

# BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

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

MAY, 1942.

### I.—SUB-ATOMICS.

Spectro-analytical determination of elements in flame and spark by direct photo-electric measurement of line intensities.—See A., 1942, I, 154.

Spectrographic analysis. Photographic aspects of the internal standard method.—See A., 1942, I, 156.

Opposed axial orientation of atoms in an electric field. J. Stark (*Physikal. Z.*, 1941, 42, 45—47).—Application of a strong coaxial electric field to He canal rays causes intensity dissymmetry in the displaced components of certain higher lines in the par-He series.  $2P, p-mP, p, 1s-mP$ , and  $2S-mP$  lines form doublets when the field is applied. It is inferred that He atoms, like H atoms (cf. A., 1938, I, 377), assume opposed axial orientations in an electric field.

A. J. E. W.

Measurement by ionisation methods of real energy absorption from an X-ray beam. J. R. Clarkson (*Phil. Mag.*, 1941, [vii], 31, 437—451).—Ionisation currents were measured at low pressure in gases contained in chambers having walls of several different metals, graphite, and "Elektron" alloy, for a narrow range of  $\lambda$ . The electronic real energy absorption coeffs. measured from the slopes of the ionisation-pressure curves are < theoretical vals., except for substances of at. no. < 12.

L. J. J.

Elastic scattering of fast electrons by nitrogen nuclei. F. C. Champion (*Nature*, 1941, 148, 727).—A discussion. Evidence is now strong that the N nucleus exhibits excess scattering of electrons at energies > 1 Mv.

L. S. T.

Distribution of energy among the cathode rays of a glow discharge. R. M. Chaudhri (*Nature*, 1941, 148, 727—728).—Experiments to determine the energy distribution among electrons originating in the cathode dark space of the glow discharge through gases show that (i) at low pressures and high voltages where the discharge is abnormal, the issuing electrons are substantially homogeneous in energy, and (ii) at higher pressures and lower voltages, the electron beam possesses a wide range of energies; the general form of this energy distribution is independent of current and voltage. Except at the highest pressures, there is no support for the view that ionisation is uniform throughout the cathode dark space.

L. S. T.

Space-charge effects in velocity-modulated electron beams. W. H. J. Fuchs and R. Kompfner (*Proc. Physical Soc.*, 1942, 54, 135—150).—Mathematical. Two different mathematical models of velocity-modulated beams are constructed. The first model is applied to the study of drift tubes working as high-frequency amplifiers and conclusions are deduced and discussed. The second or "domain" model is devised so as to allow a simple analysis of the process of "bunching" in the presence of space charge.

N. M. B.

Angular distribution of current from a point in hydrogen. W. H. Bennett (*Physical Rev.*, 1942, [ii], 61, 53—56; cf. A., 1941, I, 66).—The angular distribution of current of electrons from a sharp point in  $H_2$  was measured for various currents and sizes of wire. Evidence is obtained for the crit. effect of the potential drop in the ionisation sheath.

N. M. B.

Ionisation of gases by collisions of their own accelerated atoms and molecules. H. W. Berry, R. N. Varney, and S. Newberry (*Physical Rev.*, 1942, [ii], 61, 63—64; cf. A., 1936, 1041).—Apparatus for producing fast neutral atom beams with energies up to 8000 e.v. and measuring ionisation due to collisions is described. Preliminary results show that ionisation of A atoms appears to be similar to ionisation by electron collisions in that the efficiency reaches a peak and falls off again with increasing speed. Ionisation of  $N_2$  by neutral N was observed but the efficiency was  $\ll$  for A, and the nature of the ionisation function was not definitely established. This is the first evidence of ionisation of  $N_2$  by collisions of heavier particles in the energy range < that of  $\alpha$ -particles.

N. M. B.

Current-potential curves in ionised gas flames.—See A., 1942, I, 157.

Isotope report, 1940. S. Flüge and J. Mattauich (*Physikal. Z.*, 1941, 42, 1—5; cf. A., 1940, I, 185).—Mass, packing-fraction, and mass-defect data are tabulated for elements from H to V, and for 161

$^{56}\text{Fe}$ , and evidence for changes is reviewed. Revised relative abundance data for Mo are given.

A. J. E. W.

Production of 2.5 litres of the pure  $^{22}\text{Ne}$  and  $^{20}\text{Ne}$ .—See A., 1942, I, 152.

Direct determination of slow-neutron velocity distributions.—See A., 1942, I, 158—159.

Developments in ion accelerating tubes.—See A., 1942, I, 158.

Magnetic scattering of neutrons. M. Hamermesh (*Physical Rev.*, 1942, [ii], 61, 17—18).—Discrepancies between theory and experiment in results previously reported (cf. A., 1941, I, 359) are removed by a recalculation of the form factor of the  $3d$  shell of Fe, using Hartree functions for Fe instead of adjusted functions for Cu.

N. M. B.

Single scattering of fast electrons. E. Bleuler, P. Scherrer, and W. Züti (*Physical Rev.*, 1942, [ii], 61, 95).—Elastic scattering of fast electrons ( $Ra-B + -C$ ) by N, F, and A nuclei was investigated with a cloud chamber. The total scattering is somewhat > theoretically expected. The scattering cross-section as a function of energy and angle agrees with the predictions of theory.

N. M. B.

Scattering of protons by deuterium. R. F. Taschek (*Physical Rev.*, 1942, [ii], 61, 13—17).—Investigations in the energy interval 200—300 ke.v. and as a function of angle over  $20^\circ$ — $90^\circ$  show that the ratio of observed scattering to that expected on Rutherford's formula differs appreciably from unity and increases with increasing energy and angle (cf. Tuve, A., 1937, I, 5).

N. M. B.

Photo-disintegration of beryllium and deuterium. F. E. Myers and L. C. Van Atta (*Physical Rev.*, 1942, [ii], 61, 19—22).—Thresholds redetermined with high-voltage X-rays are  $1.627 \pm 0.010$  and  $2.183 \pm 0.012$  Mv., respectively. The ratio of cross-sections ( $\sigma_{Be}/\sigma_D$ ) at 15 kv. above the threshold voltage is  $\sim 10$ . The angular distribution of the neutrons from the photo-disintegration of D, investigated with X-rays of 2.43 Me.v. max. energy, is approx. isotropic. From these data the estimated ratio of the photo-magnetic to photo-electric cross-section is 6:1.

N. M. B.

Penetrating cosmic-ray showers. L. Jánossy (*Proc. Roy. Soc.*, 1942, A, 179, 361—376).—The existence of showers penetrating at least 50 cm. of Pb is reported. These penetrating showers are parts of extensive air showers; they are neither energetic cascades nor knock-on showers, and are probably connected with the production of mesons. The connexion of the penetrating showers observed at sea-level with the production of mesons in the atm. is discussed under two alternative assumptions: that the mesons are produced (1) by photons, (2) by protons and possibly neutrons.

G. D. P.

Electrical and anomalous scattering of mesotrons. R. P. Shutt (*Physical Rev.*, 1942, [ii], 61, 6—13).—Photographs obtained without a magnetic field in a large counter-controlled cloud chamber containing Pb plates of two different thicknesses are analysed by Williams' scattering theory (cf. A., 1939, I, 291) with regard to the scattering of mesotrons in Pb. The scattering is > that expected from the theory. The average cross-section calc. for this anomalous large-angle scattering agrees with the results of Code (cf. A., 1941, I, 190), and accords with the assumption of a mesotron spin of  $\frac{1}{2}$  and a Hartree energy distribution. Spin 0 is possible, but spin 1 is definitely excluded. The observed anomaly may be explained by electromagnetic effects or by nuclear scattering of the proton component instead of mesotrons.

N. M. B.

Absorption of extensive atmospheric showers of cosmic rays in air and lead. P. Auger and J. Daudin (*Physical Rev.*, 1942, [ii], 61, 91—92).—Barometric coeff. and intensity measurements were made during 8 months by double coincidences of two horizontal counters at 3 m. separation. At sea-level a decrease of 1 cm. of Hg atm. pressure gives rise to  $9 \pm 1\%$  increase in the no. of showers; the resulting mass absorption coeff. is  $0.0068 \pm 0.0007$  sq. cm. per g. A comparison with counters at 3 m. and 13 m. separation gives the vals.  $11 \pm 2\%$  and  $23 \pm 5\%$ , respectively, for the coeffs.; the variation suggests a difference in origin of the narrow local air showers and the extensive showers. Measurements at 2900 m. altitude (cf. A., 1939, I, 593) are recalcul. for comparison and give  $\sim 11\%$  for the pressure coeff. and  $0.008 \pm 0.0008$  sq. cm. per g. for the mass absorp-



tion coeff. A discussion of results and those for absorption in Pb shows difficulties in reconciliation with the cascade theory.

N. M. B.

**Diurnal variation of extensive showers.** P. Auger and J. Daudin (*Physical Rev.*, 1942, [ii], 61, 95).—Curves of automatic counts by two unshielded coincidence counters show only a feeble max. (6%) at noon. This max. may be due to a thermal effect.

N. M. B.

**Aromatic problem: density distribution and zero-point energy of conductivity electrons in graphite.** O. Schmidt (*Physikal. Z.*, 1941, 42, 36–45).—The occurrence of a "metallic" type of linking in graphite and aromatic compounds is discussed with reference to the  $B$ -electron distribution. In graphite the axial quantum no. ( $n$ ) in the ground state is 1, and the  $B$ -electrons are conc. in the C atom layers. Their mean density is  $17.63 \times 10^{22}$  per c.c., a val.  $>$  any known val. for a metal. The mean zero-point energy is 6.83 e.v. (157 kg.-cal.), which approx. equals the max. val. for Cu; since the binding energy is only  $\sim 1$  e.v. the  $B$ -electrons are free. In the excited state  $n = 2$ . Reaction of graphite with electron-acceptors occurs by removal of electrons in a direction perpendicular to the C atom layers; chemical attack consequently proceeds initially in this direction. The constitution and electrical conductivity of certain "graphite salts" (cf. Rüdorff *et al.*, A., 1938, I, 410; Z. anorg. Chem., 1940, 245, 121) are discussed.

A. J. E. W.

**Is the Dirac theory of the positron Lorentzinvariant?** H. Hönl (*Physikal. Z.*, 1941, 42, 19–23).—Theoretical.

A. J. E. W.

**Separation of nuclear isomerides.** E. P. Cooper (*Physical Rev.*, 1942, [ii], 61, 1–5).—Chemical separation cannot be explained on the recoils involved, but, with  $K$  capture or with internal conversion accompanying the isomeric transition, the positive charge built up by the Auger effect during the electronic readjustment is enough to cause mol. dissociation. The calc. probabilities for Auger effect and for  $X$ -rays for all shells of the Br atom show an excess charge as high as 4.7e. The effect on homopolar binding is examined by using a  $H_2$  mol. model. Results show that excess charges  $\ll 4.7e$  should cause dissociation in Br.

N. M. B.

**Interaction between a molecule and a metal surface.** E. J. R. Prosen and R. G. Sachs (*Physical Rev.*, 1942, [ii], 61, 65–73; cf. Bardeen, A., 1941, I, 30).—Mathematical. A treatment by the perturbation theory shows that the interaction energy  $\propto 1/R$ , where  $R$  is the distance between metal and mol., if the electron degeneracy in the metal is not taken into account, and  $\propto R^{-2} \log R$  if it is taken into account. Considerations are here limited to  $R \approx$  the Bohr radius since electron-electron interaction is not taken into account.

N. M. B.

**Detection of the neutrino.** K. C. Wang (*Physical Rev.*, 1942, [ii], 61, 97).—When a  $\beta$ -radioactive atom captures a  $K$  electron instead of emitting a positron, the recoil energy and momentum of the resulting atom will depend solely on the emitted neutrino. It is suggested that the mass and energy of the neutrino could be found by measuring the recoil energy and momentum of the resulting atom alone. This is illustrated by the decay processes of  ${}^7\text{Be}$  (43 days). Alternatively, for certain  $K$ -capture atoms, especially those having isomeric properties so that the  $K$ -capture is followed by an  $\alpha$ -decay, if the radioactive substance is prepared to form some non-polar compound, the recoil energy of the resulting atom would break the bond and thus be detected chemically.

N. M. B.

**Nature of temperature.** W. E. Benham (*Proc. Physical Soc.*, 1942, 54, 121–128).—Mathematical. Some difficulty exists in reconciling temp. as energy per unit mass with the radiation theory conception of temp. Evidence is given to support the view that the ultimate significance of temp. is that it is measured by the thinness of a pulse of electromagnetic radiation. A new (unpublished) theory of radiation, which requires that central orbits shall be non-radiating when circular, is used to support a dimensional treatment in which the energy density of radiation is a function of the mass, rather than of the charge, of an electron and of the abs. temp. The dimensions of temp. appear to be  $1/L$ , and this is reconciled with energy per unit mass by attributing dimensions to "Newton's const."  $N$ . This and the gravitational const. have the dimensions  $[N] = T^2/L^3$ ,  $[G] = 1/M$ . Dimensions of thermal quantities are listed and discussed.

N. M. B.

## II.—MOLECULAR STRUCTURE.

**High-pressure carbon band system.** R. K. Asundi and D. D. Pant (*Current Sci.*, 1941, 10, 520–521).—It has been proposed by Fox *et al.* (A., 1937, I, 595) that the high-pressure  $C_2$  bands are part of the Swan system. This view is untenable because it has been found that under certain discharge conditions the high-pressure bands only appear to the exclusion of all other  $C_2$  bands, including the Swan bands. It is considered that it would be impossible to bring about the selective production of a single excited vibrational level.

A. J. M.

**Ultra-violet band spectrum of mercurous iodide.** M. G. Sastry (*Current Sci.*, 1941, 10, 521; cf. A., 1941, I, 362).—The class-I

band system of HgI in the ultra-violet, reported by Wieland (A., 1929, 1127), is found to consist of two systems, designated  $\alpha_1$  and  $\beta_1$ , having a common final level, probably a  ${}^2\Sigma$  state. A new system of HgI, designated  $A$ , and similar to the class-II system of HgCl, has been found in the region  $\lambda$  2540. It arises from the transition  ${}^2\Pi \rightarrow {}^2\Sigma$ , and shows 4 component heads; the electronic separation in the  ${}^2\Pi$  state is  $126 \text{ cm}^{-1}$ . Vibrational consts. for the  $\alpha_1$ ,  $\beta_1$ , and  $A$  systems are tabulated.

A. J. M.

**Molecular spectra and fractionation of rare earths.**—See A., 1942, I, 154.

**Effect of intermolecular fields on the N-H vibration.** G. Jung and E. Wygash (*Z. physikal. Chem.*, 1941, B, 49, 205–218).— $\text{NH}_2\text{Me}$  has a series of absorption bands extending into the visible, which may be regarded as overtones of the fundamental at  $3 \mu$ . The third overtone at  $0.8 \mu$  has been investigated for gaseous, liquid, and dissolved  $\text{NH}_2\text{Me}$ . Solutions of  $\text{NH}_2\text{Me}$  in  $\text{H}_2\text{O}$ ,  $\text{MeOH}$ ,  $\text{EtOH}$ ,  $\text{PrOH}$ , dioxan, and  $\text{C}_6\text{H}_6$  were used. There is a displacement of the absorption bands dependent on  $[\text{NH}_2\text{Me}]$ , and the effect of the solvents is in the same order for  $\text{NH}_2\text{Me}$  as for  $\text{NH}_3$ . There is a characteristic increase in the frequency displacement towards higher  $\lambda$  with increasing concn. for each solvent. The effect is the same for both  $\text{NH}_2\text{Me}$  and  $\text{NH}_3$  in aq. and alcoholic solutions. The displacements for dioxan and  $\text{C}_6\text{H}_6$  solutions are  $\gg$  for solutions in  $\text{H}_2\text{O}$  or alcohols. An analysis of the displacements into one fraction depending on the interaction between solvent and solute, and another depending on interaction between the dissolved particles, shows that the effect of solvents on the NH vibration increases in the order  $\text{H}_2\text{O}$ , alcohols,  $\text{C}_6\text{H}_6$ , dioxan.

A. J. M.

**Complete analysis of absorption spectra. IV. Physico-chemical properties of the chromophoric groups, azomethine ( $\text{CH}=\text{N}$ ) and azomethinevinylene ( $\text{CH}=\text{CH}-\text{CH}=\text{N}$ ).** E. Hertel and (Frl.) M. Schinzel (*Z. physikal. Chem.*, 1941, B, 48, 289–308).—The acceptor variability of doubly-bound N atoms of  $\text{CH}=\text{N}$  is  $<$  that of singly-bound N of amines. The transference of induced effects of substituents on N in  $\text{CH}=\text{N}$  through a system of conjugated double bonds is extremely small. Compared with Ph,  $\text{CH}=\text{CH}$  is the stronger variator. The effects of other substituent groups and the influence of location of the groups are discussed.

W. R. A.

**Absorption spectra of terpenoid compounds. II. Iron.** A. E. Gillam and T. F. West (*J.C.S.*, 1942, 95–98).—The absorption spectrum of iron from two different sources in EtOH solution has been investigated. The results show that the active chromophoric group is  $\text{C}=\text{C}=\text{C}=\text{O}$  and not  $\text{C}=\text{C}=\text{C}=\text{C}=\text{O}$ . Using Woodward's generalisation, it is inferred that only one of the 3 H capable of being attached to the  $\text{C}=\text{C}$  linkage is replaced by other groups, so that the chromophore is either  $\text{CHR}=\text{CH}=\text{CR}=\text{O}$  or  $\text{CH}_2=\text{CR}=\text{CR}=\text{O}$ . It is concluded that iron is a  $\beta$ -substituted  $\alpha\beta$ -unsaturated ketone. Although the absorption spectra of iron from two different sources agree in giving a short- $\lambda$  band at 2280  $\text{\AA}$ , they differ sufficiently to show that the natural ketone is a mixture. This is confirmed by examination of the crude thiosemicarbazones derived from the two samples.

A. J. M.

**Absorption spectra of mono-, di-, and tri-chloroamines and some aliphatic derivatives.** W. S. Metcalf (*J.C.S.*, 1942, 148–150).—The absorption spectra of  $\text{NH}_2\text{Cl}$ , some mono- and di-substituted chloroamines,  $\text{NHCl}_2$ , monosubstituted dichloroamines, and of  $\text{NCl}_3$  have been investigated. Me, Et, and Pr<sup>n</sup> derivatives have the same absorption spectra. The chloroamines examined have a characteristic absorption band lying between the limits  $\nu_{\text{max.}} = 40,800 \text{ cm}^{-1}$ ,  $\epsilon_{\text{max.}} = 416$ , and  $\nu_{\text{max.}} = 29,400 \text{ cm}^{-1}$ ,  $\epsilon_{\text{max.}} = 255$ . The less is the polarisability of the groups attached to the  $\text{N}=\text{Cl}$  chromophore, the greater is the  $\nu$  of max. absorption.

A. J. M.

**Relation between absorption spectra and chemical constitution of dyes.**—See A., 1942, II, 89.

**Structure and absorption spectra. III. Normal conjugated dienes. IV.  $\alpha\beta$ -Unsaturated ketones.**—See A., 1942, II, 161, 164.

**Colour and constitution.**—See A., 1942, II, 153.

**Photochemically derived binding energy of gaseous mercuric chloride.** K. Wieland (*Helv. Chim. Acta.*, 1941, 24, 1285–1298).—A photochemical val. for the energy of dissociation of a triat. mol. can be obtained if the resulting excited diat. radical emits a fluorescence spectrum. In this way a val. for the energy of the  $\text{Cl}-\text{HgCl}$  linkage in agreement with thermochemical vals. is obtained.

