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## BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

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

SEPTEMBER, 1943.

#### I.—SUB-ATOMICS.

Atomic beams in spectroscopy.—See A., 1943, I, 209.

Zeeman effect of the spectrum of singly-ionised argon in fields of 55,000 Gauss. R. Bezler (Z. Physik, 1940, 116, 480—494).—The Zeeman effect of 81 A II lines has been investigated, with a field of 55,000 gauss. Some very narrow, formerly unresolved Zeeman lines, and further anomalous g-vals., have been observed, especially with the  $4d^4D_4$  (3p) term.

A. J. M.

Zeeman effect in xenon spark spectrum, Xe II. H. Angenetter (Z. Physik, 1939, 114, 636—650).—Data are recorded for 32 classified and 45 unclassified spark lines of Xe between 3811 and 6344 A.

Determination and explanation of the limits of layers emitting sodium fluorescence radiation in evening light. G. Cario and U. Stille (Z. Physik, 1940, 116, 122—136).—The height of 60 km. found by Bernard (A., 1938, I, 543) for the layer of glowing Na is only a min. val. for the upper limit, obtained by supposing that the troposphere is perfectly transparent to light. If absorption in the troposphere is taken into account, the upper limit for the height of the glowing Na layer is calc. to be 78 km., the lower edge being at 69 km.

A. J. M.

Influence of concentration on the intensity of spectral lines in the spark. F. de Boer (Z. Elektrochem., 1940, 46, 591—594).—Measurement of the intensities (I) of the lines in the spark spectra of Pb-Sn alloys shows that the relation  $\log I = a \log c + b$  (c = concn., a and b are consts.) approaches a simpler form with a = 1 at low vals. of c. Deviations of a from unity are attributed to absorption in the vapour. The ratio of the concns. of the metals in the vapour is approx. that in the electrodes, no distillation effect being observed. Similar results are obtained with Sn in Ag or Cd and for Cd in Zn.

Distribution of the intensities of spectral lines over the path of the spark. F. de Boer (Z. Elektrochem., 1940, 46, 594—595).—The relative intensities of various Sn and Pb spectral lines have been measured during the passage of sparks between electrodes of pure Sn and of Sn containing 7 at.—% of Pb. The average intensity of the Pb lines over the whole path when the alloy is anode is  $\sim\!40\%$  > when it is the cathode. The variation of the relative intensities of various Pb lines along the path of the spark can be explained by assuming that the outer vapour shell of the spark comprises mainly material from the anode, which is the hotter electrode. J. W. S.

Continuous spectrum of the carbon arc light. II. H. Maecker (Z. Physik, 1940, 116, 257—266; cf. A., 1940, I, 183).—The construction of a stabilised C arc in a quartz tube 10 mm. in diameter, filled with  $N_2$ , is described. A current of 30—50 amp. and a c.d. of 2600 amp. per sq. cm. were obtained. The temp. was  $13,000^{\circ}$  κ. and the electron pressure 60 mm. The continuous spectrum of the arc light was investigated. The variation of the absorption coeff. with  $\lambda$  and temp. was examined, and its abs. val. determined. The experimental curve is similar in shape to the theoretical curve for the absorption coeff. of free electrons, but the latter is somewhat the same of the absorption coeff.

B.p. of carbon and the high-current arc. E. Podszus (Z. Physik, 1940, 116, 352—358).—The characteristics of high-current arcs are discussed.

A. J. M.

So-called minimal arcing potential. P. Rossbach and R. Seeliger (Z. Physik, 1940, 116, 68—72).—It is pointed out that the min. arcing potential, i.e., the smallest potential under which it is possible to maintain an arc between given electrodes, can be determined by the usual method to an accuracy of only 1 v. It represents the sum of the anode and cathode drops.

A. J. M.

Calculation of the eigenfunction and energy of the ground state of the valency electrons in alkaline-earth atoms. P. Gombås (Z. Physik, 1940, 116, 184—193).—A method formerly described (A., 1940, I, 149) is used to calculate the eigenfunction and energy of the valency electrons of the alkaline-earth atoms in the ground state. For the Ca atom, the calc. vals. of the first and second ionisation energies are 5.78 and 11.19 e.v.

A. J. M.

Experimental test of the wave-mechanical theory of field electron emission. R. Haefer (Z. Physik, 1940, 116, 604—623).—Former 213 I (A., I.)

investigations of the field electron emission from points have been difficult on account of an incomplete knowledge of the true form of the point, but this can now be obtained by means of the electron microscope. W points were used with a field strength of  $3\times 10^7~\rm v.$  per cm. The wave-mechanical theory was confirmed for pure W. Theory requires that the c.d. should be  $\propto$  (emission work)  $^{1.5}$ . Deviations from this for Ba adsorbed on W are due to an increase in the field strength on account of crystallite formation. The wave-mechanical theoretical results can also be verified for crystallite-free, electron-microscopically controlled layers of Ba, K, and Cs.

Electronics of natural cleavage surfaces of metallic single crystals. I. Formation of cleavage surfaces of single crystals of zinc in a high vacuum and preliminary photo-electric measurements. W. Kluge and H. Steyskal (Z. Physik, 1940, 116, 415—427).—The cleavage of a single crystal of a metal in a high vac. provides a method of determining the effect of crystal orientation on the electronic properties of various boundary surfaces. The effect of secondary structure and impurities is discussed. A method is described for determining the photo-emission of a (0001) face of a Zn single crystal. The  $\lambda$  limit of the photo-effect is  $\lambda_0=290\pm0.7$  mm., and the val. of the emission work-function is 4.26 e.v.

Internal motion of the electron. III. H. Hönl and A. Papapetrou (Z. Physik, 1940, 116, 153—183; cf. A., 1939, I, 394; 1940, I, 185).—Theoretical. The relationship between the Dirac electron and polar-dipolar particles is investigated. The details of macroand micro-motion of the electron, the characteristic impulse moment, and the energy function are obtained. The polar-dipolar particle may be regarded as the classical model of the Dirac electron.

A. J. M.

Theory of electronic plasma vibrations. R. Seeliger (Z. Physik, 1942, 118, 618—623).—Mathematical (cf. Tonks and Langmuir, A., 1929, 1369).

W. R. A.

Significance of ternary collisions in energy relations of discharges in gases. R. Rebsch  $(Z.\ Physik,\ 1939,\ 114,\ 620-635)$ .—The energy transfer between two electrons colliding in the presence of a neutral atom is derived from wave-mechanical principles. The energy relations of discharges in gases still present difficulties even if such ternary collisions are taken into account.

L. J. J.

Cathodic sputtering by oblique ionic bombardment. H. Fetz (Z. Physik, 1942, 119, 590-601).—Sputtering of thin wires by ions of long free-path increases rapidly with decreasing thickness of the wire, owing to the greater sp. effect of oblique impact. L. J. J.

Physical chemistry of a cooling planet. P. G. Nutting (J. Washington Acad. Sci., 1943, 33, 121—125).—A tentative sketch of the stages of the probable early physical history of the earth on a temp. instead of a time scale, based on known data (m.p., b.p., crit. temp. and pressure) for the materials composing its surface. N. M. B.

Behaviour of hydrogen bromide in nuclear processes of bromine.—See A., 1943, I, 206.

Artificial radioactive isotopes of lead and neighbouring elements, produced from uranium and thorium lead. W. Maurer and W. Ramm (Z. Physik, 1942, 119, 602—629).—3·3-hr.  $^{209}\mathrm{Pb}$ , from  $^{209}\mathrm{Bi}$  (n, p) and  $^{208}\mathrm{Pb}$  (n), has target area  $10^{-27}$  sq. cm. for addition of thermal neutrons and a greater val. for fast neutrons, and emits electrons of 750 ke.v. without y-radiation. 52-hr.  $^{203}\mathrm{Pb}$ , from  $^{204}\mathrm{Pb}$  (n, 2n), is not formed with neutrons <5·3 Me.v.; it emits  $\beta$ -radiations of 180 and 330 ke.v. by internal transformation of two y-quanta of 270 and 420 ke.v., and strong y- and X-radiations. 68-min.  $^{204}$  or  $^{205}\mathrm{Pb}$ , from  $^{204}\mathrm{Pb}$  with unretarded (Li + a) neutrons, has target area <7 × 10- $^{28}$  sq. cm. for addition of thermal neutrons. It emits several  $\beta$ -lines up to 750 ke.v. and y-radiation up to 900 ke.v.  $^{209}\mathrm{Pi}$  absorbs fast neutrons, and thermal neutrons with target area  $10^{-27}$  sq. cm. 13-day  $^{202}\mathrm{Tl}$  emits strong X-radiation of  $\sim$ 70 ke.v., and y-radiation of 400 ke.v.  $^{5.5}\mathrm{-min}$ .  $^{205}\mathrm{Hg}$  is formed from  $^{205}\mathrm{Tl}$  (n, p) and  $^{203}\mathrm{Pb}$  (n, a). 30—60-day  $^{203}\mathrm{Hg}$  is formed from Tl (n, p). 48-min.  $^{200}\mathrm{Cay}$  as formed from  $^{205}\mathrm{Tl}$  (n, p) and from Hg (n, p).

Energy threshold of disintegration neutrons from uranium. W. Bothe and W. Gentner (Z. Physik, 1942, 119, 568—574).—The energy spectrum of neutrons emitted from U disintegrated by

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thermal neutrons from the  $^{14}{\rm N}$  (n, a) reaction is shown by a photographic method to extend to slightly  $>\!10$  Me.v. L. J. J.

Nuclear structure of the elements. L. H. Sensicle (Chem. and Ind., 1943, 234—235).—The suggestion previously advanced (A., 1943, I, 79) for a nuclear model based on the equilateral triangle, one edge of which represents an electron, and two a proton, is extended. As the periodic table is ascended, some nuclei may be given alternative model structures, involving principally the icosahedron. It is shown how isotopes of U can be built up in this way. The single icosahedron type of model is present in Fe, Ni, and Co, and it is suggested that on this account atoms of these elements have a preferred axis of rotation. This tends to fix the axis of revolution of the orbital electrons, and is characteristic of ferromagnetic elements. The structure of Er is also discussed.

A. J. M.

Nuclear isomerism of strontium. H. Reddemann (Z. Physik, 1940, 116, 137—143; cf. A., 1940, I, 383).—The product from pure  $^{87}$ Sr irradiated with neutrons, with half-life 3 hr., is identified with a radioactive isomeride of stable  $^{87}$ Sr. The effective cross-section of the reaction  $^{87}$ Sr (n,n)  $^{87*}$ Sr has been obtained for D + D neutrons.

Electrical quadrupole moment of the iodine nucleus. K. Murakawa (Z. Physik, 1939, 114, 651—652; cf. A., 1939, I, 290).—A correction.

Solar half-day period of cosmic rays at the equator. W. Rau (Z. Physik, 1940, 116, 105—114).—The twice-daily variation in intensity of the hard components of cosmic rays, found in the ocean, has been confirmed by experiments [by H. Hoerlin] carried out in the Peruvian mountains, near the equator. The amplitude of variation is  $\pm 0.8\%$ , and the phase agrees with that found in experiments carried out at a depth of 40 m. of H<sub>2</sub>O. The layers in the upper atm., in which the mesotrons of the hard components are produced, must undergo a twice-daily variation, so that the mesotrons have different path-lengths.

A. J. M.

Cloud chamber investigations with hard secondary radiation from cosmic rays. S. Liesegang (Z. Physik, 1940, 116, 515—524).—The hard secondary rays liberated from Pb by cosmic rays have been investigated. It is shown that the second max. at  $\sim\!\!30$  cm. Fe ( $\sim\!\!20$  cm. Pb), observed by Maass, is produced by non-ionised particles, which are converted into ionised particles in the secondary radiation. A. J. M.

Observations of showers in air and nuclear fissions with cosmic rays in the ionisation chamber. H. Euler (Z. Physik, 1940, 116, 73—104).—The theory of extended showers in air is compared with the observation of Hoffmann collisions in an uncovered ionisation chamber. The larger collisions in the Hoffmann effect can be quantitatively explained as the effect of air showers, if assumptions are made concerning the energy of electrons in space. The effect of temp, and pressure on these collisions is calc. The smaller collisions cannot be explained as the result of air showers, but correspond to nuclear fission brought about by cosmic rays. The small frequency of air showers provides evidence for the view that the electrons observed at sea level are not produced by a cascade effect from the electrons of space, but by secondary processes from the hard radiation.

A. J. M.

Cascade theory with collision loss. H. J. Bhabha and S. K. Chakrabarty (*Proc. Roy. Soc.*, 1943, A, 181, 267—303).—Subject to certain assumptions, a solution of the cascade equations is given in the form of a series which is so rapidly convergent that in general it is necessary only to calculate the first term. This term alone gives to a high degree of accuracy the whole energy spectrum of electrons from the highest energy to energies below the crit. level.

Liberation of single secondary electrons by mesotrons and electrons. E. Stuhlinger (Z. Physik, 1940, 116, 281—297).—Wilson photographs indicate that of 100 mesotrons,  $\sim$ 10 liberate one or more secondary electrons of energy  $<10^4$  e.v. when passed into a Pb sheet 9 mm. thick. About the same no. of electrons were liberated from a similar Al sheet.  $\sim$ 75% of the light electrons rich in energy are doubled or quadrupled when passed into a 9-mm. Pb sheet. Experiments with counter tubes give somewhat smaller nos. of secondary electrons liberated by mesotrons, and show that the no. produced in a Pb sheet is < that produced in an Al sheet of mass-equiv. thickness. The no. of secondary electrons is compared with the theoretical val. of Bhabha, the energy spectrum of mesotrons obtained by Blackett being employed.

Thermodynamic method for Planck's radiation law. E. Lohr (Z. Physik, 1940, 116, 454—468).—Theoretical. It is shown that the supposition of the coexistence of a "radiation gas" with radiation leads to the Rayleigh-Jeans radiation law. The "radiation gas" is then replaced by a gas mixture, and the Planck law is deduced.

Quantum-mechanical treatment of atomic collisions.
(Naturwiss., 1942, 30, 533—534).—Mathematical.

A. J. M.
E. Lindholm
L. J. J.

Origin of gravitational field. E. Reichenbächer (Z. Physik, 1942, 119, 630—658).—Theoretical. The author's non-relativistic theory

leads to the Newtonian law and the Einstein effect as first and second approximations, respectively.

L. J. J.

Gravitational effects between polar-dipolar particles. A. Papapetrou (Z. Physik, 1940, 116, 298—309).—The gravitational force between two macroscopic polar-dipolar particles at rest has been calc. If the particles are widely separated the mean attraction is identical with the Newtonian attraction between simple mass poles. The momentary val. of the gravitational force, however, shows considerable variations about this mean val., owing to the internal motion of the particle.

A. J. M.

#### II.—MOLECULAR STRUCTURE.

Intensity distribution in the quartet-doublet bands. I. A. Budó and I. Kovács (Z. Physik, 1940, 116, 693—700).—Theoretical. The intensity distribution in the branches of the inter-combination bands  $^4\Sigma^{\pm}-^2\Sigma^{\pm}$ ,  $^4\Sigma^{\pm}-^2\Sigma^{\mp}$ ,  $^4\Sigma^{-2}\Pi(a)$ , and  $^4\Sigma^{-2}\Pi(b)$  is calc.

Explanation of perturbations in the nitrogen bands. L. Gerö and R. Schmid (Z. Physik, 1940, 116, 246—248).—Perturbations in the N<sub>2</sub> and N<sub>2</sub><sup>+</sup> bands can be explained by taking nuclear spin into account. The usual J-quantum no. is replaced by the corresponding total rotational impulse quantum nos. The Zeeman effect observed by Parker (A., 1933, 879) with perturbed N<sub>2</sub><sup>+</sup> lines can also be simply explained by introducing nuclear spin.

A. J. M.

Rotational analysis of the IV positive bands of the nitrogen molecule. L. Gerö and R. Schmid (Z. Physik, 1940, 116, 598—603).—An analysis of the bands  $\lambda$  2351 A. (0–1) and  $\lambda$  2448 A. (0–2) of the  $D-B^3\Pi$  system of  $N_2$  is given. The bands consist of 15 branches, of which 5 are edge-forming. The lines show intensity variations within the branch. For even rotational quantum nos., the  $S_1$ ,  $Q_1$ ,  $R_2$ ,  $P_2$ ,  $Q_3$ , and  $Q_3$  lines are the strongest. The rotational consts. for the  $D^3\Sigma_u^+$  state of  $N_2$  are  $B_0=1.961$  cm. and  $D_0=2\times10^{-5}$  cm. A. J. M.

Formation of molecules in binary collisions. I. Aluminium hydrides. G. Stenvinkel (Z. Physik, 1939, 114, 602—619).—The spectrum of AlH obtained by heating Al in H<sub>2</sub> by means of an electric furnace shows enhanced intensity in the lines which are missing in the arc spectrum. This anomaly depends on the time elapsed since the beginning of the experiment, and the temp. and pressure in the furnace. A continuous spectrum is obtained at sufficiently high temp. and pressure. These effects are explained by the formation of AlH in the <sup>1</sup>H state by binary collisions.

L. J. J.

Completion of the term scheme of lead hydride. L. Gerō (Z. Physik, 1940, 116, 379—384).—Perturbations in the PbH spectrum have been investigated, and the anomalous behaviour of the rotation consts. of the initial term of the  ${}^2\Sigma \rightarrow {}^2\Sigma$  bands is ascribed to  $\Delta\Lambda=0$  perturbations. Investigation of the possibility of dissociation shows that the excited PbH terms cannot be dissociated in the at. terms of the Pb fundamental electron configuration.

Ultra-violet radiation of a non-self-dependent gas discharge. W. Schwiecker (Z. Physik, 1940, 116, 562—575).—An apparatus involving a counter tube has been used to investigate the properties of the ultra-violet radiation from a non-self-dependent gas discharge in air and  $H_2$ , using plane electrodes. The intensity of various  $\lambda$  regions of the radiation has been determined. The absorption coeff. of the radiation in the gas was also obtained. 400% of the radiation has  $\lambda < 1000 \, \text{A}$ . The absorption coeff. in air is  $\sim 0.4 \, \text{cm}^{-1}$  (200 mm. pressure) or  $\sim 1.5 \, \text{cm}^{-1}$  (760 mm. pressure). In  $H_2$  the absorption coeffs. are about half these vals.

Combination frequencies in the electronic-vibrational spectrum of rare earth salts. K. H. Hellwege and A. Roever (Z. Physik, 1939, 114, 564-570).—A no. of weak lines in the absorption spectra of rare earth salts at  $20^{\circ}$  K. are identified with superposition of combinations of different anharmonic lattice vibrations on a single electronic transition.

Ion association and absorption spectrum. III. H. von Halban and M. Litmanowitsch (Helv. Chim. Acta, 1943, 26, 771—788).—The deviations from Beer's law for solutions of picric acid (I) in moist dioxan (II) decrease with increasing degree of purification of (II), and their dependence on the concn. of (I) or of added mineral acid suggests the presence of a basic impurity. The observed absorption spectra are compounded of those for undissociated (I) and for associated ion pairs of  $H_3O$  and the ion of (I) (cf. A., 1941, I, 237).

Absorption spectra of explosives.—See B., 1943, I, 348.

Structure of sodium borate glasses as affected by temperature. A. E. Badger, H. C. Johnson, and J. O. Kraehenbuehl (J. Amer. Ceram. Soc., 1942, 25, 395—401).—Spectral transmission curves were determined for Na<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> glasses containing 0—30% of Na<sub>2</sub>O and coloured with 0·1% of Co<sub>2</sub>O<sub>4</sub>, at temp. up to the softening point. An abrupt rate of change of transmission with temp occurred at or near the transformation temp., and a clearly defined

break occurred in the property-composition curve at  $\sim 15\%$  of Na<sub>2</sub>O. Theoretical deduction indicates that glasses containing 10 and 20% of Na<sub>2</sub>O correspond with stable configurations. K<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> glasses show similar changes. The use of colour indicators to show changes in the high-temp, structure of glasses is a reliable method.

Absorption lines of water vapour in the spectral wave-length range 0-15—0-5 mm. H. Hopf (Z. Physik, 1940, 116, 310—316).—A spectrophotometer for the long- $\lambda$  infra-red has been constructed. It can be used for determinations in the range  $150-400~\mu$ ., with a slit-width of  $18~\mu$ . Individual lines in the absorption spectrum of H<sub>2</sub>O vapour in this range have been investigated. The max. occur at 220 and  $325~\mu$ ., and there are min. at 212 and  $304~\mu$ . A. J. M.

Absorption of liquid water and deuterium oxide in the infra-red region between 5  $\mu$ . and 27  $\mu$ . M. Sohm (Z. Physik, 1940, 116, 34—46).—The absorption spectra of  $H_2O$  and  $D_2O$  in thin layers have been determined in the near infra-red. For  $H_2O$ , the absorption gradually increases from 10 to  $15\,\mu$ , after which there is a regular series of absorption max. The absorption curve for  $D_2O$  is similar to that for  $H_2O$ , but there is a displacement of the intramol. vibration bands to longer  $\lambda\lambda$ , indicated by the fact that the regular series of absorption max. does not begin before  $19\,\mu$ . The separation of these max. (41 cm.-1) is somewhat < that for  $H_2O$  (52 cm.-1). If the mol. is capable of free rotation the separation in the case of  $D_2O$  should be approx. half that in the case of  $H_2O$ . The absorption spectrum of liquid  $H_2O$  shows many similarities to that of the vapour.

Infra-red absorption spectrum and configuration of cyclohexane. R. S. Rasmussen (J. Chem. Physics, 1943, 11, 249—252).—32 infra-red absorption frequencies are recorded between 673.4 and 4330 cm.<sup>-1</sup> for cyclohexane vapour at 5 and 40 mm. Hg and room temp. Five bands are found in the C-C stretching and CH<sub>2</sub> rocking and twisting range, in agreement with the chair structure (symmetry D<sub>24</sub>) rather than the cradle or planar structure. The band envelopes agree with Gerhard and Dennison's theory (A., 1933, 337).

L. J. J.

Quantitative photographic absorption determinations on the CH bands of aliphatic alcohols at  $\lambda$  9100 A. R. Ziegler (Z. Physik, 1940, 116, 716—728).—The absorption spectra ( $\lambda$  8500—13,000 A.) of MeOH, EtOH, PraOH, PrBOH, BuaOH, BuBOH, BuPOH, iso- and tert.-C<sub>5</sub>H<sub>11</sub>-OH, n-C<sub>6</sub>H<sub>12</sub>-OH, (CH<sub>2</sub>-OH)<sub>2</sub>, and glycerol were determined with the pure alcohols and with solutions. The integral absorption of the bands of the third CH overtone at 9100 A., and the positions of the neighbouring OH bands, were determined. With most of the alcohols there is a widening and splitting of the CH bands, due to association, which is dependent on the dilution in the case of solutions of the alcohols in non-polar solvents. In consequence of the effect of association, the integral absorption of the bands of the individual alcohols is not  $\alpha$  no. of CH vibrations in the mol. Diffuse OH bands indicate the existence of association, although sharp OH bands due to single mols. are also found. The fine structure of these sharp OH bands is compared with previous data; it can be explained as a rotational splitting. If this occurs, however, free rotation in solution is not possible with MeOH and Pr $\beta$ OH, as the OH bands of these substances show no splitting.

