification in the ternary systems allylthiocarbimide-sulphur-amines. E. F. Shuravlev (J. Gen. Chem. Russ., 1940, 10, 1926—1938).—Regions of stratification have been determined for the systems CH<sub>2</sub>:CH·CH<sub>2</sub>·NCS-S-o-toluidine (120° and 140°), -NPhMe<sub>2</sub> (80°, 90°, 100°, 110°, and 120°), and -NHPhMe (100°, 110°, 120°, 130°, and 140°). R. T.

Ternary system toluene-m-xylene-naphthalene. V. M. Kravtschenko (J. Phys. Chem. Russ., 1940, 14, 248—252).— This system forms an eutectic at  $-104\cdot2^{\circ}$ ,  $C_{10}H_8$  2, PhMe 79, m-xylene 19 mol.-%. The position of the eutectic point can be approx. calc. assuming the solution to be ideal.

Application of the method of sections to determination of equilibria in ternary systems with solid phases. R. V. Mertzlin and I. L. Krupatkin (J. Gen. Chem. Russ., 1940, 10, 1999—2004).—n-composition curves are given for the system Pb(NO<sub>3</sub>)<sub>2</sub>-NaNO<sub>3</sub>-H<sub>2</sub>O, at 15°, and the results are treated geometrically, by the "method of sections" (Mertzlin, Bull. Res. Inst. Perm Univ., 1937, 2, 1). The compositions of the solid phases and solutions in contact with them are thus derived.

R. T.

Dehydration of molten carnallite. J. E. Vilnianski and N. P. Golubtschenko (J. Appl. Chem. Russ., 1941, 14, 39—45). —The b.p. of fused carnallite falls from 715° to 516° as the  $[H_2O]$  of the salt rises from 0·12 to 0·51%. The composition of the vapour phase over the fused salt varies according to the temp, and the  $H_2O$  content of the salt; the equilibrium coeff. is given by  $K = [HCl]^2/[MgCl_2][H_2O]$ . R. T.

Ternary systems. VII. Sodium phthalate-sodium carbonate-water. S. B. Smith and E. I. Hoegberg (J. Amer. Chem. Soc., 1941, 63, 1866—1869).—The solubility relations between Na phthalate (I), Na<sub>2</sub>CO<sub>3</sub>, and H<sub>2</sub>O have been determined at 25°, 30°, 33°, and 40°. No compound or solid solution is formed between (I) and Na<sub>2</sub>CO<sub>3</sub>. (I),7H<sub>2</sub>O and Na<sub>2</sub>CO<sub>3</sub>,10H<sub>2</sub>O, Na<sub>2</sub>CO<sub>3</sub>,7H<sub>2</sub>O, and Na<sub>2</sub>CO<sub>3</sub>,H<sub>2</sub>O have been found as solid phases and the composition of solutions at the quintuple point and the transition temp. at the quintuple point have been determined. W. R. A.

Equilibria of manganese hydroxide,  $Mn(OH)_2$ , in solutions of hydrochloric acid and sodium hydroxide. R. K. Fox, D. F. Swinchart, and A. B. Garrett (J. Amer. Chem. Soc., 1941, 63, 1779—1782).—The solubility of  $Mn(OH)_2$  in  $H_2O$ , in  $H_2O$ , and in NaOH has been determined at  $25^\circ$  and from the data it is concluded that  $Mn(OH)_2$  is a strong base reacting in acid solution  $Mn(OH)_2 + 2H' = Mn'' + 2H_2O$  (i) and in basic solution  $Mn(OH)_2 + OH' = HMnO_2' + H_2O$ . The solubility product const. from (i) is  $1.6 \times 10^{-13}$  whilst that from solubility in  $H_2O$  is  $2.8 \times 10^{-13}$ . The ion product of the acidic dissociation  $Mn(OH)_2 = H' + HMnO_2'$  is  $1 \times 10^{-13}$ . Corresponding vals. of  $\Delta G_{298}^\circ$  have been calc. W. R. A.

Sodium arsenites: system  $Na_2O-As_2O_3-H_2O$  at 35°. O. A. Nelson (J. Amer. Chem. Soc., 1941, 63, 1870—1872).—Two new Na arsenites,  $Na_2O,3As_2O_3$  and  $2Na_2O,3As_2O_3,7H_2O$ , have been revealed but the existence of  $5Na_2O,2As_2O_3,26H_2O$  has not been substantiated (cf. A., 1917, ii, 206). The behaviour of different arsenites with  $H_2O$  has been discussed. W. R. A.

Necessary and sufficient number of sections for the construction of univariant curves in ternary and quaternary systems. D. Petrov (Acta Physicochim. U.R.S.S., 1941, 14, 387—402).—It is shown by geometrical reasoning that in systems consisting of eutectics without solid solutions or compounds it is necessary and sufficient for the construction of the univariant curves to determine only three sections of a ternary, or six sections of a quaternary, system.

Application of the co-node method to the determination of univariant curves for ternary and quaternary eutectic mixtures with mixed crystals. D. A. Petrov (Acta Physicochim. U.R.S.S. 1941, 14, 497—502).—The method described in the previous abstract is extended to systems with mixed crystals.

F. L. U.

Possible errors in determination of the heat of formation of cuprous sulphide. I. A. Korschunov (J. Phys. Chem. Russ., 1940, 14, 134—136).— $\Delta H$  for the formation of  $\alpha$ -Cu<sub>2</sub>S from Cu heated in  $H_2$  and then in  $N_2$ , and rhombic S, is  $-19,300\pm500$  g,-cal. at 25°. This val. is less probable than -18,500 g,-cal. from electrochemical measurements. J. J. B.

Heat of formation of silver sulphide. A. F. Kapustinski and I. A. Korschunov (J. Phys. Chem. Russ., 1940, 14, 131—133).—Ag powder treated with  $\rm H_2$  combines with rhombic S so rapidly after being ignited with a hot wire that the heat of formation of Ag<sub>2</sub>S can be measured directly.  $\Delta H = -7560 \pm 350$  g.-cal. at 25°. J. J. B.

Standard free energies of formation of metallic sulphides from e.m.f. I. A. Makolkin (Acta Physicochim. U.R.S.S., 1940, 13, 361—368).—The e.m.f. of the cells Pt|H<sub>2</sub> (1 atm.)| KCl (0·01N.)|KCl (0·01N.)|H<sub>2</sub>S (1 atm.)|CdS or ZnS or MoS<sub>2</sub> have been measured at 25° and the following thermodynamic vals. for the formation of the sulphides are evaluated; ΔG<sub>2881°K</sub>. CdS —32,970, ZnS —46,730, and MoS<sub>2</sub> —53,960 g.-cal. per g.-mol., ΔH<sub>298.1°K</sub>. CdS —34,000, ZnS —47,860, and MoS<sub>2</sub> —55,930 g.-cal. per g.-mol., ΔS<sub>298.1°K</sub>. CdS —3455, ZnS —3790, and MoS<sub>2</sub> —6608 entropy units per g.-mol.

J. W. S. Heat of reaction of sulphur with lead and tin. I. A. Korschunov (J. Gen. Chem. Russ., 1940, 10, 2087—2090).—The heat of formation of PbS is -22·38, of SnS -18·61, of PbMg<sub>2</sub> -42·0, and of SnMg<sub>2</sub> -48·0 kg.-cal. per g.-mol.

Partial pressure of hydrogen bromide over its solution in benzene and heat of dissolution of hydrogen bromide in benzene. A. F. Kapustinski and V. A. Maltzev (J. Phys. Chem. Russ., 1940, 14, 105—109).—The v.p. of HBr rises linearly with its molarity: at 30° from 0.01003 to 0.7455 atm. for 0.000612m. to 0.04713m., and at 50° from 0.1667 to 0.8325 atm. for 0.00686 to 0.03418m. These results agree

neither with Raoult's law nor with Hildebrand's rule. For the heat of dissolution 4197 g,-cal. per mol. is calc.

Thermodynamics of the manganese ion. Entropy of aqueous ions. A. F. Kapustinski (Acta Physicochim. U.R.S.S., 1941, 14, 503—522).—The heat of dissolution of cryst. MnCO<sub>3</sub> in Im-HCl to give 0.05m-MnCl<sub>2</sub>, and the heat of dilution of Im- to 0.05m-MnCl<sub>2</sub>, were measured at 20°, giving  $\Delta H_{298} = -3.68 \pm 3.5\%$  kg.-cal. for the reaction MnCO<sub>3</sub> (cryst.) + 2HCl (1m.) = MnCl<sub>2</sub> (1m.) + CO<sub>2</sub> (gas) + H<sub>2</sub>O (liquid). This result, combined with known vals. of other necessary quantities, leads to  $\Delta H = -207.8 \pm 1\%$  cal. for Mn (cryst.) + C (graphite) + 1.5O<sub>2</sub> (gas) = MnCO<sub>3</sub> (cryst.), and  $\Delta H = -49.13$  cal. for Mn (cryst.) = Mn'' (1m.). The entropy of the hydrated Mn ion at 298·1° κ. is calc. to be 19·1±0·6 units. Theoretical considerations about aq. ions in general lead to the conclusions (a) that the entropy of ions of equal dimensions is a linear function of the ionic charges, and (b) that the entropy of ions of equal valency is a linear function of the reciprocal of the ionic radius. These rules are applied to calculate the entropies of other ions for which the radii are known.

#### VII.—ELECTROCHEMISTRY.

Dispersion of current in solutions. N. A. Schpigel (J. Gen. Chem. Russ., 1940, 10, 2077—2086).—In general, for dil. solutions, increase in conductivity  $d\kappa$  with increasing vol V of solution may be expressed by the formula  $d\kappa/\kappa = (\phi - 1)/(a + b\phi)$ , where  $\phi = V/V_0$ , and a and b are consts. Scattering of current in conc. solutions is < in dil. ones. R. T.

Antimony electrode. F. Hovorka and G. H. Chapman (J. Amer. Chem. Soc., 1941, 63, 2024).—Correction (cf. A., 1941, I, 268). W. R. A.

Metastability of cadmium sulphate and its effect on the e.m.f. of saturated standard cells. G. W. Vinal and L. H. Brickwedde (J. Res. Nat. Bur. Stand., 1941, 26, 455—465).—Solubility and e.m.f. measurements indicate that the transition point between 3CdSO<sub>4</sub>,8H<sub>2</sub>O (I) and CdSO<sub>4</sub>,H<sub>2</sub>O (II) is 43·4°. The solubility of (I) increases, and that of (II) decreases, with rise of temp. The temp. coeff. of the Cd amalgam|(I) electrode is negative, and that of the Cd amalgam|(II) electrode is positive. Both forms tend to persist in a metastable state. The thermodynamics of the interchange are discussed:

Derivation of expressions for the e.m.f. of concentration cells from the principle of the Donnan membrane equilibrium. S. G. Chaudhury (J. Proc. Inst. Chem. India, 1941, 13, 62—80).

—By applying the Donnan principle and Boltzmann's distribution law to the liquids (double layer plus bulk solution) surrounding two reversible electrodes, equations identical with those generally used are derived for the e.m.f. of concn. cells with transference.

F. L. U.

Decomposition potentials of salts in liquid ammonia. A. Murtazaev and I. Abljaev (J. Phys. Chem. Russ., 1940, 14, 69—72).—Decomp. potentials in NH<sub>3</sub> at 0° for N. solutions are: NaNO<sub>3</sub> 2·52, KI 2·87, KBr 2·43, NH<sub>4</sub>NO<sub>3</sub> 1·34, NH<sub>4</sub>Cl 1·07, and NH<sub>4</sub>Br 0·92 v. They are > in H<sub>2</sub>O for Na and K salts, and < in H<sub>2</sub>O for NH<sub>4</sub> salts, since NH<sub>4</sub> salts in NH<sub>3</sub> are acids:

J. J. B.

Photogalvanic processes on a silver electrode. V. I. Veselovski (Acta Physicochim. U.R.S.S., 1941, 14, 483—496).—Ag covered with Ag<sub>2</sub>O, when immersed in dil. alkali and illuminated, acquires a stable negative potential with respect to that of a similar electrode in the dark. The max. effect is in the red region and is attained in a fraction of a sec. The relations between the effective (measured) and true vals. of the e.m.f. and the max. current are established, and the latter is obtained as the product of the estimated capacity, 640  $\mu\text{F}$ . per sq. cm., and the rate of change of potential (from oscillograms) near the beginning of the charging process; with the illumination used and the electrode in 0·1n-NaOH  $I_{\text{max}} = 25.6~\mu\text{a}$ . per sq. cm. of apparent surface. Measurements of the true photogalvanic current for different times of anodic polarisation, with an electrode illuminated by monochromatic light of const. intensity, indicate a quantum yield approaching 1 for sufficiently large positive vals. of the potential. F. L. U.

Polarisation during the electrolytic reduction of titanium ions. O. Essin (Acta Physicochim. U.R.S.S., 1940, 13, 429—442).—When solutions of low [TiV] are electrolysed using flowing Hg electrodes, the anodic polarisation increases steadily at first with increasing current, and then increases slowly as the current approaches its saturation val. The cathodic polarisation curve, however, shows two distinct branches attributed to the transitions  $\text{Ti}^{\text{IV}} \rightarrow \text{Ti}^{\text{III}}$  and  $\text{Ti}^{\text{III}} \rightarrow \text{Ti}^{\text{II}}$ , respectively. It is shown that both processes are accompanied by slow discharge complicated by an inadequate rate of diffusion of ions and retarded dissociation, particularly of complex  $\text{Ti}^{\text{IV}}$  ions. It is suggested that the existence of an electrolytic saturation current influences the form of the voltage–current curve for the reduction of Ti, but its calc. magnitude is > the saturation c.d. observed.