F. J. G.

**Extinction of fluorescence by ascorbic acid.** K. Weber (*Radio-logica*, 1938, 2, 57–64, 237; *Chem. Zentr.*, 1938, ii, 3911).—Fluorescence of quinine sulphate, fluoronone, or pinakryptol-yellow is extinguished by ascorbic acid (I) (0.001–0.05M), probably owing to the reversible oxidisability of (I). Addition of (I) to solutions of uranine, eosin, or resorcin reduces the intensity of fluorescence and liberates the free acid from the dye. (I) has no effect on the fluorescence of chlorophyll or aetioporphylin.

A. J. E. W.

**Phosphorescence and its applications.** J. N. Bowtell and E. E. Miles (*G.E.C. J.*, 1941, 11, 256–265).—A short historical summary introduces a general account of phosphorescent and fluorescent



substances, effect of  $\lambda$  on excitation efficiency, effect of infra-red radiation on phosphorescence, and the theoretical explanation of luminescence. A survey is given of practical applications, brightness decay curves, sources of long- $\lambda$  ultra-violet radiation for excitation, stability of materials, phosphorescent paints, solid synthetic resins and vitreous enamel, and painting processes. N. M. B.

**Hydrogen bond formation. I. Amides.** A. L. S. Rao (*J. Indian Chem. Soc.*, 1941, 18, 337—349).—The effects of varying temp. and concn. on the Raman spectra of aq.  $\text{HCO}\cdot\text{NH}_2$ ,  $\text{NH}_2\text{Ac}$ , and  $\text{CO}(\text{NH}_2)_2$  have been studied. It is concluded that high polymerides are present which dissociate at higher temp. or on dilution. F. J. G.

**Raman effect. CXXIV. cyclohexane and oxalyl chloride.** K. W. F. Kohlrausch and H. Wittek. **CXXV. Chlorotrifluoromethane.** L. Kahovec and J. Wagner (*Z. physikal. Chem.*, 1941, B, 48, 177—187, 188—192).—CXXIV. Raman frequencies and polarisation data for cyclohexane and  $(\text{COCl})_2$  are recorded. The observations support the "chair"-shaped structure rather than the planar structure for cyclohexane.

CXXV. Raman frequencies for liquid  $\text{CClF}_3$  are recorded and are discussed in relation to the frequencies and polarisation data for  $\text{CF}_4$ ,  $\text{CCl}_2\text{F}_2$ ,  $\text{CCl}_3\text{F}$ , and  $\text{CCl}_4$ . J. W. S.

**Raman effect. CXXVI. Carbonyl sulphide and cyanogen chloride. CXXVII. Compounds containing nitrogen. XIX. Quinuclidine.** J. Wagner (*Z. physikal. Chem.*, 1941, B, 48, 309—315, 316—320).—CXXVI. The polarisations of the Raman lines of COS and CNCl have been measured. COS is non-linear; CNCl is linear. Further evidence for these structures is added from the isotope splitting of lines.

CXXVII. Raman spectra of quinuclidine (I) and 1-aza-(1:2:2)-dicycloheptane are recorded. Frequency formulæ for the valency force model of (2:2:2)-dicyclooctane have been derived. A satisfactory frequency description of (I) could not be obtained. W. R. A.

**Electrical conductivity of titanium dioxide.** M. D. Earle (*Physical Rev.*, 1942, [ii], 61, 56—62).—Experiments show that  $\text{TiO}_2$  is an electronic semi-conductor in which the current carriers are free electrons, in contrast to the hole conduction of the other type of semi-conductors. The variation of conductivity with  $\text{O}_2$  pressure accords with the decomp.  $\text{TiO}_2 \rightarrow \text{Ti}^+ + \text{O}_2 + e^-$ . The variation with temp. is represented by  $\sigma = Ae^{-E/kT}$ , where  $E$ , the activation energy for producing free electrons, is  $\sim 1.7$  e.v. Approx. measurements of the Hall effect show that the mean free path for the conduction electrons is very small. N. M. B.

**Dielectric constant of carbon tetrachloride from 15° to 40°.**—See A., 1942, I, 158.

**Dipole moments of gallium chloride and its molecular compounds.** H. Ulich and G. Heyne (*Z. physikal. Chem.*, 1941, B, 49, 284—292).—The prep. of  $\text{GaCl}_3$  from Ga and HCl is described. When  $\text{GaCl}_3$  is dissolved, with warming, in org. solvents, the solution is brown or yellow if ordinary solvents are used, but if specially purified and dried liquids are employed, the solutions are clear and colourless. The following additive compounds have been prepared:  $\text{GaCl}_3\cdot\text{PhCN}$  (I), m.p. 125°,  $\text{GaCl}_3\cdot p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$  (II), m.p. 95°,  $\text{GaCl}_3\cdot\text{BzCl}$  (III), m.p. 46°. The following dipole moments have been determined:  $\text{GaCl}_3$  in  $\text{C}_6\text{H}_6$ ,  $\text{CS}_2$ , and  $\text{CCl}_4$ ; (I) in  $\text{C}_6\text{H}_6$ , (II) in  $\text{C}_6\text{H}_6$ , (III) in  $\text{CCl}_4$ . The moments of the additive compounds are of the same order as those of similar compounds with  $\text{AlCl}_3$ ,  $\text{AlBr}_3$ ,  $\text{BCl}_3$ ,  $\text{BeCl}_2$ ,  $\text{BeBr}_2$ ,  $\text{TiCl}_4$ , and  $\text{SnCl}_4$ . A. J. M.

**Field of electrets in the presence of gaseous ions.** A. Gemant (*Physical Rev.*, 1942, [ii], 61, 79—83; cf. Good, A., 1940, I, 41).—Calculations show that, contrary to available experimental evidence, the field of electrets ought to be completely shielded by the ions in the atm. Experimental facts on the electret field and the use of electrets in discharge tubes are discussed (cf. Sheppard, A., 1941, I, 449). N. M. B.

**Refractive indices of  $\text{PF}_5$  and  $\text{OsO}_4$  and the dielectric constants of  $\text{OsO}_4$ ,  $\text{SF}_6$ ,  $\text{SeF}_6$ , and  $\text{TeF}_6$ .** R. Linke (*Z. physikal. Chem.*, 1941, B, 48, 193—196).— $n$  for  $\text{PF}_5$  and  $\text{OsO}_4$  vapours has been determined by the interferometer method at pressures 27—314 mm. and 2.5—11.9 mm., respectively.  $\epsilon$  has been determined for  $\text{SF}_6$ ,  $\text{SeF}_6$ , and  $\text{TeF}_6$  at  $\sim 293^\circ\text{K}$ . and for  $\text{OsO}_4$  at  $429.2^\circ$  and  $561.2^\circ\text{K}$ . The results indicate that  $\text{OsO}_4$  has zero dipole moment. From these and previous data the total and electronic ( $P_E$ ) polarisations of  $\text{OsO}_4$ ,  $\text{PF}_5$ ,  $\text{SF}_6$ ,  $\text{SeF}_6$ ,  $\text{TeF}_6$ ,  $\text{BF}_3$ ,  $\text{HgCl}_2$ ,  $\text{HgBr}_2$ , and  $\text{HgI}_2$  are calc. and the at. polarisations ( $P_A$ ) are derived. The vals. for  $P_A$  range between 16 and 67% of  $P_E$ , being the higher the more polar are the linkings in the compound concerned. J. W. S.

**Molecular refraction nomograph.** D. S. Davis (*Ind. Eng. Chem.*, 1942, 34, 258).—A nomograph has been constructed for solving the Lorentz-Lorenz equation  $R = M(n^2 - 1)/d(n^2 + 2)$ , where  $R$  = mol. refraction,  $M$  = mol. wt.,  $n$  = refractive index, and  $d$  = density. C. R. H.

**Structural algebra in chemistry.** A. A. Balandin (*Acta Physico-chim. U.R.S.S.*, 1940, 12, 447—479).—The relations between the elements of a geometrical structure are represented symbolically

by structural matrices, and the algebra of such matrices is developed. Applied to chemistry, this structural algebra affords a concise and quant. representation of structures, equilibria, etc., and in some cases facilitates calculations. F. J. G.

**Mechanisms of covalent-bond fission.** W. A. Waters (*J.C.S.*, 1942, 153—157).—In the case of an unsymmetrical covalent bond, there is a close connexion between the electrostatic dipole energy and resonance energy. The Coulombic energy of a bond is usually the greater part of the ionic resonance energy, and thus often gives a better criterion of the extent of internal resonance in a polar bond than does the dipole moment alone. The energy requirements for unimol. dissociations are considered, and the electrostatic factors determining the activation energies of both ionic and neutral reactions are compared. The favoured mechanism for a unimol. dissociation is largely determined by the dielectric const. of the solvent. Available experimental data confirm these conclusions. The activation energies of bimol. reactions are also considered. A. J. M.

**Application of the  $p$ -hydrogen method to some problems of organic constitutions.** I. G. M. Schwab and E. Schwab-Agallidis (*Z. physikal. Chem.*, 1941, B, 49, 196—204; cf. A., 1938, I, 625).—The effect of org. substances on  $p\text{-H}_2$  can be used as a test for their radical nature, and the method is applicable where the determination of magnetic susceptibility cannot be used. The method was applied to protoporphyrin (I) and monobromobenzanthrone (II). (I) has no action on  $p\text{-H}_2$  and does not therefore exist as di-radicals. Similarly (II) is found not to be a mono-radical. These results agree with those obtained by the magnetic method. A. J. M.

**Rotating bubble method for the determination of surface and interfacial tensions.**—See A., 1942, I, 159.

### III.—CRYSTAL STRUCTURE.

**Diffuse spots in X-ray photographs.** (Sir) W. H. Bragg (*Nature*, 1941, 148, 780; cf. A., 1942, I, 135).—Simple diffraction formulæ, which are independent of elastic consts., predict accurately the positions of all the diffuse spots, but the theory that ascribes the spots to the interaction of the structural periodicities of the crystal and the periodicities of the elastic waves does not do so. L. S. T.

**Thermal scattering of X-rays in crystals.** J. Weigle and C. S. Smith (*Physical Rev.*, 1942, [ii], 61, 23—34).—Mathematical. The reciprocal lattice of a crystal with heat waves is calc. under simplifying assumptions, and a simple representation of the principal facts concerning observed diffuse scattering max. is obtained. The assumptions are justified and the problem of scattering from waves of large amplitude is considered. N. M. B.

**Scattering of polarised X-rays by ferromagnetic substances.** E. Rodgers (*Physical Rev.*, 1942, [ii], 61, 35—38; cf. A., 1937, I, 55).—If high-frequency polarised X-rays are scattered by some substance, the total intensity of the scattered rays should be altered by anything leading to special orientations of the spins of the scattering electrons. Experimental attempts to detect the effect on intensity due to changes in spin orientations in ferromagnetics when magnetised were unsuccessful. An attempt to reconcile these and the results of gyro-magnetic experiments leads to orientations of the spin, giving the spin magnetic quantum nos.  $\frac{1}{2}$  and  $-\frac{1}{2}$ . N. M. B.

**Evaluation of X-ray back-reflexion pictures.**—See A., 1942, I, 156.

**Structure of tricalcium aluminate.** H. F. McMurdie (*J. Res. Nat. Bur. Stand.*, 1941, 27, 499—505).—X-Ray diffraction measurements by the powder method indicate that  $\text{Ca}_3\text{Al}_2\text{O}_6$  has a cubic unit cell with  $a_0$  15.24 Å. and containing 24 mols. Comparison with data for  $\text{CaTiO}_3$  and  $\text{Na}_2\text{CaSiO}_4$  indicates that the metal atoms are arranged in a body-centred cubic lattice with  $a_0$  3.81 Å. This is confirmed by measurements on  $\text{Sr}_3\text{Al}_2\text{O}_6$ , which has a cubic unit cell with  $a_0$  15.82 Å. No conclusions can be drawn concerning the arrangement of the O atoms. Since many compounds have a lattice with  $a_0$  3.81 Å., and structures with some irregularity will not show a strong-line pattern, it is suggested that the patterns obtained with slowly quenched glass from Portland cement (Brown-miller, B., 1938, 654) were caused by submicroscopic growths of a metastable cryst. compound. J. W. S.

**Diffraction of fast electrons in thin films of hydrated cellulose.** V. A. Kargin and D. I. Leipunskaia (*Acta Physicochim. U.R.S.S.*, 1940, 12, 397—410).—The scattering of fast electrons by thin films of hydrated cellulose gives an intensity curve agreeing with that calc. for the cellobiose mol., and showing no sign of an ordered structure. F. J. G.

**Variation with temperature of the principal elastic moduli of rock-salt near the m.p.** L. Hunter and S. Siegel (*Physical Rev.*, 1942, [ii], 61, 84—90; cf. Durand, A., 1936, 1329).—Measurements are reported over the range 20—804°, the m.p., by means of a tripartite piezoelectric oscillator consisting of a quartz crystal driver, an intermediate fused  $\text{SiO}_2$  bar, and the NaCl specimen. The shear consts.  $C_{44}$  and  $C_{11} - C_{12}$  decrease nearly linearly with temp., reaching non-zero vals. at the m.p. The compressibility increases



with temp., but drops suddenly close to the m.p. Results are compared with predictions based on Born's theory of the stability of crystal lattices. N. M. B.

"Flow" in stressed solids; an interpretation. R. W. Goranson (*Bull. Geol. Soc. Amer.*, 1940, 51, 1023—1033).—The mechanism involved in "creep," "plastic flow," and "pseudo-viscous" flow is interpreted (cf. A., 1942, I, 188). Plastic flow in solids is regarded as taking place by means of a change-of-phase transfer mechanism as solid  $\rightarrow$  fluid  $\rightarrow$  solid or solid  $\rightarrow$  solution  $\rightarrow$  recrystallisation of solid. Expressions are derived from consideration of the thermodynamic potential relations for different physical conditions. L. S. T.

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

Mol. wt. of sulphur vapour. W. Klemm and H. Kilian (*Z. physikal. Chem.*, 1941, B, 49, 279—283).—New determinations of the v.d. of S between 450° and 850° give vals. for the mol. wt. somewhat > those obtained by Preuner *et al.* (A., 1910, ii, 118). A. J. M.

External electrical potential of metals in a temperature gradient. H. Lämmermann and E. Lange (*Z. physikal. Chem.*, 1941, B, 49, 219—234).—For a metal in a temp. gradient in moist air, the temp. coeff. of the potential  $d\psi/dT$  has a definite val., whereas in vac. and for dry gases,  $d\psi/dT$  is almost zero. This difference is due to adsorbed  $H_2O$ . Approx. the same vals. for  $d\psi/dT$  are obtained if  $N_2$  is substituted for air. A. J. M.

Names of electrical units. E. A. Guggenheim (*Nature*, 1941, 148, 751).—The charge that repels a similar charge at a distance of 1 cm. with a force of 1 dyne is called a franklin. Units of the most important electrostatic quantities in cm.-g.-sec.-franklin and in m.-kg.-sec.-coulomb units are tabulated. L. S. T.

Velocity of sound in methyl methacrylate polymeride. L. R. Weber and F. P. Goeder (*Physical Rev.*, 1942, [ii], 62, 94—95).—A preliminary report of measurements by compressional forces on rods of various sizes and by a modification of the electrostatic method shows widely divergent results. Explanations are suggested. N. M. B.

Refractive indexes of gases at high radio frequencies. F. J. Kerr (*Nature*, 1941, 148, 751—752).—At 58 Mc. per sec., 100°, and 1 atm., the vals. obtained are  $1.00024(0) \pm 0.000006$  and  $1.0030(1) \pm 0.00007$  for dry air and  $H_2O$  vapour, respectively. L. S. T.

P-V-T relations and derived quantities for hexanes. E. A. Kelso and W. A. Felsing (*Ind. Eng. Chem.*, 1942, 34, 161—163).—Mol. vols. of liquid  $Pr_6$  over the temp. and pressure ranges 100—225° and 5.6—311.8 atm. are tabulated. Data for the sp. vol. under its own v.p. and P-V-T data in the gaseous state are also tabulated. The data, together with similar data for  $n-C_6H_{14}$  and  $Pr^*Pr_6$ , have been utilised to evaluate vals. of  $pV/RT$  and fugacity-pressure ratios. C. R. H.

Pressure-temperature chart for vapours. M. Hirsch (*Ind. Eng. Chem.*, 1942, 34, 174—182).—Mathematical. A new method of plotting logarithmic pressures using convergent isotherms results in straight lines parallel or inclined to the pressure axis according to whether the ordinary plots of  $\log p$  against  $1/T$  are linear or curved. The application of the method to the solution of problems connected with Trouton's rule and the Clapeyron and van der Waals expressions is illustrated. C. R. H.

Cellulose and its derivatives as liquids of fixed structure. K. Ueberreiter (*Z. physikal. Chem.*, 1941, B, 48, 197—218).—The V-T relationships of cellulose and its derivatives over the solidification range indicate that they can be regarded as a "liquid of fixed structure," i.e., a solid with structure similar to that of a liquid (cf. A., 1942, I, 84). Hydrocellulose forms relatively rigid macro-mols., but nitration and acetylation increase the mobility of the links in the macro-mol. chains, leading to "internal softening." "External softening" has been studied by measurement of the V-T relations for ethylcellulose or cellulose nitrate to which  $(C_6H_5Me)_3PO_4$  (I) has been added. The solidification point is depressed considerably by small additions of (I), but further additions produce decreasing effects. Swelling of cellulose in  $H_2O$  is a special case of external softening. The V-T curves of artificially produced cellulose fibres show anomalous inflexions on initial heating, attributable to strains in the macro-mols. Polystyrenes show similar phenomena. J. W. S.

Thermal expansion of pure metals. II. Molybdenum, palladium, silver, tantalum, tungsten, platinum, and lead. F. C. Nix and D. MacNair (*Physical Rev.*, 1942, [ii], 61, 74—78; cf. A., 1942, I, 50).—High-precision measurements made interferometrically from room temp. to liquid- $N_2$  temp. are reported, and comparisons with the Grueneisen theory are made. N. M. B.

Critical state. VI. Vapour pressure curve of naphthalene up to the critical point. E. Schröder (*Z. physikal. Chem.*, 1941, B, 49, 271—278).—Apparatus for the determination of crit. data is described. The crit. data of  $C_{10}H_8$  have been determined. The crit.

temp. is 478.5—480°; crit. pressure 42 kg. per sq. cm.; crit. d 0.314 g. per c.c. The v.p. curve is given between 200° and 500°.

A. J. M.

Explorations toward the limit of utilisable pressures.—See A., 1942, I, 159.

[Viscosity of air by rotating-cylinder method.] G. Kellström (*Phil. Mag.*, 1941, [vii], 31, 466—470; cf. A., 1937, I, 231).—Corrections for the influence of the air on the effective moment of inertia of the inner cylinder and the end-correction to the length of the inner cylinder are applied to the author's earlier data, giving  $1.8204 \pm 0.0003 \times 10^{-4}$  at 20° and  $1.8352 \pm 0.0030 \times 10^{-4}$  at 23° as final vals. for  $\eta$ . L. J. J.

Method of successive approximations for the solution of the boundary layer equations. J. H. Preston (*Phil. Mag.*, 1941, [vii], 31, 452—465).—The author's iteration method (*ibid.*, 1938, [vii], 26, 791) for flow at high Reynolds nos. gives results of limited accuracy when experimental pressures are used. The position of the breakaway may be uncertain even when a large no. of approximations are used. L. J. J.

#### V.—SOLUTIONS AND MIXTURES (INCLUDING COLLOIDS).

Self-diffusion of hydrogen chloride and hydrogen bromide. H. Braune and F. Zehle (*Z. physikal. Chem.*, 1941, B, 49, 247—256).—The diffusion of DCl with respect to HCl, and of DBr with respect to HBr, has been investigated. The difference in the diffusion coeff.  $D_{DCl} - D_{HCl}$  is 0.1246 at 295° K., and  $D_{DBr} - D_{HBr}$  is 0.0792 at 295.3° K. The results are discussed. A. J. M.