A. J. M. Absorption of light by az-dien- $\gamma$ -inenes in the region 2300—2900 A. H. Bastron, R. E. Davis, and L. W. Butz (J. Amer. Chem. Soc., 1943, 65. 973—975).—Absorption spectra (2300—2900 A.) are recorded for the following in EtOH, figures quoted being for the max.: (CH<sub>2</sub>·CMe-C<sub>2</sub>)<sub>2</sub> (b.p. 82—85°/101 mm.) 2525 A. (z 14,500); a- $\Delta$ 1-cyclopentenyl- (b.p. 81°/13 mm.) 2615 A. (z 13,000) and (mainly 2-)methyl- $\Delta$ 1-cyclopentenyl- $\Delta$ 7-buten- $\Delta$ 8-inene (b.p. 90°/14 mm.) 2600 A. (z 11,500); a- $\Delta$ 1-cyclopentenyl- $\beta$ - $\Delta$ 1-cyclohexenyl- (b.p. 110—113°/1 mm.) 2650 (z 15,000) and 2780 A. (z 11,500) [min. at 2750 A. (z 10,500)] and  $-\beta$ -4-methoxy- $\Delta$ 1-cyclohexenyl-acetylene (b.p. 136°/1·5 mm.) 2645 (z 14,750) and 2770 A. (z 11,500) [min. at 2720 A. (z 11,000)];  $a\beta$ -di- $\Delta$ 1-cyclohexenyl- (b.p. 130°/2 mm.) 2625 (z 12,500) and 2755 A. (z 9000) [min. at 2725 A. (z 8000)], and a- $\Delta$ 1-cyclohexenyl- $\alpha$ 1-cyclohexenyl-acetylene (b.p. 118—121°/0·5 mm.) 2650 A. (z 12,000). Introduction of one or more rings progressively moves the principal absorption max. to longer  $\alpha$ 1-cyclohexenylethylene [max. at 2611 A. (z 45,600)] and  $\alpha$ 3-di- $\alpha$ 1-cyclohexenylethylene [max. at 2690 A. (z 22,900)] shows that replacement of C.C by C.C shifts the principal max. to longer  $\alpha$ 2 And considerably decreases z.

Quantitative determination of the absorption of benzene and benzene derivatives in the near infra-red. H. Kempter (Z. Physik, 1940, 116, 1—18).—A photo-electric method for the rapid determination of absorption in the near infra-red (7000—11,000 a.) to within 0·1% is described. Determinations were made by the null method, and for the Cs cell used the compensation voltage was  $\alpha$  intensity of illumination. Beer's law holds accurately for solutions of  $C_eH_e$  in CCl4, and Lambert's law was tested in the case of  $C_eH_e$ , PhMe, xylene, and  $C_eH_3Me_3$ . The absorption of  $C_eH_e$ , PhMe, p-xylene, s-C\_eH\_3Me\_3, PhEt, PhNO\_2, BzOH, polystyrene, styrene, and PhCl was determined. The proportionality between absorption in the

CH band and the no. of CH valencies of the same degree of saturation is verified.

A. J. M.

Spectrophotometric study of green colour in peas and okra.—See

Aromatic hydrocarbons and their derivatives. XXXII. Influence of angular anellation on the absorption spectra of aromatic hydrocarbons. E. Clar (Ber., 1940, 73, [B], 596-606; cf. A., 1940, II, 273).—Absorption spectra data are recorded for 1:2:3:4-1:2:5:6-, and 1:2:7:8-di- and 1:2:3:4:5:6-tri-benz-anthracene, 1:2:9:10-dibenztetracene, pentaphene, isopentaphene, 1:2-benzpentaphene, phenanthrene, chrysene, 3:4- and 8:9-benztetraphene, anthracene, etc., and the relationship of the spectra to mol. structure is discussed.

A. T. P.

Orientation of molecules produced photochemically in rigid solvents. G. N. Lewis and J. Bigeleisen (J. Amer. Chem. Soc., 1943, 65, 520—526).—Long conjugated mols., e.g., benzidines, after illumination in solid media with plane-polarised light show max. absorption for light polarised parallel and min. absorption for polarisation perpendicular to the exciting radiation (normal orientation). In abnormal orientation, as with Wurster's blue (I), the absorption relationship is inverted. Max. polarisability axes of the mol. and photochemically produced ion are parallel and perpendicular, respectively, in normal and abnormal orientations. Max. orientation is calc. and compared with observed vals. Oriented solutions of (I) lost orientation when warmed, and at higher temp. the colour also faded.

W. R. A.

Ultra-violet dispersion frequencies of the alkali-metal oxides. W. Rauch (Z. Physik, 1940, 116, 652—656).—The prep. of thin films of alkali-metal oxides on quartz is described. The ultra-violet dispersion frequencies have been obtained. The position of the first max. of the bands is satisfactorily given by an empirical formula.

A. J. M.

Measurement of relaxation time of fluorescence. W. Kirchhoff (Z. Physik, 1940, 116, 115—121).—An improved fluorometer for measuring relaxation times is described. The vals. obtained for fluorescein (4.90  $\times$  10-9 sec.) and eosin (4.82  $\times$  10-9 sec.) agree well with vals. formerly obtained. With  $\psi$ -isocyanine and two of its derivatives and quinoline-red the relaxation time found was <10-9 sec. This is the smallest val. yet obtained, and can be explained if it is supposed, with Scheibe, that the fluorescence is due not to a single mol. but to a polymeric complex, which is regarded as a system of coupled resonators; this assumption is not necessary, however, and it is possible to explain the small relaxation time if the mol. is regarded as a normal oscillator. A. J. M.

Mechanical and optical "excitation" of colour centres. A. Smekal (Z. Physik, 1940, 116, 525—546).—The colour band of NaCl crystals is not, in general, a single F-band, but consists of an F- and an F'-band very close together, which cannot be separated optically. Their presence is indicated by the magnitude of the half-val. widening and its dependence on the state of the crystal. The mutual thermal and optical transformation of F- and F'-centres depends on the state of the crystal. In optical excitation phenomena, F-, F'-, and  $F_2$ -centres all take part. The state of the crystal is also responsible, at least partly, for the general space arrangement of colour centres. A. J. M.

Behaviour of phosphors when irradiated intermittently with electrons. M. Knoll (Z. Physik, 1940, 116, 385—414).—The behaviour of phosphors when irradiated intermittently with electrons is investigated, with special reference to the screens of cathode-ray tubes. The period elapsing before the phosphor responds, and the time for which it remains glowing after the removal of the excitation, are examined at low temp. These periods depend, in the case of ZnS-CdS phosphors, on the electron concn. and not on the temp. (0° to -190°) of the screen. The decrease of brightness on warming to 0° is investigated for ZnO and ZnS-CdS on glass and metal carriers. With intermittent excitation there is a decrease in brightness with increase of electron concn. Cooling of the phosphorescent screen shows this to be a temp. effect; it is greater with glass than with metal screens. Charging and secondary emission phenomena are also considered.

A. J. M.

Determination of chlorine vibrations in dichlorobenzenes from intensities and polarisations of their Raman lines. G. Nordheim and H. Sponer (J. Chem. Physics, 1943, 11, 253—262).—Theoretical. Raman tensors for Cl vibrations in  $C_0H_4Cl_2$  are calc. by adding or subtracting single C–Cl contributions for a series of axes fixed with respect to the mol., and intensity ratios are deduced for symmetrical valency and unsymmetrical deformation vibrations. Very small depolarisation factors are found for the former and complete depolarisation for the latter, for all permitted Raman lines.

Thermodynamics and molecular structure of benzene and its mthyl derivatives. III. Vibration frequencies of benzene. IV. Vibration frequencies of toluene, o-, m-, and p-xylenes, and mesitylene. K. S. Pitzer and D. W. Scott (J. Amer. Chem. Soc., 1943, 65, 814—817,

817-824; cf. A., 1943, I, 223).—III. Wilson's numbering scheme (cf. A., 1934, 829) being followed,  $\nu\nu$  vals. for the normal modes 3,

14, 15, and 17 have been assigned on the  $C_p$  data, as follows: 3, 1298; 15, 1170; 14, 1693; 17, 985 cm.<sup>-1</sup>

IV. With the aid of a product ratio analogous to the Teller-Redlich product rule for isotopic substitution, assignments of vibrational vv have been made from calorimetric and spectroscopic data for mesitylene, PhMe, and o-, m-, and p-xylene.

Ionisation potential of the nitrogen molecule. U. Stille (Z. Physik, 1940, 116, 144-152).—The occurrence of negative bands in the spectrum of the after-glow of N<sub>2</sub> is discussed. The possibility of the ionisation of N<sub>2</sub> by a collision process in active N is discussed in relation to the val. of 13·3 v. obtained for the ionisation potential of N<sub>2</sub> by Rypdal and Vegard (*Geofys. Publ. Oslo*, 1940, 12, No. 12) with an electron-collision apparatus, in which the intensity of the emitted light was measured as a function of the velocity of the exciting electrons. This result for the ionisation potential is compared with vals. formerly obtained, which are all >13.3 v. Acceptance of the new val. brings disagreement with a no. of well-established data.

Dependence of column ionisation by a-rays on pressure. E. Helbig (Z. Physik, 1940, 116, 444—453).—The effect of pressure (p)on column ionisation produced by a beam of a-rays perpendicular to the electric field has been investigated in air, CO2, H2, A, and air-CO<sub>2</sub> mixtures. The theory of column ionisation is presented. The p effect given by the theory is verified in the case of irradiation perpendicular to the electric field. Large deviations occur only for  $H_2$  and A for small fields, and these are due to ion loss in consequence of diffusion to the walls. The recombination coeffs for air and CO<sub>2</sub> are calc. For both gases it decreases with increasing

Secondary production of electrons through the photo-effect in a non-self-dependent discharge in air. H. Costa (Z. Physik, 1940, 116, 508—514).—The proportion of secondary electrons produced in a Townsend discharge in air up to near the breakdown point has been determined by a reathed similar to that used for H. he a Townsend discharge in air up to hear the bleakdown point has been determined by a method similar to that used for H<sub>2</sub> (A., 1940, I, 2). Vals. vary from 50% to 20% according to pressure, the lower val. being obtained at higher pressure. In addition to the photo-effect another process was detected depending on the nature of the cathode surface, which may be due to the collision of positive ions on the cathode.

Composite photo-cathodes. II. P. Görlich (Z. Physik, 1940, 116, 704—715).—The emission work of [Ag]–Cs<sub>2</sub>O,Cs,Ag–Cs cathodes has been determined thermally and photo-electrically. In the temp. range  $350-460^\circ$   $\kappa.$  the Richardson curve is followed, but temp. range 350—400 R. the Richardson curve is followed, but there are deviations at temp.  $<350^{\circ}$ . The emission mechanism of the above, and of [Ag]–Cs<sub>2</sub>O,Cs–Cs cathodes, is discussed. Experiments with cathodes of the type [Ag]–Cs<sub>2</sub>O,X,Cs–Cs (where X = Mo, Al, Pb, Ni, Mn) show that the long- $\lambda$  max. increases the smaller is the at. vol. of X, but the rule does not hold if X is an alkali or alkaline-earth metal, or Ag. The extent to which the long- $\lambda$  max. is altered by X depends on the quantity of X present. The sensitivity was increased by the addition of the foreign metal in every case except Mo. Addition of foreign metals to the Ag in the case except Mo. Addition of foreign fletals to the Ag in the cathode [Ag]—Cs<sub>2</sub>O,Ag,Cs—Cs nearly always decreased the sensitivity. Comparison of cathodes of the type [Y]—Cs<sub>2</sub>O,Cs—Cs and [Y]—Cs<sub>2</sub>O,Y,Cs—Cs (Y = Be, Mn, Pb, Cu) indicates that the introduction of the foreign metal (Y) causes a displacement of the long- $\lambda$  max. towards the red, and there is an increase in efficiency owing to diffusion of the added metal. For cathodes of the type [Z]—Cs<sub>2</sub>O,Ag,Cs—Cs (Z = Al, Mn, Pb), there was a small displacement of the long- $\lambda$  max. towards the red, and an increase in sensitivity. the long- $\lambda$  max. towards the red, and an increase in sensitivity. The foreign metal not only affects the conductivity and position of the long-\(\lambda\) max. but there is also an interaction between the ionisable Cs atoms and the foreign metal atoms, affecting the photo-ionisation of the Cs atoms, and thus the sensitivity. Ag occupies a special place as such a metal. A bibliography of literature on alloy cathodes A. J. M.

Theory of boundary surface rectifiers. W. Schottky (Z. Physik, 1942, 118, 539—592).—A mathematical theory, with special reference to Se and  $\mathrm{Cu}_2\mathrm{O}$  rectifiers, has been developed. W. R. A. ence to Se and Cu<sub>2</sub>O rectifiers, has been developed.

Anomalous dispersion and loss angle in amorphous organic solids at high frequencies. W. Holzmüller (Z. Elektrochem., 1941, 47, 129).—Theoretical discussion (cf. A., 1942, I, 8). C. R. H.

Apparent ionic volume in infinitely dilute solutions.—See A., 1943, I, 198.

Anomalous reflexion at optical line gratings. K. Artmann (Z. Physik, 1942, 119, 529—567).—The bright bands produced by high-order reflexion of polarised light at metallic gratings, due to anomalous intensification of approx. tangentially reflected rays, are due to synchronisation of an infinite no. of multiply deviated waves. Quant. expressions are derived for the intensity dis-

Magnetic rotation in doubly-refracting media. F. Gabler (Z. Physik, 1940, 116, 271—280).—The equations governing the be-

haviour of doubly-refracting media in a magnetic field are discussed. If the magnetic rotation is small it disappears rapidly as soon as marked double refraction begins. If the magnetic rotation is large, it increases at first with the double refraction, and then shows a periodic variation of decreasing amplitude, representing gradual approach to a limiting val. Apparatus for testing these conclusions is described. The double refraction is produced in a Kerr cell filled with PhNO<sub>2</sub>. From determinations of the degree of polarisation of light response to the described that the second second control of the degree of polarisation of light response to the degree of polarisation of the degree of the deg ation of light passing through the cell in a magnetic field, very good A. J. M. agreement between theory and experiment is obtained.

Paramagnetism of molecules depending on electron spin. Neugebauer (Z. Physik, 1940, 116, 428—435),—Mathematical. The paramagnetic susceptibility and the Cotton-Mouton const. are obtained in the case for which the spin moment may be considered as not completely free. From experimental vals. for quantities involved, it follows that for  $O_2$  the mean square of the magnetic moment in the direction of the axis of rotation is  $\sim 1.3\%$  > that in a perpendicular direction. This agrees with deductions from the band spectrum. The paramagnetism of S2 and SO is governed by similar considerations. A. J. M.

Magnetic double refraction in alkali metal vapours. F. Gabler (Z. Physik, 1940, 116, 495—507).—An apparatus for the investigation of the Voigt effect using a Babinet compensator is described. The dependence of the effect on the  $\rho$  of the vapour, and the observation of double refraction in the region of the forbidden Zeeman transitions, are demonstrated. The wave-mechanical theory of the Voigt effect gives results in qual. agreement with experiment.

Theory of acoustic double refraction in colloidal solutions. S. Oka (Z. Physik, 1940, 116, 632-651).—The directive effect of an ultrasonic field on suspensions of disc-shaped particles has been considered, interaction being neglected. The theory of acoustic double refraction of suspensions of such particles has been developed for the stationary case, and for the state existing after the cutting off of the field. The decay of the double refraction with time when the field is removed is exponential. The relaxation time is calc. for particles of various dimensions and liquids of different  $\eta$ .

Application of group theory to isomerism in general. T. L. Hill (J. Chem. Physics, 1943, 11, 294—297).—Polya's theorem (A., 1936, 322, 1358) can be applied to determine not only the no. of structural isomerides of org. compounds, but also the no. of isomerides of org. compounds, but also the no. of optical and geometrical isomerides of C compounds and co-ordination compounds corresponding with any co-ordination no.

Structure of the boron hydrides. H. C. Longuet-Higgins and R. P. Bell (J.C.S., 1943, 250-255).—It is suggested that the B hydrides contain the H bridge linkage >B<H>B<, which can be formulated as a resonance hybrid between structures containing only normal electron-pair bonds. It is shown that this type of

linkage is as probable as the accepted structure containing oneelectron bonds, and that B and Ga are the only elements known to form covalent hydrides likely to contain such a linkage. The borohydrides of Be and Al are accounted for on the same hypothesis. Experimental data for the electron diffraction, Raman and infra-red spectra, and sp. heat of B<sub>2</sub>H<sub>8</sub> are analysed and shown to support a bridge configuration rather than one resembling C<sub>2</sub>H<sub>8</sub>. Structures are suggested for the higher B hydrides.

Ionic radii and the periodic system. E. Kordes (Z. Elektrochem., 1941, 47, 152—155).—The Pauling and Goldschmidt formulæ for calculating ionic radii are discussed and successfully applied, after calculating ionic radii are discussed and successful making certain assumptions, to electrons in lower valency states.  $C_{\rm e} R_{\rm e} H_{\rm e}$ 

Proton affinity of O' and O' and electron affinity of O and O'. G. Briegleb (Naturwiss., 1942, 30, 532—533).—Lattice energies and heats of dissolution in  $\rm H_2O$  of alkaline-earth halides give for proton (P) and electron (E) affinities the vals.  $P_0$ , 608,  $P_0$ , 356,  $E_0 \rightarrow 0$ , -150,  $E_0 \rightarrow 0$ , 56,  $E_0 \rightarrow 0$ , -206, and  $E_{0H} \rightarrow 0H$ , 45 kg.-cal. (all vals.  $\pm 10$ —20 kg.-cal.).

Optical method of measuring the angle of contact. S. J. Khambata and A. B. Sahiar (J. Univ. Bombay, 1943, 11, A, Part 5, 52-55). The contact between turpentine and glass in air has a fine fringe extending beyond that previously observed. The angle can be calc. by photographing interference fringes in the liquid and is 0.4° at 28.6°, instead of 17° as previously recorded. The angle for H<sub>2</sub>O and clean glass is 0°.

Dependence of size of liquid drops on their rate of formation. H. Neumann and R. Seeliger (Z. Physik, 1939, 114, 571—578).—Data are recorded for the variation of drop size with rate of formation for a no. of liquids of different surface tension and viscosity.

#### III.—CRYSTAL STRUCTURE.

Weissenberg controlled-temperature technique.—See A., 1943, I.

Crystal chemistry. I. Isotypism and isomorphism. H. Strunz (Naturwiss., 1942, 30, 526—531).—The term "isomorphism" is restricted to substances with analogous constitution, close similarity of cryst. structure, and the power of forming homogeneous mixed crystals. In the absence of the latter property the term "isotypism" is preferred. "Diadochism" is interchangeability of individual ions without change of cryst. form.

L. J. J.

Isomorphous replaceability of chalkogens in organic compounds.—See A., 1943, II, 263.

Molecular structure of liquids in experiments with models. H. A. Stuart (Z. Elektrochem., 1941, 47, 110—112).—Technical details in the prep. of a film illustrating liquid structure are discussed.

Molecular structure of supercooled and of glassy ethyl alcohol. W. Kast and A. Prietzschk (Z. Elektrochem., 1941, 47, 112—116).—At  $-150^{\circ}$  EtOH shows pronounced chain structure; the chains become linked together on addition of  $H_2O$ , the resulting increase in  $\eta$  inhibiting crystallisation and leading to the formation of the glassy state.

C. R. H.

Lattice constants of calcite determined by the rotating-crystal method. A. Ievips and M. Straumanis (Z. Physik, 1940, 116, 194—206).—The lattice consts. of calcite specimens of varying degrees of purity have been determined at different temp. by the rotating-crystal method, the asymmetric process being used. The purest crystals had  $d_{100}$  3·02900 a. at 18°. Eight samples showed a variation in this val. of 0·00123 a. The val. is usually the lower the more impure is the crystal. The presence of  $\rm MnCO_3$  and  $\rm MgCO_3$  lowers it, but  $\rm SrCO_3$  raises it. The rhombohedral angle  $a=101^\circ$  54′ 5″.

Isotypism with occupation of vacant lattice spaces.  $\mathbf{Fe^{++}}_2[\mathbf{PO}_4]_2, \mathbf{4H}_2\mathbf{0}$  and  $\mathbf{Fe^{++}}_3[\mathbf{PO}_4]_2, \mathbf{4H}_2\mathbf{0}$ . H. Strunz (Naturwiss., 1942, 30, 531).—Phosphosiderite,  $\mathbf{Fe^{++}}_2[\mathbf{PO}_4]_2, \mathbf{4H}_2\mathbf{0}$  (I), and phosphophyllite,  $(\mathbf{Fe^{++}}, \mathbf{Zn})_3[\mathbf{PO}_4]_2, \mathbf{4H}_2\mathbf{0}$  (II), have the following isotypic monoclinic lattice dimensions: (I)  $a_0$  5·28,  $b_0$  9·75,  $c_0$  8·71 A.,  $\beta$  90° 36′, space-group  $C_{2h}^2 - P_2, |m|$ ; cell content  $\mathbf{4Fe^{+++}}, \mathbf{4PO}_4, \mathbf{8H}_2\mathbf{0}$ ; (II)  $a_0$  2 × 5·30,  $b_0$   $\frac{1}{2}$  × 10·18,  $c_0$  2 × 8·88 A.,  $\beta$  90° 28′, space-group  $C_{2h}$ ; half-cell content  $\mathbf{6}(\mathbf{Fe^{++}}, \mathbf{Zn}), \mathbf{4PO}_4, \mathbf{8H}_2\mathbf{0}$ . PO<sub>4</sub> and H<sub>2</sub>O have the same basic lattice in both minerals, with octahedral co-ordination centres occupied by  $\mathbf{4Fe^{+++}}$  and free lattice spaces in (I), and by  $\mathbf{6}(\mathbf{Fe^{++}}, \mathbf{Zn})$  in (II).

Crystal structure of 4:4'-dinitrodiphenyl  $[\mathbf{C}_{12}\mathbf{H}_8(\mathbf{NO}_2)_2]$ . J. N. van Niekerk (*Proc. Roy. Soc.*, 1943, **A, 181**, 314—329).—It is shown that the crystal is monoclinic but can be referred to an orthogonal unit cell with a 3.77, b 9.56, c 15.39 A., which contains two mols.; space-group Pc. The method of Fourier analysis has been applied and projections of electron density on two of the axial planes are given. The packing of the mols. in the structure is discussed.