Polarisation capacity of a smooth gold electrode. G. Deborin and B. Erschler (Acta Physicochim. U.R.S.S., 1940, 13, 347—360).—By the capacity method (cf. A., 1938, I, 624) it has been shown that after Au has been heated in air at 900° ~4 at. layers of O<sub>2</sub> are bound on its surface. The cathodic potential required to remove this layer in acid solutions is > in basic solutions. Charging curves for a smooth Au electrode in N-H<sub>2</sub>SO<sub>4</sub>, -HCl, and -KOH have been obtained. Preliminary oxidation of the Au causes distortion of the shape of the charging curves, attributed to firmly bound O<sub>2</sub>, which appears not to be removed on subsequent cathodic polarisation of the electrode up to the reversible H potential. During anodic polarisation of a Au electrode which has been cleaned from the firmly bound O<sub>2</sub> 0.5—1 at. layer of O is taken up. This O is less easily deposited and more easily removed in bases than in acids.

J. W. S.

Hydrogen overvoltage at high current densities. V. Decay of hydrogen overvoltage. A. Hickling and F. W. Salt (Trans. Faraday Soc., 1941, 37, 450—462).—An improved interruptor circuit is described which permits observation of the decay of overvoltage ( $\eta$ ) from a min. time of  $5 \times 10^{-5}$  sec. Measurements with cathodes of 18 different materials show the occurrence of two distinct processes, one of which, operative at c.d. >10<sup>-3</sup> amp. per sq. cm., leads to a rapid fall of potential in  $10^{-3}$  sec., and depends mainly on the magnitude of the polarising c.d. The other process, operative at all c.d. vals., results in a slower decay of  $\eta$  which, after a time that decreases with increase of the polarising c.d., becomes  $\alpha$  log time; the rate of decay then depends only on the electrode material. None of the theories of overvoltage so far proposed is capable of explaining the observations.

Overvoltage of hydrogen on nickel in acid solutions. A. Legran and S. Levina  $(J.\ Phys.\ Chem.\ Russ.,\ 1940,\ 14,\ 211—216).$ —Overvoltage  $(\eta)$  is independent of c.d. (i) when i is  $<10^{-6}$  amp. per sq. cm. At higher c.d.  $\eta=a+b\log i$ ; b is 0.093 in dil, solutions and rises to 0.103 in conc. solutions. The vals. of  $\eta$  are identical in HCl, HBr, and H<sub>2</sub>SO<sub>4</sub>; they increase with dilution between 0.01N. and 1N. and are independent of it at lower concns. La salts slightly reduce  $\eta$  at low i vals. and mostly raise it slightly at higher i. At higher i the overvoltage is due to a retardation of H discharge but its mechanism at low i is obscure.

Use of dropping mercury electrode for measuring overvoltage. Z. A. Iofa and A. N. Kolitschev (J. Phys. Chem. Russ., 1940, 14, 58—68).—For the coeff. b in the equation  $b = d\eta/d \log i$ ,  $\eta$  being the overvoltage and i the c.d., different vals. were obtained when using stationary and dropping electrodes (cf. Heyrovsky, A., 1937, I, 525). This discrepancy disappears if (a) the variation of the surface tension and, therefore, of the drop vol. with the applied potential is considered; this correction eliminates the apparent rise of b at high vals. of i; (b) the current used up for charging the growing drop is subtracted from the observed i; this correction eliminates the abnormally low vals. of b at low b; and b0 is referred to the average surface area of the drop which fluctuates between a very small and a max. val. b1 = 4·6 B1/B1 for both stationary and dropping electrodes. The experiments were carried out in 0·01—6·5n-HCl and in 1—5·5n-HBr.

J. J. B.

Corrosion of lead in an oxidising medium. E. V. Krivolapova and B. N. Kabanov (J. Phys. Chem. Russ., 1940, 14,
279).—The polarisation of Pb in 7n-H<sub>2</sub>SO<sub>4</sub> at 0·2 ma. per sq. cm.
and its depolarisation in 1n-Na<sub>2</sub>SO<sub>4</sub> at 20 ma. per sq. cm. are
studied by potential measurements. In addition to potentials

corresponding with the reactions  $PbO_2 \rightarrow PbSO_4$  and  $PbSO_4 \rightarrow Pb$  another potential is noticed which is presumably due to decomp. of a compound between  $PbO_2$  and  $PbSO_4$ . Stearic acid and HCl strongly increase the anodic corrosion of Pb; octoic acid, palmitic acid, AcOH, and NiSO<sub>4</sub> are less effective. 0·1%  $CoSO_4$  lowers the corrosion by 50% and increases the life of accumulators.

J. J. B.

Electrochemical properties of mineral membranes. I. Estimation of potassium ion activities. C. E. Marshall and W. E. Bergman (J. Amer. Chem. Soc., 1941, 63, 1911—1916).

—The electrochemical behaviour of apophyllite (I) and montmorillonite (II) membranes to K' ions has been investigated. (I) proved unsuitable, but with membranes of (II), particularly if dried at >200°, reproducible results were obtained. The effect of the anion on the determination of K' ion activities has been investigated and membrane potentials in the presence of bivalent cations have been measured. At <0·1N. K' ion activities can be determined within 5%.

W. R. A.

#### VIII.—REACTIONS.

Mechanism of two-stage ignition. D. A. Frank-Kamenetzki (J. Phys. Chem. Russ., 1940, 14, 30—35).—Reactions the rate of which increases to ignition, decreases, and then rises to a second ignition (cf. Belov and Neumann, A., 1938, I, 256) can take place if  $dx/dt = k_1ax - k_2xy$  and  $dy/dt = k_2xy - k_3ay$ , a, x, and y being the concus. respectively of the combustible substance A, of an intermediate product X formed from A, and of another intermediate product Y originating from X. In combustion of hydrocarbons the product X is probably a per-acid, and Y an aldehyde.

J. J. B.

Carbon monoxide—oxygen flame. VII. The OH radical in the flame of moist carbon monoxide. E. Kondrateeva and V. Kondrateev (J. Phys. Chem. Russ., 1940, 14, 1—5).—A mixture of CO 15.5, O<sub>2</sub> 15.5, and H<sub>2</sub>O 0.5 mm. Hg was passed through a quartz tube at 690°. The selective absorption of the radiation 3064 A. showed that the pressure of OH was 0.004 mm. This concn. is 100 times the equilibrium [OH] at the temp. of the flame (810°). OH is produced in a chemical reaction and consumed by oxidation of CO.

Ignition temperatures of acetylene-air and acetylene-oxygen mixtures. G. W. Jones and W. E. Miller (U.S. Bur. Mines, 1941, Rept. Invest. 3567, 5 pp.).—Data on the ignition temp. of air- $C_2H_2$  mixtures over a wide range of composition, and also of  $O_2$ - $C_2H_2$  mixtures having a high % of  $C_2H_2$ , are given. The ignition temp. of air- $C_2H_2$  mixtures depends markedly on the composition, decreasing rapidly as the % of  $C_2H_2$  increases up to  $\sim 30\%$ , when it becomes const. at  $\sim 305^\circ$ .

F. J. G.

Dependence of the induction period of acetaldehyde cool flame on the composition of the mixture. N. P. Keyer and M. B. Neumann (Acta Physicochim. U.R.S.S., 1941, 14, 451—462).—The cool flame induction period  $\tau$  is related to the composition of the mixture by  $\tau = (h_1[O_2]^2 + h_2)/k_3[\text{MeCHO}]^2[O_2]^2$ . This expression is deducible from the authors' theory of the mechanism of the reaction (cf. A., 1941, I, 340) and its correctness is established by experiments over the temp. range  $231-265^\circ$ . The oxidation of MeCHO is an example of a chain reaction with degenerate branching which occurs on triple collisions between  $AcO_2H$  mols. and those of MeCHO and  $O_2$ .

Cold and hot flame of ethyl ether. K. I. Ermakova (J. Phys. Chem. Russ., 1940, 14, 148—156).—The pressure in  $\rm Et_2O$ —air and  $\rm Et_2O$ —02 mixtures varies in the course of their slow combustion in six different ways according to temp. and concn. of the mixtures. The boundaries of the six regions are determined; for the mixture  $\rm Et_2O + O_2$  the regions of cold flame are confined between 10 and 140 mm. Hg and between 170° and 320°. In one of the regions the induction period of ignition can be measured; it decreases when pressure and temp. increase.

J. J. B.

Explosive properties of nitrogen trichloride. A. J. Apin (Acta Physicochim. U.R.S.S., 1940, 13, 405—422).—In the absence of air NCl<sub>3</sub> undergoes spontaneous decomp. with the emission of light at all pressures < a definite upper limit (40, 70, and 115 mm. at 20°, 40°, and 60°, respectively). The decomp. is propagated by local explosions. The ignition is accelerated by an unstable active intermediate compound,

some of which remains in the vessel after decomp. is apparently complete. Liquid  $NCl_3$  in fused glass bulbs heated at 60° explodes after an average time of 13 sec., but at 55° no explosion occurs. Dilution with the decomp. products raises the temp. of the explosion. Below the explosion temp. liquid  $NCl_3$  decomposes slowly. The mechanism of the explosion of  $NCl_3$  and of  $NH_3,NI_3$  is discussed. J. W. S.

Combustion of nitroglycol. A. F. Belaiev (Acta Physicochim. U.R.S.S., 1941, 14, 523—546).—Experiments with (CH₂·O·NO₂)₂ are described in support of the author's theory of explosions (cf. B., 1939, 554, 781). The calc. temp. of combustion is 1350°. The relations between rate of combustion and the kinetic consts. of the reaction, calc. with the equations of Zeldovitsch and Frank-Kamenetzki (A., 1938, I, 625), are in accord with observation. F. L. U.

Quantitative studies of the oxidation of fatty acids by hydrogen peroxide.—See A., 1941, I, 278.

Kinetics of the polymerisation of  $\Delta^{\alpha\gamma}$ -butadiene in presence of potassium phenylisopropyl. O. Mamontova, A. Abkin, and S. Medvedev (J. Phys. Chem. Russ., 1940, 14, 36—48).—The rate of polymerisation was determined from the reduction of vol. of gaseous (CH<sub>2</sub>:CH)<sub>2</sub> (I) over a solution of K·C<sub>6</sub>H<sub>4</sub>Pr<sup>\beta</sup> (II) in Et<sub>2</sub>O, the pressure \(p\) of (I) being kept const. When \(p\) increased (between 540 and 620 mm. Hg), the rate increased at first slowly, then rapidly, and then again slowly; the highest rate at 25° was about 6 c.c. of gas per min. and per c.c. of solution. The effect of the concn. of (II) (between 10<sup>-3</sup> and 6 × 10<sup>-2</sup>N.) was indefinite. An increase of the surface area of glass in contact with solution raised the rate but < proportionately to the area. From measurements at 5°, 15°, and 25° the activation energy was calc. to be 7600 g.-cal. The reaction chains probably started at the surface, grew in the bulk of solution, and broke down both at the surface and in the bulk. Saturated solutions of (I) in Et<sub>2</sub>O are 0.3M, and 0.73M, at  $p_{25} = 572$  and 637 mm. Hg respectively.

Chemical warfare materials. XXIII. Hydrolysis of  $\beta\beta'$ -dichlorodiethyl sulphide. H. Mohler and J. Hartnagel (Helv. Chim. Acta, 1941, 24, 564—570).—The velocity of hydrolysis of (Cl·[CH<sub>2</sub>]<sub>2</sub>)<sub>2</sub>S by H<sub>2</sub>O is independent of  $p_{\rm H}$ , and is greatly diminished in aq. alcohols, confirming the view that the measured rate is that of ionisation of the Cl. The energy of activation is  $\sim$ 17.5 kg.-cal. The rate is not appreciably affected by the presence of metallic salts. F. J. G.

Exchange reaction between gaseous and combined nitrogen. Y. Nishina, T. Iimori, H. Kubo, and H. Nakayama (J. Chem. Physics, 1941, 9, 571—572).—By leaving radioactive <sup>13</sup>N<sub>2</sub>, prepared by bombarding amorphous C with deuterons from a cyclotron, in contact with 0·025—0·1M. solutions of NaNO<sub>2</sub>, NaNO<sub>3</sub>, NH<sub>2</sub>OH,HCl, NH<sub>4</sub>Cl, KCN, N<sub>2</sub>H<sub>4</sub>,H<sub>2</sub>SO<sub>4</sub>, Na<sub>3</sub>Co(NO<sub>2</sub>)<sub>6</sub>, 8-hydroxyquinoline acetate, and CO(NH<sub>2</sub>)<sub>2</sub> and, after removing the gas, pptg. the N from solution, it has been shown that interchange occurs between the N<sub>2</sub> and N compound. With NaNO<sub>2</sub> the rate of interchange decreases with increasing [NaNO<sub>2</sub>] and becomes undetectable in 2M. solution.