Condensation of vapours in a carrier gas. F. Frey (*Z. physikal. Chem.*, 1941, B, 49, 83—101).—An apparatus is described with which it is possible to determine fog formation as a result of adiabatic expansion to high supersaturation. The relationship between the no. of drops per unit vol. and the degree of supersaturation has been estimated. In the absence of ions the crit. supersaturation is higher and the increase in the no. of drops occurs more slowly than when ions are present; reasons for this are advanced. The necessary conditions for the adiabatic process have been established and the influence of liberated heat on the condensation is discussed. W. R. A.

Viscosity of binary liquid mixtures and associated liquids. R. Linke (*Z. physikal. Chem.*, 1941, A, 188, 191—197).— $\eta$  has been determined for the systems  $COMe-CHCl_3$  and  $C_6H_5-CCl_4$  at 10—50° and for  $PhNO_2$  at 10—180°. The results are discussed as illustrating the influence of compound formation and association. F. J. G.

Specific viscosity of suspensions and solutions. E. W. J. Mardles (*Trans. Faraday Soc.*, 1942, 38, 47—54).—A detailed account of experiments leading to the conclusions previously announced (A., 1942, I, 16) is given. F. L. U.

Viscosities of aqueous solutions of some phenanthrenesulphonic acids. T. R. Bolam and J. Hope (*J.C.S.*, 1941, 850—854).— $\eta$  for aq. solutions of  $p-C_6H_4MeSO_3H$ , phenanthrene-3-sulphonic acid, 9-chloro- and 9-bromo-phenanthrene-3-sulphonic acid are recorded. The  $\eta$ -conc. curves for the phenanthrene acids show abnormalities corresponding with those for A, and indicating micelle formation. F. J. G.

Relaxation times in mixtures of polar and non-polar liquids. H. Spengler (*Physikal. Z.*, 1941, 42, 134—143).—The relaxation time of  $PhNO_2$  in  $C_6H_6$  and of  $PhCl$  in  $C_6H_6$  has been determined as a function of concn. by the method of high-frequency heating. It is to be expected that, in consequence of the greater moment of  $PhNO_2$  compared with that of  $PhCl$ , there will be a stronger coupling in the case of  $PhNO_2$ , and a more rapid decrease of relaxation time with concn. This is demonstrated by experiment. A. J. M.

Influence of differences in the molecular volumes of liquids on the vapour pressure curves of their binary mixtures. K. Fredenhagen (*Z. physikal. Chem.*, 1941, B, 48, 219—227).—The conclusions of Frahm (A., 1940, I, 19) are criticised. Thermodynamic and kinetic considerations indicate that the v.p. of a binary mixture depends on the mol. vols. of the components. In most cases vol. or energy changes during mixing also modify the v.p. With components which have equal intermol. forces and do not react, the free energies of the components with lower and higher mol. vol. are increased and decreased, respectively, and consequently the partial v.p.-composition curves of these components are lowered and raised, respectively, relative to the straight-line relations of Raoult's law. J. W. S.

Constitution of sodium silicate solutions. R. C. Ray, P. B. Ganguly, and A. B. Lal (*Trans. Faraday Soc.*, 1942, 38, 104—108).—The diffusion of Na silicates with initial compositions varying from  $Na_2O/SiO_2 = 0.5$  to 0.25 has been examined by analysing successive layers. In all cases the ratio  $Na_2O/SiO_2$  increases with distance and tends to the val. 2.0. Measurements of  $p_H$  as well as published data indicate that hydrolysis is inadequate to account for the



observed changes, and the conclusion reached is that the solutions studied contain a single species of salt, viz.,  $\text{Na}_2\text{SiO}_4$  or  $\text{Na}_2\text{H}_2\text{SiO}_4$ , and that the remaining  $\text{SiO}_2$  is present as colloidal  $\text{SiO}_2 \cdot \text{H}_2\text{O}$ .

F. L. U.

**Order in the alloy  $\text{Cu}_3\text{Au}$ .** L. H. Germer, F. E. Haworth, and J. J. Lander (*Physical Rev.*, 1942, [ii], 61, 93).—Electron diffraction patterns for thin films indicate that order is produced by heating for 16 hr. at  $170^\circ$ , but diffuseness indicates the presence of anti-phase domains (cf. Nix, A., 1942, I, 17). Stronger and sharper superstructure rings are obtained from films which have been heated at higher temp. An ordered specimen on heating shows no marked change of pattern up to  $\sim 300^\circ$ ; above this temp. the superstructure rings become broader and less prominent, reaching a steady state at  $\sim 370^\circ$ . At  $370$ – $550^\circ$  the diffraction pattern shows unresolved superstructure rings, confirming the existence of short-range order above the Curie point ( $380$  or  $390^\circ$ ).

N. M. B.

**Variation of the magnetic properties of antimony with electron concentration.** S. H. Browne and C. T. Lane (*Physical Rev.*, 1941, [iii], 60, 895–899).—The susceptibilities perpendicular  $\kappa_1$  and parallel  $\kappa_{11}$  to the principal (trigonal) axis were determined for single crystals of pure Sb and solid-solution alloys of Sb with Sn, Ge, Pb, and Te. As the % of alloying metal increases  $\kappa_1$  changes very little and remains diamagnetic, but  $\kappa_{11}$  decreases sharply, and, for Sn and Ge changes to paramagnetic beyond 1.17 at.-% Sn and 1.25 at.-% Ge. The calc. no. of electrons which overlap into the second Brillouin zone in Sb is  $10^{-2}$  per atom. The bearing of results on the current theory of metals is discussed. (Cf. following abstract.)

N. M. B.

**Temperature variation of the magnetic susceptibilities of antimony-tin alloys.** S. H. Browne and C. T. Lane (*Physical Rev.*, 1941, [iii], 60, 899–905; cf. preceding abstract).—Measurements on single crystals of pure Sb and of Sb–Sn alloys up to 4.1 at.-% Sn in the temp. range  $77^\circ\text{K}$ . to room temp. show that  $\kappa_1$  (diamagnetic) is practically independent of temp. for all the alloys;  $\kappa_{11}$  (diamagnetic and paramagnetic) decreases with rise of temp. except for the alloy of 1.06 at.-% Sn, but this is brought into agreement by a correction of the temp.-independent diamagnetic susceptibility of the lattice ions. Experimental  $\kappa_{11}$  are compared with Stoner's expressions for the susceptibilities of free electrons, assuming that  $\kappa_{11}$  is due to the electrons overlapping into the second Brillouin zone. The degeneracy temp. of these electrons is found to be  $\sim 475^\circ\text{K}$ ,  $\sim 0.25$  of what it would be for free electrons. Effective masses of the electrons, which occur as parameters in the energy equation, are calc. Theoretical consequences are discussed.

N. M. B.

**Equilibrium relations in the solid state of the iron-cobalt system.** W. C. Ellis and E. S. Greiner (*Trans. Amer. Soc. Met.*, 1941, 29, 415–434).—Redeterminations by thermal analysis of the temp. of the  $\gamma$ - $\alpha$  transformation and the Curie point of Fe–Co alloys with <70 at.-% Co confirmed previous studies. In alloys with 70–90 at.-% Co the phase boundaries were determined by X-ray diffraction methods, and an extended region of  $\alpha + \gamma$  equilibrium was established. At  $600^\circ$ , the  $\alpha + \gamma$  region exists from 78.5 to 88.5 at.-% Co. The lattice consts. of the  $\alpha$  phase were measured at  $25^\circ$ ; additions of Co increase the cell size from 2.8607 Å. for Fe to 2.8611 Å. for 20.5 at.-% Co alloy; further additions then decrease the size rapidly. In alloys with 40–67 at.-% Co the cell size is slightly larger after quenching from  $575^\circ$  than after quenching from  $800^\circ$ . This effect is associated with an order-disorder change, the crit. temp. of which was located by thermal analysis. The ordered cell has a CsCl structure.

J. C. C.

**Nature of a satellite in the X-ray pattern of  $\alpha$ -crystals, and differentiation of a new phase,  $\alpha'$ , by the surface recrystallisation method in certain ternary alloys. I. Iron-nickel-aluminium system.** S. Kiuti (*Aeronaut. Res. Inst. Tokyo Imp. Univ.*, Rept. 207, 1941, 16, 167–204; *Bull. Iron Steel Inst.*, 1941, No. 74, 158A).—In view of the importance of the discovery of a new  $\alpha'$  phase in the magnetic Fe–Ni–Al system (*ibid.*, Rept. 203, 1940, 15, 601), experimental data obtained in the course of early studies of this phase are reported. In these studies the possibility of differentiation of the  $\alpha'$  phase by the surface recrystallisation method was considered theoretically and verified experimentally by X-ray analysis. The conclusion from calculations was that the  $\alpha'$  phase is a body-centred cubic lattice with a simple cubic superstructure of the CsCl type.

R. B. C.

**X-Ray study on mechanism of the splitting phenomenon of  $\alpha$  crystals in interiors of some ternary alloys. I. Iron-nickel-aluminium system.** S. Kiuti (*Aeronaut. Res. Inst. Tokyo Imp. Univ.*, Rept. 207, 1941, 16, 271–298; *Bull. Iron Steel Inst.*, 1942, No. 74, 158A).—The discovery of a new  $\alpha'$  phase in the surface layers of magnetic Fe–Ni–Al alloys (cf. preceding abstract) raised the question whether the same phase occurs in the interior of the specimens. After subjecting specimens to prolonged annealing at const. temp., the splitting of the  $\alpha$  crystals was found by X-ray examination to have taken place in the interior also; this confirmed the author's earlier conclusion obtained by the surface recrystallisation method.

R. B. C.

**Solubility of calcium carbonate in tropical sea-water.** C. L. Smith (*J. Marine Biol. Assoc.*, 1941, 25, 235–242).—The solubility pro-

duct of  $\text{CaCO}_3$  in sea- $\text{H}_2\text{O}$  of salinity 3.6% at  $29.7^\circ$  has been determined as  $\sim 1.16 \times 10^{-6}$ .

J. W. S.

**Solubility of nickel ions in aqueous alkaline carbonate-tungstate solutions.** M. L. Holt and D. A. Swalheim (*Trans. Electrochem. Soc.*, 1942, 81, Preprint 2, 11–25).—Measurement of the solubility ( $s$ ) of  $\text{NiSO}_4$  in  $\text{Na}_2\text{CO}_3$ -tungstate solutions shows that  $s$  depends on time as well as on the composition of the solvent.  $s$  decreases with time and with decrease in  $[\text{Na}_2\text{CO}_3]$ , and  $s$  is also influenced by the amount and nature of the tungstate, increasing with increase in tungstate concn. and being greater for solutions prepared from  $\text{Na}_2\text{WO}_4$  than for solutions of the same equiv.  $[\text{H}_2\text{WO}_4]$  prepared from  $5\text{Na}_2\text{O} \cdot 12\text{WO}_3$ . Under conditions which favour  $\text{NaHCO}_3$  formation and in solutions containing added  $\text{NaHCO}_3$  there is an increase in  $s$ . This suggests that it is  $\text{NaHCO}_3$  which favours  $\text{NiSO}_4$  dissolution rather than the formation of sol. Ni tungstate complexes, a view which is supported by electrolysis experiments which are described. The presence of  $\text{NaHCO}_3$  may affect  $s$  by forming sol.  $\text{Ni}(\text{HCO}_3)_2$  or, what is more likely in view of the electrolysis data,  $\text{Na}_2\text{Ni}(\text{CO}_3)_2$ .

C. R. H.

**Nephelometric method for determination of solubilities of extremely low order.** W. W. Davis and T. V. Parke, jun. (*J. Amer. Chem. Soc.*, 1942, 64, 101–107).—A nephelometric method capable of measuring the solubilities of polycyclic hydrocarbons down to  $\sim 1 \mu\text{g}$ . per l. is described. Data for the solubilities in  $\text{H}_2\text{O}$  of 3:4 benzpyrene, 10-ethyl-1:2-benzanthracene, and phenanthrene are reported. Extensions and limitations of the method are discussed.

W. R. A.

**Solubility of carcinogenic and related hydrocarbons in water.** W. W. Davis, M. E. Krah, and G. H. A. Clowes (*J. Amer. Chem. Soc.*, 1942, 64, 108–110).—Using the nephelometric method (preceding abstract) the solubility of 31 polycyclic hydrocarbons in  $\text{H}_2\text{O}$  at  $27^\circ$  has been determined.

W. R. A.

**Solubility and chemical constitution.** E. Leikola (*Suomen Kem.*, 1940, 13, B, 13–17).—The solubility of  $\text{H}_2\text{O}$  in mixtures of non-ionising ( $\text{C}_6\text{H}_6$ , PhMe, *o*-, *m*-, and *p*-xylene, 1:3:5- $\text{C}_6\text{H}_3\text{Me}_3$ , PhNO<sub>2</sub>,  $\text{NH}_2\text{Ph}$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ ,  $\text{CS}_2$ , and *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{MeOH}$ ) with semi-ionising ( $\text{MeOH}$ ,  $\text{EtOH}$ ,  $\text{Pr}^i\text{OH}$ ,  $\text{Pr}^n\text{OH}$ ,  $\text{COMe}$ ,  $\text{AcOH}$ ,  $\text{EtCO}_2\text{H}$ ,  $\text{Pr}^i\text{CO}_2\text{H}$ , and  $\text{C}_6\text{H}_5\text{N}$ ) liquids has been studied. In mixtures with  $\text{MeOH}$ ,  $\text{EtOH}$ ,  $\text{AcOH}$ ,  $\text{EtCO}_2\text{H}$ , or  $\text{C}_6\text{H}_5\text{N}$  (but not  $\text{Pr}^i\text{OH}$ ,  $\text{Pr}^n\text{OH}$ ,  $\text{Pr}^i\text{CO}_2\text{H}$ , or  $\text{COMe}$ )  $\text{H}_2\text{O}$  is decreasingly sol. with increasing replacement of H by Me in  $\text{C}_6\text{H}_5$  or by Cl in  $\text{CH}_3$ . In mixtures with  $\text{MeOH}$   $\text{H}_2\text{O}$  is sol. in  $\text{C}_6\text{H}_6 < \text{PhNO}_2 < \text{NH}_2\text{Ph}$ , *o*- < *p*- < *m*- $\text{C}_6\text{H}_4\text{MeOH}$ , but equally in all three xylenes. The solubility of  $\text{H}_2\text{O}$  in  $\text{C}_6\text{H}_6$  (or  $\text{CHCl}_3$ ) is with  $\text{EtOH} > \text{MeOH} > \text{Pr}^i\text{OH} > \text{Pr}^n\text{OH}$ , in PhMe (or  $\text{CCl}_4$ ) with  $\text{EtOH}$ ,  $\text{Pr}^i\text{OH} > \text{MeOH}$ , and in xylene with  $\text{Pr}^i\text{OH} > \text{EtOH}$ ,  $\text{MeOH}$ . Similar variation with size of the alkyl group is found with  $\text{AcOH}$ ,  $\text{EtCO}_2\text{H}$ , and  $\text{Pr}^i\text{CO}_2\text{H}$  in the two lipid series. In general, the size of the alkyl group of the semi-ionising solvent giving max. solubility of  $\text{H}_2\text{O}$  increases with increasing no. of Me or Cl groups in the lipid solvent.

M. H. M. A.

**Difference in heat of adsorption of ortho- and para-hydrogen.** E. Cremer (*Z. physikal. Chem.*, 1941, B, 49, 245–246).—The difference in the heat of adsorption of *o*- and *p*- $\text{H}_2$  on solid  $\text{O}_2$  is  $< 90$  g.-cal. This can be explained as due to the hindrance of rotation imposed on the *o*- $\text{H}_2$  mol. by the action of neighbouring mols. of the adsorbing agent.

A. J. M.

**Van der Waals adsorption of gases ( $\text{N}_2$ , A, CO,  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{D}_2\text{O}$ , etc.) on glass plates.** A. van Itterbeek and W. Vereycken (*Z. physikal. Chem.*, 1941, B, 48, 131–147).—The adsorption isotherms for A,  $\text{N}_2$ , CO,  $\text{CH}_4$ , and  $\text{O}_2$  at the temp. of liquid  $\text{O}_2$ , for  $\text{CS}_2$  and  $\text{COMe}_2$  between  $294^\circ$  and  $213^\circ\text{K}$ , and for  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  between  $45^\circ$  and  $0^\circ$ , on glass plates have been determined. In the case of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  no further adsorption takes place above  $180^\circ$ . This is also true of  $\text{H}_2$  and  $\text{O}_2$  at high temp. In the range of pressures where the equilibrium pressure is of the same order as the saturation pressure the adsorption curves rise rapidly, but the slope decreases where a layer 2 mols. thick is formed. Where the equilibrium pressure is small compared with the saturation pressure, a unimol. layer only is formed, and the adsorption curve can be analysed by means of Langmuir's equation. The results for bimol. layers agree with the theory of Brunauer *et al.* (A., 1938, I, 190), except in the case of  $\text{O}_2$ , where they are in agreement with the theory of Zeise (A., 1928, 1182).

A. J. M.

**Mixed adsorption of amylene and ethylene on activated charcoal.** A. Magnus and A. Spalt (*Z. physikal. Chem.*, 1941, B, 49, 187–195).—The adsorption of amylene (I) at  $100^\circ$  and of  $\text{C}_2\text{H}_4$  at  $0^\circ$  and  $100^\circ$  on activated C has been investigated. The results do not agree well with the simple adsorption formulae of Freundlich and Langmuir, but in the case of  $\text{C}_2\text{H}_4$  at  $100^\circ$  the data fit the formula  $1/A = 0.0202 + (27.55/p) - (1200/p^2)$  with fair accuracy ( $A$  = wt. adsorbed,  $p$  = pressure in mm.). The adsorption of a mixture of (I) and  $\text{C}_2\text{H}_4$  was also studied. (I) blocks the most active spots without being affected by the  $\text{C}_2\text{H}_4$ .

A. J. M.

**Van der Waals sorption of chlorine by silica gel at low temperatures.** L. H. Reyerson and C. Bemmels (*J. Physical Chem.*, 1942, 46, 31–35).—The sorption of  $\text{Cl}_2$  by  $\text{SiO}_2$  gel at  $30.2^\circ$ ,  $0^\circ$ , and



—25–3° over the pressure range 0–732 mm. Hg has been determined in order to extend the range of earlier data (cf. A., 1937, I, 611). The data conform to Brunauer's sorption theory. C. R. H.

**Van der Waals sorption of gaseous hydrogen chloride, hydrogen bromide, and hydrogen iodide by silica gel.** L. H. Reyerson and C. Bemmels (*J. Physical Chem.*, 1942, 46, 35–42).—The sorptions of HCl, HBr, and HI by SiO<sub>2</sub> over a wide range of temp. and pressure have been determined. The sorptions of the three acids show regular behaviour and are very similar, and also appear similar to the sorption of Cl<sub>2</sub>. The data are in general agreement with Brunauer's sorption theory. C. R. H.

**Adsorptive properties of synthetic resins.** V. S. S. Bhatnagar and M. Sarup (*J. Indian Chem. Soc.*, 1941, 18, 447–452).—Acids are adsorbed by basic resins (A., 1937, I, 234) in the order HI > HCl > HBr; HNO<sub>3</sub> > H<sub>2</sub>SO<sub>4</sub> > H<sub>3</sub>BO<sub>3</sub>; and H<sub>2</sub>CrO<sub>4</sub> > HClO<sub>4</sub> > H<sub>2</sub>SO<sub>4</sub> > H<sub>3</sub>PO<sub>4</sub>. Bases are adsorbed by both basic and acid resins in the order Ba(OH)<sub>2</sub> > Sr(OH)<sub>2</sub> > Ca(OH)<sub>2</sub> and KOH > NaOH > LiOH > NH<sub>4</sub>OH. For basic resins halogens are adsorbed in the order I > Br > Cl, and in salts Rb<sup>+</sup> > K<sup>+</sup> > Na<sup>+</sup> > Li<sup>+</sup> and I<sup>-</sup> > Br<sup>-</sup> > Cl<sup>-</sup>. It is concluded that at the resin-H<sub>2</sub>O interface of a basic resin, the mol. of the sorbate will orient itself in such a way that the polar group is towards the resin, so that the greater is the polarisability of the sorbate in solution the greater will be the adsorption. The reverse holds for acid-condensed phenolic resins. F. R. G.