G. D. P.

X-Ray study of hydrocarbon from phthiocerol. E. Stenhagen
(J. Biol. Chem., 1943, 148, 695—697).—X-Ray examination of the
parent hydrocarbon of phthiocerol suggests that it is a normal
straight-chain hydrocarbon, probably n-tetratriacontane.

Diffraction experiments with very fine electron beams. H. Boersch (Z. Physik, 1940, 116, 469—479).—The crystal structures of thin foils of Au and films of NH<sub>4</sub>Cl and NaCl were determined by using a very fine beam of electrons (diameter 0.005 mm.). The diffraction of the primary beam in Au foil shows a four-fold axis of symmetry, indicating that the foil is composed of polycryst. material. The crystallites are the more regularly oriented the nearer they are together. The passage of electrons through thin films of insulating material can give rise to charges, which can, under suitable conditions, lead to an image of the object. The lens effect of the charges decreases as the diameter of the primary beam increases.

Occurrence of black lines in the electron-microscopic images of crystalline lamellæ. M. von Ardenne (Z. Physik, 1940, 116, 736—738).—The black lines observed are not due to any difference of  $\rho$  in the object, and no satisfactory explanation of their existence can be advanced.

A. J. M.

Morphology of finely-powdered lead oxide sublimate. R. Meldau and M. Teichmüller (Z. Elektrochem., 1941, 47, 191—196).—The results of an electron-microscopical examination of both modifications of PbO are discussed and illustrated with micrographs.

Electron interferometric measurement of free molecules. Isomerism of the nitrogen atom. F. Rogowski (Z. Elektrochem., 1941, 47, 152).—Interferometric data for MeNO<sub>2</sub> show that the C—N and N—O distances are 1·47 and 1·22 a., respectively, with the O-N-O angle 130—140°. For MeO·NO\* the C—O, O—N, and N—O\* distances are 1·44, 1·37, and 1·22 a., respectively (all distances ±0·02 a.).

Influence of supersonic vibrations on the magnetic properties of nickel. G. Schmid and U. Jetter (Z. Elektrochem., 1941, 47, 155—162).—The influence of supersonic vibrations (frequency 10—20 kHz.) on the magnetic properties of hard-drawn Ni tubing has

been investigated. The changes in properties are mostly irreversible. The increase in magnetic properties brought about by the vibrations increases with the amplitude of the latter. The max. magnetisation attained, viz.,  $\sim\!\!8$  times the initial magnetisation, is only  $\sim\!\!40\%$  of the ideal magnetisation val. The effect of the vibrations is to narrow the hysteresis loops. The vibrations apparently increase magnetisation by loosening the crystal structure. C. R. H.

Theory of anomalous reflexion of atomic rays at crystal surface layers. I. K. Artmann (Z. Physik, 1942, 118, 624—658).—An optical theory of the anomalous reflexion of at rays at crystal surface layers has been developed, a layer on the surface being assumed in which matter waves may be totally reflected. The thickness of the surface layer depends on the magnitude of the van der Waals forces.

W. R. A.

Mechanical properties of polymeric materials.—See B., 1943, II, 257.

Elasticity of rubber.—See B., 1943, II, 264.

Characteristic movements in crystal lattices. U. Dehlinger and A. Kochendörfer (Z. Physik, 1940, 116, 576—585).—A formula is deduced for the no. of at. transitions in unit time for thermal excitation of crystals, and the vals, of the consts. involved are estimated. The mathematical demonstration of an aperiodic motion of a series of atoms in the lattice put forward by Frenkel and Kontorova (A., 1941, I, 159) is only a special case of a migration of displacements and chain reactions through the lattice, proposed previously. Such movements as plastic deformation and twinning must have their origin in transitions in single atoms excited thermally. Long-λ vibrations recently discovered by Förster et al. (Z. Metallk., 1940, 32, 165) are intermediate between aperiodic vibrations and the normal small-λ vibrations.

Micrographic observations of slip lines in a-brass. R. G. Treuting and R. M. Brick (Amer. Inst. Min. Met. Eng., 1941, Tech. Publ. 1356, 6 pp.; Met. Tech., 8, No. 5).—The formation of slip lines on a plane surface polished along the length of a cylindrical single-crystal tensile specimen of a-brass was studied. The crystal was strained 0.074 in. and then annealed at 850° for 15 hr., when it recryst. to form two grains. Slip planes did not become visible until after flow had begun.

J. C. C.

Polymorphism of phosphoric oxide. W. L. Hill, G. T. Faust, and S. B. Hendricks (f. Amer. Chem. Soc., 1943, 65, 794—802).—The m.p. and monotropic relation of the three forms of  $P_2O_5$  have been determined. The phase diagram ( $70-600^\circ$ ) for  $P_2O_5$  includes three liquid-vapour-solid triple points, corresponding with the hexagonal, orthorhombic, and stable forms. Two liquids have been established, differing in degree of polymerisation, and obtained by melting the hexagonal and stable forms, respectively. n,  $\rho$ , and thermal, hygroscopic, and structural properties of the various phases have been determined. Superheating in solid-solid transitions is discussed. W. R. A.

**Polymorphism of arsenious oxide.** J. H. Schulman and W. C. Schumb ( $J.\ Amer.\ Chem.\ Soc.$ , 1943, 65, 878—883).—Solubilities in M-HCl at 2—35° and v.p. at 171—297° of monoclinic and octahedral  ${\rm As_2O_3}$  have been determined. Monoclinic  ${\rm As_2O_3}$  is thermodynamically stable from 2° to the m.p. Solubility data establish the enantiotropic relation between the two forms, with transition temp.  $-13^\circ$ . The latent heat of transition has been calc. from solubilities in M-HCl and heats of dissolution in 4M-NaOH.  ${\rm H_2O}$  vapour catalyses the octahedral  $\rightarrow$  monoclinic transformation at  $180^\circ$ . Existence of three other supposed forms of  ${\rm As_2O_3}$  is rendered uncertain by X-ray examination of products prepared as previously described.

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

Mol. wt. of polyisobutylenes.—See A., 1943, I, 199.

Electrical conductivity of liquid dielectrics and its variation by ultrasonic waves. F. Seidl (Z. Physik, 1940, 116, 359—365).—The conductivity of  $C_6H_{14}$ , PhMe, and  $CCl_4$  is increased when they are exposed to ultrasonic waves. Small field strengths were used. The results can be explained by supposing that the complex groups of mols. are broken down by the ultrasonic waves, and that there is a simultaneous recombination of ions. When the ultrasonic waves are cut off, the current decreases, usually to its original val.

Superconduction and magnetic exchange interaction. H. Welker (Z. Physik, 1939, 114, 525—551).—The theory of superconduction presented is based on London's theory and postulates an "electron-liquid" structure for the conduction electrons, which are constrained by coulombic repulsion to preserve a definite mean separation. A magnetic exchange force is postulated to account for an electronic "velocity superstructure." L. J. J.

Absolute diamagnetism of superconductors. T. Neugebauer (Z. Physik, 1942, 119, 581—589).—Theoretical. The assumption  $\chi=-(4\pi)^{-1}$  leads to more intense magnetic fields in the interior of super-

conductors than in ambient space, whereas London's theory leads to vanishing field intensity within a superconductor. L. J. J.

Electric moments of substituted benzoic acids. II. Moments of o-, m-, and p-fluoro- and of o-chloro- and o-bromo-benzoic acids. M. E. Hobbs and A. J. Weith, jun. (J. Amer. Chem. Soc., 1943, 65, 967—971).—Vals. of  $\mu$  of o-, m-, and p-fluoro- (I), o-chloro- and -bromo-benzoic acids in dioxan are 2·10, 2·16, 1·99, 2·43, and 2·50 p. The angle between the resolved CO<sub>2</sub>H group moment and the Ph-C axis, calc. from  $\mu$  of (I), is 74°, in good agreement with previous vals. from data on p-chloro- and -bromo-benzoic acids. Factors operative in the vector addition of moments are discussed.

Ferritin. III. Magnetic properties of ferritin and some other colloidal ferric compounds. L. Michaelis, C. D. Coryell, and S. Granick (J. Biol. Chem., 1943, 148, 463—480).—Measurements were performed by a modified Gouy procedure using both the macro-(A., 1937, I, 293) and the micro-method (A., 1942, I, 14). The Fe atoms of colloidal Fe(OH)3 in any one prep. were in different magnetic states. The two extremes of all the cases occurring were represented either by those with almost all Fe atoms in the 5 odd-electron state or by those having most of the Fe atoms in the 1 odd-electron state depending on the way in which the compound had been prepared. The Fe of ferritin (I) is always in the 3-electron state, as is also the Fe in the amorphous Fe(OH)3 prepared from (I) by pptn. with alkali. The susceptibility corresponded with that for the 3 odd-electron state with spin contributions alone. It is suggested that "Fe(OH)3" does not exist as individual mols. of Fe(OH)3 or Fe(OH)3 but that partial dehydration takes place, establishing O bridges from one Fe atom to another, and thus producing neighbouring octahedral complexes with shared corners and edges. The O of such a bridge may be bound either by covalent or by ionic bonds, according to the valency angles established. The effects of temp. and of Fe-Fe interaction are discussed. Reduction of (I) by Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> gave a Fe<sup>II</sup> compound of the same magnetic state as FeSO<sub>4</sub>. No F or CN complex of (I) could be detected by either magnetic or optical methods.

Reversible processes in magnetic materials with small internal strains. W. Döring ( $Z.\ Physik$ , 1939, 114, 579—601).—Change of elasticity modulus with strain, reversible permeability at the remanence point, and change of remanence with tension are correlated with initial susceptibility and deduced for magnetic materials in which crystal energy is > the effect of internal strain. Internal strains are assumed isotropic. L. J. J.

Effect of elastic compression on the susceptibility maximum of nickel. Characteristic strains. (A) S. Velayos. (B) H. Bittel (Z. Physik, 1940, 116, 340—348, 349—351).—(A) The effect of longitudinal compression on the magnetic susceptibility ( $\chi$ ) of Ni rods has been examined. The max. val. of  $\chi$  is increased with increasing compression, and this val. is reached at a smaller field strength with increasing compression. The actual vals. of  $\chi$  also depend on the internal strains in the metal. The internal strain can be calc. from observations of other magnetic properties, e.g., permeability, magnetisation, and magnetostriction. The vals. obtained agree satisfactorily with those obtained from the effect of compression on  $\chi$ .

(B) The work of Velayos (see above) indicates that the coercivity is  $\alpha$  mean val. of the internal strain when no external strain is applied. This holds even if the strains are produced by different thermal or mechanical treatment. It follows that the magnetic field strength for max.  $\chi$  must be  $\alpha$  internal strain, and the results of Velayos agree with this.

A. J. M.

Specific heats at low temperatures of manganese carbide and dioxide. K. K. Kelley and G. E. Moore (J. Amer. Chem. Soc., 1943, 65, 782—785).—Vals. of  $C_p$  of  $\mathrm{Mn_3C}$  and  $\mathrm{MnO_2}$  have been measured at 51—298° K.  $\mathrm{MnO_2}$  shows an anomaly between 85° and  $100^\circ$  K., with the max. at  $92\cdot12\pm0\cdot05^\circ$  K. Vals. of  $S_{298\cdot16}$  and  $\Delta G_{298\cdot16}$  are:  $\mathrm{Mn_3C}$   $23\cdot6\pm0\cdot3$ ,  $\mathrm{MnO_2}$   $12\cdot7\pm0\cdot1$  g.-cal. per degree per g.-mol.;  $\mathrm{Mn_3C}$  -22,800,  $\mathrm{MnO_2}$  -109,900 g.-cal. per g.-mol.

Heat capacities of hydrocarbon gases. D. R. Stull and F. D. Mayfield (Ind. Eng. Chem., 1943, 35, 639—645).—In order to make heat capacity calculations over a wide temp. range the authors have coupled the Bennewitz and Rossner method (cf. A., 1938, I, 303) with the rotational modification suggested by Dobratz (cf. A., 1941, I, 369), retaining the use of Einstein functions. Tables of bonding frequency contributions to mol. heat capacity for temp.  $250-1500^{\circ}\,\text{K}$ . and of solutions to the Einstein function for one degree of freedom are presented. Calc. heat capacities for 29 hydrocarbons over the same temp. range show an average difference of  $\pm4\%$  from published vals.

Thermodynamics and molecular structure of benzene and its methyl derivatives. I. Thermodynamic measurements on the pure substances. Heat capacities, heats of fusion and vaporisation, vapour pressures, and entropies of benzene, toluene, and the xylenes. K. S. Pitzer and D. W. Scott (J. Amer. Chem. Soc., 1943, 65, 803—811).— The m.p. of the xylenes are: o-,  $247\cdot82\pm0\cdot1^\circ$ ; m-,  $225\cdot27\pm0\cdot15^\circ$ ; p-,  $286\cdot39\pm0\cdot05^\circ$  K. Vals. of  $C_p$  have been determined calorimetrically at  $15-350^\circ$  K. The following expressions for  $\log p$  have

been derived from v.p. data: PhMe  $(0-50^\circ)$ ,  $-2866\cdot53/\theta-6\cdot7\log\theta+27\cdot6470$ ; o-xylene  $(0-60^\circ)$ ,  $-3327\cdot16/\theta-8\cdot0\log\theta+31\cdot7771$ ; m-xylene  $(0-60^\circ)$ ,  $-2871\cdot66/\theta-5\cdot0\log\theta+22\cdot9270$ ; p-xylene  $(13\cdot23-60^\circ)$ ,  $-3080\cdot31/\theta-6\cdot7\log\theta+27\cdot8581$ ,  $(0-13\cdot23^\circ)$ ,  $-3141\cdot33/\theta+11\cdot6092$ . Heats of fusion and vaponsation are: PhMe —,  $9115\pm50$ ; o-xylene  $3250\pm10$ ,  $10\cdot470\pm50$ ; m-xylene  $2784\pm15$ ,  $10\cdot160+50$ ; p-xylene  $4090\pm20$ ,  $10\cdot110\pm50$  g.-cal. per g.-mol. Entropies for gas at 1 atm. and  $298\cdot16^\circ$  K. are:  $C_0H_6$   $64\cdot39\pm0\cdot3$ ; PhMe  $76\cdot44\pm0\cdot3$ ; o-  $84\cdot50\pm0\cdot3$ , m-  $85\cdot60\pm0\cdot3$ , and p-xylene  $84\cdot27\pm0\cdot3$  g.-cal. per degree per g.-mol. Gas heat capacities for all these and CCl, have been determined. W. R. A.

Physical data of monoalkylcyclo-pentenes and -pentanes.—See A., 1943, II, 222.

Thermodynamic properties of propane. W. V. Stearns and E. J. George (Ind. Eng. Chem., 1943, 35, 602—607).—P-H and S-t charts, and tables of d (liquid and vapour), l, P, S, and H, are given for  $C_3H_8$  in the in.-lb.-°F. system from  $-80^\circ$  to  $200^\circ$ F. and  $5\cdot65$ —575·0 lb. per sq. in. abs. M. H. M. A.

Equation for the isotherms of pure substances at their critical temperatures. C. H. Meyers (J. Res. Nat. Bur. Stand., 1942, 29, 157—176).—The empirical equation of state given represents the crit. isotherms of 12 out of 13 substances up to 1·1 times the crit. density with  $<\frac{1}{2}\%$  error. The exception is  $\rm H_2O$  with  $\frac{1}{2}\%$  error. Fugacity vals. along the crit. isotherm can be calc. L. J. J.

Correlating fluid viscosity. A. S. Smith and G. G. Brown (Ind. Eng. Chem., 1943, 35, 705—711).—The equation  $\eta/\sqrt{M}=\mathrm{f}(T_r,P_r)$ , where  $M=\mathrm{mol}$ . wt. and the suffix r refers to the reduced state, which has been derived from the theory of corresponding states, is applied to  $\eta-T$  data for gases and liquids at atm. and higher pressures and under saturated conditions. The equation is applicable to homologous series and to diat. gases.  $\eta$  data for  $\mathrm{C_2H_8}$  and  $\mathrm{C_3H_8}$  over the pressure range 100—5000 lb. per sq. in. and temp. range 15—200° are recorded.

C. R. H.

Motion of a mercury index in a capillary tube. H. G. Green (Phil. Mag., 1943, [vii], 34, 393—395; cf. Yarnold, A., 1938, I, 452; Proc. Physical Soc., 1940, 52, 191, 196).—Mathematical. An alternative analysis, with extended velocity range, shows that results are comparable with those obtained in large-scale continuous flow experiments.

N. M. B.

#### V.—SOLUTIONS, DISPERSIONS, AND MIXTURES.

Autodiffusion of xenon and krypton. W. Groth and P. Harteck (Z. Elektrochem., 1941, 47, 167—172).—The autodiffusion coeffs. of light and heavy Kr (at. wt. difference  $1\cdot74$ ) and Xe (at. wt. difference  $2\cdot95$ ) at  $20^\circ/760$  mm. are  $0\cdot044_3\pm0\cdot002_2$  and  $0\cdot093\pm0\cdot004_5$  sq. cm. per sec., respectively. Between 0 and 760 mm. the difference in abs. pressure between Xe isotope mixtures rich in heavy Xe and those rich in light Xe is  $<0\cdot02$  mm. In the case of similar Kr mixtures the difference in pressure is  $\sim0\cdot3\%$  of the abs. pressure, the heavier mixture having the lower pressure. C. R. H.

Fluidity of mixtures which obey Batschinski's law. F. Kottler (J. Physical Chem., 1943, 47, 277—293).—Derived equations defining the fluidity of ideal and non-ideal mixtures which obey Batschinski's law (A., 1913, ii, 26, 928) have been tested by published data for mixtures of  $C_6H_6$  with PhBr, PhCl, PhI, CCl<sub>4</sub>, and CH<sub>2</sub>Ph·OBz, and for CS<sub>2</sub>-MeI mixtures. Agreement is good in all cases except the last, where experimental errors are the probable cause of the discrepancies. C. R. H.

Autodiffusion of liquids. H. Rögener (Z. Elektrochem., 1941, 47, 164—167).—A method of following the diffusion of two liquids by measuring changes in n is described, and its application to the diffusion of isotopic liquids is illustrated.

C. R. H.

Volatility, diffusion, and vapour pressure in the system acetophenone–Novolak. E. Jenckel and J. Komor (Z. Elektrochem., 1941, 47, 162—163).—The volatility of COPhMe from the system COPhMe-Novolak  $\alpha$  the v.p. if the proportion of synthetic resin is  $>\!30\%$ . At higher resin concns. the reduced diffusion coeff. of COPhMe in the system leads to the volatility being < expected. C. R. H.

Behaviour of mercuric chloride and determination of its parachor. W. V. Bhagwat and P. M. Tosniwal (J. Indian Chem. Soc., 1942, 19, 492—494).—Vals. for the parachor of  $HgCl_2$  in various solvents range from 150 to 250. The apparent mol. wt. (ebullioscopio) in  $H_2O$  is 220-260, and in various org. solvents 290-360. Its coagulating effect on  $As_2S_3$  and  $Sb_2S_3$  sols is between those of Al and Ba salts.

Intermetallic phases with partial heteropolar linkings. U. Dehlinger (Z. Elektrochem., 1940, 46, 627—634).—Rules for the formation of heteropolar intermetallic compounds have been formulated and are applied to Hume-Rothery alloys (bronzes) and combinations of alkalis, alkaline earths, rare earths, Al, Ga, In, Cu, Ag, Au, and the transition elements with other metals.

C. R. H.

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Preferred orientation in rolled magnesium and magnesium alloys. P. W. Bakarian (Amer. Inst. Min. Met. Eng., 1941, Tech. Publ. 1355, 6 pp.; Met. Tech., 8, No. 5).—Pole figures of pure Mg and of Mg alloys with 0·15 and 0·20% of Ca respectively were determined, using small cylindrical specimens 0·038 in. in diameter cut with the axis at various angles to the rolling direction of hot-rolled sheet. The additions of Ca greatly altered the texture of pure Mg.

Ternary cadmium alloys.—See B., 1943, I, 340.

Magnetic study of the two-phase iron-nickel alloys. II. K. Hoselitz and W. Sucksmith (*Proc. Roy. Soc.*, 1943, A, 181, 303—313; cf. A., 1940, I, 318).—The method of using measurements of magnetic saturation intensity for the determination of the equilibrium phase boundaries has been extended. The phase diagram of the system Fe-Ni has been determined in the temp. range 525—365°. The mechanism of phase segregation from the single-phase a-state has been studied; one of the phases crystallises out in its equilibrium concn. whilst the residue of the alloy progressively approaches equilibrium composition.

G. D. P.

Superheated steam as a solvent. O. Fuchs (Z. Elektrochem., 1941, 47, 101—110).—When NaCl, KCl, and NaOH volatilise with superheated steam the concn. of salt in the vapour increases rapidly with pressure. The effect of the volatilised salt on the electrical conductivity and dielectric const. of the vapour is negligible.

C. R. H.

Solubility of solids in "gases" or "vapours." G. W. Morey and E. Ingerson (Amer. Min., 1942, 27, 227—228).—The transport of solid material in significant amount by a gas or vapour at high tempand pressure depends on the solubility of the solid in the vapour, i.e., in unit vol. of vapour the solid content is > corresponds with its own v.p. at the given temp. and pressure. Transport and deposition of corundum, rutile, sillimanite, quartz, and amorphous SiO<sub>2</sub> by H<sub>2</sub>O at temp. from 500° to 1000° and at pressures from 3000 to 15,000 lb. has been obtained experimentally. Suitable definitions of "gas" and "vapour" are proposed. L. S. T.

Solubility of hydrogen chloride in cyclohexane. F. Wiegner (Z. Elektrochem., 1941, 47, 163—164).—Solubility data, expressed as v.p. of HCl, over the range 13—40° are recorded. C. R. H.

Solubility of ammonium chloroplatinate in ammonium chloride solutions. P. S. Belonogov (Zavod. Lab., 1939, 8, 217).—100 ml. of a solution containing x% of NH<sub>4</sub>Cl dissolve y g. of (NH<sub>4</sub>)<sub>2</sub>PtCl<sub>6</sub> at 25°; for x=0, 1·86, 9·81, 19·74, 28·36 y=0·5530, 0·0432, 0·0276, 0·0245, 0·0082, respectively. Addition of HCl lowers y.

Solubility of metals in mercury.—See B., 1943, I, 341.

Hysteresis in sorption. X. Open pore volume in relation to particle radius. K. S. Rao and V. R. Thiruvenkatachar (*Proc. Indian Acad. Sci.*, 1943, 17, A, 46—49).—Mathematical. In an assemblage of packed spheres of equal size and of const. total mass the total open pore vol.  $(v_1)$  and total cavity vol.  $(v_2)$  decrease as particle radius increases, whereas  $v_1/v_2$  increases. W. R. A.