J. W. S. Halogenation of phenolic ethers and anilides.—See A., 1941, II, 287.

Oxidation with molecular oxygen. III. Kinetics of the autoxidation of protected blue cobalt hydroxide. W. Feitknecht [with W. Bédert] (Helv. Chim. Acta, 1941, 24, 694—702).—The kinetics of the oxidation by  $O_2$  of blue  $Co(OH)_a$ , stabilised by glucose, have been studied. At const.  $p_{O_1}$  the course of reaction is represented by  $dx/dt = k(a-x)^{2+6}$ . The curves of k against  $p_{O_2}$  resemble adsorption isotherms. The temp. coeff. is small, corresponding with an apparent activation energy of 9 kg.-cal. It is concluded that the reaction depends on activation of  $O_2$  by adsorption.

Oxidation of isomeric ketones by selenium dioxide.—See A., 1941, II, 281.

Oxidation of substituted acetophenones with selenium dioxide.—See A., 1941, II, 323.

Velocity of high-temperature reactions. I. Kinetics of reduction of magnesium oxide by various reagents. A. S. Mikulinski. II. Reduction of phosphorites. A. S. Mikulinski and F. S. Maron (*J. Appl. Chem. Russ.*, 1941, 14, 19—29, 30—38).—I. The temp. of initiation, θ, of the reaction between MgO and various reducing agents varies parallel with pres-

sure. In high vac. (<1 mm.) the vals. of  $\theta$  are: C 1380°, CaC<sub>2</sub> 1290°, Al 1200°, Fe-Al 1210°, Fe-S 1330°. II. The velocity of the reaction Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> + 3SiO<sub>2</sub> + 5C  $\rightarrow$  $3\text{CaSiO}_3 + \text{P}_2 + 5\text{CO}$  is inversely of diameter of the granules of substrates. The reaction is completed in 17 min. at 1400-1450° when the granule diameter is 2-3 mm., and in 120 min. when this is 7-14 mm.

Kinetics of dissociation of pyrites. V. S. Udintzeva and G. I. Tschufarov (f. Appl. Chem. Russ., 1941, 14, 3—10).— The velocity of the reaction  $FeS_2 \rightleftharpoons FeS + S$  is, within certain limits,  $\infty$  temp., and inversely  $\infty$  diameter of the granules and to the pressure. No induction period could be detected. The rate of advance of the reacting surface within each The rate of advance of the reacting surface within the granule is const. until ~70% of the mass has reacted. At 525° the rate of decomp. of mono-crystal is 300 times < of R. T.

Mechanism of catalytic reactions of halogens and their derivatives. I. Kinetics of the catalytic displacement of hydrogen in benzene. N. E. Breshneva and S. Z. Roginski (J. Phys. Chem. Russ., 1940, 14, 49-57).—The initial rate of consumption of Br in a solution of Br and ZnBr, in C6H6 or in  $C_0H_6$ —Et<sub>2</sub>O at 60°  $\propto$  [ZnBr<sub>2</sub>][ $C_6H_6$ ][Br<sub>2</sub>], when [ZnBr<sub>2</sub>] varies from 1 to 30 g., [Br] from 3 to 18 g., and [ $C_6H_6$ ] from 25 to 100 c.c. per 100 c.c. of solvent. In later stages the apparent reaction coeff. decreases. This decrease is due to an inhibition by PhBr; in a mixture of C<sub>6</sub>H<sub>6</sub> 15, PhBr 85 the reaction is 15—150 times as slow as in a mixture of C<sub>6</sub>H<sub>6</sub> 15, amyl ether 85 and is strictly unimol. After correction for the effect of PhBr 45 strictly unimol. rection for the effect of PhBr the reaction coeff. is  $1.5 \times 10^{-2}$ ,  $6\times10^{-4},$  and  $3\cdot3\times10^{-4}$  at 80°, 60°, and 40°, respectively; the activation energy is 8000 g.-cal. The inhibiting effect of PhBr is probably due to formation of a complex with ZnBr<sub>2</sub>.

Oxidation with molecular oxygen. I. W. Feitknecht (Helv. Chim. Acta, 1941, 24, 670—675).—Oxidation by mol. O2 (autoxidation) is discussed and a no. of theories are summarised and compared. It is suggested that in the oxidation of a solid phase, or of a dissolved substance in presence of a solid catalyst, the first stage is activation of O2 by adsorption. For testing this theory, instances in which the oxidation of a a solid proceeds without a change of phase, i.e., through a continuous series of solid solutions, are particularly suitable. Examples of this kind are the first stages of the oxidation of the green basic Co salts and of blue Co(OH)2.

Order of reactions of hydrogenation and dehydrogenation. M. A. Grechnev and I. G. Eroschevski (J. Gen. Chem. Russ., 1940, 10, 2005—2013).—Reactions of hydrogenation or dehydrogenation in presence of excess of catalyst may be of the first, second, or third order. If only a small proportion of substrate is in contact with the active centres of the catalyst at any given moment, or if the reaction is a slow one, it will be apparently of zero order. If the reaction at these centres is very fast, it will be of the first order. These considerations are illustrated by the reactions of dehydrogenation of borneol and isoborneol at a C-Cu catalyst.

Velocity of decomposition of hydrocarbons during destructive hydrogenation. I. Naphthalene, tetra- and deca-hydronaphthalene, and dodecane. A. V. Lozovoi and S. A. Senjavin (J. Appl. Chem. Russ., 1941, 14, 96—109).—The hydrocarbons were hydrogenated at 360—475°/180—220 atm. (MoS<sub>2</sub> catlyst). The velocities of hydrogenation were, taking that of tetrahydrogenathylana (T) as a latter of the company of the compa tetrahydronaphthalene (I) as  $1: n\text{-}C_{12}H_{26}$  56·8, decahydronaphthalene 2·2,  $C_{10}H_8$  0·27. Hydrogenation of  $C_{10}H_8$  involves the reactions  $C_{10}H_8 \rightarrow$  (I) (rapid reaction)  $\rightarrow$  PhBu (slow)  $\rightarrow$  PhMe and PhEt (rapid)  $\rightarrow$   $C_6H_6$ . R. T.

Kinetics of the para-ortho transformation of hydrogen on charcoal. R. Burschtein (J. Phys. Chem. Russ., 1940, 14, 157–160).—The half-val. time of the p-o-transition of H<sub>2</sub> at 90° k. in presence of well (950°) degassed charcoal & the amount of H<sub>2</sub>. When charcoal after being degassed at 950° was allowed to adsorb at 500° 0.2 c.c. of H<sub>2</sub> per g., the half-val time becomes executed to receive the property of the property val. time became, except at pressures <4 mm. Hg, independent of the amount of H<sub>2</sub> and  $\gg$  that on pure charcoal. The H<sub>2</sub> adsorbed at 500° poisoned the active centres of charcoal; on the remaining surface the reaction was of the first instead J. J. B. of zero order.

[Catalytic] synthesis of benzene hydrocarbons from methane. —See B., 1941, II, 325.

Activation of ammonia synthesis by means of alkali ions.— See B., 1941, I, 443.

Catalytic vapour-phase oxidation of aliphatic kerosene fractions.—See B., 1941, I, 435.

Electrolytic replacement of sodium by ammonium in glass. -See B., 1941, I, 450.

Lead oxides. III. Radioactive indicator method applied to the lead storage cell.—See B., 1941, I, 419.

Formation of nitrogen oxides in a torch discharge of an ultrahigh frequency. P. A. Serebriakov (J. Phys. Chem. Russ., 1940, 14, 175-179).-A torch discharge occurs when a highfrequency current (~10° cycles) passes through a needle electrode in air at atm. pressure. The min. voltage required for lighting is 1000-1500 v.; then the torch burns also at 600-800 v. The vol. of the torch  $\propto$  the no. of watts supplied, and the density of its energy is independent of the power W. When torch discharge takes place in streaming air, NO is produced. [NO] in the outgoing gas increases with W (30—140 w.) and decreases when the rate v of flow (9—250 l. per hr.) increases; [NO] as a function of W/v(i.e., of the energy spent per unit vol. of air) is independent of W. At low v it becomes also independent of v; its val. then is 3%. The yield of NO is at 750—1100 mm. Hg > at 250-600 mm. The highest yield observed was 63 g. of J. J. B. HNO, per kw.-hr.

Photosensitisation by solids. II. Photosensitised oxidation of ammonia in aqueous solution with titania as the photosensitiser. G. Gopalarao and K. S. Murty (J. Indian Chem. Soc., 1941, 18, 127—137).—NH<sub>3</sub> in aq. solution is oxidised on exposure to visible light in presence of TiO2. The reaction is of zero order, and with increasing amount of TiO2 its rate at first increases linearly and then tends to reach a max. The rate increases with increasing pH in the range 7.5-9.6, and is diminished by addition of electrolytes, the effect increasing in the order NaCl, BaCl<sub>2</sub>, AlCl<sub>3</sub>. NH<sub>3</sub> oxidation is rapid in light of  $\lambda$  4050 A., but slow in light of longer  $\lambda$ . The mechanism of the reaction is discussed. It probably involves activation of adsorbed NH<sub>3</sub> by an excited Ti<sup>\*\*\*</sup> ion in the surface. F. J. G.

Photochemical primary process of ions in aqueous solutions. J. Weiss (Trans. Faraday Soc., 1941, 37, 463—469).—The primary process in the case of I', HS', and RS' can be represented generally by X', $H_2O + h\nu = X + H + OH'$ , and the observed effects of irradiating solutions of these ions under various conditions are adequately explained by taking into account secondary chemical processes. The energy required for these reactions, and for those of Fe", Cr", Ce", and Co", are calc. from the corresponding oxidation-reduction potentials. The thermal formation of H<sub>2</sub> from Fe<sup>II</sup> solutions and of O2 from Com solutions is discussed.

Efficiency in the primary photochemical process in solution. K. Atwood and G. K. Rollefson (J. Chem. Physics, 1941, 9, 506—512).—The quantum yield (n) in the photochemical decomp. of  $(COBr)_2$  in  $CCl_4$  solution at 2650 A. is  $\sim 0.9$ , approx. the same as in the gas phase, but it decreases with increasing  $\lambda$ , particularly between 3130 and 3650 A., and becomes  $\sim 0.3$  at 4358 A. In the decomp. of NOCl in CCl in presence of  $O_2$  to prevent the back reaction n varies from 0.7 at 3650 a. to 0.5 at 5790 a., as compared with  $\sim\!\!2$  for all  $\lambda\lambda$  in the gas phase. The results are discussed with reference to the Franck-Rabinovitsch hypothesis and it is suggested that the lower vals. of n for the solutions are more probably due to deactivation by the solvent than to high efficiency of recombination. The equilibrium const. of the reaction  $N_2O_4 \rightleftharpoons 2NO_2$  in CCl<sub>4</sub> solution at 25° is  $6.4 \times 10^{-5}$  (concns. in mol. fractions). J. W. S.

Application of electron microscope to the study of photographic phenomena. C. E. Hall and A. L. Schoen (J. Opt. Soc. Amer., 1941, 31, 281—285).—Photographic emulsions have been examined by means of an electron microscope of resolving power <50 A. Ag halide crystals exposed to the electron beam are at first opaque but on continued exposure develop holes and cracks due to migration of Ag; a stable state is finally reached. Ag crystals remain after treatment with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. Latent image particles produced by exposure to light have not been identified. Developed Ag shows a filamentary structure; the length and thickness of the filaments depend on the developer. Physical development and  $p\text{-}\mathrm{C_6H_4(NH_2)_2}$  produce massive clumps of Ag. Lippmann emulsions produce on development a long single filament from each particle. L. J. J.

Rebromination theory of photographic solarisation. J. H. Webb and C. H. Evans (J. Opt. Soc. Amer., 1940, 30, 445—454).—The effect on the density-log exposure curves of three emulsions of exposure temp. from 58° to -196° has been investigated. With decreasing temp. the max. density val. decreases and below -73° the position of the max. shifts to longer exposures. At temp. <-100° the max. density val. increases and solarisation decreases until at -196° it disappears. Introduction of Br acceptors into the emulsion causes decrease in solarisation. Removal of AgBr from the film after exposure by immersion in dil. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> decreases solarisation but on long immersion causes a decrease in max. density. The position of the max. in the solarisation curve is the same for chemical and physical development. With reduced intensity of illumination greater total exposures, exposure time × intensity, are required to produce solarisation. These facts are interpreted as supporting the rebromination theory of solarisation.

Optical sensitisation of photographic emulsions. I. Rôle of adsorption in optical sensitisation. J. N. Gorochovski, A. A. Kriukov, and V. I. Fedotova. II. Spectral properties of emulsions consisting of various silver halides. J. N. Gorochovski, A. J. Smirnov, and V. I. Fedotova (J. Phys. Chem. Russ., 1940, 14, 180—187, 188—194).—I. From the variation of the e.m.f. of cells Agldye solution saturated KCl] Hg<sub>2</sub>Cl<sub>2</sub>|Hg on addition of AgNO<sub>3</sub> to the dye solution it is concluded that erythrosin (I) forms a compound with Ag, pinaverdol iodide (II) ppts. AgI, and pinaflavol iodide and cryptocyanin iodide (III) first ppt. AgI and then affect AgNO<sub>3</sub> otherwise (? reduction). Adsorption of (I) by AgBr is lessened the more markedly by KBr the higher is [KBr] and adsorption of (II) and (III) is increased by KBr and reduced by AgNO<sub>3</sub>. Adsorption of pinacyanol (IV) is min. in absence of both KBr and AgNO<sub>3</sub>. Sensitisation is defined as the ratio of the photosensitivity in the point of max. sensitisation to the max. sensitivity of Ag halide emulsion; this ratio is strongly lowered by KBr for (I), but is almost independent of [KBr] up to 10<sup>-3</sup>M. for (II), (III), and (IV). There is a similarity between the effect of KBr on adsorption of, and on sensitisation by, (I); this similarity is masked for (II), (III), and (IV) by their colloidal nature.