**Application of the Gibbs adsorption equation to solutions of paraffin-chain salts.** A. E. Alexander (*Nature*, 1941, 148, 752).—A discussion. L. S. T.

**Sorption of soluble dyes by gelatin.** S. E. Sheppard, R. C. Houck, and C. Dittmar (*J. Physical Chem.*, 1942, 46, 158–176).—The sorption of tartrazine, Alizarin Rubine R, anthraquinone-blue, thiacarbocyanine, and methylene-blue by two types of gelatin, CaO-process with isoelectric point at  $p_H$  4.77 and acid-process with isoelectric point at  $p_H$  8.2, has been investigated. The dye is taken up according to a reversible action between protein cation and dye anion in the case of acid dyes, and between protein anion and dye cation in the case of basic dyes. Dye distribution is governed by  $p_H$ , neutral salt content, and dye concn. Buffered solutions dye more strongly than the unbuffered, particularly below the isoelectric point. C. R. H.

**Calculation of the surface area of microporous solids from measurements of heat conductivity.** S. S. Kistler (*J. Physical Chem.*, 1942, 46, 19–31).—A derived equation connecting the mean free path,  $L$ , in a microporous solid with the internal surface area,  $A$ , permits the calculation of  $A$  from thermal conductivity data. The calc. vals. of  $L$  for samples of SiO<sub>2</sub> aerogel are  $\sim 6 \times 10^{-6}$  cm. which yield  $\sim 4 \times 10^6$  sq. cm. per g. for  $A$ , a val. verified by adsorption data. The thermal conductivity of SiO<sub>2</sub> aerogel diminishes slightly as the density increases from 0.025 to  $\sim 0.2$ , but further increase in  $d$  is accompanied by a rapid increase in thermal conductivity. C. R. H.

**Structure of surfaces of solutions.** A. E. Alexander (*Trans. Faraday Soc.*, 1942, 38, 54–63).—Contrary to the interpretation by McBain and co-workers of surface tension and surface pressure data (cf. A., 1941, I, 333; 1940, I, 356, and earlier abstracts), which assumes the formation of a surface pellicle or of a complex adsorption layer, a study of force-area curves for Ph-[CH<sub>2</sub>]<sub>2</sub>-CO<sub>2</sub>H and C<sub>12</sub>H<sub>25</sub>-SO<sub>3</sub>H solutions indicates that all the experimental data are consistent with the formation of no more than a unimol. layer, when due account is taken of the slowness of the rate of dissolution of surface layers when compressed. Failure of the Gibbs theorem is apparent only when the solutions studied are so conc. that they contain aggregated mols. or micelles. F. L. U.

**Diffusion of gases through high-polymeric substances. I. Simple apparatus for measurement of diffusion of gases through films.** F. H. Müller (*Physikal. Z.*, 1941, 42, 48–53).—In one type of apparatus gas passing through the film under test is condensed in a small reservoir and measured manometrically. In a second type for non-condensable gases the measurement is made in an adapted McLeod gauge in which gas diffuses directly into the larger reservoir. The apparatus gives results accurate to 5–10%; the time taken by a measurement (excluding time required to reach the stationary state) is from 1 min. [permeable films, e.g., cellulose acetate (I)] to  $>1$  hr. (rubber 1 mm. thick). Typical diffusion const. data are given for H<sub>2</sub>O in polystyrene, polyvinyl chloride, benzylcellulose, and (I), and for H<sub>2</sub>, He, H<sub>2</sub>O, Ne, O<sub>2</sub>, A, Kr, and Xe in (I). A. J. E. W.

**Structure and electrical behaviour of colloid membranes. III. Base-exchange properties of colloidion.** K. Sollner, C. W. Carr, and I. Abrams (*J. Gen. Physiol.*, 1942, 25, 411–429; cf. A., 1941, I, 466; Beutner, *et al.*, A., 1933, 900).—Although theoretical considerations indicate that the electrochemical properties of colloidion are determined by its content of dissociable acidic groups and that the base-exchange capacity of colloidion preps. is a measure of that content, chemical and electrometric titration of preps. of varied origin, pretreated in various ways and having widely varying electrochemical properties, shows no regular correlation between electro-

chemical activity and base-exchange capacity. Although large capacity is apparently always associated with moderate or great activity, very low capacity is associated sometimes with high, sometimes with low, activity. The significance of these findings for the problem of the structure of colloidion membranes is discussed. W. McC.

**Thirty years of colloid chemistry.** W. D. Bancroft (*J. Physical Chem.*, 1942, 46, 1–9).—A lecture. C. R. H.

**Foam time. I. Method of measuring foam time. Experiments with saponin and methylcellulose. II. Experiments with aliphatic alcohols. Relation between chain length and foam time. Critical foam time and conjugate foaming solutions.** F. Schütz (*Trans. Faraday Soc.*, 1942, 38, 85–93, 94–104).—I. Foam time ( $t_f$ ) is defined as the duration of foam produced under standard conditions, and is a more satisfactory criterion of stability than vol., height, or size of bubbles.  $t_f$  is influenced by the temp. and humidity of the external air, by the time of passage of gas bubbles through the liquid, and in many cases by the age of the solution. An arrangement is described in which these factors can be controlled. Measurements with saponin (I) solutions show that  $t_f = ac^b$  ( $c$  = concn.); two samples of (I) showing only very small differences in surface tension gave relatively large differences in  $t_f$ . A similar relation was found with fractions of H<sub>2</sub>O-sol. methylcellulose of different mol. wts.; with these the log  $t_f$ -log  $c$  graphs are approx. parallel and  $t_f$  increases with the mol. wt.

II.  $t_f$ - $c$  curves for aq. solutions of the first five saturated aliphatic  $n$ -alcohols exhibit a max. at concns. ( $c'$ ) that diminish with the mol. wt. according to  $c' = ab^n$ , where  $n$  is the no. of C atoms in the alcohol and  $a$  and  $b$  are consts. With BuOH the  $n$ - and  $sec$ -alcohols show a definite max.; BuOH and Bu'OH do not. Solutions on either side of the max. having equal  $t_f$  vals. are termed conjugate foaming solutions; their foams behave differently towards staining reagents and are therefore not identical, although they have the same stability.  $t_f$ - $c$  curves for mixtures still exhibit the max. characteristic of one or more of the components. F. L. U.

**Electrochemical character of colloids. Relation between the activity and conductivity coefficients.** W. Pauli (*Helv. Chim. Acta*, 1941, 24, 1253–1284).—A review. F. J. G.

**Intermediate colloid state in the formation of gold and platinum ions.** C. G. Fink (*J. Physical Chem.*, 1942, 46, 76–81).—When Au and Pt dissolve anodically they pass through an intermediate colloid phase which can be isolated if the rate of formation of colloid from cryst. metal is  $>$  the rate of transition of colloid into metallic ion. The working conditions leading to such isolation of colloid have been investigated. Similar experiments with Cu and Ag have been unsuccessful. Possible applications of the method are discussed. C. R. H.

**Study of the surface of colloidal particles of zirconium dioxide sols.** I. V. A. Kargin and V. V. Kiseleva (*Acta Physicochim. U.R.S.S.*, 1940, 12, 377–396).—Absorption spectra of dyes adsorbed on ZrO<sub>2</sub> sols and in presence of various electrolytes are recorded and compared. It is concluded that the ion which determines the potential of the colloidal particles is [Zr<sub>2</sub>O<sub>3</sub>. $n$ H<sub>2</sub>O]<sup>+</sup>. F. J. G.

**Depolarisation of the Tyndall-scattered light of bentonite and ferric oxide sols.** C. R. Hoover, F. W. Putnam, and E. G. Wittenberg (*J. Physical Chem.*, 1942, 46, 81–93).—An apparatus, based on the Cornu method, has been devised for determining the degree of depolarisation of the transversely scattered light of colloidal dispersions and has been tested with bentonite and Fe<sub>2</sub>O<sub>3</sub> sols. The Krishnan relation is valid for both sols whether unoriented or oriented by an electric field. The application of the method to the determination of particle size is described. C. R. H.

**Studies on solubilisation.** R. C. Merrill, jun., and J. W. McBain (*J. Physical Chem.*, 1942, 46, 10–19).—Solubilisation is the spontaneous formation of thermodynamically stable colloidal particles of detergent and otherwise insol. material. The solubilities of Orange OT and Yellow AB in 1% solutions of anionic, cationic, and non-electrolytic detergents and of the former dye in 0.01N. solutions of colloidal electrolytes have been determined and compared. The solubilisation of liquids and the passage of solubilised dyes through semipermeable membranes are distinct from emulsification and from suspending or protective action respectively. Five theories of solubilisation are discussed. C. R. H.

**Electrochemical properties of mineral membranes. II. Measurement of potassium-ion activities in colloidal clay.** C. E. Marshall and W. E. Bergman (*J. Physical Chem.*, 1942, 46, 52–61).—Using as a membrane electrode a film of electrolysed bentonite dried at 490°, measurement of K<sup>+</sup> activities from 0.1N. to 0.0001N. in agar and in montmorillonite (I), beidellite (II), illite (III), and kaolinite (IV) have been made. The K salt of agar behaves as a typically strong electrolyte, whereas the K salts of the clays are weaker electrolytes, the order of strength being (I)  $>$  (III)  $>$  (II)  $>$  (IV). The electrochemical behaviours of (I), (II), and (III), are similar, but (IV) differs in having a low exchange capacity and showing much less evidence of passing into true solution than the other clays. The addition of KCl and K phthalate gives no evidence of interionic



effects between  $K'$  associated with the clays and those added salts. C. R. H.

**Mol. wts. of rubber and related materials. III. Correction. IV. Micellar theory of structure of rubber.** G. Gee (*Trans. Faraday Soc.*, 1942, 38, 108—109, 109—115).—III. Data in part II (A., 1941, I, 12) are corr.

IV. Data for the mol. wt. of rubber (I) obtained by the Rast method [micro-determination of f.p. of solutions of (I) in camphor (II)] have been made the basis of a theory of the micellar structure of (I). The dissolution of (I) in (II) at the required temp., 180°, in presence of air is shown to result in extensive degradation of (I). If the solutions are prepared in a vac. (II) shows no essential difference from other solvents of (I), all of which give apparent "mol. wts." that depend on the concn. and are nearly independent of the nature of (I) except in dil. solution. The evidence hitherto used in support of the micellar theory is therefore unsound, and the osmotic units the size of which has been previously recorded are to be considered as true macromols. F. L. U.

**Constitution of three-dimensional polymerides and the theory of gelation.** P. J. Flory (*J. Physical Chem.*, 1942, 46, 132—140).—Comparison is made between the accelerating effect of pressure and temp. changes on certain gas-phase explosions and the effect of a change in the total no. of intermol. linkings on the formation of gels from three-dimensional polymerides, the distinction between gel and sol being analogous to that between a liquid and its saturated vapour. The theory is applied to the consideration of raw rubber and to protein and inorg. gels. C. R. H.

**Statistical treatment of crystallisation phenomena in high polymerides.** T. Alfrey and H. Mark (*J. Physical Chem.*, 1942, 46, 112—118).—An explanation of the anomalous aspects of high-polymeride crystallisation on the basis of free energy changes in the amorphous segments is offered. The entropy of the amorphous phase depends on temp., pressure, degree of extension, and the fraction of cryst. material in the sample. The crystallisation of stretched and unstretched rubber and the spontaneous extension of rubber are explainable on the basis of the proposed theory. C. R. H.

**Rigidity and moisture hysteresis in gels.** W. W. Barkas (*Nature*, 1941, 148, 690).—A correction (A., 1942, I, 144). L. S. T.

**Denaturation of proteins and its apparent reversal. III.** H. Neurath, G. R. Cooper, and J. O. Erickson (*J. Physical Chem.*, 1942, 46, 203—211).—A crit. survey of available data offers no reliable evidence for strictly reversible denaturation. (Cf. A., 1942, III, 417.) C. R. H.

**State of aggregation of gelatin in non-gelating systems.** E. O. Kraemer (*J. Physical Chem.*, 1942, 46, 177—182).—Recent work (cf. A., 1941, I, 262) has been extended to solutions of gelatin in 1.0M-CS(NH<sub>2</sub>), 8% Na salicylate, and PO<sub>4</sub><sup>'''</sup> buffer. The difference in the sedimentation behaviour in the different solvents is not marked. The difference between the diffusion consts. is also small except for PO<sub>4</sub><sup>'''</sup> buffer, the val. being very low at 20° and very high at 34.4°. Taken as a whole, the present data confirm earlier conclusions regarding mol. state and the degree of folding and coiling of the mol. C. R. H.

**Electrophoresis of rabbit papilloma virus protein.**—See A., 1942, III, 354.

**Progressive boundary spread in electrophoresis of proteins in solution.**—See A., 1942, III, 341.

**Comparison of the effects of neutron and  $\gamma$ -ray ionisation on the electrophoretic mobility of colloidal graphite particles.** L. H. Gray, J. Read, and H. Liebmann (*Brit. J. Radiol.*, 1941, 14, 102—106).—The effects are qualitatively similar, but the amount of  $\gamma$ -ray ionisation required to produce a given change in electrophoretic mobility is  $\gg$  that of neutron ionisation, a ratio of 8 being obtained for a particular graphite sample. Implications relative to the phenomenon itself and to the problem of the biological action of neutron rays are discussed. N. M. B.

**Moving boundary methods for determination of cataphoretic speed of colloids. II.** N. C. Sen-Gupta and P. R. Sinha (*J. Indian Chem. Soc.*, 1941, 18, 489—502; cf. A., 1939, I, 78).—The Kohlrausch and Weber relation has been verified for mixtures of KCl and KIO<sub>3</sub> in which the conductivity of the micelle ions is comparable with those of the intermicellar electrolytes. Concordant cataphoretic speeds for two Fe<sub>2</sub>O<sub>3</sub> and two Al<sub>2</sub>O<sub>3</sub> sols are given by the moving boundary and the transport methods. F. R. G.

EtOH indicate that decrease of  $\epsilon$  favours Cu<sup>I</sup>. Complex formation with NH<sub>3</sub> favours Cu<sup>I</sup>, but with org. diamines favours Cu<sup>II</sup>.

F. J. G.  
**Potentiometric measurements for the determination of complex ions in cadmium salt solutions.** I. Leden (*Z. physikal. Chem.*, 1941, A, 188, 160—181).—Complex ion formation in Cd salt solutions has been studied by a potentiometric method. The following species are indicated: CdX<sup>+</sup>, CdX<sub>2</sub>, CdX<sub>3</sub><sup>+</sup> (X = Cl, Br, I, CNS), CdBr<sub>4</sub><sup>''</sup>, CdI<sub>4</sub><sup>''</sup>, CdNO<sub>3</sub><sup>+</sup>, CdSO<sub>4</sub>, and probably Cd<sub>2</sub>Br<sub>3</sub><sup>+</sup>. The concn. of the various complexes as functions of the anion concn. are recorded in composition diagrams. F. J. G.

**Steric hindrance.** I. L. Gauditz (*Z. physikal. Chem.*, 1941, B, 48, 228—237).—The proportion of semi-acetal in equilibrium mixtures arising from dissolution of EtCHO in various alcohols, with or without the presence of C<sub>2</sub>H<sub>5</sub>I<sub>18</sub>, has been determined by measurement of their absorption in the ultra-violet spectral region. The results are discussed in relation to steric hindrance effects (cf. A., 1931, 573). J. W. S.

**Disorder in the region of complexity phenomena.** A. Smits (*Z. physikal. Chem.*, 1941, B, 49, 21—26).—Certain phenomena in the Schottky effect are in close agreement with the considerations of inner equilibria. Disorder occurs in the limiting range of complexity phenomena. Within these limiting ranges lie complexity phenomena which can be elucidated only by thermodynamic studies combined with data from infra-red and Raman spectra. W. R. A.

**Elementary formulation of statistical mechanics.** H. Eyring and J. Walter (*J. Chem. Educ.*, 1941, 18, 73—78). L. S. T.

**Osmotic pressure. II.** H. Frahm (*Z. physikal. Chem.*, 1941, B, 48, 119—123; cf. A., 1940, I, 19).—Thermodynamic and kinetic considerations lead to the conclusion that the relative lowering of v.p. is independent of the vol. of the liquid phase and the no. of mols. of liquid per c.c. This is contrary to the deductions of Frenkel. A. J. M.

**Osmotic coefficients of some organic compounds in relation to their chemical constitution.** R. A. Robinson, P. K. Smith, and E. R. B. Smith (*Trans. Faraday Soc.*, 1942, 38, 63—70).—Data are tabulated for isopiestic concns. of sucrose (I) (0.27—5.86M.) against KCl, and v.p. and osmotic coeffs. of (I) solutions are evaluated. With (I) as reference substance isopiestic measurements for solutions of *d*- and *dl*-tartaric acids and of *d*-, *l*-, and *dl*-alanine disclose no difference in the v.p. of the optically active and racemic compounds. Similar measurements with succinic, maleic, malic, and tartaric acids show that the introduction of OH causes a marked increase in the osmotic coeff. of the acid. Osmotic and activity coeffs. of Na fumarate are > those of Na maleate; this is consistent with the formation of ion-pairs in the *cis*-compound. F. L. U.

**Vapour pressures and osmotic coefficients of solutions of sodium salts of fatty acids at 25°.** E. R. B. Smith and R. A. Robinson (*Trans. Faraday Soc.*, 1942, 38, 70—78).—Isopiestic data are tabulated for solutions of the Na salts of fatty acids C<sub>1</sub>—C<sub>10</sub>, the reference substance being KCl. Osmotic ( $\phi$ ) and activity coeffs. are given for molalities (*m*) 0.1—5.0. The data are consistent with micelle formation in PrCO<sub>2</sub>Na and the higher salts, together with association between Na<sup>+</sup> and the polymerised anions. In a plot of (1— $\phi$ )/ $\sqrt{m}$  against  $\sqrt{m}$  the curves for the C<sub>6</sub> and C<sub>8</sub> salts almost coincide, at the higher concns., with similar curves for Ca(NO<sub>3</sub>)<sub>2</sub> and K<sub>4</sub>Fe(CN)<sub>6</sub>, respectively. This suggests that salts C<sub>4</sub>—C<sub>6</sub> may tend to form double, and C<sub>8</sub>—C<sub>10</sub> quadruple, polymerides. F. L. U.

**Properties of solutions of long-chain compounds.** M. L. Huggins (*J. Physical Chem.*, 1942, 46, 151—158).—Mathematical. Equations for the activities of the components of a solution containing chain and non-chain mols. have been derived. With their aid relations for osmotic pressure, lowering of f.p., and solubility have been derived. C. R. H.

**Velocity of hydration and dehydration of nickel sulphate.** B. N. Ghosh (*J. Indian Chem. Soc.*, 1941, 18, 472—476).—The hydration curve of NiSO<sub>4</sub>·7H<sub>2</sub>O plotted as the no. of mols. of H<sub>2</sub>O lost as a function of the time shows sharp changes of direction at the transition points corresponding with NiSO<sub>4</sub>·4H<sub>2</sub>O and NiSO<sub>4</sub>·H<sub>2</sub>O. The process of hydration is more complex. F. R. G.