Sorption of ammonia on montmorillonitic clay. I. Cornet (J. Chem. Physics, 1943, 11, 217—226).—Parabolic or hyperbolic sorption isotherms are given by dry  $\mathrm{NH_3}$  on  $\mathrm{NH_4}$ ,  $\mathrm{K}$ , and finely ground H bentonites. Unground H bentonite shows a short initial parabolic section followed by an inflexion and subsequent second parabolic section, with widening of the c-axis spacing. The sorption occurs at exterior and interplanar surfaces and at lattice discontinuities. Thermal decomp. data for  $\mathrm{NH_4}$  bentonite show sorption at base-exchange reactive spots. Lattice OH and polarisation of  $\mathrm{H_2O}$  mols. may give rise to base-exchange capacity on grinding. L. J. J.

Absence of coprecipitation of barium ion with the chlorides of the silver group and the sulphides of the copper and tin groups in presence of ammonium ion. L. Lehrman and I. Mandel (J. Physical Chem., 1943, 47, 264—266).—No copptn. (adsorption, occlusion, or postptn.) of Ba" occurs when sulphides of the Cu and Sn groups are pptd. in presence of NH<sub>4</sub> or when chlorides of the Ag group are pptd.

C. R. H.

Surface available to nitrogen on bone black and other carbonaceous adsorbents. V. R. Deitz and L. F. Gleysteen (f., Res. Nat. Bur. Stand., 1942, 29, 191—225).—Adsorption isotherms for  $N_2$  on a no. of samples of adsorbent charcoal at liquid  $N_2$  and liquid  $O_2$  temp. are recorded. For coconut shell charcoal the results accord with unimol. adsorption and for the other samples the results at >50% of the y.p. accord with the theory of Brunauer et al. (A., 1938, I, 190), from which vals. for the available surface are calc. F. J. G.

Mechanism of formation of Orange II alumina colour lakes. A. Voet (f. Physical Chem., 1943, 47, 191—196).—An investigation of the interaction of Al(OH)<sub>3</sub> suspensions with Orange II solutions shows that all the dye is pptd. at pH <7. Below pH 5.5 the lake is a pure Al salt; between pH 5.5 and 7 the lake is a mixture of Al salt and adsorbed dye. Above pH 7 only adsorption takes place. Adsorbed lakes contain no Na, and the phenomena must be explained as an exchange adsorption, hydrolytic adsorption being ruled out in view of the absence of any pH change.

C. R. H.

Monolayers of compounds with branched hydrocarbon chains. VI. 2-[a-]Methyl- and 10-[i-]methyl-substituted carboxylic acids of high mol. wt. S. Ställberg-Stenhagen and E. Stenhagen (J. Biol. Chem., 1943, 148, 685—694).—The condensed monolayers of long-chain acids substituted with a-Me- and i-Me groups occupy an area 4-6 A. > the unsubstituted acids. An i-Me group has little effect on surface moments, whilst the effect of an a-Me group is greater in condensed than expanded monolayers, and esterification of the a-methyl-acids greatly increases the surface moment. The forcearea curves for condensed monolayers of branched-chain acids differ appreciably from those for straight-chain acids. P. G. M.

Foam and emulsion stabilities. S. Ross (J. Physical Chem., 1943, 47, 266—277).—The unit of foaminess for static foams ( $L_l$ ) is redefined as the average length of time that unit vol. of liquid can remain suspended aloft as foam. This contrasts with the unit of foaminess for dynamic foams (Bikerman's  $\Sigma$ ) which is the average length of time that unit vol. of gas remains in the foam. For static foams the unit corresponding to  $\Sigma$  is  $L_q$ .  $L_l = (1/V_0) \int_{V_0}^0 t \mathrm{d}V$  and

 $L=(1/G_0)\int_{g_0}^0t\mathrm{d}G$ , where t= time, V and G are the vols. of liquid and gas respectively in the foam after time t, and  $V_0$  and  $G_0$  are the corresponding vols. when t=0. For foams obeying the logarithmic relation for drainage the expression for  $L_1$  simplifies to  $t/2\cdot3\log{(V_0/V)}$ . Foams of Aerosol OT and laurylsulphonic acid conform to this simplified relation. An approx. drainage equation has been developed and successfully applied to certain data on demulsification. The mechanism of demulsification is discussed.

Dissolution of gels. A. Tobolsky (J. Chem. Physics, 1943, 11, 290—293).—The gel-liquid transition in three-dimensional cross-linked polymerides derived from long chain mols., swollen by suitable solvents, is reversible if carried out slowly and comparable with the melting of a solid. The "melting" temp. of a swollen gel is correlated with the entropy of disruption of the gel, which can be calc. from mol. consts.

L. J. J.

Calculation of the degree of orientation of gels from refractometric measurements. A. Frey-Wyssling (Helv. Chim. Acta, 1943, 26, 833—846).—Theoretical. Simple equations are given connecting n of a gel with its degree of orientation, this being represented by a single quantity, the scattering angle. The structure of Cellophane is discussed.

F. J. G.

Coagulation of silicic acid gels compared with that of plasma.—See A., 1943, III, 680.

Softening of thermoplastic polymers. Theoretical.—See B., 1943, II. 257.

X-Ray investigation of the highly disperse state of division in a fibre. Cellulose model. R. Hosemann (Z. Elektrochem., 1940, 46, 535—550).—A method has been developed for determining the quant. particle size distribution from the intensity distribution in the central spot obtained in the X-ray diagram, using a monochromatic X-ray beam. The method assumes that the particles behave as rotation ellipsoids and is independent of whether the particles are crystallites, distorted crystallites, micelles, or amorphous conglomerates.  $C_{31}H_{64}$  crystallites are very flat discs mainly 400 A. high and of considerable breadth which apparently attains macroscopic dimensions. In cellulose fibres the upper limit of micelle thickness is 400 A., the most frequent thickness being that of a single mol chain; purified ramie has thinner micelles than the unpurified material. The length distribution max. occurs at 3000 and 200 A. for ramie and cellulose triacetate, respectively. The latter val. is not in accord with that deduced from viscosity data. The results are discussed in relation to the structure of cellulose.

J. W. S.

Reaction of wool with alkali.—See B., 1943, II, 249.

Acid-, base-, and salt-binding capacity of salt-denaturated collagen. E. R. Theis and T. F. Jacoby (J. Biol. Chem., 1943, 148, 603—609).— KCl and CaCl<sub>2</sub> bind with collagen over a wide pH range, a max. val. being obtained in the isoelectric zone. CaCl<sub>2</sub> fixation is > that for KCl at any given ionic strength but it produces shrinkage and contraction of the collagen. The isoionic point of CaCl<sub>2</sub>-treated collagen is shifted to a lower val., whilst that for KCl remains the same as for native collagen.

J. E. P.

Migration data in solutions of a colloidal electrolyte. Lauryl-sulphonic acid. M. E. L. McBain (J. Physical Chem., 1943, 47, 196—204).—Electrolytic transference nos. (T.N.) of laurylsulphonic acid solutions (0·00116—0·3475M.) at 20° are recorded. At the lowest concn. there is practically complete dissociation into simple ions. T.N. increases rapidly with concn., attaining a max. val. of  $\pm 0.351$  at 0.0551M. With further increase in concn. T.N. falls rapidly up to  $\sim 0.07$ M. and gradually thereafter. The max. T.N. is  $\sim 6$  times the val. at the lowest concn. At the T.N. peak diffusion is at a min. and conductivity and osmotic coeff. are still diminishing. Over this range the colloid must contain much neutral material, mols., or ion pairs and the average composition must be continually

changing. A common misconception of the significance of transport of material in a colloid particle or complex ion as distinguished from the electrolytic T.N. is corr.

C. R. H.

#### VI.—KINETIC THEORY. THERMODYNAMICS.

Dissociation constants of some acids in mixed solvents. J. C. Speakman (J.C.S., 1943, 270-273).—Thermodynamic dissociation consts. at  $20^\circ$  for  $([\mathrm{CH}_2]_2\cdot\mathrm{CO}_2\mathrm{H})_2$ ,  $(\mathrm{CH}_2\cdot\mathrm{CO}_2\mathrm{H})_2$ ,  $\mathrm{CO}_2\mathrm{H}\cdot[\mathrm{CH}_2]_2\cdot\mathrm{CO}_2\mathrm{Me}$ , cis-tetrahydronaphthalene-2 : 3-dicarboxylic acid, and BzOH in  $\mathrm{H}_2\mathrm{O}$ , EtOH, and aq. dioxan are in agreement with vals. calc. from the structure of the mol. Vals. for BzOH are independent of whether the cells have liquid junctions or not. F. R. G.

Ionisation constant of secondary magnesium phosphate. H. Tabor and A. B. Hastings (J. Biol. Chem., 1943, 148, 627—632).—Conductivity data at 38° confirm the incomplete dissociation of MgHPO4 in solution and are described by the equation  $pK'_{\text{MgHPO4}} = 2\cdot87-4\cdot15(\sqrt{\mu}-0\cdot5\mu)$ . Intracellular electrolyte balance is discussed. The solubility product of MgHPO4, corr. for incomplete dissociation, is  $pK'_{\text{5-p.}} = \sim 4\cdot5$  at  $\mu=0\cdot160$ . J. E. P.

Provisional pH values for certain standard buffer solutions. R. G. Bates, W. J. Hamer, G. G. Manov, and S. F. Acree (J. Res. Nat. Bur. Stand., 1942, 29, 183—190).—pH vals. at 20°, 25°, and 30° are recorded for a no. of standard buffer solutions. F. J. G.

Titration curves of hexameta- and tripoly-phosphoric acid. H. Rudy and H. Schloesser (Ber., 1940, 73, [B], 484-492).—The titration curves of  $(NaPO_3)_a$  and  $(NaPO_3)_3$  obtained by addition of varied amounts of 0·In-NaOH and determination of pH of the resulting solutions by the Pt-H<sub>2</sub> electrode show that  $(NaPO_3)_a$  behaves like the Na salt of a strong monobasic acid and that it, like  $(NaPO_3)_3$ , has no buffering action towards alkalis.  $H_5P_3O_{10}$  has three strong and two weaker acid groups and shows distinct buffering action at pH >4. Comparison of the titration curves of  $(HPO_3)_a$ ,  $(HPO_3)_a$ ,  $H_3PO_4$ ,  $H_4P_2O_7$ , and  $H_5P_3O_{10}$  gives no evidence of the existence of  $Na_4H_2P_6O_{18}$ . The first marked change of potential occurs almost simultaneously with all the acids and at this point 1, 2, 3, and 6 acid groups are satisfied in  $H_3PO_4$ ,  $H_4P_2O_7$ ,  $H_5P_3O_{10}$ , and  $(HPO_3)_a$  respectively; hence there is one strongly dissociated acid group for each P. If several OH are present, only the first is strongly dissociated. With regard to buffering action at pH >4·5 the sequence is  $H_3PO_4$ ,  $H_4P_2O_7$ ,  $H_5P_3O_{10}$ ,  $(HPO_3)_a$ , and  $(HPO_3)_a$  is slight. The constitution of  $(HPO_3)_a$  and  $(HPO_3)_a$  is slight. The constitution of  $(HPO_3)_a$  and  $Na_5P_3O_{10}$  is discussed.

Na<sub>5</sub>F<sub>3</sub>O<sub>10</sub> is discussed.

Activity coefficients of thallous chloride in ethylene glycol-water solutions. O. D. Black and A. B. Garrett (J. Amer. Chem. Soc., 1943, 65, 862—865).—The e.m.f. of the cell Tl-Hg|TlCl|AgCl|Ag has been measured in H<sub>2</sub>O, (CH<sub>2</sub>·OH)<sub>2</sub>, and (CH<sub>2</sub>·OH)<sub>2</sub>-H<sub>2</sub>O mixtures at 25°, and the solubility of TlCl in (CH<sub>2</sub>·OH)<sub>2</sub>-H<sub>2</sub>O-KCl, (CH<sub>2</sub>·OH)<sub>2</sub>-KCl, (CH<sub>2</sub>·OH)<sub>2</sub>-H<sub>2</sub>O, H<sub>2</sub>O-morpholine, and H<sub>2</sub>O-dioxan mixtures at 25° has been determined. Activity coeffs., solubility product, and ionisation consts. of TlCl have been calc. from e.m.f. and solubility data.

W. R. A.

Ethanol-water system. Vapour-liquid properties at high pressures. J. Griswold, J. D. Haney, and V. A. Klein (Ind. Eng. Chem., 1943, 35, 701—704).—Vapour-liquid equilibrium and crit. temp. and pressure data for the system EtOH-H<sub>2</sub>O over the pressure range 1—75 atm. and temp. range 150—275° are recorded in tabular and diagrammatic form.

C. R. H.

Equilibrium still for miscible liquids. Data on ethylene dichloride-toluene and ethanol-water. C. A. Jones, E. M. Schoenborn, and A. P. Colburn (Ind. Eng. Chem., 1943, 35, 666—672).—New apparatus for determining vapour-liquid equilibria is described. Data are given for  $C_2H_4Cl_2$ -PhMe and EtOH-H<sub>2</sub>O between their b.p./760 mm. and for EtOH-H<sub>2</sub>O at 50°/ and 60°/133—366 mm.

Composition of vapours from boiling binary solutions. D. F. Othmer (Ind. Eng. Chem., 1943, 35, 614—620).—A detailed description is given of a standardised form of the author's apparatus (A., 1928, 943; 1932, 567), and its operation is discussed. Data are given for 26 systems.

M. H. M. A.

System CaO-Al<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>O at temperatures of 21° and 90°. L. S. Wells, W. F. Clarke, and H. F. McMurdie (J. Res. Nat. Bur. Stand., 1943, 30, 367—409).—Metastable and stable solubility data are recorded for the system CaO-Al<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>O at 21° and 90°. X-Ray examination shows that the so-called hexagonal tricalcium aluminate hydrate is an equimol. mixture of hexagonal 2CaO,Al<sub>2</sub>O<sub>3</sub>,8H<sub>2</sub>O (I) and hexagonal 4CaO,Al<sub>2</sub>O<sub>3</sub>,13H<sub>2</sub>O (II), cryst. in alternate layers. On keeping at room temp. (I) is slowly converted into (II) with separation of hydrated Al<sub>2</sub>O<sub>3</sub>. Both are metastable with respect to isometric tricalcium aluminate, 3CaO,Al<sub>2</sub>O<sub>3</sub>,6H<sub>2</sub>O. F. J. G.

Graphical interconversions for multicomponent systems. J. D. Leslie (Ind. Eng. Chem., 1943, 35, 495—496).—The Sun and Silverman graphical methods of converting wt., vol., and mol. fractions

into one another have been extended from binary to multiple systems (cf. A., 1942, I, 293).

C. R. H.

Interconversions of multicomponent compositions by graphical methods. K. H. Sun and A. Silverman (Ind. Eng. Chem., 1943, 35, 497—498).—The authors' graphical methods for converting wt., vol., and mol. compositions in binary and ternary systems are extended to multicomponent systems (cf. preceding abstract).

Thermochemistry of alloys. F. Weibke (Angew. Chem., 1940, 53, 74—80).—A lecture in which are described methods of determining the heat of formation of alloys and recent results obtained for Ca-Pb and Au-Cu alloys. Ca<sub>2</sub>Pb has a heat of formation of 47 kg.-cal. per mol. and reacts with Pb to form CaPb liberating 3 kg.-cal. The formation of AuCu, Au<sub>2</sub>Cu<sub>3</sub>, and AuCu is shown by well-marked peaks in the heat of formation-composition graph.

A. R. P.

Heat of formation of manganomanganic oxide and manganese dioxide. C. H. Shomate (J. Amer. Chem. Soc., 1943, 65, 785—790).  $-\Delta H_{298\cdot 16} \text{ vals. are } \text{Mn}_3\text{O}_4 - 331,650 \pm 250 \,; \quad \text{MnO}_2 - 124,640 \pm 200 \,\text{g.-cal per mol.}$ 

Heats of formation of natural and artificial carbonates. W. A. Roth, H. Berendt, and G. Wirths (Z. Elektrochem., 1941, 47, 185—190).—The heats of formation at 20° of calcite,  $\rm MnCO_3$ , malachite, and azurite, calc. from heat changes on dissolution in acid, are  $+42\cdot45\pm0\cdot05$ ,  $+15\cdot07\pm0\cdot09$ ,  $+13\cdot78\pm0\cdot09$ , and  $+20\cdot88\pm0\cdot14$  kg.-cal., respectively. Comparison with published vals. is made, and the accuracy of published vals. for the heats of formation of other compounds is discussed. C. R. H.

Heats of formation of cadmium halide compounds with amines. W. Huber and E. Reindl (Z. Elektrochem., 1940, 46, 556—558).— Mol. heats of formation at 20° from solid halide and liquid or (in parentheses) gaseous amine are:  $CdCl_2$ ,  $2C_5H_5N$  21·47 (40·89),  $CdBr_2$ ,  $2C_5H_5N$  20·86 (40·28),  $CdI_2$ ,  $2C_5H_5N$  20·31 (39·73),  $CdBr_2$ ,  $2C_5H_5N$  38·09 (96·25),  $CdI_2$ ,  $2C_5H_5N$  40·80 (99·06),  $CdCl_2$ ,  $2C_5H_5N$  38·09 (96·25),  $2C_5H_5N$  40·80 (99·06),  $2C_5H_5N$  51·86 (85·46),  $2C_5H_5N$  38·09 (83·96), and  $2C_5H_5N$  40·60 (83·20) kg.-cal. per g.-mol. The results are discussed in relation to data for Zn and Hg halide compounds with amines and for compounds with  $2C_5H_5N$  3. U. S.

Heats of formation and constitution of molecular compounds of stannic chloride. W. Hieber and E. Reindl (Z. Elektrochem., 1940, 46, 559—570).—From v.p. measurements over the temp. range 30—200° the following mean heats of vaporisation at 0—100° are deduced: SnCl<sub>4</sub> 9·24, Et<sub>2</sub>C<sub>2</sub>O<sub>4</sub> 11·86, Et<sub>2</sub> malonate 12·35, succinate 13·05, glutarate 13·40, adipate 14·16, sebacate 14·68, and EtOBz 11·90. Mol. heats of formation at 0° from the liquid or (in parentheses) gaseous components are SnCl<sub>4</sub>,Et<sub>2</sub>C<sub>2</sub>O<sub>4</sub> 18·98 (40·03), SnCl<sub>4</sub>,CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub> 22·48 (44·07), SnCl<sub>4</sub>,(CH<sub>2</sub>·CO<sub>2</sub>Et)<sub>2</sub>, 20·33 (42·62), SnCl<sub>4</sub>,[CH<sub>2</sub>]<sub>3</sub>(CO<sub>2</sub>Et)<sub>2</sub> 21·60 (44·24), SnCl<sub>4</sub>,[CH<sub>2</sub>]<sub>4</sub>(CO<sub>2</sub>Et)<sub>2</sub> 23·49 (46·89), SnCl<sub>4</sub>,[CH<sub>2</sub>]<sub>8</sub>(CO<sub>2</sub>Et)<sub>2</sub> 23·19 (47·20), SnCl<sub>4</sub>,2EtCO<sub>2</sub>Et 23·47 (50·33), SnCl<sub>4</sub>,2EtOBz 20·15 (53·19), SnCl<sub>4</sub>,2EtOH ~22·31 (~52·37), SnCl<sub>4</sub>,2Et<sub>2</sub>O 25·80 (48·44) and SnCl<sub>4</sub>,2NH<sub>2</sub>Ph 33·59 (62·35) kg.-calper g.-mol. The m.p. of these complexes are 85°, 121·5°, 111·5°, 95·5°, 79·5°, 62°, 48°, 47°, 92°, 82°, and >220° (decomp.), respectively. It is inferred that the Sn atom has co-ordination no. 6 in each of these compounds, whilst the association of the compounds with dibasic acids in org, solvents indicates that they must exist in the dimeric form with each Sn co-ordinated to two O atoms of different acid mols.

J. W. S.

Heat of combustion of benzoic acid with special reference to the standardisation of bomb calorimeters. R. S. Jessup (J. Res. Nat. Bur. Stand., 1942, 29, 247—270).—The heat of combustion per g. of BzOH under the conditions of standard bomb calorimetry is 26428.4 International joules.

F. J. G.

Heats of dilution and relative heat contents of lanthanum chloride and sulphate solutions. C. C. Nathan, W. E. Wallace, and A. L. Robinson (f. Amer. Chem. Soc., 1943, 65, 790—794).—Heats of dilution in  $\mathrm{H_2O}$  at  $25^\circ$  of  $\mathrm{Lacl_3}$  between  $6\times10^{-5}$  and  $0\cdot1\mathrm{M}$ . and of  $\mathrm{La_2(SO_4)_3}$  between  $2\times10^{-5}$  and  $0\cdot025\mathrm{M}$  have been determined, and the relative partial molal heat contents have been calc. Results do not agree with Debye–Hückel theory even at the lowest concns. W. R. A.

Thermodynamics and molecular structure of benzene and its methyl derivatives. II. Thermodynamic measurements on mixed systems. Equilibrium and heat content relationships between benzene, toluene, and each of the xylenes. F.p. diagram of the system, o-, m-, and p-xylenes. V. Statistically calculated thermodynamic quantities. Internal rotation of methyl groups attached to a benzene ring. General discussion. K. S. Pitzer and D. W. Scott (J. Amer. Chem. Soc., 1943, 65, 811—814, 824—829).—II. By using m.p. and heats of fusion (cf. A., 1943, I, 223) with thermodynamics and Raoult's law the f.p. diagram of the xylenes has been calc. Xylene mixtures were analysed by measuring n. The equilibrium composition of xylene at 50° is o- 12 $\pm$ 3, m-71 $\pm$ 5, and p-17 $\pm$ 2%. Equilibrium measurements on the reaction 2PhMe  $\rightleftharpoons$   $C_6H_8 + C_9H_4Me_2$  at 50° with anhyd. AlBr<sub>3</sub> + HBr as a catalyst are given, and thermodynamic

consts. are evaluated for  $m \to p$ ;  $m \to o$ ;  $p \to o$ ;  $m \to o$  (equilibrium) -xylene;  $2\text{PhMe} \to C_0 H_0 + m$  (and equilibrium)

-xylene. V. Statistically calc. vals. for  $S_{298^{\circ}16^{\circ}}$  for gaseous  $C_6H_6$ , PhMe, o-, m-, and p-xylene, and mesitylene are compared with experimental vals., and potential barriers restricting free rotation in the mols. have been computed. In PhMe and m- and p-xylene, the Me groups rotate relatively freely, but in o-xylene there is a barrier of  $\sim 2000$  g.-cal. From the equilibrium data the m-compound has the lowest energy, and it is suggested that m-orientation of identical or similar groups may be generally the most stable. The estimated entropies of 1:2:4-C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub> and 1:2:4:5-C<sub>6</sub>H<sub>2</sub>Me<sub>4</sub> are reported.