II. Sensitivity of emulsions of AgCl, AgBr, AgI, and their mixtures is determined for the region >400 mμ. Mixtures

II. Sensitivity of emulsions of AgCl, AgBr, AgI, and their mixtures is determined for the region >400 mμ. Mixtures of AgBr and AgI are more sensitive to long waves (>450 mμ.) than AgBr emulsions, especially if AgBr and AgI are pptd. together as distinct from being mixed after pptn. Sensitisation by (I), (III), and (IV) is equally strong for AgBr and AgBr 50, AgCl 50, but is reduced several times if the emulsion contains AgI.

J. J. B.

Mechanism of the regeneration of dye in the course of the sensitised photolysis of silver halide. S. V. Natanson and G. L. Natanson (J. Phys. Chem. Russ., 1940, 14, 278).—In absence of O<sub>2</sub> suspensions of Ag erythrosinate are decomposed by light giving Ag and decomp. products of erythrosin (I). If NaNO<sub>2</sub>, gelatin, or some other substances are added to the suspension, Ag is pptd. in light but (I) is not destroyed. It is suggested that (I) gives up an electron to Ag' and then, if substances capable of giving electrons are present, obtains one from these.

J. J. B.

Photochemistry of fluorescein dyes. G. L. Natanson (J. Phys. Chem. Russ., 1940, 14, 16—29).—Uranin (I), eosin (II), and erythrosin (III) in air-free aq. solution are transformed by the visible light of a 2-kw. lamp into coloured products having absorption max. at 495 mμ. (I), 515 mμ. (II), and 520 mμ. (III). At 20° the transformation of (II) takes 10—100 hr. During the transformation the absorption spectrum changes in a complicated manner showing that > two reaction products are formed. The solution contains Br' [from (II)] or I' [from (III)]. 10-3—10-1ν-NaOH reduces the transformation time of (II) to 1—10 hr.; the spectrum of the product has a max. at 500 mμ. Air increases the bleaching time in presence of NaOH and prevents formation of coloured products; the absorption of aq. solutions of (II) is lowered to the same extent along the whole spectrum. In this case the quantum yield is 1.5 × 10-4. In presence of 0.2M-Na<sub>2</sub>SO<sub>3</sub> (II) gives another dye. In presence of 0.3m-KI

(II) is not affected by visible light. Dry films of (II) are bleached by visible light rapidly when the air is dry  $(P_2O_5)$ , slowly in moist air, not at all in vac. or in air-free  $H_2O$  vapour; hence  $H_2O_2$  is not required for bleaching. No coloured compounds are formed when (II) is irradiated in COMe<sub>2</sub>, EtOH, or  $C_5H_5N$ .

I. J. B.

#### IX.-METHODS OF PREPARATION.

Salts of alkaloids with bromo-complexes of some heavy metals.—See A., 1941, II, 306.

Decomposition of alkali, calcium, and magnesium carbonates.—See B., 1941, III, 265.

Metallic contamination of hot water from cylinders of bare and tinned copper.—See B., 1941, I, 418.

Chlorination of barium sulphide solutions. V. M. Grinevitsch (J. Appl. Chem. Russ., 1941, 14, 63—67).—The sole products of chlorination of aq. BaS at 95—100°, using pure  $Cl_2$  or air– $Cl_2$  mixtures, are  $BaCl_2$  and S. Further chlorination of the reaction mixture leads to production of  $BaSO_4$ , by the reaction  $BaCl_2 + S + 3Cl_2 + 4H_2O \rightarrow BaSO_4 + 8HCl$ . Chlorination of aq.  $Ba(SH)_2$  involves the reaction  $Ba(SH)_2 + Cl_2 \rightarrow BaCl_2 + H_2S + S$ . The solubility of  $Ba(SH)_2$  is > that of BaS, so that the final max. concn. of  $BaCl_2$  attainable from aq.  $Ba(SH)_2$  is > that from BaS. R. T.

Certain properties of barium thiosulphate, in connexion with its use for analytical purposes. G. P. Lutschinski and V. S. Suzdaleva (J. Gen. Chem. Russ., 1940, 10, 2047—2051).

—The solubility of BaS<sub>2</sub>O<sub>3</sub> rises linearly from 0·194% at 10° to 0·399% at 60°. It falls asymptotically with increasing [EtOH] of the solution, being 2% of the val. in H<sub>2</sub>O in the case of 50% EtOH. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> forms an insol. 1:1 salt with BaS<sub>2</sub>O<sub>3</sub>.

R. T.

Reaction between sulphur dioxide and oxides of nitrogen. II. Reaction in sulphuryl chloride solution. C. B. Medinski (J. Gen. Chem. Russ., 1940, 10, 1950—1952; cf. A., 1939, I, 274).—SO<sub>2</sub> does not react with NO<sub>2</sub>-NO in SO<sub>2</sub>Cl<sub>2</sub> except in presence of H<sub>2</sub>O.

R. T.

Preparation of crystalline chromic anhydride from calcium chromate. I. G. Riss, A. E. Zajarni, and A. I. Zelianskaja (J. Appl. Chem. Russ., 1941, 14, 46—62).—CaCl<sub>2</sub> is added in 20% excess to aq. Na<sub>2</sub>CrO<sub>4</sub> at 100°, and the ppt. of CaCrO<sub>4</sub> is collected after 1 hr. The solubility of CaSO<sub>4</sub> in aq. CrO<sub>3</sub> rises with increasing [CrO<sub>3</sub>] to a max. at ~30 g. of CrO<sub>3</sub> per 100 g. H<sub>2</sub>O, thereafter falling rapidly (25°, 60°, and 95°). 95% H<sub>2</sub>SO<sub>4</sub> is added to an aq. suspension of CaCrO<sub>4</sub> at 100°, in such amount as to give a [CrO<sub>3</sub>] of 32%, and the solution is filtered. The filtrate is evaporated to a [CrO<sub>3</sub>] of 81%, again filtered, and cooled, when pure CrO<sub>3</sub> separates in good yield.

R. T.

Preparation of tervalent manganese. S. V. Gorbatschev and E. E. Schpitalski (J. Gen. Chem. Russ., 1940, 10, 1961—1967).—The concn. of Mn<sup>III</sup> obtainable by anodic oxidation of aq. MnSO<sub>4</sub> at 18° is max. in 11n-H<sub>2</sub>SO<sub>4</sub>. The reaction begins abruptly at a voltage of 1·8 (c.d. 24.5-3.770 ma. per sq. cm. The yield rises with increasing [MnSO<sub>4</sub>] to 17%. A series of complex equilibrium reactions exists, according to the acidity of the solutions, as follows:  $2\text{Mn}(\text{OH})_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Mn}(\text{OH})_4 + \text{MnSO}_4 + 2\text{H}_2\text{O} (2\text{N-H}_2\text{SO}_4); \rightarrow \text{Mn}_2(\text{SO}_4)_3 + 4\text{H}_2\text{O} \rightarrow \text{Mn}(\text{OH})_4 + \text{MnSO}_4 + 2\text{H}_2\text{SO}_4$ , and  $\text{Mn}_2(\text{SO}_4)_3 + 4\text{H}_2\text{O} \rightarrow \text{Mn}(\text{OH})_3 + 3\text{H}_2\text{SO}_4 (2-10\text{n-H}_2\text{SO}_4); \text{Mn}(\text{OH})_4 + 2\text{H}_2\text{SO}_4 \rightarrow \text{Mn}(\text{SO}_4)_2 + 4\text{H}_2\text{O} (>11\text{n-H}_2\text{SO}_4); \text{Mn}_2(\text{SO}_4)_3 \rightarrow \text{Mn}(\text{SO}_4)_2 + \text{MnSO}_4; \text{Mn}_2(\text{SO}_4)_3 + 12\text{SO}_4 \rightarrow \text{H}_2\text{Mn}_2(\text{SO}_4)_3$  (11-18n-H<sub>2</sub>SO<sub>4</sub>). The complex salt H<sub>2</sub>[Mn<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>],8H<sub>2</sub>O crystallises from solution of high acidity (15-20n-H<sub>2</sub>SO<sub>4</sub>) during electrolysis. It is collected, excess of H<sub>2</sub>SO<sub>4</sub> is removed by gentle heating, and the salt is stored in air-tight containers. It is a useful oxidising agent.

Precipitation of carbonates, borates, silicates, and arsenates. P. E. Gagnon, L. Cloutier, and R. Martineau (Canad. J. Res., 1941, 19, B, 179—204).—The influence of concn. and  $p_{\rm H}$  on the composition of several ppts. of carbonates, borates, silicates, and arsenates has been investigated. The following compounds have been isolated:  $5CoCO_3$ ,  $Co(OH)_2$  from  $Co(NO_3)_2$  and  $(NH_4)_2CO_3$ ;  $9Pb_3(AsO_4)_2$ ,  $Pb(OH)_2$  from  $Pb(NO_3)_2$  and  $K_2HASO_4$ ; and  $4Pb_3(AsO_4)_2$ ,  $Pb(OH)_2$  from  $Pb(NO_3)_2$  and  $H_3AsO_4$  in presence of  $NH_3$ . Normal  $CdCO_3$  and

PbHAsO<sub>3</sub> were obtained, but attempts to prepare NiCO<sub>3</sub>, CoCO<sub>3</sub>, BeCrO<sub>4</sub>, Zn borates, Cu silicates, and Pb arsenates always resulted in the formation of mixtures of basic salts.

C. R. H. Oxidation with molecular oxygen. II. Chemistry of the autoxidation of the blue and green basic Co<sup>II</sup> compounds. W. Feitknecht [with W. Bédert] (Helv. Chim. Acta, 1941, 24, 676—693).—When O<sub>2</sub> is bubbled through a suspension of blue Co(OH)2 (I) at room temp, the oxidation of (I) is accompanied by the transformation of (I) into pink Co(OH)<sub>2</sub> (II). This transformation is so rapid at room temp. that a pure specimen of (I) cannot be obtained, but pure (I) can be prepared at 0°. (I) has a structure in which layers of ordered alternate with layers of disordered material, there being 4 mols. of ordered per mol. of disordered material, and so may be formulated  $4\text{Co}(O\text{H})_2$ ,  $\text{Co}(O\text{H})_2$ . The first stage of oxidation proceeds without change of phase, affording a green product having the analogous composition  $4\text{Co}(O\text{H})_2$ , Co(OH)(III). Subsequent oxidation of (III) involves a change of phase, and the product is CoO(OH) (IV), identical with the product of hydrolysis of complex Co<sup>III</sup> compounds. (III) is unstable, decomp. into (II) and (IV), but can be stabilised by addition of glucose; (I) pptd. in presence of glucose is more slowly oxidised, and the reaction proceeds only as far as (III). (II) is oxidised directly, with change of phase, to (IV). The green basic chloride and bromide have structures like that of (I), i.e.,  $4\text{Co}(O\text{H})_2$ ,  $\text{Co}(O\text{H}) \times (X = \text{Cl or Br})$ , and their oxidation proceeds analogously, the disordered layers being first oxidised to a bright green intermediate product. being first oxidised to a bright green intermediate product, 4Co(OH)<sub>2</sub>,CoOX. The green basic nitrate, of empirical formula 6Co(OH)<sub>2</sub>,Co(NO<sub>3</sub>)<sub>2</sub>, consists of ordered layers alternating with disordered layers of a basic nitrate, and may be represented 4Co(OH)<sub>2</sub>,Co<sub>1,25</sub>(OH)(NO<sub>3</sub>)<sub>1,5</sub>. The first product of oxidation is 4Co(OH)<sub>2</sub>,CoO(NO<sub>3</sub>), analogous to (III), but the mechanism of the reaction is more complicated, involving extrusion of Co(NO<sub>3</sub>)<sub>2</sub> out of the disordered layers. The oxidation of the blue basic sulphate is apparently analogous F. J. G. to that of the basic halides.

#### X.-ANALYSIS.

Chromatographic analysis. A. H. Cook (Inst. Chem., April 23, 1941, 36 pp.).—A lecture.

Spectrochemical analysis of metals.—See B., 1941, I, 460.

Determination of metals in foods.—See B., 1941, III, 265.

Determination of  $p_{\rm H}$  in coloured and turbid solutions. N. A. Tananaev and L. P. Tegentzeva (J. Appl. Chem. Russ., 1941, 14, 127—129).—A colorimetric dialysis procedure is described.

Determination of  $p_{\rm H}$  value for alkali soils.—See B., 1941, III, 249.

Conductometric analysis of sodium sulphite and ammoniacal [wood-]pulping liquors.—See B., 1941, II, 340.

Hydride method of determining water in aquo-complex compounds. I. A. G. Elitzur (J. Gen. Chem. Russ., 1940, 10, 1981—1984).—The substance is immersed in abs. EtOH in presence of  $CaH_2$ ; the vol. of  $H_2$  evolved  $\infty$  [ $H_2O$ ] of the substance. The rate of evolution of  $H_2$  gives an indication of the lability of the  $H_2O$  of crystal hydrates. R. T.