**Zirconia-magnesia spinel system.** R. F. Mather (*J. Amer. Ceram. Soc.*, 1942, 25, 93—96).—The oxide mixtures were fired for a total of 6 hr. at 1650° and the thermal expansion, *d*, and microstructure of the product were determined. No stable compounds or solid solutions were found but an unstable solution, decomp. on repeated heating to 1300°, formed over the range 0—30% of ZrO<sub>2</sub>. The decomp. product was an aggregate of ZrO<sub>2</sub> and spinel. The ZrO<sub>2</sub> transformation (heating curve) at 1110° was observed throughout the range of composition but transformation points on the cooling curve were lowered, by the presence of spinel, to 990° and 630° for the ZrO<sub>2</sub>- and spinel-rich ends of the system respectively. J. A. S.

**Equilibrium between vapour and liquid phases in the system CO<sub>2</sub>-H<sub>2</sub>O-K<sub>2</sub>O-SiO<sub>2</sub>.** G. W. Morey and M. Fleischer (*Bull. Geol. Soc. Amer.*, 1940, 51, 1035—1057).—Technique and apparatus for the

## VI.—KINETIC THEORY. THERMODYNAMICS.

**Equilibrium between cuprous and cupric compounds in presence of metallic copper.** J. E. B. Randles (*J.C.S.*, 1942, 802—811).—The equilibrium  $2\text{Cu}^+ \rightleftharpoons \text{Cu}^{2+} + \text{Cu}$  is discussed theoretically, and it is shown that with simple ionic binding the equilibrium lies far over to the right, but that covalent binding tends to favour Cu<sup>I</sup>, in accordance with the known behaviour of the solid salts and their aq. solutions. Measurements on the equilibrium in anhyd. MeOH and



separation and independent analysis of liquid and vapour phases are described. Data for the equilibrium between vapour and liquid in the system  $\text{CO}_2\text{--H}_2\text{O--K}_2\text{O--SiO}_2$  at  $500^\circ$  are tabulated, and presented graphically. Partial pressures of  $\text{H}_2\text{O}$  ranged up to 400 atm., and of  $\text{CO}_2$  up to 25 atm. The mixtures had ratios of  $\text{K}_2\text{O}:\text{SiO}_2$  from 1:1 to 1:4. The distribution ratios of the fraction of  $\text{CO}_2$  in the vapour to the ratio of the % of  $\text{CO}_2$  to  $\text{H}_2\text{O}$  in the liquid indicate the tendency of the metasilicate melts to retain  $\text{CO}_2$ , and of the more siliceous mixtures to expel it. With a fall in pressure at const. temp. and ratio  $\text{K}_2\text{O}:\text{SiO}_2$ , the composition of the vapour changes towards higher  $[\text{CO}_2]$ . Data showing the rate of dissolution of quartz in aq.  $\text{KHCO}_3$  at  $340\text{--}424^\circ$  for varying times are recorded. L. S. T.

**Calorimetry of aqueous solutions of borax, ferrous sulphate, copper nitrate, and magnesium nitrate.** J. Perreu (*Compt. rend.*, 1941, 213, 286—289).—Thermochemical data for the dissolution of these salts in  $\text{H}_2\text{O}$  at room temp. are recorded. L. S. T.

**Photometric investigation of the free energy of formation of aqueous nitrosyl chloride.** H. Schmid and A. Maschka (*Z. physikal. Chem.*, 1941, B, 49, 171—186).—The equilibrium of the reaction  $\text{NOCl (aq.)} + \text{H}_2\text{O (l.)} = \text{HNO}_2\text{ (aq.)} + \text{HCl (aq.)}$  has been investigated. The  $\text{NOCl}$  was determined photometrically, making use of its strong yellow colour, and the equilibrium was studied from the right-hand side by the addition of  $\text{HCl}$  to  $\text{NaNO}_2$ . The thermodynamic equilibrium const. at  $25^\circ$ ,  $K = (a_{\text{HNO}_2} \cdot a_{\text{HCl}})/(a_{\text{NOCl}} \cdot a_{\text{H}_2\text{O}}) = (0.88 \pm 0.04) \times 10^3$ . The free energy of the reaction  $\Delta G^\circ = -4019$  g.-cal. The free energy of formation of aq.  $\text{NOCl}$  at  $25^\circ$  is 16,015 g.-cal. A. J. M.

**Heats of isomerisation of the nine heptanes.** E. J. R. Prosen and F. D. Rossini (*J. Res. Nat. Bur. Stand.*, 1941, 27, 519—528; cf. A., 1942, I, 24).—The heats of isomerisation in the liquid state at  $298^\circ \text{K.}$  and in the gas at  $298^\circ$  and  $0^\circ \text{K.}$  have been calc. for  $\beta$ - and  $\gamma$ -methylhexane from the corresponding vals. for the isomerisation of  $n$ -hexane into  $\beta$ - and  $\gamma$ -methylpentane and of  $n$ -octane into  $\beta$ - and  $\gamma$ -methylheptane. Similar data for the other heptanes have been determined from their heats of combustion in the liquid state. J. W. S.

**Free energies and equilibria of isomerisation of the butanes, pentanes, hexanes, and heptanes.** F. D. Rossini, E. J. R. Prosen, and K. S. Pitzer (*J. Res. Nat. Bur. Stand.*, 1941, 27, 529—541).—The function  $\Delta G^\circ/T$  ( $\Delta G^\circ$  = standard free energy of isomerisation) and the relative amounts of the several isomerides present at equilibrium are calc. for all  $\text{C}_4\text{H}_{10}$ ,  $\text{C}_5\text{H}_{12}$ ,  $\text{C}_6\text{H}_{14}$ , and  $\text{C}_7\text{H}_{16}$  isomerides. For mixtures containing the two butanes, two pentanes, or four hexanes the results are in accord with directly measured equilibrium concns. At  $25^\circ$  the  $n$ -isomeride is thermodynamically the least stable in each case, excepting that  $\gamma$ -ethylpentane is less stable than  $n$ - $\text{C}_5\text{H}_{12}$ , whilst the  $\beta$ - $\text{Me}_2$  isomeride is the most stable. Relative to the other isomeride the  $n$ - and  $\beta$ -dimethyl-isomerides increase and decrease in stability, respectively, with rising temp., till at  $1000^\circ \text{K.}$  they are among the most stable and least stable isomerides, respectively. J. W. S.

## VII.—ELECTROCHEMISTRY.

**Electrical conductivities of aqueous solutions of some phenanthrene-sulphonic acids.** T. R. Bolam and J. Hope (*J.C.S.*, 1941, 843—849).— $\Lambda$  and  $\rho$  for aq. solutions of  $p$ - $\text{C}_6\text{H}_4\text{MeSO}_3\text{H}$  (I), phenanthrene-2- and -3-sulphonic acid, 9-chloro- and 9-bromo-phenanthrene-3-sulphonic acid have been determined at  $18^\circ$  and  $25^\circ$  over a wide range of concn. (I) behaves throughout as a simple strong electrolyte.  $\Lambda$  for the other acids agrees with the Onsager theory at sufficiently high dilution, but micelle formation occurs at higher concn. F. J. G.

**Relation of electromotive force to the concentration of deuterium oxide in saturated standard (cadmium) cells.** L. H. Brickwedde and G. W. Vinal (*J. Res. Nat. Bur. Stand.*, 1941, 27, 479—489).—Previous measurements (A., 1938, I, 402) have been extended to standard Weston cells containing up to 98-mol.-% of  $\text{D}_2\text{O}$ . Over the range 0—50 mol.-%  $\text{D}_2\text{O}$  the e.m.f. is decreased by 3.6  $\mu\text{V.}$  per mol.-% of  $\text{D}_2\text{O}$ , but the decrease is slightly greater with >50 mol.-%  $\text{D}_2\text{O}$ , the e.m.f. in 98 mol.-%  $\text{D}_2\text{O}$  being 388  $\mu\text{V.}$  < in normal  $\text{H}_2\text{O}$ . The temp. coeff. is almost independent of the  $\text{D}_2\text{O}$  content and evidence is obtained that with high  $\text{D}_2\text{O}$  contents the hysteresis is slightly <, and the cell resistance slightly >, in normal  $\text{H}_2\text{O}$ . During 4 years the constancy of the cells was equal. The difference between the partial mol. free energy of  $\text{CdSO}_4$  in  $\text{H}_2\text{O}$  and in  $\text{D}_2\text{O}$  is calc. J. W. S.

**Electrode polarisation. Automatic control of potential of a working electrode.**—See A., 1942, I, 157.

**Effect of surface-active agents on electro-organic reductions.** C. W. Proudfit and W. G. France (*J. Physical Chem.*, 1942, 46, 42—51).—The effect of various types of wetting agents on the reduction of the depolarisers  $\text{COPhMe}$ ,  $\text{CCl}_3\text{NO}_2$ , pyrrole,  $o$ - $\text{C}_6\text{H}_4\text{MeNO}_2$ ,  $m$ - and  $p$ -tolualdehyde, and anisaldehyde is to decrease the current efficiency (C) of the process, the greatest lowering being observed

with those wetting agents which are efficient foam producers. Changes in C with increase in concn. of wetting agent conform to three types: (1) gradual reduction of C in the case of moderately strong wetting agents of the anion-active type; (2) decrease in C followed by a rise in the case of strong wetting agents of the anion-active type; (3) rapid decrease in C followed by const. C with strong wetting agents of the cation-active type. The effects of anion-active and cation-active wetting agents are respectively attributed to the ability to stabilise emulsions of org. liquids in aq. solutions, and the saturation of the cathode surface by low concns. of wetting agent which partially excludes the depolariser from the reducing zone of the cathode. C. R. H.

## VIII.—REACTIONS.

**Kinetics of the thermal decomposition of straight-chain paraffins.** R. E. Burk, L. Laskowski, and H. P. Lankelma (*J. Amer. Chem. Soc.*, 1941, 63, 3248—3250).—The constancy of the calc. energies of activation for the thermal decomp. of  $n$ -paraffins on the basis of scission of C—C bonds to form an olefine and a new hydrocarbon (A., 1931, 1131) is taken to corroborate the mechanism. A simplified chain mechanism is considered but it predicts a rate of decomp. > the experimental rate. W. R. A.

**Reaction rates of oxidation of liquid acetaldehyde.**—See B., 1942, II, 89.

**Influence of hydroxyl ion concentration on the autoxidation of quinol.** J. R. Green and G. E. K. Branch (*J. Amer. Chem. Soc.*, 1941, 63, 3441—3444).—The expression  $-d(\text{O}_2)/dt = k[\text{O}_2][\text{C}_6\text{H}_4(\text{OH})_2][\text{OH}^-]^{3/2}$  (A., 1924, i, 281) for the rate of autoxidation of quinol has been confirmed and a chain mechanism has been proposed for the reaction. W. R. A.

**Surface phenomena in the recrystallisation of supercooled liquids in thin layers.** III. G. L. Mischnevitch and I. Brovko (*Acta Physicochim. U.R.S.S.*, 1940, 12, 444—446; cf. A., 1940, I, 110).—The curve of rate of formation of nuclei in supercooled Betol (in a thin film between glass plates) against temp. usually shows two max., but after treatment of the plates with HF only one max. remains. F. J. G.

**Influence of low-frequency elastic vibrations on the crystallisation of a supercooled organic liquid.** I. G. L. Mischnevitch and P. I. Dombrovski (*Acta Physicochim. U.R.S.S.*, 1940, 12, 437—443).—Low-frequency (sound) vibrations diminish both the rate of formation of nuclei and the rate of their growth in the recrystallisation of undercooled Betol, and the effect persists for a time after the sound is cut off. F. J. G.

**Thermal decomposition of acetone catalysed by iodine.** G. M. Gantz and W. D. Walters (*J. Amer. Chem. Soc.*, 1941, 63, 3412—3419; cf. A., 1940, I, 261).—The homogeneous thermal decomp. of  $\text{COMe}_2$  is catalysed by I. The products have been analysed and from the analyses and the pressure increase it is concluded that the overall reaction is  $\text{COMe}_2 = 1.5\text{CH}_4 + \text{CO} + 0.5\text{C}$ . The decomp. is retarded by  $\text{NO}$ ,  $\text{C}_2\text{H}_6$ , and  $\text{C}_2\text{H}_4$ . The effect of adding  $\text{MeI}$  was comparable to that of I;  $\text{EtI}$  was less effective, and  $\text{Pr}^n\text{I}$  had practically no effect. As the pressure of I is increased the catalytic effect increases to a max. and then decreases to a const. val. I catalyses the decomp. of  $\text{COMeEt}$ ,  $\text{COEt}_2$ ,  $\text{Ac}_2\text{O}$ , dioxan, and tetrahydrofuran. From spectroscopic observations I disappears for a period during the decomp. W. R. A.

**Acid catalysis in relation to concentration and activity of hydrogen ions.** M. Duboux [with Rochat, Favre, Matavulj, Jaccard, and de Souza] (*Bull. Soc. vaud. Sci. nat.*, 1937, 59, 279—320; *Chem. Zentr.*, 1938, ii, 3908).—The rates of inversion of sucrose (I) and decomp. of  $\text{CHN}_2\text{CO}_2\text{Et}$  have been determined in org. solvents at  $25^\circ$  and  $75^\circ$ , in presence of various org. acids and their salts. The val. of the const.  $k_H$  in  $k = k_H[\text{H}^+]$  increases with the concn. (c) of the catalysing acid, and reference must be made to the relation between  $k_H$  and c if  $[\text{H}^+]$  is to be determined to within 1—3% by measurement of  $k$ . A study of the inversion of (I) at  $25^\circ$ , in aq.  $\text{HCl}$  or aq.  $\text{HCl}$  containing  $\text{NaCl}$ ,  $\text{NH}_4\text{Cl}$ , or  $\text{MgCl}_2$ , shows that the relation  $k = k_{\text{HAR}}$  is followed with moderate accuracy. A. J. E. W.

**Acid-catalysed hydrolysis of ethyl esters of aliphatic acids.** H. A. Smith and J. H. Steele (*J. Amer. Chem. Soc.*, 1941, 63, 3466—3469).—The kinetics of acid-catalysed hydrolysis in 70%  $\text{COMe}_2$  has been investigated for  $\text{Et } n$ - and  $iso$ -butyrate,  $n$ - and  $iso$ -hexoate,  $n$ -nonoate,  $\beta$ -methylvalerate, and cyclohexanecarboxylate. The effects of the character of an alkyl group are similar on the rate of acid- and base-catalysed hydrolysis of esters of aliphatic acids and on the rate of acid-catalysed esterification of the corresponding acids. W. R. A.

**Base-catalysed decomposition of nitramide in aqueous solution.** L. K. J. Tong and A. R. Olson (*J. Amer. Chem. Soc.*, 1941, 63, 3406—3411).—The rate coeffs. for the decomp. of nitramide in aq. solutions containing the following ions have been measured:  $\text{OH}^-$ ,  $\text{OPh}^-$ , 2:4-dichloro-, 2:4-dinitro-,  $o$ -nitro-phenoxide,  $\text{OBz}^-$ ,  $\text{CN}^-$ , and nitramide. The curve of log sp. rate of catalysis—log basic



const. of catalyst agrees with that postulated by Brønsted and Pedersen (A., 1924, ii, 306). W. R. A.

**Effect of solvent on some reaction rates.** F. H. Westheimer and W. A. Jones (*J. Amer. Chem. Soc.*, 1941, **63**, 3283—3286).—The rate of amine-catalysed dealdolisation (i) of diacetone alcohol, and the rates of uncatalysed (ii) and amine-catalysed decarboxylation of  $\text{CMe}_2\text{Ac}\cdot\text{CO}_2\text{H}$  have been measured in  $\text{H}_2\text{O}$ -EtOH and  $\text{H}_2\text{O}$ -dioxan. Since (i) and (ii) are independent of solvent the rate-determining step cannot be the decomp. of a dipolar ion or other highly polar intermediate. Possible mechanisms are discussed. W. R. A.

**Kinetics of the tervalent vanadium-oxygen reaction.** J. B. Ramsey, R. Sugimoto, and H. DeVorkin (*J. Amer. Chem. Soc.*, 1941, **63**, 3480—3486).—The reaction between  $\text{V}^{+++}$  ions and  $\text{O}_2$  has been investigated alone and in the presence of  $\text{Cu}^{++}$  and possible mechanisms have been proposed. Crit. increments have been determined. The different rate vals. obtained for the uncatalysed reaction are attributed to variation in the "dust particle" content of different stock solutions of  $\text{V}^{+++}$  ions. The rate of the uncatalysed reaction is independent of salt concn. but the  $\text{Cu}$ -catalysed reaction has a positive salt effect at ionic strengths from 0.1 to 1.0. A mechanism of the induced catalysis of the  $\text{O}_2$ -I' reaction is suggested.  $\text{O}_2$ ,  $\text{Cu}$ , and I react with hydrolysed  $\text{V}^{+++}$  at a measurable rate. W. R. A.

**Influence of halides on oxidation of ascorbic acid.**—See A., 1942, III, 329.

**Magnetism and catalysis. III. Chlorination of chloroform to carbon tetrachloride in presence of ferric chloride.** S. S. Bhatnagar, N. A. Yajnik, P. L. Kapur, and A. S. Bhatnagar (*J. Indian Chem. Soc.*, 1941, **18**, 350—358).—The chlorination of  $\text{CHCl}_3$  is accelerated by  $\text{H}_2\text{O}$ , but that of moist  $\text{CHCl}_3$  is retarded by  $\text{FeCl}_3$ , and  $\chi$  for the mixture is  $<$  calc. for additivity, suggesting that  $\text{FeCl}_3$  reacts with  $\text{H}_2\text{O}$  forming  $\text{Fe}(\text{OH})_3$  and that this is the inhibitor. F. J. G.

**Magnetism and catalysis. IV. Catalysis of the reaction between ammonium oxalate and mercuric chloride by ferric ions.** S. S. Bhatnagar, P. L. Kapur, A. S. Bhatnagar, and B. Prakash (*J. Indian Chem. Soc.*, 1941, **18**, 371—374).—During the photochemical reaction between  $\text{HgCl}_2$  and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  in presence of  $\text{FeCl}_3$ ,  $\chi$  deviates slightly from the mixture law, indicating the formation of an intermediate compound. F. J. G.

**Magnetism and catalysis. V. Catalytic decomposition of potassium chlorate by cobaltous oxide and ferromagnetic variety of ferric oxide.** S. S. Bhatnagar, P. L. Kapur, A. S. Bhatnagar, and M. A. Qayyum (*J. Indian Chem. Soc.*, 1941, **18**, 391—396; cf. A., 1940, I, 261).— $\chi$  for the products of decomp. of  $\text{KClO}_3$  catalysed by  $\text{Co}_3\text{O}_4$  is  $<$   $\chi$  of the sum of the separate constituents, indicating that there is intermediate formation of  $\text{Co}_2\text{O}_3$  thus:  $2\text{KClO}_3 + 12\text{Co}_3\text{O}_4 \rightarrow [2\text{KCl} + 12\text{Co}_3\text{O}_4 + 3\text{O}_2] \rightarrow 2\text{KCl} + 18\text{Co}_2\text{O}_3 + 3\text{O}_2$ . The spontaneous decomp. temp. of  $\text{KClO}_3$  with magnetic  $\text{Fe}_2\text{O}_3$  is  $330^\circ$  compared with  $350^\circ$  for non-magnetic  $\text{Fe}_2\text{O}_3$ , indicating that the former is a better catalyst. F. R. G.

**Catalytic decomposition of ammonia over iron synthetic ammonia catalysts.** (Miss) K. S. Love and P. H. Emmett (*J. Amer. Chem. Soc.*, 1941, **63**, 3297—3308).—The decomp. of  $\text{NH}_3$  over 3 Fe catalysts has been studied. The kinetics of the reaction over catalyst 931 (1.3%  $\text{Al}_2\text{O}_3$ , 1.59%  $\text{K}_2\text{O}$ ) differ markedly from those of the reaction over catalysts 954 (10.2%  $\text{Al}_2\text{O}_3$ ) and 973 (0.15%  $\text{Al}_2\text{O}_3$ ). The reaction over catalyst 931  $\propto p_{\text{NH}_3}^{0.6}/p_{\text{H}_2}^{0.85}$ , with an apparent energy of activation of  $45,600 \pm 2000$  g.-cal. The reaction kinetics over catalysts 954 and 973 are similar and the rates  $\propto p_{\text{H}_2}$  and  $1/p_{\text{NH}_3}$  for a considerable range of temp. Possible explanations are advanced. W. R. A.