Entropy and irreversible processes. W. Ehrenberg (Phil. Mag., 1943, [vii], 34, 396—409).—Mathematical. From an analysis of the notion "body" in thermodynamics, irreversible processes are classified as "conduction" and as "breaking-up" processes. A new derivation, from the Clausius principle, of dS = dQ/T shows that this relation holds for irreversible "conduction" processes as well as for reversible processes. Bridgman's hypothesis, the theory of Carathéodory and Born, and the bearing of the new derivation on the interpretation of the equilibrium conditions are discussed. the interpretation of the equilibrium conditions are discussed.

Absolute values of entropies of aqueous ions. F. H. Lee and Y. K. Tai (J. Chinese Chem. Soc., 1941, 8, 60—63).—From the temp. coeffs. of the potentials of the capillary electrometer and  $H_2$  electrode against the  $Hg_2Cl_2$  electrode the abs. entropy of the aq. H' ion is calc. to be -5.4 entropy units. Utilising this val. the abs. entropies of other ions are calc. The application of these vals. to the verification of the theoretically deduced entropies of hydration of gaseous ions is illustrated for K'.

#### VII.—ELECTROCHEMISTRY.

Mobility of the ferrocyanide ion in aqueous solution at infinite dilu-Modify of the terrocyanine for in aqueous solution at limite unition. E. Asmus (Z. Elektrochem., 1940, 46, 596—599).—The viscosity ( $\eta$ ) of aq. Na<sub>4</sub>Fe(CN)<sub>6</sub> has been measured over the concn. (c) range 0·0003—0·012M. at 25° and vals. of the function  $\phi = (\eta/\eta_0 - 1)/c^{0.5}$  are evaluated. The limiting val. of  $\phi$  at  $c \rightarrow 0$  is deduced graphically as 0·0405, in accord with the vals. deduced theoretically using 51 and 101 as the equiv. conductivities of Na and Fe(CN)<sub>6</sub>"", respectively, thus confirming Hölzl's val. of the mobility of Fe(CN)<sub>6</sub>" (A., 1930, 1253). 1253). Ageing of the solutions leads to lower vals. of  $\phi$ .

High mol. wt. aliphatic amines and their salts. XI. Transference numbers of primary aliphatic amine hydrochlorides in aqueous solution and their significance in the interpretation of the micelle theory. C. W. Hoerr and A. W. Ralston (J. Amer. Chem. Soc., 1943, 65, 976—983).—Transference nos. of n-primary aliphatic amine hydrochlorides containing 8, 10, 12, 14, 16, and 18 C, in H<sub>2</sub>O at 60°, and of dodecylammonium chloride at 20°, 30°, and 40°, have been determined. The results indicate the formation of both ionic and lamellar micelles, the latter name being given to large aggregates of lamellar micelles, the latter name being given to large aggregates of undissociated mols. formerly called "neutral colloid." W. R. A.

Transference phenomena in molten salts. K. E. Schwarz (Z. Elektrochem., 1941, 47, 144—147).—Electrolytic transference in the systems  $Pb[PbCl_2 + PbI_2]Pb$  and  $Sn[SnCl_2 + SnI_2]Sn$  and diffusion potential data for the system  $Ag[AgNO_3]AgNO_3 + Ag$  halide[Ag agree with predictions on the basis of the author's theory (cf. A., 1940, I, 27).

E.m.f. measurements in liquid sulphur dioxide. K. Cruse (Z. Elektrochem., 1940, 46, 571—590).—Pb-PbCl<sub>2</sub>, Hg-Hg<sub>2</sub>Cl<sub>2</sub>, Ag-AgCl, Ag-AgBr, and Pt-H<sub>2</sub> electrodes suitable for use in liquid SO<sub>2</sub> are described. The e.m.f. of the cells Pb,PbCl<sub>2</sub>|SO<sub>2</sub> +  $0\cdot$ 1M-NH<sub>2</sub>Et<sub>2</sub>Cl|Hg<sub>2</sub>Cl<sub>2</sub>,Hg and Ag,AgCl|SO<sub>2</sub> +  $0\cdot$ 1M-NH<sub>2</sub>Et<sub>2</sub>Cl|Hg<sub>2</sub>Cl<sub>2</sub>,Hg increase slowly with time and it is shown that of electrodes of this type only Ag-AgCl is reliable, being almost free from change of potential with time. The Pt-H<sub>2</sub> electrode operates very well in liquid SO<sub>2</sub> but the Pt-O<sub>2</sub> electrode is unsatisfactory. The effects of the [HCl] or [HBr] on the e.m.f. of the cells Ag,AgCl|SO<sub>2</sub> + HCl|H<sub>2</sub>,Pt and Ag,AgBr|SO<sub>2</sub> + HBr|H<sub>2</sub>,Pt have been investigated. In all cases the e.m.f. are > the theoretical vals. The results are discussed in relation to Brönsted's theory of acids and bases.

Stages of oxidation of ruthenium. II. Oxidation potential Ru<sup>III</sup>  $\rightleftharpoons$  Ru<sup>IV</sup> in hydrochloric acid solution. G. Grube and G. Fromm (Z. Elektrochem., 1941, 47, 208—211).—The Ru<sup>III</sup>  $\rightleftharpoons$  Ru<sup>IV</sup> oxidation potentials at 25° in HCl solutions of RuCl<sub>3</sub>-RuCl<sub>4</sub> mixtures (0·034 g.-mol. of Ru per l.) are 0·858, 0·874, 0·908 v. in 2·0, 1·1, and 0·5N-HCl respectively, showing that oxidation is not solely explained by changes in potential of Ru ions, but is influenced by HCl.

C. R. H. Apparatus for determination of oxidation-reduction potential and hydrogen-ion concentration in vivo by a single puncture.—See A., 1943, III, 704.

Polarisation at oxidation-reduction electrodes. I. Ferrocyanideferricyanide electrode. W. R. Carmody and J. J. Rohan (Trans. Electrochem. Soc., 1943, 83, Preprint, 11, 137—145).—Chemical polarisation is  $\sim 0.2 \text{ v.}$  per amp. per cm.² at smooth Pt and somewhat less at platinised Pt and at Au, with the Fe(CN)<sub>6</sub>""-Fe(CN)<sub>6</sub>" electrode as anode or as cathode using c.d. <100 ma. per cm.2

Polarography of stannous and cupric tartrate complexes. Amperometric titration of tin with cupric ion. J. J. Lingane (J. Amer. Chem. Soc., 1943, 65, 866—872).—Polarograms of the Sn' tartrate complex in tartrate solutions include a cathode wave due to reduction to Sn, and an equal anode wave from the oxidation to Sn''', both reactions being irreversible. A min. in the anodic diffusion current has been observed in acid media. The half-wave potential is discussed in relation to pH and the nature of the complex. In acid tartrate solutions the Cu" tartrate complex gives a cathode wave, but in alkaline media the latter is masked by the discharge of Na'. The amperometric titration of Sn" with Cu" in tartrate solutions, in which the anode diffusion current of Sn" is compensated by the cathode diffusion current of Cu" is described. cathode diffusion current of Cu", is described.

#### VIII.—REACTIONS.

Correlation of rate data. C. C. DeWitt (Ind. Eng. Chem., 1943, 35, 695—700).—Mathematical. The application of equations of growth to chemical engineering problems is considered.

Transmission coefficient in the theory of absolute reaction rates. H. M. Hulburt and J. O. Hirschfelder (J. Chem. Physics, 1943, 11, 276—290).—Transmission coeffs. are computed quantum-mechanically for a no. of idealised energy surfaces. Quantum effects are small at room temp, where isotope separation is not involved. The use of classical mechanics in Eyring's theory of rate processes is

Interaction of the van der Waals type between three atoms. B. M. Axilrod and E. Teller (J. Chem. Physics, 1943, 11, 299-300). Axilrod and E. Teller (J. Chem. Thysics, 1943). Van der Waals interaction between three atoms is calc. by a per-L. J. J.

Does a measurable excess of translational or of internal molecular energy occur when gases burn explosively? H. Zeise (Z. Elektrochem., 1941, 47, 172—177).—Discussion. C. R. H.

Thermal hydrogen-oxygen reaction; measurements in large vessels. O. Oldenberg and J. E. Morris (J. Chem. Physics, 1943, 11, 247).—Measurements of the upper explosion limit of  $H_2$ — $O_2$  mixtures as a function of temp. in the range 400— $500^\circ$ , in small and large (4 l.) vessels with KCl, BaCl<sub>2</sub>, and Pyrex surfaces, are recorded. The limiting pressure for explosion increases with temp., but the effect of size of vessel is insignificant. Vals. are lower in KCl than in Pyrex vessels. in Pyrex vessels.

Influence of turbulence on flame velocity in gaseous mixtures. G. Damköhler (Z. Elektrochem., 1940, 46, 601—626).—Experiments on the influence of turbulence on the velocity of flame propagation in C<sub>3</sub>H<sub>8</sub>-O<sub>2</sub> mixtures are described, and a mathematical treatment of the subject is presented.

Reaction kinetics of the "knocking" process. II. Spontaneous ignition of hydrocarbon-air mixtures and "knocking." H. Teichmann. III. Effect of added substances on the spontaneous ignition of adiabatically compressed heptane-air mixtures. W. Jost and H. Rögener (Z. Electrochem., 1941, 47, 297—307, 307—309).—II. An apparatus for the study of the combustion of adiabatically compressed mixtures of inflammable substances and air is described. "Knocking," after spark ignition, has been investigated by photographically recording the flames. Induction times and energies of activation for the ignition by adiabatic compression of hydrocarbon-air mixtures have been determined. Vals. of the latter are 30—

III. Addition of amyl nitrite, EtNO<sub>3</sub>, or acetone peroxide increases the inflammability of  $C_5H_{12}$ -air mixtures.  $NH_2Ph$  and  $Fe(CO)_5$  retard the ignition. The influence of  $PbEt_4$  could not be unequivocally established. It is considered that the mild conditions of  $C_5H_{12}$  ignition are insufficient to cause the decomp. of PbEt<sub>4</sub> to the "antiknock"-active substance. W. R. A.

Rate of decomposition of hydrogen peroxide in concentrated solutions. R. Livingston (J. Physical Chem., 1943, 47, 260—264).—Conc.  $H_2O_2$  (80—83%) in Pyrex vessels decomposes at the rate of  $3 \times 10^{-7}$  mol. per l. per sec. at 25°. With glyptal-varnished vessels decomp. is 2—3 times as fast, and with vessels lined with bakelite or tetracosane decomp. is extremely rapid. With Sn-lined vessels decomp is slow after an initial rapid period. Perpendict deserts decomp. is slow after an initial rapid period. Removal of dust or decomp. Is slow after an initial rapid period. Removal of dust of addition of  $H_4SNO_4$  or 2%  $H_2SO_4$  increases stability. Decomp. proceeds by at least two independent processes. One of these is not inhibited by  $H_4SNO_4$  or  $H_2SO_4$  or by removing dust. The decomp. rate is  $2.6 \times 10^{-7}$  mol. per l. per sec. and the heat of activation is <16,000 g.-cal. per mol. The other process, which is predominant in ordinary solutions, is inhibited by H<sub>4</sub>SnO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> and catalysed by dust, and its heat of activation is >20,000 g-calper mol. C. R. H.

Kinetics of aromatic halogenation. I. Bromination. P. W. Robertson, P. B. D. de la Mare, and W. T. G. Johnston. II. Chlorination of hydrocarbons. P. B. D. de la Mare and P. W. Robertson (J.C.S., 1943, 276—279, 279—281).—I. Bromination of 0.025M-NHACPh, p-C<sub>6</sub>H<sub>4</sub>Me·NHAc, mesitylene, PhOMe, and p-C<sub>6</sub>H<sub>4</sub>Me·OMe in AcOH is a third-order reaction which at lower conc. or by addition of H<sub>2</sub>O becomes of second order, and with addition of CHCl<sub>3</sub> or CCl<sub>4</sub> of a higher order involving chain reactions.

II. Rates of chlorination of PhR in AcOH are in the order  $R = Me > Et > Pr^{\beta} > Bu^{\gamma}$ . Vals. are also recorded for o-, m-, and p-xylene,  $C_6H_3Me_3$ , and  $C_6HMe_5$ .

Mechanism of reaction between alkyl halides and hydroxylic solvents. III. Reactions of *n*-butyl bromide. M. L. Bird, E. D. Hughes, and C. K. Ingold (J.C.S., 1943, 255—261).—Vals. calc. for both rate of reaction and composition of the products in the solvolysis of Bu<sup>a</sup>Br on the basis of a single pair of consts. agree with experimental results obtained in MeOH and MeOH-H<sub>2</sub>O at 59·4°, and in EtOH-H<sub>2</sub>O at 75·1°, confirming that these reactions are bimol.

Reduction of ammonium molybdate by sodium hydrogen l-ascorbate in the dark. S. K. Bhattacharyya and A. R. Sur (J. Indian Chem. Soc., 1942, 12, 514—515).—The velocity of reduction of  $(NH_4)_2MoO_4$  (I) by Na H l-ascorbate (II) is a max. when (I) and (II) are in equiv. concn., indicating that it is  $\alpha$  the concn, of a complex.

Velocity of fission of glycols with lead tetra-acetate in relation to the solvent. R. Criegee and E. Büchner (Ber., 1940, 73, [B], 563—571; cf. A., 1933, 1272).—Velocity coeffs. ( $k_{20}$ ) are recorded for reaction of Pb(OAc), and cis-cyclohexanediol in AcOH with various addenda (the accelerating effect of the latter is in the order  $H_2O > MeOH > COMe_2$ , EtOAc  $> C_0H_6$ , trans-dimethylacenaphthenediol in MeOH-AcOH (1:1), and mandelic acid in 99.5% AcOH, and curves showing increase of k with increasing additions of MeOH to AcOH are given for several other diols. Hydrobenzoin is oxidised by Pb<sub>3</sub>O<sub>4</sub>-2N-HNO<sub>3</sub> to PhCHO; pinacone hydrate affords COMe<sub>2</sub> similarly. The reaction mechanisms are discussed. A. T. P.

Velocity of fission of glycols with lead tetra-acetate in relation to the constitution of glycol. R. Criegee, E. Büchner, and W. Walther (Ber., 1940, 73, [B], 571—575; cf. A., 1933, 1272).—Vals. of  $k_{20}$  and  $k_{30}$  are tabulated for 17 diols; they decrease in the order ciscyclopentanediol > dimethylcamphanediol > isohydrobenzoin > cycloheptanonepinacone > tetrabenzonaphthalene glycol > dimethyldihydrophenanthrenediol, hydrobenzoin, fluorenonepinacone > cis-decahydronaphthalene-9: 10-dione > trans-cyclopentanediol > cyclohexanonepinacone > trans-decahydronaphthalene-2: 3-diol (I) of m.p.  $140^{\circ}$  > trans-decahydronaphthalene-9: 10-diol > cyclopentanonepinacone > (I) of m.p.  $163^{\circ}$  > d-camphorpinacone > camphenilonepinacone, and the relation between reaction velocity and mol. structure is discussed. A. T. P.

Kinetics of co-polymerisation. H. Branson and R. Simha (J. Chem. Physics, 1943, 11, 297—298).—Co-polymerisation is discussed on the basis of a steady-state method with termination involving radical chain and a stable monomeride.

L. J. J.

Restriction of the catalysed oxidation of the iodine ion by chlorate. III. Osmium tetroxide and ferric chloride as catalyst. K. Weber and M. Pichler (Ber., 1940, 73, [B], 415–423).—OsO<sub>4</sub> is the best catalyst for the reaction, 61' + ClO<sub>3</sub>' + 6H' = 3I<sub>2</sub> + Cl' + 3H<sub>2</sub>O<sub>5</sub>, being in the initial stages about 20 times as powerful as RuCl<sub>3</sub>. With increasing [HCl] the rate of reaction increases initially, but the subsequent decrease in the rate is more pronounced. The increase is more marked than corresponds with direct proportionality with [HCl], less marked than is required by [HCl]<sup>2</sup>. At 13·5°, 25°, and 40° there is little increase in the rate of reaction with increasing temp. and such increase diminishes with time and ultimately at 40° changes to a decrease. The velocity coeff. appears to be  $\propto$  log [OsO<sub>4</sub>]. The rate of the catalysed reaction is greatly lessened by NiSO<sub>4</sub>, Co", and SO<sub>4</sub>", the influence being of the same order as observed with RuCl<sub>2</sub>. Cl' has little effect and Na' is without action, Mn" has a slight accelerating effect. The catalytic activity of FeCl<sub>3</sub> is not very pronounced. HCl appears to cause a great acceleration due to the accumulation of H' in the neighbourhood of I' and a less pronounced restriction by inactivation of the catalyst by repression of the slight hydrolysis. The temp. coeff. of the change is not quite normal. Direct proportionality between rate of reaction and [FeCl<sub>3</sub>] is observed. NiSO<sub>4</sub>, CoSO<sub>4</sub>, MnSO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, NaCl, and Mn(NO<sub>3</sub>)<sub>2</sub> restrict the change slightly but MnCl<sub>2</sub> causes a slight acceleration.

Kinetics in acid media. Condensation of o-benzoylbenzoic acid. C. W. Deane with J. R. Huffman (Ind. Eng. Chem., 1943, 35, 684—694).—The condensation of o-C<sub>6</sub>H<sub>4</sub>Bz·CO<sub>2</sub>H to anthraquinone (I) in presence of conc. H<sub>2</sub>SO<sub>4</sub> and oleum is a unimol reaction. It is catalysed by  $^{\bullet}SO_3$  and inhibited by H<sub>2</sub>O and to a greater extent by (I). The average energy of activation (E) is 26,100 g.-cal., E decreasing slightly with increase in  $[SO_3]$ . The temp. coeff. for a  $10^{\circ}$  rise  $(75-85^{\circ})$  is  $\sim 3$ . Reaction mechanisms and the application of the data to problems involved in the commercial prep. of (I) are discussed.

Effects of high pressure on the inversion of sucrose and the mutarotation of glucose.—See A., 1943, III, 683.

Chemical interpretation of the mechanism of oxidation by dehydrogenase systems.—See A., 1943, III, 596.

Kinetics of ammonia synthesis. P. H. Emmett and J. T. Kummer (Ind. Eng. Chem., 1943, 35, 677—683).—Temkin and Pishev's theory of the catalytic synthesis and decomp. of  $\mathrm{NH}_3$  (cf. A., 1942, I, 207) is discussed and applied to data on the rate of  $\mathrm{NH}_3$  synthesis as a function of gas composition, pressure, space velocity, and temp. Agreement between observation and theory is very close, although the theory does not appear to be applicable to catalysts singly promoted with  $\mathrm{Al}_2\mathrm{O}_3$ . C. R. H.

promoted with Al<sub>2</sub>O<sub>3</sub>.

Cyanide-cyanamide equilibrium in the case of lithium. A. Perret and J. Riethmann (*Helv. Chim. Acta*, 1943, 26, 740—746).—LiCN is unchanged at high temp. in the absence of catalysts, but in presence of Fe the reaction 2LiCN = C + Li<sub>2</sub>CN<sub>2</sub> occurs. LiCN is stable at >1000°, Li<sub>2</sub>CN<sub>2</sub> is stable at <600°, and at intermediate temp. LiCN and Li<sub>2</sub>CN<sub>2</sub> are in equilibrium. When Li<sub>2</sub>C<sub>2</sub> is heated in NH<sub>3</sub>, or when LiN<sub>3</sub> is heated with C, the product is Li<sub>2</sub>CN<sub>2</sub> at <700°; at higher temp. increasing amounts of LiCN are also formed.

F. J. G.

Anodic oxidation of aluminium and aluminium alloys.—See B., 1943, I, 342.

Separation of metals by the mercury cathode: chromium. R. C. Chirnside, L. A. Dauncey, and P. M. C. Proffitt (Analyst, 1943, 68, 175—180).—In presence of  $(\mathrm{NH_4})_2\mathrm{SO}_4$  the rate of deposition of Cr is increased by high c.d., high temp., use of conc. solutions, and min. acidity, but decreased by rotation of the anode and addition of reducing agents. K and Na have no effect. Small amounts of Ni and traces of Ag facilitate complete deposition of Cr even in the presence of much  $(\mathrm{NH_4})_2\mathrm{SO}_4$ . Cu and Fe do not interfere.

Hard chromium-plating of aluminium and its alloys.—See B., 1943, I, 342.

Electrolysis with alternating current superposed on direct current (undulating current); reduction of nitrocarbamide to semicarbazide. E. Briner and E. Hoefer (Helv. Chim. Acta, 1943, 26, 913—922).—In the electrolytic reduction of nitrocarbamide to semicarbazide, superposition of a.c. on d.c. reduces the yield with bright Pt electrodes but not with black Pt.

F. J. G.

Optical sensitising of silver halides by dyes. IV. Optical sensitising properties of fluorescein dyes in relation to their spectral absorption and constitution. S. E. Sheppard, R. H. Lambert, and R. D. Walker (J. Chem. Physics, 1943, 11, 263—275; cf. A., 1941, I, 172).—The visible and first ultra-violet absorption bands of halogenated fluoresceins move towards longer  $\lambda\lambda$  with increasing halogen content, whilst acid dissociation consts. of •OH and •CO2H become indistinguishable and solubilities of Ag compounds decrease. The half-degree of adsorption of fluorescein dyes on Ag halides does not coincide with the isoelectric pAg of the Ag halide. Deviation from the Langmuir isotherm at low and approach to agreement at high adsorption densities can be explained by assuming an accommodation coeff. in adsorption, making the average life of adsorbed mols. dependent on adsorption density. Adsorption saturation of erythrosin agrees with an edge-on or end-on monolayer. Electrometric titration and dilution of suspensions give 4-55  $\times$  10-6 and 4-6—4-8  $\times$  10-6 mols. per 1., respectively, for solubility of Ag erythrosinate; the val. decreases with ageing and with adsorption on AgBr, and varies with particle size. Evidence favours energy rather than electron transfer as the basis of sensitisation.

Photobromination of cinnamic acid in ultra-violet light of 254 m $\mu$ . J. C. Ghosh and S. K. Bhattacharyya (*J. Indian Chem. Soc.*, 1942, 12, 503—506).—The reaction between Br and cinnamic acid (I) in CCl<sub>4</sub> solution in light of  $\lambda$  254 m $\mu$ . is unimol. with respect to Br and to (I). The rate  $\alpha$  the intensity of radiation absorbed by (I), and the quantum efficiency and temp. coeff. are both >1. A mechanism involving activated mols. of (I) is proposed.