Photo-electric method for the colorimetric determination of hydrogen peroxide with titanium [or vanadium] sulphate. C. B. Allsopp (Analyst, 1941, 66, 371).—The yellow colour produced by the action of a Ti salt on H<sub>2</sub>O<sub>2</sub> may be measured photo-electrically (e.g., in a Hilger Absorptiometer which has been calibrated against standard solutions), although it is not readily detectable visually. The probable errors are 20, 2.5, and 0.25% for concns. of 10<sup>-5</sup>, 10<sup>-4</sup>, and 10<sup>-3</sup>N., respectively. The reagent is prepared by digesting conc. H<sub>2</sub>SO<sub>4</sub> with an excess of TiO<sub>2</sub>, diluting to 15—20% concn., and filtering. A solution of V<sub>2</sub>O<sub>5</sub> in H<sub>2</sub>SO<sub>4</sub> (which changes from green to brown in presence of H<sub>2</sub>O<sub>2</sub>) is ~25% less sensitive.

Determination of total chloride content of heavy oils.—See B., 1941, I, 434.

Colorimetric detection of chlorate ion. M. B. Roy (J. Indian Chem. Soci., 1941, 18, 165—166).—A solution of  $C_bH_bN$  in  $H_2SO_4$  develops an intense and permanent violet colour with

chlorates. This may be used as a qual. test or an approx. colorimetric determination. F. J. G.

Micro-determination of sulphur. Modified bomb method.—See A., 1941, II, 344.

[Colorimetric] determination of sulphides in sewage and sewer atmospheres.—See B., 1941, III, 272.

Determination of sulphate in the presence of chromate. W. B. Meldrum, W. E. Cadbury, jun., and W. W. Lucasse (Ind. Eng. Chem. [Anal.], 1941, 13, 456—457).—SO<sub>4</sub>" is pptd. as usual, but in presence of 5 ml. of HCl per 75 ml. of solution to minimise co-pptn., the BaSO<sub>4</sub> + BaCrO<sub>4</sub> is fused with Na<sub>2</sub>CO<sub>3</sub>, and the co-pptd. CrO<sub>4</sub>" determined iodometrically in the aq. extract. The solution obtained after fusion of asbestos with Na<sub>2</sub>CO<sub>3</sub> and extraction of the fused mass with H<sub>2</sub>O liberates I from acid KI; hence a Gooch crucible and asbestos cannot be used for filtrations. Filter-paper is satisfactory, since CrO<sub>4</sub> is not reduced when ignited in contact with filter-paper in a muffle furnace. Details of procedure are given. Test data show that for 0·05—0·25 g. of Na<sub>2</sub>SO<sub>4</sub>, and ratios of Na<sub>2</sub>SO<sub>4</sub>; Na<sub>2</sub>CrO<sub>4</sub> varying from 2·5: 1 to 1: 75, the method is satisfactory.

Volumetric determination of sulphuric acid in its salts. A. Krüger (Z. anal. Chem., 1940, 119, 216—221; cf. A., 1939, I, 625).—After removal of substances likely to interfere with the purity of the pptd. BaSO<sub>4</sub>, and of free HCl and HNO<sub>3</sub> by evaporation, the solution is neutralised (Me-orange), and if poor in salts, 2 g, of NaCl are added. Excess of BaCO<sub>3</sub> [prep. from Ba(OH)<sub>2</sub> and CO<sub>2</sub> given] is added, and the solution is diluted to  $\sim\!200\,\text{c.c.}$  The containing vessel is cooled in ice, and CO<sub>2</sub> is passed into it for I·5 hr., when the reaction SO<sub>4</sub>" + BaCO<sub>3</sub> + H<sub>2</sub>CO<sub>3</sub>  $\rightarrow$  BaSO<sub>4</sub> + 2HCO<sub>3</sub>' takes place. After filtration, the ppt, is washed with ice-cold, CO<sub>2</sub>-saturated H<sub>2</sub>O. The resulting solution is evaporated to  $\sim\!100\,\text{c.c.}$  to decompose the small amounts of Ba(HCO<sub>3</sub>)<sub>2</sub> formed, filtered, and the HCO<sub>3</sub>' equiv. to the SO<sub>4</sub>" titrated with 0-5N-HCl (Me-orange). The method can be shortened by eliminating the washing of the first ppt. by means of decantation, and weighings in the manner detailed. L. S. T.

Determination of selenium in foods.—See B., 1941, III, 265.

Determination of ammonia and carbamide by modification of the Conway diffusion method. E. Kawerau (Sci. Proc. Roy. Dublin Soc., 1941, 22, 405—413).—NH<sub>3</sub> and CO(NH<sub>2</sub>)<sub>2</sub> (4—400 mg. per 100 c.c.) are determined by Abelin's method (A., 1938, III, 785), using a liquid paraffin seal and modified indicator and urease extract.

A. Lt.

Microchemistry of the azide ion. G. Denigès (Bull. Trav. Soc. Pharm. Bordeaux, 1938, 76, 69—72; Chem. Zentr., 1938, ii, 3956).—N<sub>3</sub> gives cryst. ppts. (illustrated) with TlOAc, Pb(OAc)<sub>2</sub>, and ammoniacal HgSO<sub>4</sub> and AgNO<sub>3</sub> solutions.

A. J. E. W.

Determination of nitrogen and chlorine in fertilisers.—See B., 1941, III, 250.

Sampling and analysis of phosphorus.—See B., 1941, I, 445.

Colorimetric determination of phosphate in jams, jellies, etc.—See B., 1941, III, 264.

Rapid determination of phosphate in boiler water.—See B., 1941, I, 417.

Use of bromate in volumetric analysis. Determination of arsenic and antimony using internal indicators at ordinary temperatures. G. F. Smith and R. L. May (Ind. Eng. Chem. [Anal.], 1941, 13, 460—461).—Bordeaux, B.C.I. No. 88, Brilliant Ponceaux 5R, B.C.I. No. 185, and naphthol-blue-black, B.C.I. No. 246 (1—2 drops of 0·1 to 0·2% aq. solution), are satisfactory irreversible indicators for the titration of Sb" at acidities varying from 5 to 35 vol.-% of conc. HCl, using KBrO<sub>2</sub> as oxidising agent at room temp., and for oxidation of As" in 20 vol.-% HCl. Fading of the indicator generally occurs before the equivalence point is reached, but an additional drop of indicator introduces no error. The indicator blank is negligible.

Determination of total boron in soil.—See B., 1941, III, 250.

Determination of silica in products containing fluorine, especially in cryolite. H. Spielhaczek (Z. anal. Chem., 1940, 119, 4—16).—The sample (1 g.) is mixed with 3 g. of anhyd. borax or 6 of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>,10H<sub>2</sub>O (not B<sub>2</sub>O<sub>3</sub>) and 14 g. of KHSO<sub>4</sub>

are added. The mixture is heated gradually to a high temp. F is volatilised as  $BF_3$ , and, provided that the ratio borax: F is  $displayed \leqslant 6:1$ , no loss of Si as  $SiF_4$  occurs. When cold, the fused mass is extracted with  $H_2O$  and acidified with HCl. The solution is evaporated and dried at  $105-110^\circ$  in a manner designed to overcome the difficulty of dehydrating  $SiO_2, nH_2O$  in presence of much alkali sulphate. Details of procedure and test data with different samples of cryolite are recorded and compared with results obtained by the distillation method for  $SiO_2$ . Advantages over other methods of determination are discussed.

Determination of silicon, phosphorus, and manganese in acid-resisting high-silicon iron.—See B., 1941, I, 456.

Determination of carbon monoxide by combustion over platinum in the presence of excess oxygen. J. R. Branham, M. Shepherd, and S. Schuhmann (J. Res. Nat. Bur. Stand., 1941, 26, 571—589).—The determination of CO by slow combustion has been investigated, both wet and dry gases being used and the contraction after burning,  $CO_2$  produced, and  $O_2$  consumed being measured. Under average laboratory conditions the vol. relations of the reaction are  $2CO + 1.001O_2 \rightarrow 1.986CO_2 + 1.014TC$  (TC = total contraction after burning). The effects of the loss of  $CO_2$  by dissolution and of deviations from the ideal gas laws are evaluated. In the absence of other combustible gases, the best results are obtained from  $TC + CO_2$  produced.

J. W. S.

Determination of carbon dioxide. I. F. Richter (Z. anal. Chem., 1940, 119, 109—118).—Apparatus and procedure for liberating and absorbing the CO<sub>2</sub> from carbonates in a closed system are described. The carbonate is decomposed by hot, dil. (1:10) H<sub>2</sub>SO<sub>4</sub>, and the CO<sub>2</sub> absorbed in aq. Ba(OH)<sub>2</sub>, which is finally titrated with 0·ln-HCl (cresolphthalein). Data for several carbonate-containing minerals are compared with those obtained gravimetrically. The method is accurate, and quicker than the gravimetric. L. S. T.

Determination of potassium in fruit products, jams, jellies, etc.—See B., 1941, III, 264.

Effect of temperature of alcohol in determination of potash in fertilisers.—See B., 1941, III, 251.

Determination of sodium and potassium in refractory materials and in various potassium salts.—See B., 1941, I, 451.

Recovery of uranium acetate in the determination of sodium. H. A. Puente and F. R. Marin (Anal. Asoc. Quim. Argentina, 1941, 29, 95—99).—U in the residual liquor from Na determinations is pptd. by NH<sub>3</sub> and the resulting  $(NH_4)_2U_2O_7$  purified by dissolution in HCl and repptn. until free from Zn, the  $(NH_4)_2U_2O_7$  being then converted into  $U_3O_8$  and thence successively into  $UO_2(NO_3)_2$ ,  $UO_3$ , and  $UO_2(OAc)_2$ . F. R. G.

Determination of sodium and chlorides in fruit and fruit products.—See B., 1941, III, 264.

Sensitivity of chemical reactions. III. Different types of chemical reactions. Z. Karaoglanov (Z. anal. Chem., 1940, 119, 16—55; cf. A., 1938, I, 637; 1939, I, 212).—Sensitivities, determined under varied conditions and expressed in µg. per 10 c.c., are recorded for the following reactions: Li' with Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>HPO<sub>4</sub>, Na<sub>2</sub>HASO<sub>4</sub>, or alizarin-red S (I); NH<sub>4</sub>' or NH<sub>3</sub> with HgCl<sub>2</sub>, HgCl<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub>, Graves' reagent, NaOCl and KI, aq. I, NaOPh and NaOCl, Na<sub>3</sub>Co(NO<sub>2</sub>)<sub>6</sub>, Na H tartrate, picric acid, or CuSO<sub>4</sub>; Mg" with 8-hydroxyquinoline, or (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub> and KI, and Mg" as Mg(OH)<sub>2</sub> in presence of I, diphenylcarbazide (II), (I), toluyl-orange R, azo-blue, Chicagoblue 6B, Congo-corinth, brilliant-yellow, or alizarin-yellow; Cu" with C<sub>5</sub>H<sub>5</sub>Na and NH<sub>4</sub>CNS, (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub> and KI, (II), (I), benzidine in presence of KI, NH<sub>4</sub>CNS, KBr or NaCl, or with guaiacum in presence of NH<sub>4</sub>CNS, or NaCl, or KBr. The results show that the time factor is of great importance for the sensitivity val. of a pptn. reaction, and that in many reactions sensitivity increases with a decrease in the amount of reagent. Temp. is also important in the reactions with Li". The nature of the reactions between Mg" and the dyes is discussed.

L. S. T.

Spectroscopic determination of alkaline-earth metals and of phosphate. T. Török (Z. anal. Chem., 1940, 119, 120—125; cf. A., 1939, I, 277).—The method is based on the non-reducibility and non-volatility of the alkaline-earth phosphates. N-NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> is added from a burette to the solution of Ca",

Sr", or Ba" containing Zn and HCl, until the flame reaction, as observed through a spectroscope, disappears. A filter solution of dahlia-violet to eliminate the Na flame, or of dahlia-violet + CuSO<sub>4</sub> to eliminate that of K', can replace the spectroscope. The method is sensitive to 0.4 mg. of Sr and 0.2 mg. of Ca, corresponding with 0.1 c.c. of 0.1N-phosphate solution. With the exception of SO<sub>4</sub>", anions have no effect on the method; Bi", Cu", Sn", and Tl' interfere by deposition of metal on the Zn, and inhibition of H<sub>2</sub> evolution. The method can be applied to the titration of PO<sub>4</sub>" with N-SrCl<sub>2</sub> with the appearance of the Sr flame as indicator.

Determination of hardness of water.—See B., 1941, III, 273.

Determination of calcium and sulphur of fertilisers.—See B., 1941, III, 251.

Determination of exchangeable bases in soils.—See B., 1941, III, 249.

Photometric method for the determination of magnesium. W. S. Gillam (Ind. Eng. Chem. [Anal.], 1941, 13, 499—501). —The method described is based on the use of titan-yellow and a photo-electric colorimeter. It affords a rapid means for determining 0.5—300 p.p.m. of Mg in fertilisers and soil extracts. Fading of the coloured complex is prevented by the addition of aq. NH<sub>2</sub>OH,HCl. 800 p.p.m. of Ca do not interfere with the determination of 1 p.p.m. of Mg, but the Ca", NH<sub>4</sub>', and PO<sub>4</sub>"" contents should be kept <500, 600, and 100 p.p.m., respectively. Al and Sn must be absent. Results agree with those obtained gravimetrically as Mg hydroxyquinolinate.