**Vapour-phase partial oxidation of ethyl alcohol.** L. R. Michels and D. B. Keyes (*Ind. Eng. Chem.*, 1942, **34**, 138—146).—A quant. study of the vapour-phase oxidation of EtOH and its oxidation products has been made. Using a platinised  $\text{SiO}_2$  aerogel catalyst, conversion into MeCHO increases with decrease in the velocity ( $v$ ) of EtOH over the catalyst, and the optimum ratio ( $r$ ) of air to EtOH increases with increase in  $v$ . High  $\text{CO}_2$  yields are obtained with high vals. of  $r$ . Dehydrogenation of EtOH can account for only a small proportion of the MeCHO formed during oxidation.  $\text{H}_2\text{O}$  and AcOH have only a small effect on the oxidation. The varying effect of EtOH and of  $\text{H}_2\text{O}$  on the oxidation of MeCHO at different catalyst temp., and the influence of catalyst temp. on the oxidation of AcOH and CO have similarly been investigated. Experiments with plain  $\text{SiO}_2$  catalysts have shown that the effect of Pt is to increase the conversion of EtOH into MeCHO and  $\text{CO}_2$  and to decrease the conversion into AcOH,  $\text{H}_2$ , and CO. No general theory appears able to explain the complex mechanisms involved in the oxidation. C. R. H.

**Catalytic dehydrogenation and condensation of aliphatic alcohols.** II.—See A., 1942, II, 127.

**Catalysts for the polymerisation of benzyl chloride.** O. C. Dermer and E. Hooper (*J. Amer. Chem. Soc.*, 1941, **63**, 3525—3526).—The polymerisation of  $\text{CH}_2\text{PhCl}$  is catalysed by  $\text{AlCl}_3$ ,  $\text{SbCl}_5$ ,  $\text{BCl}_3$ ,

$\text{CdCl}_2$ ,  $\text{NbCl}_5$ ,  $\text{FeCl}_3$ , Ga, In (both added as metal),  $\text{MnCl}_2$ ,  $\text{MoCl}_5$ ,  $\text{PdCl}_2$ ,  $\text{PtCl}_4$ ,  $\text{SnCl}_4$ ,  $\text{SnCl}_2$ ,  $\text{TaCl}_5$ ,  $\text{TiCl}_4$ ,  $\text{WCl}_6$ , uranyl acetate, and  $\text{ZnCl}_2$ , giving thermoplastic resins in approx. theoretical yield. Small amounts of polymeride were produced in presence of  $\text{AuCl}_3$ ,  $\text{BaCl}_2$ ,  $\text{CoCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{LaCl}_3$ ,  $\text{NiCl}_2$ ,  $\text{SeCl}_4$ , and  $\text{TeCl}_4$ . No solid polymeride was formed with  $\text{SbCl}_3$ ,  $\text{AsCl}_3$ ,  $\text{BiCl}_3$ ,  $\text{CaCl}_2$ ,  $\text{CeCl}_4$ ,  $\text{CrCl}_3$ ,  $\text{ICl}_3$ ,  $\text{PbCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{HgCl}_2$ ,  $\text{PCl}_3$ ,  $\text{PCl}_5$ ,  $\text{AgCl}$ ,  $\text{SrCl}_2$ ,  $\text{S}_2\text{Cl}_2$ ,  $\text{TeCl}_4$ ,  $\text{TiCl}_3$ , and  $\text{ThCl}_4$ . W. R. A.

**Applicability of palladium synthetic high polymer catalysts.** L. D. Rampino and F. F. Nord (*J. Amer. Chem. Soc.*, 1941, **63**, 3268).—The superiority of the synthetic Pd and Pt catalysts (A., 1942, I, 150) has been shown in the hydrogenation of benzil,  $m\text{-C}_6\text{H}_4\text{Br}\cdot\text{NO}_2$ , chaulmoogric acid, cinnamaldehyde, furfuraldehyde,  $\text{CH}_2\text{C}\cdot\text{CO}_2\text{H}$ , and quinol. W. R. A.

**Use of amalgamated aluminium as catalyst in the Friedel-Crafts reaction.**—See A., 1942, II, 136.

**Influence of behaviour of thiophen on aromatisation catalysts.**—See B., 1942, II, 137.

**Catalytic mullitisation of kaolinite by metallic oxides.**—See B., 1942, I, 195.

**Electrolytic production of ozone and anodic overvoltage.** E. Briner and A. Yalda (*Helv. Chim. Acta.*, 1941, **24**, 1328—1345).—Yields of up to 11.6 g. of  $\text{O}_3$  per kw.-hr. may be obtained by the electrolysis of  $\text{H}_2\text{SO}_4$  of the eutectic composition at  $-40^\circ$  to  $-50^\circ$ . The yields increase with increasing anodic overvoltage, and there is a parallelism between overvoltage and the potential of an  $\text{O}_2$ - $\text{O}_3$  electrode. F. J. G.

**Perborate formation at a rotating anode.** J. L. Culbertson and W. C. Teach (*Trans. Electrochem. Soc.*, 1942, **81**, Preprint 4, 33—39).—The efficiency ( $a$ ) of  $\text{NaBO}_3$  formation at a rotating Pt anode increases to a max. and then diminishes as the rotational speed ( $V$ ) increases. For a given val. of  $V$ ,  $a$  decreases continually with duration of the reaction. The val. of  $V$  at which max.  $a$  is attained in a given time interval decreases as the time interval increases. The data are examined in the light of existing theories. C. R. H.

**Oxidation of cerous sulphate at a rotating anode.** J. L. Culbertson and C. Rutkowski (*Trans. Electrochem. Soc.*, 1942, **81**, Preprint 3, 27—32).—The effect on the anodic oxidation of  $\text{Ce}_2(\text{SO}_4)_3$  of varying the speed of rotation of the anode over the range 0—5100 r.p.m. has been investigated. If other factors are kept const., current efficiency ( $a$ ) increases with increase in speed of rotation according to  $\log(a - a_0) \propto \log V$ , where  $a_0$  is the current efficiency at a stationary electrode and  $V$  is the linear velocity of the surface of the electrode. This relation breaks down as  $a$  approaches 1, since  $V$  may increase without limit. Since the relation is of the same type and order of magnitude as the heat transfer coeff. for a liquid film and since heat transfer is diffusion-controlled, diffusion control of the electrolytic reaction is indicated. C. R. H.

**Electrolysis of rare-earth acetates and separation of europium as amalgam from other rare earths.** H. N. McCoy (*J. Amer. Chem. Soc.*, 1941, **63**, 3432—3433).—By the electrolysis of aq. K citrate solutions of Eu, Yb, and Sm acetates between a heavy Pt wire anode and a Hg cathode amalgams are formed. Amalgams are also formed when aq. K citrate solutions of Eu, Yb, and Sm acetates are stirred with K amalgam. Other rare earths treated similarly gave no amalgams. It is possible that Eu and Yb can be separated from accompanying rare earths by their amalgams, the Eu amalgam being formed more readily than the Yb amalgam. W. R. A.

**Electrolytic solution of sodium hypochlorite.**—See A., 1942, III, 280.

**Effect of inorganic colloids on electrodeposition of nickel on copper.**—See B., 1942, I, 201.

**Cathodic protection of aluminium equipment.**—See B., 1942, I, 204.

**Electrolytic preparation of ethyl glyoxylate.**—See A., 1942, II, 130.

**Decomposition of hydrogen peroxide by sodium nitroprusside.** B. B. Lal (*Proc. Indian Acad. Sci.*, 1941, **14**, A, 652—669).—The decomp. of  $\text{H}_2\text{O}_2$  by  $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}$  (I) is negligibly slow in the dark, but if the mixture is previously insulated then, in the dark, decomp. is autocatalytic. In presence of  $\text{K}_3\text{Fe}(\text{CN})_6$  (II) decomp. is unimol. and more rapid. Evidently the catalyst formed during insulation is changed into a more reactive substance by interaction with (II) and is kept at a const. concn. when (II) is in excess. If fresh  $\text{H}_2\text{O}_2$  is added in the dark to the end products of the reaction an autocatalytic reaction takes place similar to that observed with pre-insulated (I). The catalyst is  $\text{Na}_2\text{Fe}(\text{CN})_5\text{H}_2\text{O}$  (III) which is reduced by (II) to  $\text{Na}_2\text{Fe}(\text{CN})_5\text{H}_2\text{O}$  which is highly reactive towards  $\text{H}_2\text{O}_2$ . The photochemical after-effect is suppressed by  $\text{CN}^-$  and  $\text{NO}_2^-$  which convert (III) into  $\text{Na}_2\text{Fe}(\text{CN})_6$  and (I), respectively. C. R. H.

**Photosensitisation by solids. III. Photosensitised oxidation of ammonia in aqueous solution with colloidal titania as the photosensitiser.** G. Gopal Rao and C. I. Varadanam (*J. Indian Chem. Soc.*, 1941, **18**, 361—370).—The rate of reaction in presence of



negatively charged  $\text{TiO}_2$  sol is independent of  $[\text{NH}_3]$  and is decreased by addition of coagulating electrolytes, indicating that the reaction occurs on the surface of the photosensitizer. The probable mechanism is discussed. F. J. G.

**Photographic factors influencing the concentration-calibration curve in quantitative methods of spectrochemical analysis.** I. Photographic intensity ratios as an expression of intensity ratios of lines in a light source. II. Failure of the reciprocity law and intensity retardation of development effect. L. W. Strock (*Spectrochim. Acta*, 1939, 1, 117—122, 123—130).—I. "Photographic intensity ( $I$ ) ratios" determined by comparison of the photographic effects of spectrum lines differ from true  $I$  ratios owing to failure of the reciprocity law. The effects of such failure are considered with reference to photographic density-log (exposure) curves with " $I$  scales" (obtained with const. exposure time and a stepped filter) or "time scales" (obtained with const.  $I$  and a rotating stepped sector). In either case the photographic  $I$  ratio must be calibrated empirically against concn. in spectrographic analysis.

II. The effects of reciprocity failure and the intensity retardation of development effect on concn.-calibration curves are separately examined, and a non-linear theoretical curve is obtained which resembles typical experimental curves. In spectrographic analysis const. development conditions are essential, even when internal standards are used. A calibration curve should be made for each emulsion. Empirical calibration curves should not be extrapolated beyond experimental points. A. J. E. W.

**Photographic factors influencing the concentration-calibration curve in quantitative methods of spectrochemical analysis.** I. Photographic intensity ratios as an expression of intensity ratios of lines in a light source. L. W. Strock (*Spectrochim. Acta*, 1940, 1, 374).—A correction (cf. preceding abstract). J. W. S.

**Number of quanta required to form the photographic latent image.**—See B., 1942, II, 127, 175.

**Distribution of the latent image in the silver bromide grain.**—See B., 1942, II, 175.

**Photolysis of methyl bromide.** A. Gordon and H. A. Taylor (*J. Amer. Chem. Soc.*, 1941, 63, 3435—3441).—The photolysis of  $\text{MeBr}$  by 2537 Å. gives a quantum yield, based on  $\text{Br}$  produced, of  $4 \times 10^{-3}$ . The principal products are  $\text{Br}$ ,  $\text{CH}_4$ , and  $\text{CO}$  and the following mechanism is suggested:  $\text{MeBr} + h\nu \rightarrow \text{Me} + \text{Br}$ ;  $\text{Me} + \text{MeBr} \rightarrow \text{CH}_4 + \text{CH}_2\text{Br}$ ;  $\text{Me} + \text{MeBr} \rightarrow \text{C}_2\text{H}_6 + \text{Br}$ ;  $\text{Me} + \text{Br} \rightarrow \text{MeBr}$ . In the presence of  $\text{NO}$  a complex reaction occurs and  $\text{NOBr}$ ,  $\text{N}_2$ , oxides of  $\text{N}$ , and  $\text{CO}$  are formed. The quantum yield on the basis of  $\text{NOBr}$  produced is  $\sim 1$ . In the presence of  $\text{Ag}$  the quantum yield, based on  $\text{CH}_4$  produced, is  $\sim 1$  and only  $\text{CH}_4$  and  $\text{CO}$  are formed. The difference of  $\sim 6$  kg.-cal. in the energies of activation for the production of  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  accounts for the absence of  $\text{C}_2\text{H}_6$ .  $\text{CO}$  is formed probably by reaction between  $\text{CH}_2\text{Br}$  and  $\text{SiO}_2$ . Increase of temp. to  $250^\circ$  does not alter qualitatively the above results. W. R. A.

**Photochemical studies. XXXIII. Photochemical decomposition of acetone in the presence of an inert gas.** J. J. Howland, jun., and W. A. Noyes, jun. (*J. Amer. Chem. Soc.*, 1941, 63, 3404—3406).—Addition of several hundred mm. of  $\text{CO}_2$  to  $\text{COMe}_2$  produces a marked increase in the amount of  $\text{CO}$  formed by the photochemical decomp. of  $\text{COMe}_2$  at low intensities, but the effect at high intensities is the production of less  $\text{CO}$  and of more  $\text{Ac}_2$ .  $\text{CO}$  appears to be produced principally by the homogeneous decomp. of  $\text{MeCO} \rightarrow \text{Me} + \text{CO}$  and only very slightly by a primary process. Production of  $\text{Ac}_2$  at low intensities appears to be largely a wall reaction. At higher intensities and higher pressure  $\text{Ac}_2$  formation becomes increasingly a homogeneous gas phase reaction. W. R. A.

**Photolysis of keten in the presence of hydrogen and methane.** C. Rosenblum (*J. Amer. Chem. Soc.*, 1941, 63, 3322—3329).—The photodecomp. of keten by ultra-violet light at  $\sim 45^\circ$  is independent of the nature of subsequent reactions. This supports the view that  $\text{CH}_2$  radicals are produced by the absorption of radiation. In the presence of  $\text{H}_2$  saturated compounds are formed possibly by reaction between  $\text{CH}_2$  and  $\text{H}_2$  yielding  $\text{Me}$  and  $\text{H}$  at the same time as  $\text{CH}_2$  combines to give  $\text{C}_2\text{H}_4$ . Saturated compounds are also formed in the presence of  $\text{CH}_4$ , owing, presumably, to the reaction between  $\text{CH}_2$  and  $\text{CH}_4$  yielding  $\text{Me}$  radicals. W. R. A.

**Photochemical oxidation of chloral sensitised by bromine.** J. Stauff and H. J. Schumacher (*Z. physikal. Chem.*, 1941, B, 48, 154—175).—The photochemical oxidation of  $\text{CCl}_3\text{CHO}$  in the presence of  $\text{Br}$  has been investigated at  $70$ — $90^\circ$ . The reaction is a chain reaction, which has a quantum yield of 8 mols. per  $h\nu$  at 100 mm. total pressure, and for the absorption of light at the rate of  $3 \cdot 3 \times 10^{13}$   $h\nu$  per c.c. per sec. The products are  $\text{COCl}_2$ ,  $\text{CO}$ ,  $\text{HCl}$ ,  $\text{BrCl}$ ,  $\text{H}_2\text{O}$ , and probably a small quantity of  $\text{CCl}_3\text{COBr}$ . The chain can be represented by 12 equations. An expression is obtained for the velocity of formation of  $\text{COCl}_2$ . The temp. coeff. for a temp. interval of  $10^\circ$  is 1.30, giving an activation of energy of 6.5 kg.-cal. A. J. M.

**Photochemical studies of rancidity. Chlorophyll value in relation to autoxidation.**—See B., 1942, II, 112.

**Molecular rearrangement induced by ultrasonic waves.** E. W. Barrett and C. W. Porter (*J. Amer. Chem. Soc.*, 1941, 63, 3434—3435).—The rate of rearrangement of benzazide in  $\text{NH}_2\text{Ph}$  has been studied at 16, 275, and 478 kc. per sec. with power inputs from 100—250 w. The rate is independent of frequency but  $\propto$  the energy of vibration (cf. A., 1938, I, 419). W. R. A.

## IX.—METHODS OF PREPARATION.

**Synthetic optical crystals.** H. C. Kremers (*Ind. Eng. Chem.*, 1941, 32, 1478—1483).—The modern method of producing large synthetic  $\text{LiF}$ ,  $\text{NaCl}$ ,  $\text{KBr}$ ,  $\text{KI}$ , and  $\text{NaNO}_2$  crystals by lowering the crucible containing the molten salt slowly through tube furnaces at suitable temp. and the methods of cutting the crystals to produce prisms etc. are described. The optical characteristics of the crystals are discussed. The method is particularly applicable to  $\text{LiF}$ , which can be substituted for  $\text{CaF}_2$  in ultra-violet spectroscopy. J. W. S.

**Hydrated lithium aluminium sulphate (lithium alum).** H. A. Horan and J. J. Duane (*J. Amer. Chem. Soc.*, 1941, 63, 3533—3534).—Additional work on the system  $\text{Li}_2\text{SO}_4\text{--Al}_2(\text{SO}_4)_3\text{--H}_2\text{O}$  at  $0^\circ$  (A., 1939, I, 612) indicates the existence of a double salt, approx.  $\text{LiAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ . W. R. A.

**Dehydration of hydrated crystals by boiling non-aqueous liquids.** R. B. Trusler (*Oil and Soap*, 1941, 19, 1—3).—Many hydrated salts of org. or inorg. acids [e.g.,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ,  $\text{Zn}(\text{OAc})_2$ , Na silicates, borates, etc.,  $\text{CaCl}_2$ ] can be dehydrated at  $<$  air-drying temp. by immersion in a boiling, distilling, non-aq. liquid—some at relatively low temp., e.g., with  $\text{CH}_2\text{Cl}_2$ ,  $\text{Pr}^n\text{O}$  ( $\text{Et}_2\text{O}$  is ineffective); others, e.g.,  $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ , are unaffected by  $\text{C}_6\text{H}_6$  but dehydrated by boiling  $\text{PhMe}$ .  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  loses 4  $\text{H}_2\text{O}$  in boiling  $\text{PhMe}$ , but requires tetralin to remove the remaining  $\text{H}_2\text{O}$ . In the experiments detailed, a Bidwell-Stirling or A.S.T.M. receiver was used, the  $\text{H}_2\text{O}$  driven off being measured volumetrically. In some cases residual salts containing  $\text{H}_2\text{O}$  of crystallisation corresponding with unusual states of hydration could be obtained. In determining  $\text{H}_2\text{O}$  by the distillation method in soaps containing hydrated salts, the actual degree of dehydration of such salts which can be procured under the experimental conditions must be taken into account. The method can also be applied to determine the original state of hydration of normally hydrated crystals which have been partly dried. E. L.

**4-Co-ordinated mercuric salts with diamines, and a new method of determining mercury.** K. L. Mandal (*Current Sci.*, 1941, 10, 522—523).—Bis-ethylenediamine-mercuric chloride, a 4-co-ordinated  $\text{Hg}^{II}$  halide, does not exist in the pure state in the solid form.  $\text{HgCl}_2$  and  $\text{HgBr}_2$  form white mono-compounds with equimol. proportions of  $(\text{CH}_2\text{NH}_2)_2$  (I), which are insol. They dissolve in excess of (I) giving  $\text{H}_2\text{O}$ -sol. products, but pure bis-ethylenediamine-mercuric halides cannot be obtained from them. Washing with  $\text{EtOH}$  or crystallising from  $\text{H}_2\text{O}$  converts them into the insol. mono-compounds. Bis-ethylenediamine-mercuric chloroplatinate (I) and bis-ethylenediamine-mercuric salts of oxyacids have been prepared. (II) is insol. in  $\text{H}_2\text{O}$ , and is unaffected when kept over  $\text{H}_2\text{SO}_4$ . This forms the basis of a method of determining  $\text{Hg}$ . Propylenediamine can be used in place of (I). A. J. M.