F. J. G.

Photochemical oxidation of mandelic acid by bromine with tungstic acid sol as sensitiser in ultra-violet light of 254 m $\mu$ . J. C. Ghosh, S. K. Bhattacharyya, and K. R. Kar (J. Indian Chem. Soc., 1942, 12, 507—509).—The oxidation of mandelic acid (I) in aq. solution by Br with  $H_2WO_4$  sol as sensitiser in light of  $\lambda$  254 m $\mu$ . is unimol. with respect to Br and to (I). The rate is independent of [Na<sub>2</sub>WO<sub>4</sub>] at const. pH, and is a min. at pH 4·05. It is of the intensity of light absorbed by the sol. The temp. coeff. is small and the quantum efficiency is between 1 and 7.

Photochemical reactions between ammonium molybdate and various organic reducing agents in [light of] wave-length 366 m $\mu$ . S. K. Bhattacharyya, K. R. Kar, and A. R. Sur (J. Indian Chem. Soc., 1942, 12, 510—513).—In light of  $\lambda$  366 m $\mu$ ., tartaric, lactic, and mandelic acids reduce (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub> to various coloured products. Some observations on the rate of the reaction are recorded. It is independent of the state of polarisation of the light. F. J. G.

Destruction of pyridoxine by light.—See A., 1943, III, 577.

#### IX.—PREPARATION OF INORGANIC SUBSTANCES.

Metastable oxygen and biological formation of hydrogen peroxide.—See A., 1943, III, 699.

Statistics of isotope distribution in condensed particles. Requirements for a separation of isotopes on the basis of density variations of condensed particles. L. Holleck (Z. Physik, 1940, 116, 624—631).—The possibility of making use of density variations in condensed particles to effect a separation of isotopes by sedimentation or centrifuging has been investigated statistically. Calculation shows that for <sup>7</sup>Li and <sup>6</sup>Li, the frequency with which variation in density occurs, even in particles of colloidal size, is so small as to make the method quite impracticable.

A. J. M.

Compounds of gallium. V. Gallium alizarin lakes, gallium salts of geometrically and optically isomeric acids, and double sulphates with ethylene- and propylene-diamine sulphates. P. Neogi and K. L. Mondal (J. Indian Chem. Soc., 1942, 12, 501–502).—Ga alizarate,  $Ga(C_{14}H_7O_4)_3$ , Ga Ca alizarate,  $Ga_2(C_{34}(C_{14}H_2O_4)_3, H_2O$ , Ga d- and 1-camphorsulphonate,  $Ga(C_{10}H_{15}SO_4)_3, 3H_2O$ ,  $[a]_{3}^{50}+18\cdot6^\circ$ ,  $-19^\circ$ , ethylenediammonium Ga sulphate,  $Ga_2(SO_4)_3, C_2H_4(NH_3)_2SO_4, 12H_2O$ , and propylenediammonium Ga sulphate,  $Ga_2(SO_4)_3, C_3H_6(NH_3)_2SO_4, 12H_2O$ , are described. F. J. G.

Reactions in solid state. III. Reaction between sodium carbonate and quartz. G. Gibson and R. Ward (J. Amer. Ceram. Soc., 1943, 26, 239—246).—Reaction at 726—805° between  $Na_2CO_3$  and quartz (<325-mesh, 5—7 and 2—3  $\mu$ .) was conducted in a stream of  $N_2$ . The reaction rate and end products for mixtures of mol. ratio  $Na_2CO_3$ :  $SiO_2$  of 1:1 to 1:2.5 were determined. The rate of reaction and the nature of the product were affected by the size of the batch, the rate of gas flow, and the duration of the reaction. In presence of sufficient  $Na_2CO_3$  the product at the higher temp. was  $2Na_2O,SiO_2$  but compounds intermediate between  $Na_2O,SiO_2$  and  $2Na_2O,SiO_2$  appear to be formed by interaction between  $Na_2O,SiO_2$  and  $Na_2CO_3$ . The latter reaction is postulated to be reversible with the smaller ions. This theory is used to explain certain anomalies. The rate of evolution of  $CO_2$  is not a criterion of the rate of reaction of the  $SiO_2$  particles.

Acidity of silicofluorides. K. Uhl and K. Klumpner (Angew. Chem., 1943, 15, 188—189).—pH vals. obtained during the progressive neutralisation and decomp. of aq.  $\rm H_2SiF_6$  by aq. NH<sub>3</sub>, KOH, NaOH, Mg(OH)<sub>2</sub>, Ca(OH)<sub>2</sub>, and Ba(OH)<sub>2</sub> are recorded, and discussed in relation to the applications of fluorides and silicofluorides in plant physiology. L. S. T.

Conductometric elucidation of complex chromium cations. I. Theoretical. II. Structure and properties of chromium sulphate complexes. S. G. Shuttleworth (J. Soc. Leather Trades' Chem., 1943, 27, 104—111, 111—116).—I. Equations are derived to calculate the amount of hydrolysed acid and the distribution of acid and OH groups inside and outside the Cr complex from conductometric titration curves.

II. Boiled 33½% basic SO<sub>2</sub>-reduced Cr sulphate liquors contain all the SO<sub>4</sub>" and OH' inside the complex. This liquor made 66½% basic by the addition of NaOH still contains the SO<sub>4</sub>" inside the complex but 25% of the OH' is attached electrovalently to the Cr complex. Freshly prepared unheated Cr alum solution contains only electrovalent groups. Boiled Cr alum solutions consist of mixtures of electrovalent Cr sulphate and the above 33½% basic Cr complex. The proportion of 33½% basic Cr complex is 50% at M./6 concn. and 75% at 0.01M.

D. P.

Preparation and properties of ammonium diuranate. H. W. Safford and A. Kuebel (J. Chem. Educ., 1943, 20, 88—91).—A procedure for the industrial extraction of  $(NH_4)_2U_2O_7$ , $xH_2O$  (I) from pitchblende, and a duplication on the laboratory scale, are described. (I) dried in air at room temp., or over CaSO<sub>4</sub>, and  $(NH_4)_2U_2O_7$  dried at  $100^\circ$  for 3 weeks, have practically identical X-ray diffraction patterns. Reddish-brown  $UO_3$  is formed by heating (I) in air at  $\sim 350^\circ$ , olive-green  $U_3O_8$  at  $750^\circ$  for 2 hr., and grey- or blue-black  $UO_2$  at  $1000^\circ$  in dry  $H_2$ .  $UO_3$  gives no definite X-ray diffraction pattern. Qual. solubilities of (I) in acids and salt solutions are recorded.

Active substances. XLVII. Transformation and reaction processes during the heating of  $\gamma$ -iron hydroxide, cadmium carbonate, and stoicheiometric mixtures thereof. II. W. Schröder (Z. Elektrochem., 1941, 47, 196—207).—An emanation method has been used to investigate the thermal behaviour of  $\gamma$ -Fe(OH)3, basic Cd carbonate, and spinel-forming mixtures thereof. The parts played by Fe(OH)3 and CdCO3 in spinel formation are discussed with reference to these and other data. C. R. H.

Activation of passive iron in nitric acid. K. F. Bonhoeffer [with H. Beinert] (Z. Elektrochem., 1941, 47, 147–150).—Fe, rendered passive by  $\rm HNO_3$ , can be reactivated by a current of  $10^{-4}$  coulomb per sq. cm., this current being approx. the same as that necessary for the reduction of a unimol. layer of Fe oxide. In  $\rm HNO_2$ -free

HNO $_3$  the potential of passive Fe drops from  $\sim 1$  to  $\sim 0.5$  v. during the passage of  $2 \times 10^{-5}$  coulomb, corresponding with a polarisation capacity of  $\sim 40~\mu \text{F}$ . per sq. cm. When the current is stopped the Fe returns to its passive state unless a limiting potential has already been attained, in which case the potential drops still further to 0.3 v. Passivity is due to an oxide layer with a higher dissociation pressure of  $O_2$  than Fe $_2O_3$ .

Decomposition of the ammonia complex of tervalent cobalt. L. M. Orlova ( $Zavod.\ Lab.$ , 1939, 8, 502).—[Co(NH<sub>3</sub>)<sub>8</sub>]Cl<sub>3</sub> is reduced to CoCl<sub>2</sub> by boiling with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and HCl. J. J. B.

#### X.—ANALYSIS.

Determination of the precision of analytical control methods. R. F. Moran (Ind. Eng. Chem. [Anal.], 1943, 15, 361—364).—The use of statistical methods based on the standard deviation is described. The analytical method is first tested under the best obtainable conditions to find the highest precision of which the method is capable. Procedure necessary for this is specified. The method is then tested in routine practice for 1 year to determine the variability under routine laboratory conditions. A limit of uncertainty within which routine analyses can be guaranteed is then calc. Normal control methods have  $1\cdot5-2\cdot5$  times as much variation under routine conditions as the same method under the best conditions. Duplicate determinations made at the same time are generally not truly random, and the averaging of such results does not appreciably improve precision. Duplicate determinations are only a safeguard against mistakes such as an error in calculation or weighing. The above methods are exemplified by data for  $\rho$  of  $\mathrm{CCl_4}$ , and other representative commercial analytical methods.

Automatic electrochemical determination of concentration. F. Lieneweg (Z. Elektrochem., 1941, 47, 130—135).—Methods of determining ionic concns. by means of conductivity, electrode potential, c.d., and depolarisation measurements are discussed. C. R. H.

Chemical war-materials. H. Mohler (*Helv. Chim. Acta*, 1943, **26**, 769—770).—A reply to Epprecht (A., 1943, I, 161). F. J. G.

Dilution process for determining hydrogen-ion concentration with one-colour indicators. J. McCrae (Analyst, 1943, 68, 183).—Equal quantities of indicator are added to the test solution and to the test solution made alkaline with NaOH so that its pH is above the range of the indicator. The second solution (I) is then diluted until there is a colour match between the two solutions. The relation, pH = pK —  $\log (D-1)$ , where D is the ratio of final vol. to initial vol. of (I) and pK is the pH at the half transformation point of the indicator, holds for one-colour nitrophenol indicators. Calibration tables for the polyacidic one-colour indicators, phenolphthalein and salicyl-yellow, are given.

Behaviour of the quinhydrone electrode in plant liquids. Y. Kauko and L. Knappsberg (Angew. Chem., 1940, 53, 187—188).—Additional data for various plant juices show that pH vals. obtained using this type of electrode are untrustworthy. Whilst pH vals. obtained with a glass electrode remain const., those given by the quinhydrone electrode show variations with time. The use of a glass electrode for measuring the pH of plant juices is recommended.

Colorimetric determination of hydrogen peroxide. G. M. Eisenberg (Ind. Eng. Chem. [Anal.], 1943, 15, 327—328).—The method is based on photo-electric measurement of the colour intensities of  $\rm H_2O_2$  solutions treated with  $\rm Ti(SO_4)_2$  in dil.  $\rm H_2SO_4$ . Beer's law holds at 380—430 m $\mu$ . The use of a 12·5-mm. cell increases the effective range of the method, and permits the determination of 0·2—3·0 mg. of  $\rm H_2O_2$  per 100 ml. of solution with an average deviation of  $\pm 0.03$  mg.

Determination of chloride in bauxite-supported anhydrous aluminium chloride catalysts. W. A. La Lande, jun., H. Heinemann, and W. S. W. McCarter (Ind. Eng. Chem. [Anal.], 1943, 15, 385—387).— Distillation of the sample with 18n-H<sub>2</sub>SO<sub>4</sub> and determination of the liberated HCl by Volhard's method gives reproducible results representing 92—96% of the total chloride present. Extraction of the catalyst with H<sub>2</sub>O by a standard procedure gives reproducible, but low (90—93%), results. Either method is satisfactory as a routine procedure. The total Cl' content can be determined accurately by combining the two methods, the distillation method being applied to the powdered residue from the H<sub>2</sub>O extraction. Details of procedure and typical data are given.

L. S. T.

Turbidimetric determination of small amounts of chlorides. E. N. Luce, E. C. Denice, and F. E. Akerlund (Ind. Eng. Chem. [Anal.], 1943, 15, 365—366).—The nephelometric method is adapted to the Hellige turbidimeter in order to eliminate the disadvantages of reference standards. The method is suitable for 0—5 p.p.m. of Cl', and its accuracy is comparable with that of the nephelometer. A determination takes 15 min. of working time.

Determination of chloride in presence of hydrosulphide or sulphide ion. M. M. Maglio and F. Fazio (Ind. Eng. Chem. [Anal.], 1943, 15,

265—266).—HS' or S'' is pptd. as CuS by adding 5% aq. Cu(NO<sub>3</sub>)<sub>2</sub> to the solution at pH 4 (HNO<sub>3</sub>). Cl' is determined gravimetrically as AgCl in the filtrate. For samples ranging from 94 to 99% NaCl (6—1% NaSH,2H<sub>2</sub>O) the average error is -0.08%, and the largest error, -0.19%. L. S. T.

Automatic determination of oxygen. I. N. Kuzminich and E. I. Surkov (Zavod. Lab., 1939, 8, 541—544).—In a standard Orsat tube a  $\mathrm{Na_2S_2O_4}$  solution cannot be substituted for the pyrogallol (I) solution as the former is too fluid; if, instead, the vessel is filled with glass tubes 1·5 cm. long a solution of  $\mathrm{Na_2S_2O_4}$  14,  $\mathrm{NaOH}$  6·7, and  $\mathrm{H_2O}$  79·3% absorbs  $\mathrm{O_2}$  better than does (I). J. J. B.

Substitution of calcium hydroxide for cadmium and zinc acetates in the determination of sulphur by Schulte's method. P. I. Schportenko and V. F. Garan (Zavod. Lab., 1939, 8, 504—505).— $H_2S$  is absorbed in a saturated Ca(OH)<sub>2</sub> solution. J. J. B.

Determination of hydrogen sulphide by titration with potassium dichromate. M. P. Babkin (Zavod. Lab., 1939, 8, 108—109).—A solution containing 10 ml. of 3% HCl, 5 ml. of 10% KI, 25 ml. of H<sub>2</sub>S solution, and a few drops of a starch solution is titrated with  $0\cdot l_N - K_2 Cr_2 O_7$  to a blue colour. J. J. B.

Separation of carbon dioxide from volatile sulphur oxides. J. Jany and I. Fenyö (J. Amer. Leather Chem. Assoc., 1943, 38, 215—218).—Sulphites are oxidised with boiling  $\rm H_2O_2$  in an atm. of  $\rm H_2$ . HCl is added and the  $\rm CO_2$  liberated is absorbed in soda-lime tubes. The  $\rm SO_3''$  is determined as  $\rm BaSO_4$  and the  $\rm CO_3''$  by the increase in wt. of the soda-lime tubes. D. P.

Determination of impurities in air and the importance of chemical analysis in meteorology and climatology. E. Quitmann (Angew. Chem., 1940, 53, 80—82).—Systematic examinations of air are limited to determination of the NH3, NO2', Cl', SO4'', and I'. The I is collected in aq. KOH whilst the other constituents are collected by condensing the  $\rm H_2O$  vapour on a spherical surface cooled internally with solid CO2 or by evaporation of EtOH, the frost then being melted and the  $\rm H_2O$  analysed; the results are converted into  $\rm \mu g$ . per cu. m. of air by measuring the R.H. and temp. of the air. Correlation of the results obtained by simultaneous analysis of the air at various altitudes and of any rain, snow, dew, or frost over a wide area affords valuable information for the meteorologist.

Determination of nitrogen in mixed fertilisers.—See B., 1943, III, 166.

Colorimetric determination of phosphorus by reduction of phosphomolybdate to molybdenum-blue. P. J. Hardwick (Analyst, 1943, 68, 183—184).—Addition of  $0\cdot1\%$  KClO<sub>3</sub> to phosphate solutions before reduction by SnCl<sub>2</sub> to Mo-blue prevented any development of green colour over a period of several hr. S. B.

**Micro-analysis of boracite.** C. O. Harvey (Analyst, 1943, 68, 211-212).— $0\cdot1$  g. of mineral suspected to be boracite (6MgO,MgCl<sub>2</sub>,8B<sub>2</sub>O<sub>3</sub>) was analysed, with duplicate determinations, each on  $0\cdot01$  g. After fusion with Na<sub>2</sub>CO<sub>3</sub> + K<sub>2</sub>CO<sub>3</sub>, the solution obtained was made neutral to Me-orange and titrated (for B) against  $0\cdot02$ N-NaOH in presence of mannitol, while aërating with CO<sub>2</sub>-free air, using phenolphthalein as indicator. Mg was pptd. as phosphate after Na<sub>2</sub>CO<sub>3</sub> fusion and removal of B by evaporations with MeOH. Cl was pptd. as AgCl after fusion with mixed carbonates. Results showed Mg: B: Cl =  $7\cdot1:16:2\cdot2$ ; SiO<sub>2</sub>0·5%, Fe<sub>2</sub>O<sub>3</sub> + Al<sub>2</sub>O<sub>3</sub>2·3%, CaO 0·2%, MnO trace.

Determination of silicic acid in presence of fluorides. A. A. Vassiliev and L. L. Laptschinskaja (Zavod. Lab., 1939, 8, 27—31).—1 g. of fluoride containing <0.05 g. of SiO $_2$  is fused with  $\rm H_3BO_3$ , strongly ignited for 50 min., dissolved in 15 ml. of conc.  $\rm H_2SO_4+20$  ml. of  $\rm H_2O$ , heated to SO $_3$  fumes, diluted with  $\rm H_2O$ , and heated again. The rapid method of Tananaev and Babko (cf. B., 1930, 1110) is also recommended.

Rapid determination of silicon and phosphorus in cast iron.—See B., 1943, I, 338.

Determination of silicates and silicides in steel.—See B., 1943, I, 339.

Direct determination of combined carbon in cast iron and steel.— See B., 1943, I, 338.

Photometric determination of potassium by a modified Jacobs-Hoffman method. A. Eden (Analyst, 1943, 68, 167—170; cf. A., 1932, 102).—For the determination of about 0·1 mg. of K (0·02 mg. per ml.) in blood sera, solutions of ashed tissues, and inorg. solutions free from NH<sub>4</sub>, slightly modified conditions of pptn. and washing are given.

S. B.

Determination of potash in fertilisers.—See B., 1943, III, 166.

Colorimetric determination of sodium. E. A. Arnold and A. R. Pray (Ind. Eng. Chem. [Anal.], 1943, 15, 294—296).—The triple UO<sub>2</sub> acetate (Zn or Mg) is treated with excess of  $(NH_4)_2CO_3$  and  $H_2O_2$  and the [U] determined colorimetrically using a wave band of 5200 A. L. S. T.

Determination of sodium by the uranyl method. V. S. Krasnova (Zavod. Lab., 1939, 8, 219).—When Na and SO<sub>4</sub> are present together, the ppt. consisting of NaZn(UO<sub>2</sub>)<sub>3</sub>(OAc)<sub>9</sub>,6H<sub>2</sub>O (I) and insol. sulphates is weighed, washed out with cold H<sub>2</sub>O to colour change, and weighed again; the loss of wt. is the amount of (I) present.

Determination of free alkali in potassium chromate. L. E. Sabinina and A. A. Babalova (Zavod. Lab., 1939, 8, 413—416).—Solutions of pure  $K_2CrO_4$  have pH  $\sim 9.8$ . The alkali in less pure samples can be determined by acidifying the solution and titrating it, using a PbO<sub>2</sub> or a glass electrode.

J. J. B.

Use of an iodine derivative of methylene-blue in qualitative analysis. L. M. Kulberg (Zavod. Lab., 1939, 8, 421—423).—Methylene-blue (I) forms with KI $_3$  in  $\rm H_2O$  a brownish-black insol. compound, probably a polyiodide. It liberates (I) in presence of Ag', Hg', Hg'', S'', S2O $_3$ '', and Sn''. 2  $\times$  10 $^{-10}$  g. of Ag or 2  $\times$  10 $^{-8}$  g. of Hg can be thus detected.

Micro-determination of magnesium with the polarograph. C. Carruthers (Ind. Eng. Chem. [Anal.], 1943, 15, 412—414).—8-Hydroxyquinoline (I) is reduced at the dropping Hg electrode, and the diffusion current is  $\alpha$  concn. Mg" is pptd. as the salt with (I) and then determined polarographically in PO4" buffer-HCl-gelatin mixture at 25°. Polarograms, typical data, and procedure for determining Mg in tissues are given.

Microchemical determination of magnesium. P. Vukulov (Zavod. Lab., 1939, 8, 494—495).—Mg is pptd. as  $Mg(OH)_2$  and the latter titrated with 0·1n-HCl. J. J. B.

Determining magnesium in plants.—See A., 1943, III, 704.

Determination of magnesium in aluminium alloys.—See B., 1943, I, 341.

Polarographic analysis of lead and its compounds. S. P. Schaikind (Zavod. Lab., 1939, 8, 567—571).—Cu, Cd, Ni, Zn, and Mn can be determined polarographically in Pb solutions. J. J. B.

Determination of copper and zinc in fertilisers.—See B., 1943, III, 166.

Determination of mercury in air with dithizone. N. S. Kuziatina (Zavod. Lab., 1939, 8, 174—177).—Air containing Hg is passed through 0·05N-KMnO $_4$  in 5%  $\rm H_2SO_4$ , and the solution is made colourless with  $\rm H_2C_2O_4$  and shaken with a solution of diphenyl-thiocarbazone in CHCl $_3$ . To a control mixture as much HgSO $_4$  is added as produces an identical coloration.

[Reineckate-thiocarbamide complexes in] colorimetric analysis. C. Mahr (Angew. Chem., 1940, 53, 257—258).—Hg, Cd, or Cu is separated from other metals in the usual way and then converted into the reineckate (I). The washed moist (I) is dissolved in COMeEt containing 2% of CS(NH<sub>2</sub>)<sub>2</sub> (II), and the sol. (I)-(II) complex determined colorimetrically. The method is particularly suitable for determination of Cd in excess of Zn, and of Cu in steel.

M. H. M. A.

Determination of aluminium as cryolite. I. V. Tananaev and S. Talipov (Zavod. Lab., 1939, 8, 23—27).—Al can be pptd. and weighed as Na<sub>3</sub>AlF<sub>6</sub> if the Al solution is added to ~3% aq. NaF, the mol. ratio NaF: AlCl<sub>3</sub> being >9. If the Al solution contains Be, the NaF solution must be ~1%. If NaF is added to AlCl<sub>3</sub>, the results are too low.

**Detection of aluminium.** V. A. Zacharievski ( $Zavod.\ Lab.$ , 1939, 8, 33—36).—Al<sup>\*\*\*</sup> gives a red coloration with a reagent made up of 0.04 g. of  $ZrO(NO_3)_2$ ,  $4H_2O$  in 10 ml. of  $H_2O$ , 0.02 g. of alizarin-red in 5 ml. of EtOH, 0.0006 mol. of KF in 1 ml. of  $H_2O$ , and ~50 ml. of 2N-HCl. OCl',  $C_2O_4$ ", and  $SO_4$ ", as well as more F', interfere.

Determination of sesquioxides in the form of phosphates. A. G. Filippova (Zavod. Lab., 1939, 8, 98—101).—For combined determination of Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub> in phosphorites the method of Charlot (A., 1937, I, 477) (slightly modified) is recommended. F' has first to be eliminated, but flotation reagents do not interfere.