Determination of magnesium and manganese in fertilisers.—See B., 1941, III, 251.

Determination of replaceable magnesium in soils, using 8-hydroxyquinoline.—See B., 1941, III, 250.

Precipitation of zinc sulphide from a solution of ammonium citrate and citric acid. S. A. Coleman and G. B. L. Smith (Ind. Eng. Chem. [Anal.], 1941, 13, 377—380).—The Waring-Fales-Ware method (A., 1919, ii, 246) has been examined critically. The use of HCO<sub>2</sub>'-HCO<sub>2</sub>H buffer is unnecessary, since a mixture of NH<sub>4</sub> citrate and citric acid not only keeps Fe in solution but also serves as an efficient buffer solution for the quant. pptn. of ZnS. As in the above method, the precision is 1 in 1000, and some Fe contaminates the ZnS; this increases with the [Fe] in the solution. The separation of Zn' from Mn'', Al''', or Ni' by the NH<sub>4</sub> citrate-citric acid method is satisfactory. Separation from Co'' is not complete, but post-pptn. of CoS is minimised by the use of NH<sub>4</sub>CNS, which serves also to salt out the ZnS. The use of ZnS, dried at 110°, as a weighing form is untrustworthy. A procedure for the analysis of Zn ores, based on the NH<sub>4</sub> citrate-citric acid method with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> or NH<sub>4</sub>CNS as the salting-out reagent, is detailed.

L. S. T.

Rapid direct determination of zinc in brass or bronze.—See B., 1941, I, 458.

Determination of zinc in foods.—See B., 1941, III, 265.

Determination of small quantities of lead by means of dithizone. H. Fischer and G. Leopoldi (Z. anal. Chem., 1940, 119, 161—188).—The single-colour process for the colorimetric determination of Pb is discussed, and improved procedure, based on that described previously (A., 1934, 381), described. Treatment of filter-paper, contamination by Pb from glassware, and purification of reagents are discussed. Pb contents of certain reagents are tabulated. Data given for the stability of dithizone in CCl<sub>4</sub> in diffuse daylight show that when solutions are kept under aq. NH<sub>2</sub>OH,HCl, or 0·1n·H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>SO<sub>5</sub>, but not 0·1n·HCl, in brown glass, they are stable for many weeks. Details of procedure, and test results, together with the best colour ranges for quant. work, are given for the titration of 1—25 μg, of Pb" by the mixed-colour process. The alkalinity of conc. solutions of KCN has no deleterious effect on the completeness of extraction of Pb dithizonate (I); this permits the determination of traces of Pb (10-3%) in Cu, Zn, Cd, Ag, Hg, etc. Data showing the determination of 24—40 μg, of Pb in 0·5—4 g, of Zn are recorded. A 20-fold excess of KCN is necessary to mask Zn and Cd, but a smaller excess suffices for other heavy metals. Traces of Cu" catalyse the oxidising action of many substances on (I), but this effect is overcome completely by adding NH<sub>2</sub>OH,HCl, and

1941, I, 457.

boiling the solution. The use of a large excess of KCN improves the detection of Pb" against Bi" and Sn" to 0.5  $\mu$ g. of Pb with 1000  $\mu$ g. of Bi and 2500  $\mu$ g. of Sn. At  $\rho$ <sub>R</sub> 9, Pb. (0.5  $\mu$ g.) can be detected in presence of a large excess of Tl. (Pb: Tl = 1: 12,000). Conditions for the determination of Pb in presence of 1000-fold excess of Bi are laid down. The separation depends on the extraction of most of the Bi at  $p_{\rm H}$  3, and on that of the Pb in the residual Bi by a large excess of KCN. Procedure for the determination of Pb against a 50-fold excess of Tl' in presence of a large excess of KCN is also given. The Pb reacts before the Tl'.

Diguanide sulphate as a reagent for the determination of copper. P. Rây and J. Roy-Chowdhury (J. Indian Chem. Soc., 1941, 18, 149—154).—Cu may be determined gravimetrically in presence of Cd, Zn, Mg, and alkalis by pptn. from ammoniacal solution with diguanide sulphate. NO<sub>3</sub> must be absent. The ppt. is dried at 50— $70^{\circ}$  after washing with  $H_2O$ , EtOH, and  $Et_2O$ , and weighed as  $[Cu(C_2N_5H_7)_2]SO_4.3H_2O$ . In absence of a large excess of NH<sub>3</sub> or NH<sub>4</sub> salts the determination may be carried out volumetrically with rubeanic acid as indicator. F. J. G.

New precipitant for metals: 5-(8'-hydroxy-5'-quinolinyl)-imino-8-keto-5: 8-dihydroquinoline ("indo-oxine") with indicator properties. R. Berg and E. Becker (Z. anal. Chem., 1940, 119, 81—90).—In dil. AcOH-OAc' solution, indo-oxine 1940, 119, 81—90).—In dil. AcOH–OAc' solution, indo-oxine forms blue or bluish-green ppts. with the following ions: Cu' (0·1—0·17), Ag' (0·1—2·0), Au'' (0·66—2·5), Mg'' (1200), Zn'' (0·4—1), Cd'' (4—8), Hg'' (0·6), Ce''' (5), Ga'' (0·4—2), Ti''' (0·2—0·6), Zr''' (1—1·4), Pb' (200), Bi'' (1·6—4), V''' (0·1—0·6), MoO₄'' (3), WO₄'' (6), Fe''' (0·1—0·6), Fe'' (0·4—0·08), Co'' (0·1—0·4), Ni'' (0·3—0·04), and Pd'' (0·4). Sensitivities, μg. per c.c., are given in parentheses. In ammoniacal tartrate solution the sensitivities are Cu'', 0·3 and 0·05; Ag' 3·4; Mg'', 0·5; Ca'', 2; Zn'', 5; Cd'', 1·8; Hg'', 12; Co'', 0·7; Ni'', 1—0·5 μg. per c.c.; in NaOH–tartrate solution, only Cu'', Cd'', Hg'', Co'', and Ni'' give ppts., and the tests are much less sensitive. The reactions can be made more selective, in certain cases, by addition of NaCl, NaCN, or selective, in certain cases, by addition of NaCl, NaCl, or citrate. In dil. solution, the indo-oxine changes colour sharply between  $p_{\rm H}$  6 and 8 (red to blue), and can be used as indicator in the titration of 0·1n-acid and -alkali. In 0·01nacid solution, or with weak acids and bases, CO2 must be removed by boiling. Cl' and CNS' can be titrated with 0·ln-AgNO<sub>3</sub> with indo-oxine as indicator in presence of AcOH; an org. solvent, MeOH, EtOH, or COMe<sub>2</sub> (50 vol.-%), must be present. Br' and I' can be titrated in neutral and dil. AcOH solutions with 0·ln-AgNO<sub>3</sub>, but for Br', titration with 0·1 or 0·01n-AgNO $_3$  is not recommended. Small amounts (0·2—1 mg.) of Cu or Ni or Hg (0·5—2·5 mg.), can be titrated directly with an EtOH solution of indo-oxine in presence of AcOH-OAc' using the filtration method to find the end-point. Addition of NaCl enables Cu" to be determined in presence of Hg. Details of procedures and test data are recorded L. S. T. test data are recorded.

Use of nitroso-derivatives as reagents in inorganic analysis. II. S. S. Guha-Sircar and S. C. Bhattacharjee (J. Indian Chem. Soc., 1941, 18, 161—163).—Cu 1-nitroso-β- and 2-nitroso-α-naphthylamine, (C<sub>10</sub>H<sub>2</sub>ON<sub>2</sub>)<sub>2</sub>Cu, are described. They are suitable for the more invariant data minimation of Cu in page are suitable for the gravimetric determination of Cu in presence of Cd. Both nitrosonaphthylamines also give ppts. with Ni", but these are not suitable for gravimetric determination. F. J. G.

Determination of copper and zinc in fertilisers.—See B., 1941, III, 251.

Analysis of beryllium-coppers.—See B., 1941, I, 458.

Determination of copper and nickel in aluminium alloys.— See B., 1941, I, 461.

Assaying mercury ores.—See B., 1941, I, 459.

Determination of cerium, and separation of thorium and Determination of cerium, and separation of thorium and cerium by means of 8-hydroxyquinoline. R. Berg and E. Becker (Z. anal. Chem., 1940, 119, 1—4).—In ammoniacal solution containing tartrate, Ce<sup>\*\*\*</sup> gives with 8-hydroxyquinoline a yellow ppt. (sensitivity 0.59 μg.) which dries in air to a greenish-grey product, Ce(C<sub>9</sub>H<sub>6</sub>ON)<sub>3</sub>. The ppt. can be dried at 110° and weighed, or ignited with H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, or determined volumetrically with BrO<sub>3</sub>-Br' after dissolution in 3N-HCl. The solution of Ce (10—50 mg. of Ce per final vol. of 100 c.c.) is first reduced by means of NH<sub>2</sub>OH,HCl. Separation from Th is effected by pptg, the Th as Th(C<sub>9</sub>H<sub>6</sub>ON)<sub>4</sub>,C<sub>9</sub>H<sub>7</sub>ON in AcOH solution, and then the Ce as indicated above. Details of procedures and test data are recorded.

L. S. T. Spectrophotometric determination of praseodymium, neodymium, and samarium. C. J. Rodden (J. Res. Nat. Bur. Stand., 1941, 26, 557—570).—In a solution containing rare earth and associated metals as nitrates, Pr, Nd, and Sm can be determined by measuring the transmittancy of the solution with a double monochromator photo-electric spectrophotometer. The most suitable absorption bands for examination are Pr 4460 A., Nd 5210 and 7980 A., and Sm 4020 A. Nd  $(NO_3)_3$ solutions of concn. > 10 g. per l. obey Beer's law, but  $\Pr(NO_3)_3$  and  $Sm(NO_3)_3$  solutions do not obey this law. The method of correcting for the interference of each element is discussed. A procedure for the analysis of the Ce group of metals is suggested.

Chemical analysis of alloy cast iron.—See B., 1941, I, 456.

Determination of iron in beer.—See B., 1941, III, 258. Oxidation of graphite in analysis of ferrous metals.—See B.,

Use of nitroso-derivatives as reagents in inorganic analysis. I. S. S. Guha-Sircar and S. C. Bhattacharjee (J. Indian Chem. Soc., 1941, 18, 155—160).—The following sparingly sol. Chem. Soc., 1941, 18, 155—100].—The following spatningly sol, inner complex Co salts with aromatic NO-compounds are described: Co<sup>III</sup> 1-nitroso-β-naphthylamine (I) and Co<sup>III</sup> 2-nitroso-α-naphthylamine, (C<sub>10</sub>H<sub>7</sub>ON<sub>2</sub>)<sub>3</sub>Co (II); Co<sup>III</sup> oximino-dimedone, (C<sub>8</sub>H<sub>10</sub>O<sub>3</sub>N)<sub>3</sub>Co (III); Co<sup>III</sup> dinitrosoresorcinol, (C<sub>6</sub>HO<sub>4</sub>N<sub>2</sub>)<sub>2</sub>Co; Co<sup>III</sup> dinitroso-orcinol, (C<sub>7</sub>H<sub>5</sub>O<sub>4</sub>N<sub>2</sub>)<sub>2</sub>Co. (I), and especially (III) are suitable for gravimetric determination of Co. mination of Co.

Critical study of qualitative reagents for cobalt cations. P. Wenger and R. Duckert [with M. Busset] (Helv. Chim. Acta, 1941, 24, 657—670).—A large no. of reagents which have been suggested for the detection of Co" have been tested, and the results, with data on sensitivity and specificity, are tabulated; these include 31 which are recommended for use under specified conditions.

Fractional detection of cobalt and lead. N. A. Tananaev and L. P. Tegentzeva (J. Appl. Chem. Russ., 1941, 14, 130—132).—Excess of Zn(OH)<sub>2</sub> is added to the neutral solution, to ppt. Cr, Fe, Al, Bi, Cu, and Hg, and the solution is filtered. Zn(OH)<sub>2</sub> and KMnO<sub>4</sub> are added to the filtrate, which is then boiled and filtered, and the ppt. is washed with aq. NH<sub>4</sub>NO<sub>3</sub> and dissolved in dil. HNO<sub>3</sub>. Pb is detected in one portion of the solution as PbSO<sub>4</sub> or PbS, and Co in a second portion by adding NH<sub>4</sub>CNS and COMe<sub>2</sub>. R. T.