**Two lower oxides of boron.** R. C. Ray and P. C. Sinha (*J.C.S.*, 1941, 742—744).—The residue after repeated extraction of  $\text{Mg}_2\text{B}_2$  by  $\text{H}_2\text{O}$  reacts slowly with conc. aq.  $\text{NH}_3$  in an atm. of  $\text{H}_2$  to yield compounds  $(\text{NH}_4)_2\text{B}_2(\text{OH})_2$  (I) and  $(\text{NH}_4)_2\text{B}_2\text{O}_6$  (II) which are stable when dry at  $<0^\circ$ . Neither compound reacts with dil.  $\text{H}_2\text{SO}_4$  and (I) gives no ppt. with  $\text{Ba}$ ,  $\text{Ca}$ , or  $\text{Mg}$  salts but (II) yields white cryst. ppts. with these salts. On heating (I) yields  $\text{NH}_3$  and  $\text{H}_2$ , whilst (II) gives  $\text{NH}_3$  only, the residues comprising the oxides  $\text{B}_2\text{O}_3$  (slightly brown) and  $\text{B}_2\text{O}_5$  (colourless), respectively. Both oxides dissolve in  $\text{H}_2\text{O}$  to give colourless solutions which on evaporation yield the acids  $\text{H}_4\text{B}_2\text{O}_4$  and  $\text{H}_4\text{B}_2\text{O}_6$ , these on heating in a vac. giving the pure oxides. The solutions are oxidised slowly in air and also by  $\text{KMnO}_4$  to  $\text{H}_3\text{BO}_3$ . The compounds  $\text{Mg}_2\text{B}_2\text{O}_6$ ,  $\text{Ba}_2\text{B}_2\text{O}_6$ ,  $\text{MgB}_2\text{O}_6$ , and  $\text{BaB}_2\text{O}_6$  have also been prepared by the interaction of the metal hydroxides and solutions of the acids in a vac. J. W. S.

**Hydration of aluminium sulphate.**—See A., 1942, I, 145.

**Formation of complex fluorides in anhydrous liquid hydrogen fluoride. I. Sodium fluoborates.** A. W. Laubengayer and C. G. Polzer (*J. Amer. Chem. Soc.*, 1941, 63, 3264—3266).—Na fluoborates are formed by crystallisation from solutions in anhyd.  $\text{H}_2\text{F}_2$  of  $\text{NaF}$  and  $\text{NbF}_5$  in mol. ratios varying from 0.5:1 to 20:1. At 1:1 ratios pure Na hexafluoroborate,  $\text{NaNbF}_6$ , is formed; at higher ratios Na heptafluoroborate,  $\text{NaNbF}_7$ , and  $\text{NaHF}_2$  are formed, but no  $\text{Na}_2\text{NbF}_8$ .  $\text{NaNbF}_6$  has  $\rho^{25}$   $2.71 \pm 0.01$ , is unstable in air, hydrolysed by  $\text{H}_2\text{O}$ , reacts with  $\text{H}_2\text{O}$ , and is insol. in  $\text{C}_6\text{H}_6$ . When  $\text{N}_2$  is passed over it and the temp. raised slowly ( $2^\circ$  per min.)  $\text{NaNbF}_6$  is stable up to  $480^\circ$  but at  $>480^\circ$  it decomposes without melting into  $\text{NaF}$  and  $\text{NbF}_5$ .  $\text{NaNbF}_7$  has  $\rho^{25}$   $3.47 \pm 0.01$ , poorly formed, biaxial, monoclinic or orthorhombic crystals, unstable in air, rapidly hydrolysed by  $\text{H}_2\text{O}$ , insol. in  $\text{C}_6\text{H}_6$ . When heated in



dry  $\text{Na}_2$  it melted at  $530 \pm 10^\circ$  and then decomposed into NaF and  $\text{NbF}_5$ . *Anal. Ind. Eng. Chem.* [Anal.] 1942, 14, 49—53. W. R. A.

**Composition and constitution of paramolybdates.** P. Rây and S. K. Siddhanta (*J. Indian Chem. Soc.*, 1941, 18, 397—406).—Analysis, dehydration, and rehydration of  $[\text{Co}(\text{dgh})_3]_2\text{Mo}_7\text{O}_{24} \cdot 9\text{H}_2\text{O}$ ;  $[\text{Cu}(\text{dgh})_2]_3\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ;  $[\text{Ni}(\text{dgh})_2]_3\text{R}_2\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  ( $\text{R} = \text{NH}_4$  or  $\text{Na}$ ;  $\text{dgh} = \text{diguandide}, \text{C}_2\text{H}_2\text{N}_4$ ) support the formula  $3\text{R}_2\text{O}_7\text{MoO}_3$ , aq. for the paramolybdates and  $[\text{Mo}_7\text{O}_{24}]^{VI}$  for the ion. F. R. G.

**Preparation of constant-boiling hydrochloric acid. Rate of approach to equilibrium.** A. C. Titus and D. E. Smith (*J. Amer. Chem. Soc.*, 1941, 63, 3266—3267).—From measurements of  $\rho$  for distillate fractions of HCl it is concluded (i) that it is safe to discard two thirds of the distillate and keep the remaining one third, if the initial  $\rho$  is  $\sim 1.10$ , (ii) that the equilibrium  $\rho^{25}$  at 647 mm. is 1.0975, and (iii) that equilibrium is more slowly attained starting with dil. acid (e.g.,  $\rho = 1.06$ ). W. R. A.

**Interaction of chloramine-T and hydrogen sulphide, phosphine, and arsine.** J. R. Bendall, F. G. Mann, and D. Purdie (*J.C.S.*, 1942, 157—163).—Aq. chloramine-T (I) and  $\text{H}_2\text{S}$  or  $\text{Na}_2\text{S}$  at room temp. give  $p\text{-C}_6\text{H}_4\text{Me} \cdot \text{SO}_2 \cdot \text{NH}_2$  (II), together with  $\text{H}_2\text{SO}_4$  or S, respectively;  $\text{H}_2\text{S}$  added to (I), with KI-starch as internal indicator, however, affords S, due probably to quick oxidation of KI. Sulphites can be determined volumetrically by (I), which converts them at room temp. into sulphates and (II);  $\text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + \text{(II)}$ , similarly.  $\text{PH}_3$  (in excess) reacts more slowly with (I), when  $\text{H}_3\text{PO}_3$  and  $\text{H}_3\text{PO}_4$  are formed, but no  $\text{H}_3\text{PO}_4$ ; when (I) is in excess, however, there is slow oxidation to  $\text{H}_3\text{PO}_4$ .  $\text{Na}_2\text{HPO}_3$  and excess of (I) at  $28.5^\circ$  (24 hr.) do not react appreciably, but addition of 2 equivs. of  $\text{AcOH}$ , to produce an equilibrium with  $\text{NaOAc}$  and  $\text{H}_3\text{PO}_4$  causes complete oxidation in 1 hr.  $\text{NaH}_2\text{PO}_3$  and excess of (I) react slowly, through  $\text{NaH}_2\text{PO}_4$ , rapidly to  $\text{NaH}_2\text{PO}_4$ .  $\text{PH}_3$  is oxidised to  $\text{H}_3\text{PO}_4$  through stages: (rapid)  $\text{H}_3\text{PO}_3 \rightarrow$  (slow)  $\text{H}_3\text{PO}_4 \rightarrow$  (rapid)  $\text{H}_3\text{PO}_4$ .  $\text{AsH}_3$  passed into (I) at  $28.5^\circ$  affords  $\text{H}_3\text{AsO}_4$  (96.5% after 1 hr.), probably through  $\text{H}_3\text{AsO}_3$ , which is oxidised rapidly. A. T. P.

**Behaviour of rhodium and of the complex thiocyanates of rhodium and molybdenum with toluene-3:4-dithiol.** C. C. Miller (*J.C.S.*, 1941, 792).— $\text{Re}$  (as  $\text{ReO}_4^-$ ) forms with toluene-3:4-dithiol ("dithiol") a green complex similar to those produced by Mo and W, but unlike the latter its formation is favoured by the use of 11N-HCl. In presence of  $\text{Bu}^+\text{OAc}$  all yield the complex in 11N-HCl, but on warming with KCNS the  $\text{Re}$  solution turns red-brown. The complex  $\text{Mo}(\text{OH})_2(\text{CNS})_2$  on heating with HCl and dithiol yields the green dithiol complex but similar treatment of  $\text{ReO}(\text{CNS})_2$  causes only a deepening of the colour to red-brown. J. W. S.

**Action of chlorine on the hydroxides of iron and chromium in presence of iodine.** R. K. Bahl and M. Lal (*J. Indian Chem. Soc.*, 1941, 18, 359—360).— $\text{Fe}(\text{OH})_3$ ,  $11\text{H}_2\text{O}$  and  $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  are formed by the action of  $\text{Cl}_2$  on aq. suspensions of I and  $\text{Fe}(\text{OH})_3$  or  $\text{Cr}(\text{OH})_3$ . F. J. G.

## X.—ANALYSIS.

**Spectrochemical analysis by the stepped sector method.** R. Breckpot (*Spectrochim. Acta*, 1939, 1, 137—163).—A detailed description and theoretical discussion of the method, which extends the range of application of the Gerlach internal standard method, are given. The calibration curve of the photographic plate for each spectrum line is automatically obtained, and frequent reference to standard specimens is obviated. The method is almost independent of plate or development factors, and can be applied visually or photometrically. Devices are described for the rapid calculation of results from data derived from the spectrograms. A. J. E. W.

**Spectrum-analytical determination of metals in microscopical preparations.** W. Gerlach (*Spectrochim. Acta*, 1939, 1, 168—172).—The cut section is placed in a cavity in the lower electrode of an intermittent d.c. arc; specially purified C rods impregnated with NaCl are employed. Typical spectrograms showing the presence of heavy metals in liver and gum tissue sections are reproduced. The method is capable of quant. application, and is  $\sim 100$  times as sensitive as high-frequency spark methods. A. J. E. W.

**Photographic factors influencing the concentration-calibration curve in quantitative methods of spectrochemical analysis.**—See A., 1942, I, 179.

**Micro-analysis.** G. H. Wyatt (*Chem. and Ind.*, 1942, 132—134).—A brief review.

**Polarographic method of analysis. I, II.** O. H. Müller (*J. Chem. Educ.*, 1941, 18, 65—72, 111—115).—I. A general review of electro-analytical methods.

II. Apparatus and manipulation in polarographic analysis are described. L. S. T.

**Titration of bromide and iodide ions with mercuric nitrate solution using diphenylcarbazide as indicator.** H. R. McCleary (*Ind. Eng. Chem. [Anal.]*, 1942, 14, 31—32).—The solution is neutralised with NaOH (phenolphthalein), and sufficient 0.2N- $\text{HNO}_3$  added so that the final solution after titration contains the equiv. of 5 c.c. of

0.2N-acid. 8 c.c. of peroxide-free dioxan (I) are added followed by 0.025N- $\text{Hg}(\text{NO}_3)_2$  to within 2 or 3 c.c. of the end-point. After addition of 15 drops of a saturated 95% EtOH solution of the indicator, the titration is continued to the end-point, canary-yellow to blue-grey, which is sharp. The final vol. of solution should be  $65 \pm 10$  c.c. The indicator blank is 0.07 c.c. of 0.025N- $\text{Hg}(\text{NO}_3)_2$ . For Br<sup>-</sup>, Roberts' method for Cl<sup>-</sup> (A., 1936, 1351) is followed. Agreement with the corresponding Volhard methods is close. Peroxide-free (I) is prepared by distillation from Na, and preserved for  $< 2$  weeks by addition of 0.5 g. of quinol per l. In presence of 10—15% of (I),  $\text{HgI}_2$  is pptd. in the yellow form. The method of Dubsky and Trtilek (A., 1934, 744) gave erratic results. L. S. T.

**New indicators for iodate-iodine monochloride Andrews analytical procedures.** G. F. Smith and C. S. Wilcox (*Ind. Eng. Chem. [Anal.]*, 1942, 14, 49—53).—Naphthol-blue-black (I), B.C.I. No. 246, brilliant-ponceau 5R (II), B.C.I. No. 185, and amaranth (III), B.C.I. No. 184, are not destroyed by high [HCl] in presence of small amounts of I or ICl, but are rapidly destroyed by a trace of  $\text{IO}_3^-$  under the same conditions. No indicator correction is necessary, and a tendency to fade as the equivalence point is reached is counteracted by delayed addition of the indicator. Determinations with these indicators follow the usual Andrews-Jamieson procedure, except that  $\text{CCl}_4$  or  $\text{CHCl}_3$  is not required. Data obtained by both methods show agreement in determining  $\text{As}^{III}$ ,  $\text{S}_2\text{O}_3^{2-}$  [(III) preferred as indicator],  $\text{CNS}^-$ ,  $\text{SO}_3^{2-}$  [(III) preferred],  $\text{H}_2\text{O}_2$  [(III) preferred],  $\text{N}_2\text{H}_4$  [(II) and (III) preferred], and  $\text{NHPh} \cdot \text{NH}_2$  [(II) preferred]. For Sb, the new method gives the same results as the  $\text{KBrO}_3$  method (Bordeaux) (A., 1941, I, 426) and the potentiometric end-point; for Fe, it gives the same results as Heisig's modification (A., 1928, 861) of Andrews' method. In this determination,  $\text{KIO}_3$  must be standardised against Fe as low results are obtained if  $\text{As}_2\text{O}_3$  is used as a standard of reference. With (III), the new method can be used for Fe in presence of org. matter. In the determination of  $\text{Ti}^{IV}$ , the method agrees with the Andrews-Jamieson procedure and the  $\text{Ce}(\text{SO}_4)_2$  potentiometric method of Willard and Young (A., 1930, 312). L. S. T.

**Methods of determining fluorides [in water supplies].**—See B., 1942, III, 93, 119.

**Determination of thiosulphate in presence of sulphite.** R. P. Donnelly (*Chem. and Ind.*, 1942, 114; cf. Pankhurst, A., 1942, I, 153).—The procedures of Kurtenacker *et al.* (A., 1925, ii, 239) and Boot and Ward (B., 1935, 535) are recommended. W. McC.

**Colour reaction for sulphurous acid etc.**—See A., 1942, II, 159.

**Use of electrodeless annular discharge in a high-frequency magnetic field in spectrum-analytical detection of traces.** E. Fenner (*Spectrochim. Acta*, 1939, 1, 164—167).—Electrodeless excitation [by a solenoid surrounding the evacuated discharge tube, supplied with a.c. (A 6 m.) from an oscillator] permits detection of traces of impurity in Se (e.g., 0.003% of Cd) which are undetected by arc or spark methods. Traces of Se in other materials can be detected similarly. Hg in air is detected at concns. too low to give arc or spark lines. A high-frequency spark method is proposed for poor conductors. A. J. E. W.

**Conductometric determination of ammonia. Application to nitrogen distribution studies.** R. H. Hendricks, M. D. Thomas, M. Stout, and B. Tolman (*Ind. Eng. Chem. [Anal.]*, 1942, 14, 23—26).—When sintered-glass bubblers and sufficient excess of  $\text{H}_3\text{BO}_3$  are used, the absorption of  $\text{NH}_3$  by  $\text{H}_3\text{BO}_3$  after vac. distillation or volatilisation by aspiration is satisfactory.  $\text{BuOH}$  must be used in the absorbent in certain cases. Change in conductance affords an accurate measurement of the amount of  $\text{NH}_3$  absorbed.  $\text{H}_2\text{SO}_4$  is a better absorbent than  $\text{H}_3\text{BO}_3$  for  $\text{NH}_3$ , and gives a larger change in conductance; it may be more suitable, particularly in micro-analyses. The method has been applied to N distribution in plant materials, and to automatic analysis of traces of  $\text{NH}_3$  in air (data given). Apparatus for absorption is described, and data concerning the stability of  $\text{NH}_4$  borate, the vac. distillation of  $\text{NH}_3$  at  $40-50^\circ$ , the relation between temp. and alkaline reagent ( $\text{MgO}$ ,  $\text{NaOH}$ ,  $\text{K}_2\text{CO}_3$ , or  $\text{NaOH-Na}_2\text{B}_4\text{O}_7$ ) to time of aspiration, and N distribution in a seed-ball extract are recorded and discussed. L. S. T.

**Cheaper Nessler's reagent by use of mercuric oxide.** L. F. Wicks (*J. Lab. Clin. Med.*, 1941, 27, 118—122).—Red  $\text{HgO}$  is used instead of  $\text{HgI}_2$  thus:  $\text{HgO} + 4\text{KI} + \text{H}_2\text{O} = \text{K}_2\text{HgI}_4 + 2\text{KOH}$ . C. J. C. B.

**Decomposition of Nessler's solution.** W. E. James, F. A. Slesinski, and H. B. Pierce (*J. Lab. Clin. Med.*, 1941, 27, 112).— $\text{COMe}_2$  in the air may cause rapid decomp. of Nessler's solution. C. J. C. B.

**Determination of hydrazine. Rapid ferricyanide-cerimetric method.** C. J. Dernbach [with J. P. Mehlig] (*Ind. Eng. Chem. [Anal.]*, 1942, 14, 58—60).—The  $\text{N}_2\text{H}_4$  is oxidised by means of aq.  $\text{NaOH-K}_3\text{Fe}(\text{CN})_6$  and the  $\text{Fe}(\text{CN})_6^{3-}$  produced titrated with 0.1N- $\text{Ce}(\text{SO}_4)_2$ . The procedure consists of adding  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$  to an excess of  $\text{K}_3\text{Fe}(\text{CN})_6$ , making alkaline with NaOH, shaking for 0.5 min., keeping for 2 min., acidifying with HCl, diluting, and titrating with  $\text{Ce}(\text{SO}_4)_2$ , which contains sufficient  $\text{Fe}^{III}$  to form colloidal  $\text{Fe}^{III}$



ferrocyanide during the titration and gives a green colour. This disappears sharply at the end-point.  $\text{FeCl}_3$  can be added to provide  $\text{Fe}^{+++}$  if necessary. The amount of  $\text{K}_3\text{Fe}(\text{CN})_6$  must be carefully controlled, and acidity during the final titration should be  $>1.8\text{M}$ , with respect to  $\text{HCl}$ . Results are reproducible to  $<0.1\%$ , and the titration is simpler than that of the Jamieson iodate method.

L. S. T.

**Spectrophotometric determination of phosphorus.** T. D. Fontaine (*Ind. Eng. Chem. [Anal.]*, 1942, 14, 77–78).—The transmittance- $\lambda$  curve for the blue colour obtained by the reduction of  $\text{MoO}_4^{+}$  in presence of  $\text{PO}_4^{+}$  shows a min. at  $820\text{ m}\mu$ . An improved micro-method, based on earlier procedures and using  $\text{SnCl}_2$  as reducing agent, is described. The  $[\text{SnCl}_2]$  can be varied without affecting the intensity of the developed colour, acidity ( $\text{H}_2\text{SO}_4$ ) can vary between  $1.7$  and  $2.1\text{N}$ , and the colour is stable for  $<24\text{ hr}$ .