Colorimetric determination of small amounts of indium. T. Moeller (Ind. Eng. Chem. [Anal.], 1943, 15, 270—272).—The In compound of 8-hydroxyquinoline (I), In(C<sub>9</sub>H<sub>6</sub>ON)<sub>3</sub>, dissolves in CHCl<sub>3</sub> giving yellow solutions which show an absorption band at 395—400 mμ. At 400 mμ. such solutions obey Beer's law in concns. >18·0 mg. of In per l. of CHCl<sub>3</sub>. In is completely extracted from aq. solution at pH 3·2—4·5 by shaking with (I) in CHCl<sub>3</sub>. Al", Sn", Bi", Fe", Fe", Co", Ni", Cu", Tl", and Ga" are also extracted at pH 3·5, and thus interfere. In can be accurately determined in presence of Zn", Cd", and Pb", but not of Fe", by the method described. Results are accurate for 0·3—20 mg. of In per l. of CHCl<sub>3</sub>, or 0·015—1·00 mg. of In in 25 ml. of aq. solution.

Ferrocyanidometric determination of iron. M. A. Bodin (Zavod.Lab., 1939, 8, 32—33).—To 100 ml. of a solution containing >3 mg. of Fe",  $\sim$ 10 g. of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, and  $\sim$ 10 g. of H<sub>2</sub>SO<sub>4</sub>, 5 ml. of

10% NH<sub>4</sub>CNS is added, and the solution is shaken with 10 ml. of iso-C<sub>5</sub>H<sub>11</sub>·OH and titrated with 0·5% K<sub>4</sub>Fe(CN)<sub>6</sub> solution until the C<sub>5</sub>H<sub>11</sub>·OH becomes colourless. A control sample must be titrated using the same [H<sub>2</sub>SO<sub>4</sub>]. J. B.

Vanadometric volumetric micro-determination of iron. V. V. Stepin (Zavod. Lab., 1939, 8, 262—264).—Fe''' is reduced to Fe'' by SnCl<sub>2</sub> and then titrated with NH<sub>4</sub>VO<sub>3</sub> in presence of phenylanthranilic acid. Procedures for determining Fe in limestone, a Mn ore, and ceramic materials are given.

J. J. B.

Separation of rare metals by electrolysis with a mercury cathode. I. P. Alimarin and B. I. Frid (Zavod. Lab., 1939, 8, 496).—Fe is electrodeposited from a solution of Fe<sup>\*\*\*</sup> and various rare metals (Ce, La, Sm, Er, Pr, Nd) in 1% H<sub>2</sub>SO<sub>4</sub>.

J. J. B.

Determination of ferrous iron in vivianites. V. A. Kararinova-Oknina and N. A. Nikitina (Zavod. Lab., 1939, 8, 498—499).—Vivianite is dissolved in HCl and titrated with I in presence of NH<sub>4</sub>F and K<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.

J. J. B.

Determination of iron in presence of chromium and titanium with the Jones reductor. F. S. Grimaldi, R. E. Stevens, and M. K. Carron (Ind. Eng. Chem. [Anal.], 1943, 15, 387—388).—H<sub>2</sub>SO<sub>4</sub> solutions of Ti<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and CrSO<sub>4</sub> solutions, obtained by passage through the Jones reductor, are oxidised by aeration for 5—10 min. in presence of CuSO<sub>4</sub> as catalyst. The Fe" is essentially unoxidised, and is titrated by 0·05N-KMnO<sub>4</sub> (o-phenanthroline). 3 ml. of 0·0001M-CuSO<sub>4</sub> per 300 ml. of solution give the best results. Larger amounts of Cu" lead to low results for Fe" when both Ti and Cr are present. Details of procedure and typical data for the method, which is applicable to all Fe: Ti: Cr ratios, are given. Mo and V must be absent. Simple air-oxidation of Ti" is untrustworthy (cf. A., 1943, I, 24).

Extraction and colorimetric determination of certain metals as derivatives of 8-hydroxyquinoline. T. Moeller (Ind. Eng. Chem. [Anal.], 1943, 15, 346—349).—Spectrophotometric examination of CHCl<sub>3</sub> solutions of the following 8-hydroxyquinoline (I) complexes shows absorption max. at 470 and 570 mµ. for Fe<sup>1II</sup>, 395 mµ. for Al, Bi, and Ni, 420 mµ. for Co, and 410 mµ. for Cu. Agitation of aq. solutions containing these ions with (I) in CHCl<sub>3</sub> gives complete extraction in the following optimum ranges of pH: Fe 1·9—3·0, Al 4·3—4·6, Bi 4·0—5·2, Co  $<6\cdot8$ , Ni  $<6\cdot7$ , and Cu 2·7—7·0. CHCl<sub>3</sub> solutions containing the equiv. of >20 mg. of these metals per l. show little or no deviation from Beer's law at the  $\lambda\lambda$  given, and hence are suitable for colorimetric determinations. Cu can be determined in presence of 40 times as much Cd or Zn by extraction at pH 4·0 and transmittancy measurement at 410 mµ. pH vals. for hydrous oxide or hydroxide formation, pptn. as complex with (I), and extraction as this complex are correlated.

Determination of ferrous iron in difficultly-soluble materials.—See B., 1943, I, 328.

Colorimetric determination of cobalt with o-nitrosoresorcinol. L. G. Overholser and J. H. Yoe (Ind. Eng. Chem. [Anal.], 1943, 15, 310-313).—The red colour given by Co" and o-nitrosoresorcinol (I) is used as the basis of a colorimetric method for determining Co". Spectrophotometric data for solutions of (I), for the Co complex, and for complexes with Cd, Zn, Ni, Cu, and Pd are recorded. For Co, Beer's law holds at 430 and 450 m $\mu$ . Procedures for determining Co" alone and in presence of Ni" are given, and data showing the effect of pH on the colour of (I), and of the Co complex, are recorded. (I) is slightly less sensitive as a reagent for Co" than is 2:1-NO-C<sub>10</sub>H<sub>3</sub>·OH, but the Co complex is stable for several weeks. The complex could not be extracted by an immiscible solvent.

Determination of small amounts of cobalt in presence of large amounts of iron. P. V. Faleev (Zavod. Lab., 1939, 8, 381—383).—0.5—10 mg. of Co can be determined in presence of 0.4—4 g. of Fe by pptg. with 30% solution of KNO<sub>2</sub> in a solution containing 7—8% of free AcOH and leaving the ppt. overnight. J. J. B.

Applicability of the pressed-pellet electrode method to spectrographic analysis of nickel alloys.—See B., 1943, I, 341.

Determination of chromic oxide in presence of chromium trioxide. W. J. Agnew (Analyst, 1943, 68, 182).— $Cr_2O_3$  is pptd. as  $Cr(OH)_3$  from solutions just acid to litmus, filtered on asbestos, washed and redissolved in 1:3  $H_2SO_4$  (20 ml.), diluted to  $\sim 600$  ml., and oxidised with  $KMnO_4$ . The excess of  $KMnO_4$  is removed by  $MnSO_4$  at the b.p., the solution cooled, and  $CrO_3$  determined by adding an excess of  $Fe(NH_4)_2(SO_4)_2$  and titrating with  $KMnO_4$ . Small "blanks" due to  $Cr_2(CrO_4)_3$  or adsorbed  $K_2Cr_2O_7$  are determined on the solution of the  $Cr(OH)_3$  ppt. before oxidation.

Spot test for chromium in steels.—See B., 1943, I, 339.

Precipitation of uranium with hydrogen sulphide in presence of hexamethylenetetramine. E. A. Ostroumov and R. I. Bomschtein (Zavod. Lab., 1939, 8, 558—561).—H<sub>2</sub>S at 60° ppts. from a solution of UO<sub>2</sub>Cl<sub>2</sub> and (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub> a "U-red," (NH<sub>4</sub>O·UO<sub>2</sub>·O)<sub>4</sub>U(OH)·S·SNH<sub>4</sub> (I). (I) has X-ray spacings of 7·60, 3·74, 3·52, 3·19, 2·55, 2·04, 1·96, 1·70, and 1·65 A. The pptn. of (I) is quant. and one pptn.

separates U from Ca, Mg, K, and Na. For analytical purposes (I) is heated, giving U<sub>3</sub>O<sub>8</sub>.

Rapid determination of titanium in ferrotitanium.—See B., 1943, I. 339.

#### XI.—APPARATUS ETC.

Theory of the electric arc furnace. P. Drossbach (Z. Elektrochem., 1940, 46, 643—646).—Mathematical. Equations for the extent of the melting zone and for the energy distribution in the electric arc furnace have been derived. C. R. H.

Experimental details for a precision high-temperature control utilising the Hull circuit. C. E. Waring and G. Robison (Rev. Sci. Instr., 1943, 14, 143—146).—A method of temp. control applicable to electrically heated air-baths and furnaces which may be regulated to  $\pm 0.05^{\circ}$  is described, the regulation being obtained by the oscillation of a galvanometer beam across a photo-cell which controls a thyratron circuit. The galvanometer is operated by a Pt-resistance thermometer-bridge circuit.

J. L. E.

Obtaining helium temperatures without using specially liquefied hydrogen. K. Seiler (Z. Elektrochem., 1941, 47, 116—119).—An apparatus which dispenses with the need for large quantities of liquid  $H_2$  and requires only a small amount for precooling the He is described. C. R. H.

Plug-in thermocouple head. S. R. Jones (J. Sci. Instr., 1943, 20, 116).—The arrangement described allows rapid replacement of a couple which fails or develops faults at a crit. stage of pyrometric measurements.

N. M. B.

Ultra-violet photometer for analysis of solutions. I. M. Klotz (Ind. Eng. Chem. [Anal.], 1943, 15, 277—278).—Results obtained with PhOH, KNO<sub>3</sub>, and sulphanilamide are described. Min. changes in concn. detectable are  $3\times 10^{-5}$ ,  $3\times 10^{-3}$ , and  $2\times 10^{-6}$  g., respectively, per l. of  $H_2O$ .

Modification of Cenco spectrophotometer permitting measurements of reflexion and fluorescence spectra. H. J. Dutton and G. F. Bailey (Ind. Eng. Chem. [Anal.], 1943, 15, 275—277). L. S. T.

Colorimetry and spectrophotometry as analytical methods. G. Kortüm and J. Grambow (Angew. Chem., 1940, 53, 183—187).—Calibration curves obtained for solutions of  $K_2 \text{CrO}_4$ , benzopurpurin, and naphthol-yellow with the Zeiss step-photometer and the Lange photo-electric spectrophotometer at different lamp voltages show the extent of the error introduced by the non-monochromatic nature of the light used. These errors are eliminated by using a two-step immersion colorimeter. L. S. T.

Two-colour prism or screen for observing colorimetric test-tubes. V. F. Petrov (Zavod. Lab., 1939, 8, 337).—A device for improving illumination is described.

J. J. B.

Step weakener for spectrochemical analysis in the ultra-violet. N. S. Sventitzki (Zavod. Lab., 1939, 8, 512—514).—The intensity of ultra-violet light is reduced by passing it through a layer of soot deposited on a quartz plate.

J. J. B.

Determination of optical constants of metals by reflectivity measurements. J. R. Collins and R. O. Bock (Rev. Sci. Instr., 1943, 14, 135—141).—The reflectivity of linearly polarised light at various angles of incidence on plane evaporated samples of pure metals is measured throughout the spectral range from 4800 to 24,000 A. By use of the electromagnetic equations describing the reflexion process a graphical method for obtaining the optical consts. from the data is worked out.

J. L. E.

Simple method of demonstrating diffraction grating effects. (Sir) L. Bragg and H. Lipson (J. Sci. Instr., 1943, 20, 110—111).—The apparatus described allows Fraunhofer diffraction at very small angles to be observed, and provides a simple way of demonstrating diffraction by comparatively large objects; the orders of diffraction from gratings of ~1 mm. spacing are well separated. Effects produced by deliberate ruling errors simulate observed X-ray diffraction effects. Several gratings are described and diffraction patterns are discussed with reference to X-ray diffraction effects from transition structures in alloys (Cu<sub>4</sub>FeNi<sub>3</sub> and AuCu<sub>3</sub>).

N. M. B.

Simple and permanent Tyndall cone apparatus. H. J. Abrahams and A. Dubner (J. Chem. Educ., 1943, 20, 61—62). L. S. T.

Mirror used to show spot plate tests. G. P. Percival (J. Chem. Educ., 1943, 20, 87).—Colours produced in drop reactions are reflected to an audience by a mirror suspended at an angle above the plate.

L. S. T.

Simple photo-electric absorptiometer.—See B., 1943, I, 310.

Preparation of manganese filters for absorption of the  $K\beta$  radiation of X-ray tubes with an iron anode. E. N. Kisliakova and M. F. Medvedev (Zavod. Lab., 1939, 8, 114—115).—Prep. of filters from Mn<sub>2</sub>O<sub>3</sub> and shellac is described.

J. J. B.

Apparatus for detecting luminescent ores. G. F. Komovski (Zavod. Lab., 1939, 8, 514—516).—Ores are illuminated by a spark from a hand-operated magneto; scheelite, e.g., can be found in this way. For irradiation with cathode rays a portable hand pump giving a vac. of  $5 \times 10^{-3}$  mm. Hg is used. J. J. B.

Determination of X-ray amorphous substances in presence of crystalline materials. R. Fricke (Z. Elektrochem., 1940, 46, 641— 642).—Small points of experimental technique are discussed.

C. R. H. Apparatus for rapid X-ray structure tests and X-ray motion pictures. L. V. Altschuler and V. A. Zukerman (Zavod. Lab., 1939, 8, 449—458).

X-Ray tube for analysis of fluorescence spectra. A. I. Krasnikov (Zavod. Lab., 1939, 8, 458-461). J. J. B.

Stabilisation of the alternating current arc used for quantitative spectrochemical analysis. N. S. Sventitzki (Zavod. Lab., 1939, 8, 470—471).—The arc is permanently illuminated by a small spark; the photo-electric effect thus produced prevents extinguishing of the arc. J. J. B.

Micro-electrodes for measuring local oxygen tension in animal tissues.—See A., 1943, III, 704.

Electrographic methods of surface analysis [of metals].—See B., 1943, I, 343.

Application of the electrode couple platinum and graphite for potentiometric titration in neutralisation and oxidation-reduction reactions. A. S. Tichonov (Zavod. Lab., 1939, 8, 17—19).—The pair Pt-pencil core can be used for oxidation and reduction titrations but not for neutralisation.

Dual alternating current titrometer. C. J. Penther and F. B. Rolfson (Ind. Eng. Chem. [Anal.], 1943, 15, 337—340). L. S. T.

Device for determining the kinetics of dissolution of metals. Maltzev (Zavod. Lab., 1939, 8, 73—76).—An apparatus is constructed which permits a simultaneous measurement of the potential of dissolving metal and of the rate r of gas evolution. For Mg in HCl r is const. for a const. [HCl] which was varied between  $5 \times 10^{-4}$  and J. J. B.

Experimental mass spectrometer. N. D. Coggeshall and E. B. Jordan (Rev. Sci. Instr., 1943, 14, 125—129).—An all-metal, sectorshaped magnetic field type mass spectrometer is so designed that it may be disassembled, repaired, or modified without altering its focussing properties, and having a removable ion source unit. instrument was designed for investigating different source arrange-

Rapid  $\gamma$ -ray inspection technique.—See B., 1943, II, 268.

Effect of ray potential on the electron-microscope image. Borries and E. Ruska (Z. Physik, 1940, 116, 249-256).-With bright field images, increasing ray potential gives greater transmission through the object, and with thicker objects, brings out finer details. With dark-field images, the thickness for max. brightness is greater for higher than for lower potentials.

Sub-optical microscopic resolution of the images of surfaces in the electron microscope. B. von Borries (Z. Physik, 1940, 116, 370—378).—If a metallic surface is placed at a small angle with the objective axis of an electron microscope, and irradiated with electrons at a small angle, a magnification of 14,000 can be obtained. It is possible to obtain a direct resolution of 50 m $\mu$ ., so that the resolving power of the electron microscope when used to investigate surfaces in this manner exceeds that of optical microscopy. Etched specimens of different types of Fe show characteristic differences in the images. Surface microscopy can also be used for the control of the planeness of surfaces. Foreign bodies in smooth surfaces can also be detected and measured. A. J. M.

Representation of electron-irradiated surfaces. E. Ruska and H. O. Müller (Z. Physik, 1940, 116, 366—369).—Apparatus is described for the production of an image of a surface irradiated with electrons, by means of the electron microscope, instead of the electrons passing through the object. The process is of special use in metallography, is applicable at all temp., and requires no special prep. of the surface.

Reproducibility of weighings made on microchemical balances. (A.C.S. Committee Report). C. J. Rodden, J. A. Kuck, A. A. Benedetti-Pichler, A. Corwin, and E. W. D. Huffman (Ind. Eng. Chem. [Anal.], 1943, 15, 415—416; cf. A., 1941, I, 224).—The test consisted in weighing 1-g. wts. one against the other, each weighing being followed by a rest-point determination, and the rider being reset for each weighing and each rest-point. 29 micro-balances of 4 different makes were used. The stradget desiration of individual 4 different makes were used. The standard deviation of individual weighings (median val.) is  $\pm 3\cdot 4~\mu g$ ., the probable error of individual weighings  $\pm 2.3 \mu g$ ., and the largest error to be expected in any one weighing  $\pm 7 \mu g$ . 7-mg. samples should be taken for an analysis when an accuracy of 0.1% is desired for sample wts. L. S. T.

Gas balance. V. G. Fastovski and I. G. Gurvitsch (Zavod. Lab., 1939, 8, 77-82).—The density balance of Stock and Ritter (A., 1926, 669) is improved and used for the quant. analysis of gas mixtures. The range of usefulness of a particular balance is enlarged by incorporating a magnet into the balance beam; this makes it possible to shift the zero point of the balance by means of a magnet.

Improved micrometer burette. P. F. Scholander, G. A. Edwards, and L. Irving (J. Biol. Chem., 1943, 148, 495—500).—The burette (cf. A., 1942, I, 250) has interchangeable parts for titration and for the calibration of other instruments. It delivers the total capacity with an accuracy of 1 part in 6000—7000 and is easier to clean and to assemble than the original apparatus. J. E. P. and to assemble than the original apparatus.

Method of viscosity measurement in the region of 10<sup>8</sup> poises. S. M. Cox (J. Sci. Instr., 1943, 20, 113—114).—A simple method by spherical imprint is especially suited for glasses in their softening range. The formula for  $\eta$  in terms of radius of imprint a, compressive force P, time t, and radius of sphere R is shown by analogy with elastic displacement to be  $\eta = 9PRt/16a^3$ . N. M. B.

Apparatus for purification of hydrocarbons by recrystallisation.—See A., 1943, II, 286.

Protractor for a direct measurement on a screen of contact angles. M. E. Lipetz (Zavod. Lab., 1939, 8, 336—337).

J. J. B.

Universal apparatus for gas evolution. V. M. Galak (Zavod. Lab., 1939, 8, 502—504).—An improved Kipp apparatus is described.

Liquid absorber for hydrogen. G. J. Veinberg (Zavod. Lab., 1939, 8, 549—552).—Na anthraquinonedisulphonate (cf. Bonney and Huff, A., 1937, I, 323) is the best absorber; stabilised Pd sols or PdCl<sub>2</sub> activated with Co are almost as good.

Filtration cylinder. R. J. DeGray and E. P. Rittershausen (Ind. Eng. Chem. [Anal.], 1943, 15, 392).—The crucible and its adapter are fitted into a rubber bung which rests on the top of a heavy glass cylinder, fitted with a side-arm, and large enough to enclose a 100-ml. volumetric flask or a 4-oz. bottle.

Sintered glassware. I. C. P. Smith (Ind. Chem., 1943, 19, 317-321, 393-398).-Filter crucibles, Buchner funnels, pressure filters, centrifuge filters, micro-chemical apparatus, extractors, supports for fillings, and apparatus for gas manipulation are described. Graphs relating rate of air flow and pressure for various porosities are reproduced. I. G.

Simplification of glass cleaning with chromic-sulphuric acid. C. Tropp and F. Geiger (Biochem. Z., 1940, 304, 81—83).—An apparatus for storage of the cleaning mixture and for transferring it to dirty apparatus is described.

Molecular still designed for small charges [0.25—5 g. of oil]. R. Matchett and J. Levine (Ind. Eng. Chem. [Anal.], 1943, 15, 16). L. S. T.

**Low-pressure gauge.** F. E. E. Germann and K. A. Gagos (*Ind. Eng. Chem. [Anal.*], 1943, **15**, 285—286).—A gauge of the floating barometer type is described. With Hg as confining liquid the range is  $10^{-2}$  to  $10^3$  mm. of Hg, and with Apiezon B oil the lower range is extended to  $6\cdot4\times10^{-4}$  mm.

Mercury-balance pressure regulator. A. J. Bailey (Ind. Eng. Chem. [Anal.], 1943, 15, 283—284). L. S. T.

Forceps with platinum-covered tips. E. W. Balis and H. A. Liebhafsky (*Ind. Eng. Chem.* [Anal.], 1943, 15, 350).—An improved method for covering the tips of forceps with Pt foil is described.

Apparatus for preparing an average sample. P. I. Boshenov (Zavod. Lab., 1939, 8, 211—213).—The powder to be tested is passed through a funnel which separates a representative sample.

Low-holdup laboratory [macro- and semi-micro-fractionating] columns. J. R. Bower, jun., and L. M. Cooke (Ind. Eng. Chem. [Anal.], 1943, 15, 290—293).

L. S. T.

Large-scale laboratory extractor of the Soxhlet type. K. E. Rapp, C. W. Woodmansee, and J. S. McHargue (Ind. Eng. Chem. [Anal.], 1943, 15, 351).

Mixed solvent extraction. J. H. Wiegand (Ind. Eng. Chem. [Anal.], 1943, 15, 380—383).—The methods of analytical geometry are applied to the computation of mixed solvent extraction problems involving four components.

Improved meter for the measurement of gas flow rates. W. G. Appleby and W. H. Avery (Ind. Eng. Chem. [Anal.], 1943, 15, 349-350).

L. S. T.

Measurement of the rate of outflow of liquids. M. Kaliko (Zavod. Lab., 1939, 8, 599—600).—A kind of Pitot tube is used.

Theory of calibration of rheometers. M. I. Temkin (Zavod. Lab., 1939, 8, 597-599).—Equations are given for calculating the rate of flow of a gas if that of another gas through the same flow meter J. J. B.

Flow manostat for various purposes, including candy test. M. J. Proffitt  $(J.\ Res.\ Nat.\ Bur.\ Stand.,\ 1942,\ 29,\ 143-155)$ .—The manostat described has a floating orifice modulator and const. discharge nozzles, whereby the flow of a gas from a source of moderately variable pressure is regulated. L. J. J.