Detection of certain metals in minerals and ores. Ammonium hypophosphite fusion method. H. B. Van Valkenburgh and T. C. Crawford (Ind. Eng. Chem. [Anal.], 1941, 13, 459—460).—0·1 g. of mineral or ore is heated with 2 g. of NH<sub>4</sub>H<sub>2</sub>PO<sub>2</sub> (not Na or K salt), and the colour of the fused mass alone or after treatment with H<sub>2</sub>O or H<sub>2</sub>O<sub>2</sub> is the basis of detection. Co, Ti, and W give blue melts, but the Co melt turns pink on cooling. With W, the blue colour changes to violet when the warm melt is moistened with H<sub>2</sub>O, and with Ti the change is to faint rose colour, which is turned orange-red by addition of H<sub>2</sub>O<sub>2</sub>. V, Cr, and U give green melts; that due to V is red when hot. Mo minerals, except molybdenite, give a reddish-brown melt. Mn minerals yield a clear melt, which gives the permanganate colour when a clear melt, which gives the permanganate colour when excess of  $\mathrm{HNO}_3$  is added and then removed by boiling. Te minerals are reduced to metal, which eventually gives a wine-red colour; H<sub>2</sub>O changes this colour to black. Nb and Ta give no colour, but black particles can be seen throughout the melt. Any one of the above metals can be detected by these tests in their minerals, but not necessarily in presence of any or all of the others. Mn can be detected in presence of Ag, Pb, Hg, Bi, Cu, Cd, As, Sb, Sn, Co, Ni, Cr, Al, and Zn.

Analysis of platinum-iridium ores.—See B., 1941, I, 460.

#### XI.—APPARATUS ETC.

Differential calorimeter. N. Fontell (Soc. Sci. fenn., Comm. phys.-math., 1938, 10, No. 5, 18 pp.; Chem. Zentr., 1938, ii, 3839).—A differential colorimeter of simple design is described; quantities of heat of -35 to -350 g.-cal. can be determined with an accuracy of 0.1% (H<sub>2</sub>O-val. 1000 g.; temp. differences measured to ±0.00015°). Data for the heat of dissolution of KCl are in good agreement with the results of Lange and Monheim (A., 1930, 1152).

A. J. E. W. Copper blocks and optical system for determining b.p. (Emich method) and m.p. A. A. Morton and J. F. Mahoney (Ind. Eng. Chem. [Anal.], 1941, 13, 498—499).—Details of construction are illustrated.

L. S. T.

Circuit for temperature controls. B. Noyes (Science, 1941, 93, 286—288).—Apparatus utilising the Ward Leonard 106 type relay and a Hg thermometer with Pt contacts is described and illustrated.

L. S. T.

Use of the term "resolving power" in spectroscopy. S. Tolansky (Nature, 1941, 148, 54).—Examples showing that the classical resolving power as an index of an instrument should be replaced are discussed. A more useful and practical measure of the effective applicability of an instrument is the "resolving limit," now defined as  $dv = v.d\lambda/\lambda$ , i.e., the instrumental line width in cm.-1 at a given  $\lambda$ .

Photo-electric colorimetric technique for the dithizone system. F. L. Kozelka and E. F. Kluchesky (Ind. Eng. Chem. [Anal.], 1941, 13, 484—487).—A technique adapted to photo-electric colorimeters for the determination of one component in a two-component system is described. It is especially suitable for the dithizone (I) system; it eliminates the necessity of removing excess of (I), and of the use of standard solutions of (I).  $\pm 1~\mu g$ . of Pb can be recovered.

Modified eyepiece micrometer for use in dust counting. W. B. Harris (*J. Ind. Hyg.*, 1941, **23**, 148—150).—The micrometer is made by fixing strands of glass wool on the diaphragm of the eyepiece to form a grid of 25 squares; it is calibrated against a stage micrometer.

E. M. K.

Direct-reading microphotometer. G. O. Langstroth, K. B. Newbound, and W. W. Brown (Canad. J. Res., 1941, 19, A, 103—108).—In the direct-reading photo-electric microphotometer described the photographic plate, the observation screen containing the slit admitting light to the photo-cell, and the galvanometer scale are grouped together in a vertical row so as to minimise the fatigue of observation. The operation of the instrument, which is designed for use in spectrographic analysis, is described in detail. J. W. S.

Recording photometer with photo-cell. G. Weber (Licht, 1938, 8, 145—147; Chem. Zentr., 1938, ii, 3839).—The construction and use of a photometer employing barrier-layer cells are described. As the cells are colour-corr. the instrument may be used for sources giving light of different colours in different directions.

A. J. E. W.

Subjective " $V_{\lambda}$ -true" photometry. M. Richter (*Licht*, 1938, 8, 127—128; *Chem. Zentv.*, 1938, ii, 3839).—The spectral brightness curve for an individual observer can be corr. to any standard curve by supplying the observer with suitable ocular filters, the design of which is discussed.

Use of step weakness in photographic photometry. G. E. Moore and H. W. Webb (J. Opt. Soc. Amer., 1940, 30, 413—414).—The calibration of a step weakener of five steps formed by a Pt sputtered 5° quartz wedge is described. Comparison of intensities of spectral lines in two spectra was made with an accuracy of from 1 to 5% by use of the wedge. No measurable change in the sputtered films had occurred after 2½ years. A Hg arc giving const. intensity distribution and total intensity was obtained by cooling with air jets controlled by a relay in the arm of a Wheatstone bridge and maintaining the voltage across the lamp to ±0.2 v. O. D. S.

Spectrophotometer for measurement of optical filters. S. W. Seeley and E. I. Anderson (Rev. Sci. Instr., 1941, 12, 392—395).—A disc revolving at 1800 r.p.m. has two apertures in its circumference at 180° to each other. The optical filter is mounted in one aperture. Light passes through both on to a photo-cell and oscilloscope. The ratio of the amplitude of the two superimposed curves gives the transmission of the filter. Simultaneous measurements of several filters may be made by increasing the no. of apertures in the disc.

D. F. R.

Photo-electric photometer for colorimetric determinations in water and sewage.—See B., 1941, III, 274.

New technique for making thin [X-ray] targets. L. T. Pockman and D. L. Webster (Rev. Sci. Instr., 1941, 12, 389—392).—A 10-sq. cm. cellulose acetate film,  $5\times 10^{-6}$  cm. thick, is deposited from solution on to a glass plate and then floated off by  $\rm H_2O$  across a circular opening in a brass holder. From there it is stretched over the flat ends of 6 U-shaped wires, 0-003 in. diameter, mounted in the target holder. A Ni film,  $10^{-6}$  cm. thick, is then deposited on the cellulose acetate by evaporation.

Use of infra-red film for electrophoretic and ultracentrifugal analyses. H. P. Treffers and D. H. Moore (*Science*, 1941, 93, 240).—Infra-red films or plates can often be used for systems opaque to visible light. Protein solutions containing dyes or bacterial pigments, or solutions of I in CCl<sub>4</sub>, can be thus examined.

L. S. T.

Adjustable infra-red absorption cell for liquids. E. S. Barr (Rev. Sci. Instr., 1941, 12, 396—397).—The device, which replaces the use of foil or mica washers, regulates cell thickness by means of a micrometer screw and wedge arrangement. Films of non-volatile liquids are readily prepared to within  $1 \mu$ ., up to  $200 \mu$ ., without estimation. D. F. R.

Preparation of high-melting alloys with the aid of electron bombardment. R. Hultgren and M. H. Pakkala (J. Appl. Physics, 1940, 11, 643—646).—In the electron bombardment vac. furnace described, a refractory crucible is surrounded by a positively charged Ta cup bombarded with electrons emitted by a W filament. The m.p. of Ta (2850°) was attained with the expenditure of 700 w. Pt, Ir, Fe, Co, V, Ti, and Zr were melted without difficulty in Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> crucibles.

Construction of glass bellows. D. J. Pompeo and E. Meyer (Rev. Sci. Instr., 1941, 12, 368—369).—Glass bellows (alternative to helical tubes for preventing breakage due to differential expansion) can be made in tubes >5 in. in diameter if the tube is held accurately centred in a glass lathe and rotated while the convolutions are being formed with a hand blowpipe and C rod. Thorough annealing is necessary.

Preparation of quartz ultrasonic oscillators. R. R. Bajpai and V. I. Vaidhianathan (*Proc. Indian Acad. Sci.*, 1941, 13, A, 504—509).—Details of selection of natural quartz crystals free from twinning and heterogeneity, and of the cutting and grinding of thick X-cut sections, are given. L. J. J.

Refrigerating condenser. Application in vacuum distillation assembly. G. Hunter (Canad. Chem., 1941, 25, 447—450).— The condenser described consists of a box of monel metal fitted with a commercial refrigerating unit and attached to a vac. line. Details of assembly and operation, and performance in recovering large vols. of H<sub>2</sub>O or org. solvents, are given. Large vols. of extracts can also be reduced to a small vol. with little change in heat-labile or easily-oxidised materials.

L. S. T.

Immersed capillarimeter. A new form of device for measuring surface tension of liquids in closed space. M. P. Poljakov (J. Phys. Chem. Russ., 1940, 14, 137—138).—An inverted U-tube composed of two different capillaries is immersed in liquid and the difference between the capillary rises measured.

Evaporation technique for beryllium, rhodium, and silicon. Y. Moriya (*Electrotech. J.*, 1938, 2, 219; *Chem. Zentr.*, 1938, ii, 3955).—The vessel described, which is constructed from W wire and sintered ThO<sub>2</sub>, permits evaporation of highly infusible materials in a vac., but is itself almost non-volatile.

A. J. E. W.

Labelling bottles. C. Gurchot and J. K. Finnegan (Science, 1941, 93, 288).—Paper labels can be protected with cellulose transparent tape. L. S. T.

Mechanical polishing [of minerals] with a film of abrasive. J. O. Fuller (*Econ. Geol.*, 1941, 36, 199—211).—An improved method, utilising a film of abrasive on metal laps, is described. A mounted surface can be ground and polished in <1 hr., and the resulting surface is free from scratches and relief. Details of procedure are given.

L. S. T.

Condenser for use during digestion operations. R. Szymanowitz (Ind. Eng. Chem. [Anal.], 1941, 13, 455).—A

round-bottomed Pyrex flask, fitted with inlet and outlet tubes for H<sub>2</sub>O, fits in the mouth of a beaker. L. S. T.

Pendulum method for measuring settling velocities. J. H. McMillen, L. F. Stutzman, and J. E. Hedrick (Ind. Eng. Chem. [Anal.], 1941, 13, 475—478).—Procedure and apparatus for determining the stability of a suspension and the rate of particle fall, utilising a compound pendulum, are described. The method is particularly suitable for opaque liquids, and it has been applied to suspensions of coal particles in oil fuel, and the settling of paint pigments and of milk in cream. The theory of the method is described, and approx. expressions for calculating velocities of fall are given. L. S. T.

Gas distributors using alundum discs. S. E. Jolly (Ind. Eng. Chem. [Anal.], 1941, 13, 478).—The sealing of alundum discs into Pyrex tubing is described.

L. S. T.

Automatic continuous percolator. M. S. Schechter and H. L. Haller (Ind. Eng. Chem. [Anal.], 1941, 13, 481—482).
—Improvements in the apparatus described previously (A., 1938, I, 478) are detailed and illustrated. Large quantities of ground plant material can be extracted with little loss of solvent.

L. S. T.

Power compactor for air-permeation experiments. E. L. Gooden (Ind. Eng. Chem. [Anal.], 1941, 13, 483—484).—
The construction and use of a device for compacting powders are described. A column of any desired height is built up in the sample tube by simultaneous compacting and deposition of the sample. The device is suitable for use with the self-calculating air-permeation apparatus for measuring surface mean diameter of powders. Comparative results obtained by this and vibration methods are given for powders of talc, diatomaceous earth, As<sub>2</sub>O<sub>3</sub>, and synthetic cryolite.

60-Plate low-hold-up laboratory fractionating column. A. J. Bailey (Ind. Eng. Chem. [Anal.], 1941, 13, 487—491).—
The all-glass column described and illustrated is filled with glass helices. It has an efficiency of ~60 theoretical plates, and a hold-up of <0·1 ml. per plate. It can be used for the laboratory separation of complex mixtures. A flexible still head permits operation under total reflux, or variable or total take-off, and at atm. or reduced pressure. L. S. T.

Analysis of a single drop of liquid by micro-fractionation. A. A. Morton and J. F. Mahoney (Ind. Eng. Chem. [Anal.], 1941, 13, 494—498).—A procedure and apparatus for collecting 30—70 fractions from a single drop of liquid are described. The fractionation is performed with one of two types of capillary, packed with glass wool, heated in a Cu block. The b.p.-fraction no. curve shows the existence of more than one component and the % composition. Curves for numerous mixtures of org. liquids illustrate the results obtainable.

L. S. T.

Nomograms for correction of barometer readings for temperature and gravity. G. Barr and H. A. Sloman (J.S.C.I., 1941, 60, 203—205).—Since an accuracy of  $\pm 0.1$  mm. in the reading of the barometric height is ample in most routine chemical analyses, there is a temptation to ignore the correction for temp., which may, however, vary by 1 mm. or more on different days. The sum of the corrections for temp. and (at a fixed station) for gravity may be read off very simply from a nomogram, and it is desirable to mount a chart alongside the barometer so that readings may be corrections. The principle of construction of a nomogram for use with the Fortin-type barometer is detailed, and a reproduction is given of one for use with a Kew-type barometer.

Comparative tests of chemical glassware.—See B., 1941, I, 450.

#### XIII.—GEOCHEMISTRY.

Theory of ground-water motion. M. K. Hubbert (J. Geol., 1940, 48, 785—944). L. S. T.

Geochemical studies of the volcanoes of Japan. XXIV. Radon content of mineral waters in Masutomi. S. Oana and K. Kuroda (Bull. Chem. Soc. Japan, 1940, 15, 485—486). —Data on Rn content, temp., and  $p_{\rm H}$  of a no. of mineral springs are given. F. J. G.

Analysis of some mineral waters from Ancash. L. A. Saldaña (Bol. Soc. Quim. Peru, 1941, 7, 76—84).—Ionic concn.,

hardness, and total solids are recorded for seven samples of mineral  $H_2O$  collected in the province of Ancash (Peru).

Temperatures and salinities under the ice in a shallow inlet. A. W. H. Needler  $(J.\ Fish.\ Res.\ Bd.\ Canada,\ 1941,\ 5,\ 236—243).—In Bideford "River," an arm of Malpeque Bay, a layer of <math>H_2O$ , 6 in.—3 ft. in thickness, of low salinity, is formed under the ice and persists until the disappearance of the ice. The min. possible temp. of this layer is > the f.p. of the bottom  $H_2O$  and convectional mixing of the surface and bottom  $H_2O$  is largely prevented. The temp. of the bottom  $H_2O$  is lowest early in winter when open  $H_2O$  is relatively near, then the temp. gradually rises as winter progresses until it approx. that of the surface  $H_2O$ .

Metamorphism of sediments of the deep well near Wasco, California, and of the deeply-buried Eocene sediments near Ventura, California. J. B. Lyons (J. Geol., 1940, 48, 436—443).—The sandstones and shales of this well, which were buried to a depth of 15,000 ft. and heated to 146°, have undergone no metamorphism other than the recrystallisation of the clay material to kaolinite. The similar sedimentary beds from the Ventura Basin, which were buried to a greater depth, have only minor amounts of sericite, chlorite, and epidote as metamorphic products. These facts indicate the inefficiency of load metamorphism in some Cenozoic strata.

Problems in the study of meteorites. W. F. Foshag (Amer. Min., 1941, 26, 137—144).—A review of present knowledge, and a discussion of such problems as structure and origin.

Nature of the ore-forming fluid. W. J. Bichan (Econ. Geol., 1941, 36, 212—217; cf. A., 1940, I, 379; 1941, I, 61).—Shortcomings of hydrothermal solutions as important orecarriers or as agents of ore-deposition are pointed out and discussed.

L. S. T.

Petrified wood composed of iron oxide. L. B. Roberts (J. Geol., 1940, 48, 212—213).—Petrified wood composed essentially of  $Fe_2O_3$  occurs in the Wilcox Eocene sand at Shreveport, Louisiana. L. S. T.

Origin of the Surigao [Mindanao] iron ores. D. F. Frasché (Econ. Geol., 1941, 36, 280—305).—This Fe ore deposit occurs as a superficial mantle over serpentised ultrabasic rocks. The ores are residual in origin, having been formed in situ by the subaerial decomp. of the serpentine rock. Chemical analyses [H. C. Witt] of samples taken at uniform intervals from a vertical section of serpentine rock and Fe ore are recorded; they show the changes that have taken place during the formation of the ore from the rock. Petrographic examination of the country rock reveals destruction of olivine, pyroxene, and serpentine minerals with accompanying formation of Fe oxides. Graphs of progressive chemical changes that have occurred during the formation of the ore indicate rapid losses of the more sol. constituents such as SiO<sub>2</sub> and MgO, and gains of Al<sub>2</sub>O<sub>3</sub>, Fe, Cr, Ni, and Co. Chemical analyses of 2000 samples show that the ore is fairly uniform in grade. The average analysis is Fe 47·77, Al<sub>2</sub>O<sub>3</sub> 7·93, Cr<sub>2</sub>O<sub>3</sub> 4·19, Ni–Co 0·78, SiO<sub>2</sub> 1·33, P 0·03, S 0·17, H<sub>2</sub>O 40·38%. The Surigao and Cuban laterites are similar in physical character, mineralogy, and chemical composition.

Ore minerals of the La Plata mountains, Colorado, compared with other telluride districts. F. W. Galbraith (Econ. Geol., 1941, 36, 324—334).—The main stages in the history of the ore formation are (i) deposition of quartz and pyrite (I), (ii) carbonates and other minor gangue minerals, (iii) vein sulphides in the order (I), sphalerite and chalcopyrite, tetrahedrite, and galena, (iv) tellurides, contemporaneous in age, and (v) native Au. Hessite is the most abundant of the tellurides, coloradoite the most widespread, krennerite is much less abundant and widespread, whilst calaverite, sylvanite, petzite, and native Te are present only sparingly. Supergene alteration of the ores is relatively unimportant, but the occurrence of native Te as a supergene replacement product of telluride minerals in ores from both Cripple Creek and Porcupine is probably the first of the kind to be described.

Pre-Cambrian crystalline rocks of north-central Utah. A. J. Eardley and R. A. Hatch (*J. Geol.*, 1940, 48, 58—72).—Sedimentary rocks, siliceous igneous rocks, injection gneisses, and

mafic rocks, all metamorphic, are described, and mineral analyses given. L. S. T.

Dilation and replacement dykes. G. E. Goodspeed (J. Geol., 1940, 48, 175—195).—Investigation of dykes in the Pacific Northwest, ranging from basalt and diabase to aplite and pegmatite, gives evidence of two contrasting mechanisms of dyke formation, viz., dilation concomitant with magmatic injection, and replacement.

Tentative classification of sand dunes; its application to dune history in the Southern High plains. F. A. Melton (J. Geol., 1940, 48, 113—145).

L. S. T.

Progressive metamorphism of siliceous limestone and dolomite. N. L. Bowen (J. Geol., 1940, 48, 225—274).—The metamorphism of siliceous dolomitic limestone is discussed with the aid of a composition tetrahedron which suggests that the changes can be referred to 13 grades or steps of increasing decarbonation, taking place at successively higher temp. at any given pressure. At the temp. appropriate to each step a certain phase assemblage becomes unstable, and each step is characterised by the disappearance of this assemblage. In 10 of the steps this disappearance is accompanied by the more conspicuous appearance of a new phase, a metamorphic mineral. In order of the increasing temp. steps at which they are produced the 10 minerals are tremolite, forsterite, diopside, periclase, wollastonite, monticellite, akermanite, spurrite, merwinite, and larnite. Examination of their natural occurrence suggests that these minerals are produced mainly under conditions that permit their use as temp. indicators.

Contact and endomorphic phenomena associated with a part of the Idaho batholith. A. L. Anderson and V. Hammerand (J. Geol., 1940, 48, 561-589).-Hydrothermal changes are described.

Artificial helicities and gypsum flowers. L. C. Huff (J. Geol., 1940, 48, 641-659).—Deposits similar to natural helictites have been formed in the laboratory by allowing aq. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, CaCl<sub>2</sub>, and CuSO<sub>4</sub> to evaporate. These deposits indicate that natural helicities grow at the free and not at the attached end, and assume their shape as a result of the chance orientation of crystals. Artificial formations similar to gypsum flowers indicate that porous rock is necessary for the growth of the natural flowers, which grow at the attached end, and assume their curvature, not as a result of strain, but of differential rate of growth.

Rigidity of rocks at high pressure. F. Birch and D. Bancroft (J. Geol., 1940, 48, 752—766).—Previous work (A., 1938, I, 480) is extended to pressures of 9000 kg. per sq. cm. and temp. up to 150° for certain igneous rocks. Changes of velocity on heating to 150° at 4000 kg. per sq. cm. for sedimentary and metamorphic rocks have also been determined. The dependence of velocity on composition is discussed.

Diorite-kinzigite formation in the surface deposits of the Dent Blanche (Valpellina range), in the Aosta region. E. Sanero (Period. Min., 1938, 9, 35—52; Chem. Zentr., 1938, ii, 3904).—A geological and petrographic study of quartz diorite, micaceous schist, contact rocks, and pegmatites from the deposit is reported. A. J. E. W.

Luminescent minerals; (A) fluorite; (B) fluorescence in the sodalite group and related groups; (c) natural zinc compounds, M. Deribéré (Ann. Soc. géol. Belg. [Bull.], 1937, 60, 377—381; 1938, 61, 52—55, 104—108; Chem. Zentr., 1938, i, 268, 2501; ii, 3894).—(A) Specimens from different sources have been examined; their photo- and thermo-luminescence show no inter-relation. The photoluminescence is violet unless the colour is influenced by rarer elements or hydrocarbons; the latter produce yellow fluorescence in a brown fluorite from Ontario.

(B) Previous observations are in general confirmed. Ontario hackmannite contains two distinct constituents showing pink and blue fluorescence, which have d 3.4, 3.3,

and hardness 5.5, 5, respectively.

(c) Wide variations with the source, composition, and mode of formation are observed. Oxides, carbonates, and hydroxides give little characteristic fluorescence. Some Zn blendes show fluorescence or triboluminescence. Some willemite specimens do not fluoresce, but others (particularly specimens containing Mn) show a strong green fluorescence in ultra-violet light. A. J. E. W.

Morenosite from Valtournanche, A. Cavinato (Period. Min., 1938, 9, 141—142; Chem. Zentr., 1938, ii, 3903).—A very pure specimen has the composition  $NiSO_4.6.5H_2O$  (NiO 27·16,  $SO_3$  29·58,  $H_2O$  42·49%). A. J. E. W.

Natural basic carbonates of copper and zinc. C. Lauro (Period. Min., 1938, 9, 105—136; Chem. Zentr., 1938, ii, 3903).—A chemical and X-ray examination of paraurichalcites (including a specimen associated with malachite at Tsumeb) and other basic Cu Zn carbonates shows the existence of two groups,  $2R^{II}CO_3, 3R^{II}(OH)_2$  and  $R^{II}CO_3, R^{II}(OH)_2$ , in which CuO: ZnO is < or >1, respectively. The first group includes aurichalcite and the second, which shows similarities to malachite, includes rosasite, paraurichalcite-I and -II, and cuprozincite.

Barytes from Campo Pisanu (Iglesias). C. Lauro (*Period. Min.*, 1938, 9, 139—141; *Chem. Zentr.*, 1938, ii, 3903).—The mineral consists of aggregates of small crystals which are tabular on  $\{001\}$  and somewhat prolonged along [010]; the angles correspond with a:b:c=0.8152:1:1.3136.

Quicksilver deposits of the Terlingua Region, Texas. C. P. Ross (Econ. Geol., 1941, 36, 115—142).—A detailed account of work already noted (A., 1940, I, 422). The gangue minerals, especially, the calcite especially the calcite, were derived probably from the sedimentary rocks with some addition of material from deep sources. L. S. T.

Quartz xenocrysts in olivine basalt from the southern Sierra Nevada of California. R. W. Webb (Amer. Min., 1941, 26, 321—337).—Isolated bodies of little-known volcanic rocks are described. Olivine basalts containing well-defined quartz xenocrysts are common. The quartz may be derived from the alteration of numerous inclusions of granodiorite in the

Thermoluminescence of quartz after irradiation with X-rays. Thermontaininescence of quartz area framation with  $\lambda$ -rays. T. Futagami (*Proc. phys.-math. Soc. Japan.* 1938, [iii], 20, 458—466; *Chem. Zentr.*, 1938, ii, 3894).—Quartz becomes opaque on exposure to X-rays and afterwards emits a blue luminescence on warming. The absorption spectrum of the irradiated quartz extends from the infra-red into the ultraviolet, with flat max. at 302 and 390 m $\mu$ . The thermoluminescence spectrum (385—610 m $\mu$ ) has a max. at 469 m $\mu$ . the intensity distribution and its variation with time and temp. are examined.

Gray quartz breccia ore body of the Highland Mine, Butte, Montana. R. C. Newcomb (Econ. Geol., 1941, 36, 185—198).—The auriferous-quartz ore body of this mine is an open-textured siliceous sponge-breccia, which occurs as a replacement of Cambrian dolomite. The sponge texture is secondary; it has arisen from the abstraction of sulphides, mainly pyrite. Volumetric accommodation to the leaching was marked by the collapse of many primary ore structures, and by considerable slumping. The fragments are now cemented weakly by SiO<sub>2</sub>. The leaching, by residual concn., improved the grade of the ore.

Mineral resources of Mayurbhanj State. D. C. Nag (Quart. Geol. Soc., India, 1940, 12, 61-71).—The following are described briefly: hæmatite, extensive V-bearing magnetite, and Cu belts, deposits of Au, Ti, Mn, refractory and building materials. The genesis of the ore deposits is discussed.

Unusual occurrence of carbon in cavities of limestone. N. L. Sharma and K. B. Swamy (Quart. J. Geol. Soc., India, 1940, 12, 73—76).—The limestone of Baraduar area, Bilaspur district, C.P., contains cavities lined with calcite, the interspaces of which are filled with soft, jet-black lumps of finelydivided, impalpable C. Meteoric waters were probably responsible for the deposition of the C and the limestone. The C is of org. origin.

Fuller's earth deposits of Jodhpur State, Rajputana. K. L. Bhola (Quart. J. Geol. Soc., India, 1940, 12, 83—97).— Deposits at Kapurdi, Rohli, Joranada, and Dip-ki-Dhani are described. The occurrence, properties, mining, and uses of the earth are described. Fuller's earth from Kapurdi contains SiO<sub>2</sub> 47.00, Al<sub>2</sub>O<sub>3</sub> 23.30, Fe<sub>2</sub>O<sub>3</sub> 6.95, CaO 2.90, MgO trace, K<sub>2</sub>O + Na<sub>2</sub>O 5.92, loss on ignition 13.55, total 99.62%.

Analysis of Washington coals.—See B., 1941, I, 429.

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