#### XII.—LECTURE EXPERIMENTS AND HISTORICAL.

Representation of periodic properties of the elements. T. H. Hazlehurst and F. J. Fornoff (*J. Chem. Educ.*, 1943, 20, 77—79).
L. S. T.

The first chemical reagent. M. Nierenstein (Analyst, 1943, 68, 212—213).—Pliny's reagent for the detection of Fe in verdigris by papyrus soaked in a solution of gall nuts (60 A.D.) is compared with later modifications.

S. A. M.

#### XIII.—GEOCHEMISTRY.

Distribution of helium and radioactivity in rocks. V. Rocks and associated minerals from Quebec, Ontario, Manitoba, New Jersey, New England, New Brunswick, Newfoundland, Tanganyika, Finland, and Russia. N. B. Keevil (Amer. J. Sci., 1943, 241, 277—306).—Radioactive contents and He indexes of >25 rocks and associated minerals are reported and discussed. Variations in He indexes are due generally to loss of radiogenic He and occasionally to the presence of extraneous He. Distribution of radioactivity in rocks is not uniform; the mafic minerals are usually three times as active as the felsic constituents of a rock. Concn. of the radioactivity of a rock in the accessory minerals often occurs. The difference in activity between mafic and felsic constituents tends to be the greater the higher is the activity of the rock as a whole. He ages are not completely trustworthy, but He indexes are useful guides when more exact information is not available. Felsic samples, porphyries, and altered rocks give the least trustworthy indications of age. Ages for various rocks are discussed in the light of the data obtained.

L. S. T.

Causes of variations in radioactivity data [for rocks]. N. B. Keevil, A. R. Keevil, W. N. Ingham, and G. P. Crombie (Amer. J. Sci., 1943, 241, 345—365).—Data recorded for rocks show variations by a factor of ₹50 in the radioactive content from specimen to specimen. The greatest differences occur in certain granitic rocks, the least in sedimentary sections. Regional variations are not pronounced, but relatively high radioactive provinces are indicated in Colorado and Great Slave—Great Bear Lakes areas, and relatively barren areas in parts of Ontario and Quebec. Variation in sp. radioactivity of a rock can be due to inadequate sampling of the specimen, irregular localisation of radioactive elements in crystals of accessory minerals, and the effects of differentiation in the distribution of radioactive minerals within the intruded mass. Further evidence of the concn. of radioactivity in zircon and apatite is available. In the Bourlamaque batholith radioactivity is conc. near the borders of the intrusive.

Radioactive aureoles around some ore deposits. N. B. Keevil (Amer. Min., 1942, 27, 225). L. S. T.

Autoradiography of ores. C. Goodman and G. A. Thompson (Amer. Min., 1942, 27, 223; cf. A., 1942, I, 115).—Autoradiographic studies of Mn-, Au-, Cd-, and P-bearing ores have been made using stray, slow neutrons from a cyclotron on elements having large nuclear cross-sections for  $(\eta, \gamma)$  reactions and yielding radioactive isotopes of convenient half-periods. The locus and relative concus. of these elements in the constituent minerals are determined by placing polished sections of the activated ores in contact with photographic film. The source of the effective  $\beta$ -radiation is determined from the decay rate and intensity of the activity.

Specific gravity relationships of australites. G. Baker and H. C. Forster (Amer. J. Sci., 1943, 241, 377—406).—A statistical examination of the sp. gr. vals. of >1000 specimens of australites shows that they are distributed according to chemical composition, and indicates that there is  $\Rightarrow$  one fraternity of australites within each of the shape groups (buttons, lenses, ovals, etc.) from each locality. There is no significant relationship between wts. and sp. gr. Fusion experiments show that volatilisation of greater quantities of heavier than of lighter components from australite glass results in a decrease of sp. gr. L. S. T.

Miarolitic pegmatites in monzonite, Beaver Creek stock, Bearpaw mountains, Montana. W. T. Pecora and B. Fisher (Amer. Min., 1942, 27, 229).

L. S. T.

Paragenesis of the McDonald pegmatite near Hybla, Ontario. K. K. Landes (Amer. Min., 1942, 27, 226). L. S. T.

Gold mineralisation in minor igneous intrusions. W. W. Moorhouse (Amer. Min., 1942, 27, 227).—Evidence that replacement and intrusion by albitic material were accompanied by the Au-pyrite mineralisation is discussed.

L. S. T.

Geology of the nickel silicate deposit near Riddle, Oregon. W. T. Pecora and S. W. Hobbs (*Econ. Geol.*, 1941, 36, 841).—On Nickel Mountain, an irregularly distributed blanket of weathered rock contains discontinuous boxwork veinlets of quartz and garnierite (I). The deposits richest in Ni are underlain by unserpentinised peridotite. (I) contains 2—36% of Ni, and is a Ni-rich deweylite (II). The Ni and Mg were probably derived from weathering of olivine in the unserpentinised peridotite. Under present climatic conditions, (II) [Ni-poor (I)] is chemically attacked by surface waters causing Ni enrichment of (II) in situ to form (I), ptn. of SiO<sub>2</sub> to form quartz, and supergene deposition of (I) itself in open fractures.

Nickel deposit near Dracut, Massachusetts. W. H. Dennen (*Econ. Geol.*, 1943, 38, 25—55).—A small pyrrhotite (I)—pentlandite—chalcopyrite deposit between Lawrence and Lowell, Massachusetts, occurs in a Paleozoic noritic stock in Cambrian quartzite. The deposit has been worked for Au, Ag, Fe, Cu, and Ni. Spectrographic analysis of (I) shows the presence of 1.5% Ni and 0.62% Co. The ore minerals, formed subsequently to the crystallisation of the silicates, show unusual mineragraphic characteristics which are described.

L. S. T.

Scheelite-powellite minerals of the Seven Devils district, Idaho. R. S. Cannon, jun., and F. S. Grimaldi ( $Econ.\ Geol.$ , 1941, 36, 839—840).—Minerals having the physical appearance of scheelite occur in most of the pyrometasomatic Cu deposits. Chemical analyses show that these minerals are not pure  $CaWO_4$ , but are members of the isomorphous series scheelite-powellite. L. S. T.

"Opalite" type of quicksilver deposit. R. G. Yates and R. J. Roberts (*Econ. Geol.*, 1941, 36, 839).—The opalite is composed mainly of chalcedony (I) with minor amounts of quartz and opal. Cinnabar (II), intimately mixed with SiO<sub>2</sub>, occurs in fractures, cavities, etc., and is disseminated also in the massive rock. Deposits were formed probably at shallow depths. Existing rock was first replaced by opal, which either dehydrated to or was replaced by (I). (II) was deposited from siliceous H<sub>2</sub>O after the major silicification was over.

L. S. T.

Some concepts on the geology of quicksilver deposits in the United States. J. Pollock (*Econ. Geol.*, 1943, 38, 149—153; cf. A., 1943, I, 171). L. S. T.

Mineralogy of Pinchi lake. A. C. Freeze (Amer. Min., 1942, 27, 221—222).—Glaucophane (I) is widespread, and is present in rocks of both sedimentary and igneous origin. An introduction of Na<sub>2</sub>O is necessary to account for the distribution and amount of (I). The cinnabar mineralisation and the accompanying mineral suite are much younger than the (I) and related minerals.

L. S. T.

Bismuth-ochre, bismutite, bismutosphaerite, basobismutite, bismite, and bismoclite. C. Frondel (Amer. Min., 1942, 27, 222).—41 specimens of bismutite (I), Bi-ochre, and bismutosphaerite (II) from 34 localities have been examined by X-ray, optical, and chemical methods. (I), supposedly a hydrated Bi carbonate, contained only non-essential H<sub>2</sub>O, and is identical with (II), Bi<sub>2</sub>CO<sub>5</sub>. Basobismutite also is identical with Bi<sub>2</sub>CO<sub>5</sub>. So-called Bi-ochres proved to be Bi<sub>2</sub>CO<sub>5</sub>, Bi arsenate, cerussite, etc. Artificially-prepared hydrous Bi carbonate and (I) give a smooth dehydration curve to ~290°, when the CO<sub>2</sub> is lost and a-Bi<sub>2</sub>O<sub>3</sub> remains. Definite hydrates could not be synthesised. The identity of bismite (III), supposedly Bi<sub>2</sub>O<sub>3</sub>, is uncertain; 22 specimens labelled (III) from 15 localities showed neither Bi<sub>2</sub>O<sub>3</sub>,3H<sub>2</sub>O, nor any of the 4 polymorphs of Bi<sub>2</sub>O<sub>3</sub>; 8 were Bi<sub>2</sub>CO<sub>5</sub>, 2 were bismoclite (IV), and 4, a rare carbonate of Bi and Ca. (IV), BiOCl, hitherto known only from S. Africa, is described from Bygoo, N.S.W., and Tintic, Utah. (III) reported from Goldfield, Nevada, is also (IV). Reported syntheses of Bi<sub>2</sub>O<sub>3</sub>,H<sub>2</sub>O and other hydrates could not be confirmed; most are a-Bi<sub>2</sub>O<sub>3</sub>,H<sub>2</sub>O and other hydrates could not be confirmed; most are a-Bi<sub>2</sub>O<sub>3</sub>,nH<sub>2</sub>O.

Settling of heavy minerals in a granodiorite dyke at Bradford, Rhode Island. A. Quinn (Amer. Min., 1943, 28, 272—281).—The proportion of heavy minerals increases systematically towards the base of the dyke. This is probably due to crystal settling which occurred when the low- $\eta$  magma moved upwards along the dyke.

Crystallography of hureaulite. J. Murdoch (Amer. Min., 1943, 28, 19).—Hureaulite, hardness 3—4, formed close to the end of a sequence of phosphate minerals at Pala, California, shows good crystals with a:b:c=1.9037 [?]: 1:1.0470,  $\beta$  96° 40′. X-Ray photographs give  $a_0$  17.42,  $b_0$  9·12,  $c_0$  9·50 A.,  $a_0:b_0:c_0=1.908:1:1.040$ ; space-group probably  $C_{2h}^4$ , 4 mols. per unit cell, and  $\rho_{\rm calc.}$  3·23. New crystallographic forms are recorded.

Size of the unit cell and the coefficient of expansion of high-cristobalite. J. S. Lukesh (Amer. Min., 1942, 27, 226).—a<sub>0</sub> for artificial high-cristobalite is 7.031(7) A. at 275°, and 7.044(0) A. at 480°.

Equilibrium studies on mixtures of pyroxenes, pyroxenoids, melilites, and olivines containing lime, magnesia, alumina, and silica. E. F. Osborn (Amer. Min., 1942, 27, 228).—Data for the system

 ${\sf CaSiO_3-diopside}$  (I)—anorthite have been completed. Wollastonite  $[\beta\text{-CaSiO}_3$  with (I) in limited solid solution] has a field of stability, but the alleged compound  $5{\sf CaO,2MgO,6SiO_2}$  does not appear. The (I) in this system is aluminous. L. S. T.

Mineralogy of the [Rolla] Missouri hæmatite sinks. F. H. Pough (Amer. Min., 1942, 27, 230).—The hæmatite (I) formed by oxidation of the sulphide varies in texture from soft red "paint ore" to cryst. specularite. Minor quantities of azurite, malachite, brochantite, olivenite, and native Cu are associated with the (I). Small amounts of an unidentified Cu vanadate were also found. The origin of the deposits is discussed.

L. S. T.

Supergene magnetite. J. S. Brown (*Econ. Geol.*, 1943, 38, 137—148).—Evidence relating to occurrences of magnetite (**I**) believed to be of supergene origin is discussed. Such assemblages are common, but economically unimportant. The (**I**) is formed only below the H<sub>2</sub>O table, or in a H<sub>2</sub>O basin, where an unstable balance between oxidation and reduction tendencies exists, and a suitable precipitant such as CaCO<sub>3</sub>, or a hydroxide, is present. The resulting (**I**) is usually fine-grained and associated with larger amounts of soft, earthy hæmatite.

Hydrothermal replacement in deep-seated iron ore deposits of the Lake Superior region. H. M. Roberts and M. W. Bartley (*Econ. Geol.*, 1943, 38, 1—24).—Hæmatite (I) deposits at Steep Rock Lake, Ontario, are regarded as hydrothermal replacements. A comparison with deposits of the Vermilion and Marquette Fe range is made, and current hypotheses as to origin are reviewed. The formation of massive (I) at great depth is explained.

Diffuse diffraction and disorder in maucherite. M. A. Peacock (Amer. Min., 1942, 27, 229).—Rotation and Weissenberg photographs give  $a_0$  3·422,  $c_0$  21·83 A., with the symmetry  $D_{4h}^{10} = I4/amd$ . The crystal as a rule has the composition Ni<sub>11</sub>As<sub>8</sub> or Ni<sub>12-1</sub>As<sub>8</sub>, and the disorder is probably related to shortage in Ni. L. S. T.

Sternbergite and frieseite. M. A. Peacock  $(Amer.\ Min.,\ 1942,\ 27,\ 229)$ .—Sternbergite  $(\mathbf{I}),\ \rho$  4·25, from Jáchymov, Bohemia, has  $a_0$  6·62,  $b_0$  11·58,  $c_0$  12·65 A., containing  $8[\mathrm{AgFe_2S_3}]$ ; space-group  $D_{2h}^{21} = Cmma$ , or  $C_{2\nu}^{16} = C2ma$  or Cm2a. Freiseite  $(\mathbf{II}),\ \rho$  4·18—4·31, has  $a_0$  6·60,  $b_0$  11·59,  $c_0$  12·61 A.; space-group as in  $(\mathbf{I})$ . Powder photographs of  $(\mathbf{II})$  show only the pattern of pyrite  $(\mathbf{III})$  with weak extra lines corresponding with the strongest lines of  $(\mathbf{I})$ .  $(\mathbf{II})$  appears to have altered by at rearrangement to oriented  $(\mathbf{I})$  and  $(\mathbf{III})$  according to the scheme  $\mathrm{Ag_2Fe_5S_8}$   $(\mathbf{II}) \rightarrow 2\mathrm{AgFe_2S_3}$   $(\mathbf{I}) + \mathrm{FeS_2^*}(\mathbf{III})$ . L. S. T.

Quartz veins in the Ouachita mountains of Arkansas and Oklahoma: their relationships to structure, metamorphism, and metalliferous deposits. H. D. Miser (*Econ. Geol.*, 1943, 38, 91—118).— The quartz veins and crystals, and the associated minerals, are hydrothermal deposits of probable magmatic origin. The metalliferous deposits of these mountains appear to have been formed at the time of the quartz vein deposition.

L. S. T.

**Amblygonite.** C. Palache, W. E. Richmond, and C. W. Wolfe (Amer. Min., 1943, 28, 39—53).—Amblygonite from Hebron, Maine, has  $a_0$  5·18,  $b_0$  7·11,  $c_0$  5·03 A., a 112° 02½′,  $\beta$  97° 49½′,  $\gamma$  68° 07½′, and the unit cell contains 2[LiAlPO<sub>4</sub>(OH,F)]. Crystal measurements give a:b:c=0.7255:1:0.7028, a 111° 59½′,  $\beta$  97° 46½′,  $\gamma$  68° 16½′. L. S. T.

Aluminium-bearing scorodite from Hobart Butte, Oregon. R. M. Denning (Amer. Min., 1943, 28, 55—57).—Evidence for an Al-bearing scorodite, with Al replacing Fe<sup>III</sup>, is presented. L. S. T.

Grunerite in Western Australia. K. R. Miles (Amer. Min., 1943, 28, 25—38).—New occurrences in W. Australia are described. Grunerite (I) has been found only amongst the metamorphosed banded Fe formations of the Older Greenstone Series of W. Australia. It has been formed as a result of the interaction of Fe and SiO<sub>2</sub> during recrystallisation of these rocks under conditions of both regional and contact thermal metamorphism. These metamorphosed banded Fe formations are similar in mineralogical and chemical composition, and probably origin, to the (I)-bearing rocks of the Lake Superior region. Mineralogy, optical properties, and chemical analyses of several samples of (I) are recorded and discussed. A blue-green hornblende often associated with the (I) is described.

Occurrence of sodic scapolite at Falls of French Creek, Pennsylvania. W. H. Tomlinson (Amer. Min., 1943, 28, 110—113).—The occurrence and origin are described, and chemical analyses recorded.

Graphical representation of the calciferous amphiboles. A. F. Hallimond (Amer. Min., 1943, 28, 65—89).—196 analyses of amphiboles have been calc. to at. ratios according to the standard formula  $(Ca,Na)_2Na_{1-2}(Mg,Al)_5(Si,Al)_8O_{22}(OH,F)_2$ . There is a well-defined upper limit at Ca=2 atoms, and a fairly sharp lower limit to Si at 6 atoms. The analyses are represented on a triangular diagram having as co-ordinates the no. of atoms of Si, and the no. of alkali atoms allotted to the vacant space. Nearly all the present minerals

can be derived from tremolite by two substitutions, Al<sub>4</sub>/Si<sub>2</sub>Mg<sub>2</sub> and Na<sub>2</sub>Al<sub>2</sub>/Si<sub>2</sub>, whilst a third substitution, NaAl/CaMg, gives rise to glaucophane-like minerals. A general relationship exists between the type of amphibole and the nature of the parent-rock.

Unique occurrence of bobierrite,  $\mathbf{Mg_3}(\mathbf{P0_4})_2, \mathbf{8H_2O}$ . J. W. Gruner and C. R. Stauffer (Amer. Min., 1943, 28, 339—340).—An occurrence in a fossil elephant tusk is described. Mg phosphate has developed from Ca phosphate to the complete exclusion of the Ca. L. S. T.

Preliminary description of the new mineral partridgeite. J. E. de Villiers (Amer. Min., 1943, 28, 336—338).—Natural Mn<sub>2</sub>O<sub>3</sub>, found in the Postmasburg Mn ores associated with braunite (II) and staparite (III), is named partridgeite (I). (I) resembles (III) in the hand specimen, but unlike (II), is etched by a mixture of equal parts of  $\rm H_2SO_4$  (1:1) and 10%  $\rm H_2O_2$ . Chemical analyses [C. F. J. van der Walt] of a ferriferous (I) and a (II)–(I)–pyrolusite ore are given.

Gamagarite, a new vanadium mineral from the Postmasburg [Cape Province] manganese deposits. J. E. de Villiers (Amer. Min., 1943, 28, 329—335).—Gamagarite, Ba<sub>4</sub>(Fe,Mn)<sub>2</sub>V<sub>4</sub>O<sub>15</sub>(OH)<sub>2</sub>, prismatic monoclinic, dark-brown, hardness  $4\frac{1}{2}$ —5,  $\rho$  4·62; a 2·016,  $\beta$  2·040,  $\gamma$  2·130 (all  $\pm$ 0·01), pleochroic, red-brown to salmon-buff, occurs in the Mn ores of this district. A chemical analysis [C. F. J. van der Walt] is given.

Iridescent garnet from the Adelaide mining district, Nevada. E. Ingerson and J. D. Barksdale (Amer. Min., 1943, 28, 303—312).—Garnets from a CaO-rich layer in the contact zone of a granodiorite stock show brilliant iridescence both on striated crystal faces and in thin section. This is due to fine polysynthetic twinning, with the intensity of the iridescence dependent on the thickness of the individual lamellæ.

L. S. T.

Mineralogy of the calcium phosphates in insular phosphate rock. C. Frondel (Amer. Min., 1943, 28, 215—232).—The chief constituent of insular phosphate rock is a member of the apatite (I) series, usually a carbonate-hydroxyl-fluorine-apatite. Collophane (II) is not an amorphous species distinct from (I). X-Ray investigation of insular and continental phosphate rock, fossil bone and teeth, urinary calculi, and other materials corresponding with (II) shows that (II) is a sub-microcryst. variety of (I). The name should be retained for fine-grained, isotropic, hydrous types of (I). The identity of other specimens of ill-defined Ca phosphates has been investigated by X-ray and optical methods, and the results are discussed. L. S. T.

Effect of electrolytes on the solubility of metal sulphides in vein solutions. R. M. Garrels (Econ. Geol., 1941, 36, 848).—E.m.f. measurements of cells containing mixed electrolytes approximating to the composition of vein solutions show that (i) addition of electrolytes to metal sulphide solutions may increase or decrease the solubility many thousand-fold, (ii) small amounts (>0·lm.) of electrolytes increase the solubility of metal sulphides, and (iii) the effect of larger amounts of electrolytes is unpredictable, and may cause a further increase in solubility, or a rapid decrease, depending on the system involved.

Relationship of the clay minerals halloysite and endellite. L. T. Alexander, G. T. Faust, S. B. Hendricks, H. Insley, and H. F. McMurdie (Amer. Min., 1943, 28, 1—18).—Chemical, electron-microscopical, X-ray, and petrographical investigation show that halloysite (I), Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>, is formed by partial dehydration of the more highly hydrated, related mineral now called endellite (II), Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>, 2H<sub>2</sub>O, and that (I) has the same type of Al silicate layers as kaolinite, but the layers are usually superimposed in a less orderly manner. (II) has a structure in which kaolinite-type layers alternate with single layers of H<sub>2</sub>O mols. (II) may be formed by alteration of the constituents of a basic igneous rock, or its metamorphic equiv. Chemical analyses of (II), dehydrated at 110°, are recorded.

L. S. T.

Formation of petroleum. A. Treibs (Angew. Chem., 1940, 53, 202—204).—Petroleum is derived from marine plankton deposits such as occur in the Black Sea. The conversion cannot have been due to high temp. since porphyrins and optically active constituents have survived; rather was it due to biochemical elimination of O as  $\rm H_2O$  and  $\rm CO_2$  under anaërobic conditions. Different types of petroleum may have resulted from differential adsorption in neighbouring strata of hydrocarbons of the aliphatic, naphthenic, and aromatic series. Asphalt is not a product of cracking or oxidation since its  $\rm H:C$  ratio is nearly the same as that of petroleum. It is probably derived from biological material of special character which yielded primarily an oil containing reactive constituents.

Origin and composition of coals.—See B., 1943, I, 318.

Coal measure sequence in the Taff Valley, Glamorgan, and its correlation with the Rhondda Valley sequence. L. R. Moore and A. H. Cox (Proc. S. Wales Inst. Eng., 1943, 59, 189—265).

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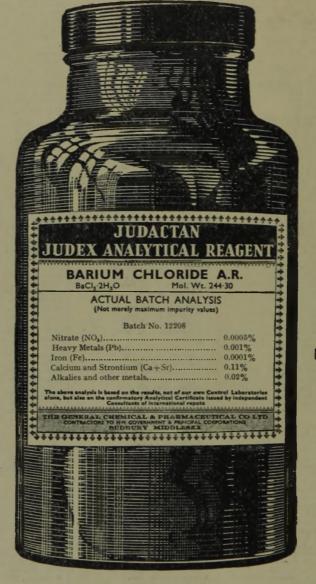
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