L. S. T.

**Acidimetric orthophosphoric acid assay.** J. A. Calamari and R. Hubata (*Ind. Eng. Chem. [Anal.]*, 1942, 14, 55–56).— $\text{H}_3\text{PO}_4$  in reagent-grade acid, in alkali orthophosphates, in detergents, and in pharmaceutical preps. is determined by titration with  $0.5\text{N-HCl}$  from the  $\text{H}_2\text{PO}_4^{+}$  to the  $\text{HPO}_4^{+}$  end-point in a solution saturated with  $\text{NaCl}$ , using cresol-red and bromophenol-blue indicators, respectively, and a colour standard for each of the two end-points. The  $p\text{H}$  of the  $\text{H}_2\text{PO}_4^{+}$  and  $\text{HPO}_4^{+}$  end-points in saturated  $\text{NaCl}$  are  $\sim 3.15$  and  $7.65$ , respectively, at  $25^\circ$ . Org. acids must be removed by charring,  $\text{CO}_3^{+}$  by boiling with  $\text{HCl}$ ,  $\text{SiO}_3^{+}$  by dehydration ( $\text{HCl}$ ), and meta- and pyro-phosphates converted into orthophosphate by boiling in presence of  $\text{HCl}$ . Results given by the method agree with those obtained potentiometrically or gravimetrically.

L. S. T.

**Colorimetric determination of readily soluble phosphate in soils.**—See B., 1942, III, 65.

**Colorimetric micro-determination of arsenic after evolution as arsine.** E. B. Sandell (*Ind. Eng. Chem. [Anal.]*, 1942, 14, 82–83).—The  $\text{AsH}_3$  is absorbed in a  $\text{H}_2\text{SO}_4$  solution of  $\text{HgCl}_2$  containing  $\text{KMnO}_4$ , which oxidises the  $\text{As}^{\text{III}}$  in one step to  $\text{AsO}_4^{+}$ . This is determined by adding an excess of  $\text{NH}_4$  molybdate +  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$ , and heating to obtain Mo-blue. The procedure detailed is designed for  $1$ – $15\text{ }\mu\text{g}$ . of  $\text{As}$ , and a determination takes  $\sim 1\text{ hr}$ . to make. Apparatus for the absorption of  $\text{AsH}_3$  is described, and test data are recorded.  $5$ – $10\text{ }\mu\text{g}$ . of  $\text{As}$  can be determined with an accuracy of  $5\%$ , and  $1$ – $2\text{ }\mu\text{g}$ . with one of  $10\%$ . Results tend to be low. Small amounts of  $\text{Sb}$  do not interfere. Acid  $\text{KMnO}_4$  alone does not absorb  $\text{AsH}_3$  completely.  $\text{Ce}(\text{SO}_4)_2$  and  $\text{KBrO}_3$  cannot replace  $\text{KMnO}_4$  in the absorbent.  $\text{AsH}_3$  is liberated by the A.O.A.C. method.

L. S. T.

**Micro-determination of arsenic.** E. Cahill and L. Walters (*Ind. Eng. Chem. [Anal.]*, 1942, 14, 90–91).—The A.O.A.C. method is modified by replacing cotton wool by glass beads soaked in  $\text{Pb}(\text{OAc})_2$ , and using cotton threads impregnated with  $\text{HgBr}_2$  by a special method instead of Hanford-Pratt strips of paper. For the determination of  $1\text{ }\mu\text{g}$ . of  $\text{As}$ , thread in glass capillaries gives a more sensitive, more const., and more definite stain than the paper strips. The closer the thread fits the capillary, the more const. is the stain. Data obtained with  $1\text{ }\mu\text{g}$ . of  $\text{As}$  are given.

L. S. T.

**Determination of silicon in aluminium and its alloys.**—See B., 1942, I, 204.

**Accurate analysis of gaseous mixtures.** C. H. Bamford and R. R. Baldwin (*J.C.S.*, 1942, 26–29).—Apparatus in which confining liquids and absorbents are eliminated is described. Determinations, accurate to  $0.03\%$ , depend on pressure measurements after separation of constituents (e.g.,  $\text{CO}_2$ ) by cooling or (e.g., hydrocarbons) by oxidation.

F. J. G.

**Ruthenium dipyriddy, a new oxidimetric indicator.** J. Steigman, N. Birnbaum, and S. M. Edmonds (*Ind. Eng. Chem. [Anal.]*, 1942, 14, 30).—Ru dipyriddy enters into a mobile reversible oxidation in which the reduced bivalent form is orange-red and the oxidised trivalent form green in conc. solution. At dilutions comparable with those of indicator solutions, the corresponding colour change is from yellow to colourless on oxidation. Both forms of the new indicator are stable towards acid, and do not dissociate appreciably, even at  $100^\circ$ . The oxidation potential of the indicator is close to that of  $\text{Ce}^{+++}$  in  $\text{SO}_4^{+}$  solution, and the indicator cannot be used satisfactorily with  $\text{Ce}(\text{SO}_4)_2$ , but the end-point is sharp with  $\text{Ce}(\text{NO}_3)_4$  in  $\text{HNO}_3$ . The direct titration of  $\text{Na}_2\text{C}_2\text{O}_4$  in  $2\text{M-HClO}_4$  at room temp. with  $\text{Ce}(\text{NO}_3)_4$ , using two drops of  $0.02\text{M}$ -indicator solution per  $100\text{ ml}$ , is rapid, precise, and accurate. Agreement to  $<0.1\%$  was obtained between this titration and standardisation by means of  $\text{FeSO}_4$  and  $\text{Ce}(\text{SO}_4)_2$  ( $\alpha$ -phenanthroline  $\text{Fe}^{\text{II}}$  complex).

L. S. T.

**Qualitative analysis of the alkali metal group.** M. E. Hobbs (*J. Chem. Educ.*, 1941, 18, 90–91).—Part of the filtrate from the  $(\text{NH}_4)_2\text{CO}_3$  group is boiled with  $\text{NaOH}$  until  $\text{NH}_3$  is expelled completely, and then tested for  $\text{K}^+$  by means of  $\text{AcOH}$  and  $\text{Na}_2\text{Co}(\text{NO}_3)_6$ . The other portion is tested for  $\text{Na}^+$  by addition of  $\text{AcOH}$  and  $\text{Zn}$  and  $\text{UO}_2$  acetate (I). High  $[\text{K}^+]$  also gives a ppt. with (I), and if  $\text{K}^+$  is present most of it is first removed by addition of  $\text{HClO}_4$ . Details of procedure for semi-micro- and macro-analyses are given.

L. S. T.

**Modified methods for the determination of total alkali, sulphate, nitrate, and phosphate in highly coloured solutions of high organic matter content.** N. V. R. Iyengar (*Proc. Indian Acad. Sci.*, 1941, 14, A, 636–642).—The total alkali,  $\text{SO}_4^{+}$ ,  $\text{NO}_3^{+}$ , and  $\text{PO}_4^{+}$  in highly coloured effluents from industrial works can be determined after almost completely decolorising the liquid with  $\text{H}_2\text{O}_2$ , and boiling until colourless. Before determining  $\text{PO}_4^{+}$  by Denigès' colorimetric method, excess of  $\text{H}_2\text{O}_2$  must be decomposed by boiling with  $\text{PO}_4^{+}$ -free alkali.  $\text{SO}_3^{+}$  and  $\text{NO}_2^{+}$  are oxidised, thus adding to the proportions of  $\text{SO}_4^{+}$  and  $\text{NO}_3^{+}$  already present.

C. R. H.

**Spectrochemical analysis of alkali products.**—See B., 1942, I, 192.

**Base-exchange capacity determination in soils by means of a rapid colorimetric method.**—See B., 1942, III, 65.

**Determination of calcium in lead alloys.**—See B., 1942, I, 202.

**Determination of radium by a photographic method.** H. Meyer (*Brit. J. Radiol.*, 1942, 15, 85–91).—In the method described three exposures, one with the prep. to be measured and two with a standard prep., are made on the same strip of film. The standard exposures should be  $\sim 10\%$  higher and  $10\%$  lower than that of the measured prep., thus giving a linear relation between density and exposure. The method is comparatively unaffected by external influences and errors due to variations of emulsion and uneven development of separate films are eliminated. Full details, calculation of results, corrections, and test data are given.

N. M. B.

**Spectrum-analytical studies on magnesium content of blood in various diseases.**—See A., 1942, III, 370.

**Determination of lead content of commercial ciders and vinegars by spectrographic methods.**—See B., 1942, III, 105.

**Polarographic method for determination of lead and zinc in paints.**—See B., 1942, II, 114.

**Oxanilic acid thioamide as an analytical reagent.** A. K. Majumdar (*J. Indian Chem. Soc.*, 1941, 18, 415–418).— $\text{NHPh}\cdot\text{CO}\cdot\text{CS}\cdot\text{NH}_2$  can be used to detect  $\text{Cu}$  ( $1$  in  $75 \times 10^4$ ),  $\text{Co}$  ( $1$  in  $4 \times 10^5$ ), and  $\text{Ni}$  ( $1$  in  $2 \times 10^6$ ) in aq. solution.  $\text{Cu}$ ,  $\text{Co}$ , and  $\text{Ni}$  can be determined with an error  $>0.2\%$ .

F. R. G.

**Quinoline-8-carboxylic acid as an analytical reagent.** I. A. K. Majumdar (*J. Indian Chem. Soc.*, 1941, 18, 419–422).—Quinoline-8-carboxylic acid with a neutral solution of  $1$  part of  $\text{Cu}$  in  $4 \times 10^4$  gives a light blue ppt.  $\text{Cu}^{+}$  in acid solution is determined as  $(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_2\text{Cu}$  with an error  $>0.05\%$  at  $p\text{H}$   $7.0$ . At lower  $p\text{H}$  the error is but little greater. Free  $\text{AcOH}$  prevents complete pptn.

F. R. G.

**Determination of copper in country spirits.**—See B., 1942, III, 78.

**Determination of mercury.**—See A., 1942, I, 180.

**Assay of ointments of mercuric oxide, ammoniated mercury, and mercurous chloride.**—See B., 1942, III, 112.

**Determination of aluminium in metals and alloys by means of the mercury cathode.**—See B., 1942, I, 204.

**Rapid determination of aluminium in magnesium alloys by means of 8-hydroxyquinoline.**—See B., 1942, I, 204.

**Quantitative spectrum analysis of hydronalium alloys.**—See B., 1942, I, 204.

**Micro-analytical method for the determination of ferrous and ferric iron in minerals.** J. Das-Gupta (*J. Indian Chem. Soc.*, 1941, 18, 375–380).—The mineral is dissolved in  $\text{HF} + \text{HCl}$  in an inert atm. and titrated first with  $\text{Ce}(\text{SO}_4)_2$  and then with  $\text{TiCl}_3$ , using  $\alpha\text{-NHPh}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  acid and  $\text{KCNS}$  as indicators.

F. J. G.

**Determination of traces of tin in malt beverages.**—See B., 1942, III, 105.

**Determination of antimony in lead-antimony alloys.**—See B., 1942, I, 202.

**Volumetric determination of bismuth as caffeine tetraiodobismuthate.** R. S. Beale and G. C. Chandlee (*Ind. Eng. Chem. [Anal.]*, 1942, 14, 43–44).—The sample ( $\sim 0.03\text{ g}$ . Bi) is dissolved in conc.  $\text{H}_2\text{SO}_4$ , the acidity regulated by evaporation of the acid, dilution, and addition of  $\text{NaOH}$ , and the Bi pptd. by means of caffeine sulphate solution followed by aq.  $\text{KI}$ . The washed  $(\text{Bi}_2\text{O})$  ppt. is decomposed by boiling with  $\text{NaOH}$ , acidified with  $\text{HCl}$ , and, after addition of  $\text{KCN}$ , titrated with aq.  $\text{KIO}_3$  to the ICN end-point. The method has been used with  $1.2\text{ mg}$ . of Bi, and, with suitable modifications, for the determination of Bi in presence of  $\text{Hg}^{+}$ ,  $\text{Ca}^{+}$ ,  $\text{Sr}^{+}$ ,  $\text{Ba}^{+}$ ,  $\text{Na}^{+}$ ,  $\text{K}^{+}$ ,  $\text{Mg}^{+}$ ,  $\text{Be}^{+}$ ,  $\text{Fe}^{+}$ ,  $\text{UO}_2^{+}$ ,  $\text{Al}^{+}$ ,  $\text{Ni}^{+}$ ,  $\text{Co}^{+}$ ,  $\text{Zn}^{+}$ ,  $\text{Mn}^{+}$ ,  $\text{Cr}^{+}$ ,  $\text{MoO}_4^{+}$ ,  $\text{As}^{+}$ ,  $\text{Pb}^{+}$ ,  $\text{Cd}^{+}$ ,  $\text{VO}_2^{+}$ ,  $\text{Sn}^{+}$ ,  $\text{Sn}^{+}$ ,  $\text{Sb}^{+}$ ,  $\text{AsO}_4^{+}$ , and  $\text{PO}_4^{+}$ .  $\text{Cu}^{+}$ ,  $\text{Ag}^{+}$ , and  $\text{Hg}^{+}$  must be absent. Data for determinations in presence of most of these ions are given.

L. S. T.

**Qualitative semimicro-analysis with reference to Noyes and Bray's system. Copper and tellurium group.** C. C. Miller (*J.C.S.*, 786–792; cf. A., 1941, I, 175).—Working details are given of a scheme for the detection and approx. determination of  $0.25$ – $50\text{ mg}$ . of Bi, Cd, or Cu,  $0.25$ – $10\text{ mg}$ . of Mo, Re, Ir, Rh, or Te, and  $0.25$ – $2\text{ mg}$ . of Pb in mixtures containing  $>50\text{ mg}$ . of these metals. The



ppt. containing the metals as sulphides is treated with HCl and  $H_2O_2$ , any dark residue being extracted with aqua regia. After evaporation with NaCl, Se and Te are separated as the elements, Te being confirmed with  $Ca(H_2PO_4)_2$ . In portions of the filtrate Cu is detected as Cu Zn Hg thiocyanate, Bi with  $CS(NH_4)_2$ , Rh by reduction with  $SnCl_2$  and extraction with  $Bu^4OAc$ , Ir by oxidation to the blue compound, Re and Mo as complex thiocyanates, Cd with cadion, and Pb with Na rhodizonate. J. W. S.

Spectro-analytical determination of niobium and tantalum in highly alloyed iron and steel samples.—See B., 1942, I, 201.

## XI.—APPARATUS ETC.

Low temperature adiabatic calorimeter. Calibration of the platinum resistance thermometers. D. M. Yost, C. S. Garner, D. W. Osborne, T. R. Rubin, and H. Russell, jun. (*J. Amer. Chem. Soc.*, 1941, 63, 3488—3492).—Constructional and operational features are given of (i) an adiabatic low-temp. calorimeter which requires only 2 l. of liquid  $H_2$  for a complete series of  $C_p$  measurements from  $14^\circ$  to  $90^\circ$  K., (ii) a calorimeter for measuring v.p. and heats of vaporisation. The calibration of Pt resistance thermometers for the range  $14^\circ$  K. to  $200^\circ$  C. is described. W. R. A.

Electrically-heated funnel heater for small conical funnels. W. C. Tobie (*J. Chem. Educ.*, 1941, 18, 90—91). L. S. T.

Modifications in the Dumas micro-method for [determination of] nitrogen. Automatic apparatus for combustion micro-methods.—See A., 1942, II, 183.

Infra-red as an analytical tool: dehydration of silicic acid derived from feldspars. E. W. Koenig (*Bull. Amer. Ceram. Soc.*, 1941, 20, 447—450).—The complete recovery of the  $SiO_2$  from the acidified silicate alkali fusion was possible after only one evaporation if the surface of the solution was heated by a 260-w. infra-red lamp at a distance of 1.5 in. This method is also much quicker. The effect may be due to the opacity of quartz to radiation of  $>7000$  Å. The method is also recommended for charring filter-papers, cupferron, etc. J. A. S.

Infra-red spectrometer for industrial use.—See B., 1942, I, 179.

Applications of wave-length turbidimetry in the infra-red. C. E. Barnett (*J. Physical Chem.*, 1942, 46, 69—75).—Opacity caused by reflexion and scattering of light by suspensions of fine particles is discussed with special reference to earlier work of the author (cf. B., 1937, 809) and of Pfund (cf. A., 1934, 130). C. R. H.

Colour measurement. J. W. Perry (*Nature*, 1941, 148, 691—692).—A discussion concerning standardisation and the need for increased precision in certain colour measurements. L. S. T.

Recording colour of opaque objects. M. E. Stansby and J. A. Dassow (*Ind. Eng. Chem. [Anal.]*, 1942, 14, 13—15).—Colours of opaque objects are compared by preparing photographic colour transparencies, and obtaining spectral distribution curves by means of a photo-electric spectrophotometer. Whenever possible, errors due to variations in illumination during exposure and in processing of the film are eliminated by taking photographs of objects to be compared on the same negative. Application of the method is illustrated by spectral distribution curves for fresh and for stored frozen salmon. L. S. T.

Nature and measurement of whiteness. J. G. Holmes (*Proc. Physical Soc.*, 1942, 54, 81—86).—The uniqueness of white is discussed from the visual and colorimetric points of view. The sensitivity of the eye to departures from white and the extent of compensation by visual mechanism for changes in illumination are considered. Instrumental methods of colorimetry for whiteness measurement are briefly described. N. M. B.

New Bausch and Lomb refractometer.—See B., 1942, III, 103.

Rapid processing of photographic plates for routine spectrographic analysis. H. B. Vincent and R. A. Sawyer (*Spectrochim. Acta*, 1939, 1, 131—136).—The apparatus described consists of a mechanical agitator for the processing solutions, a plate washer in which a flat stream of  $H_2O$  is projected across the emulsion, and an electric dryer. Details are given of suitable developing, hardening, and fixing solutions. Processing of a spectrogram can be completed in  $>5$  min. A. J. E. W.

Line absorption and total absorption of copper resonance lines and determination of radiation temperature in the gas column of the copper arc. H. Schnautz (*Spectrochim. Acta*, 1939, 1, 173—196).—A form of Cu arc which gives intense resonance lines without self-reversal is described; the emergent light beam is passed through a hole in the anode. The mean temp. of the gas column in a Cu arc at atm. pressure, determined by comparison with the positive crater of a C arc, is  $5473 \pm 9.3^\circ$  K.; the temp. increases as the cathode is approached. The variation of the intensity ratio of the 3248 and 3274 Å. Cu lines with temp. is examined, and explained qualitatively in terms of simultaneous Doppler and dispersion

broadening of the lines; the Doppler effect is particularly strong. The derived variation of total absorption with concn. is anomalous. A. J. E. W.

Dependence of intensity of arc resonance lines of an element on concentration. R. Mannkopff (*Spectrochim. Acta*, 1939, 1, 197—206).—A comparison of an ordinary Cu arc with an arc free from self-reversal (cf. preceding abstract) shows that the non-linear concn.-dependence of the absorption of spectrum lines is due to self-absorption in the emitting layer, and not to self-reversal in the arc envelope. The anomalous variation of total intensity is ascribed to depletion of atoms within the arc by ionic migration effects; the intensity-concn. curve for the 3130—3131 Å. doublet of Be, in which such effects are negligible, is normal. A. J. E. W.

Dropping mercury electrode for lead analyses.—See A., 1942, III, 428.

Preparation of Weston standard cells. W. C. Vosburgh and P. F. Derr (*J. Chem. Educ.*, 1941, 18, 87—89).—Directions for the prep. of these cells are given, and performance is described. L. S. T.

Glass electrode as a reference electrode in electrometric titrations. L. Lykken and F. D. Tuemmler (*Ind. Eng. Chem. [Anal.]*, 1942, 14, 67—69).—The use of a glass electrode as a reference electrode is recommended for all redox and pptn. titrations that yield potential-vol. curves with realisable inflexion points and that can be carried out between  $0^\circ$  and  $50^\circ$ . Curves for typical titrations are reproduced, and the advantages of the glass over conventional reference electrodes discussed. L. S. T.

Sodium-hydrogen Geissler tube. F. M. Goyan (*Ind. Eng. Chem. [Anal.]*, 1942, 14, 60—61).—Details of construction of a Geissler tube capable of emitting a strong Na D line are given. The tube is made of Pyrex glass, and is charged with commercial metallic Na and tank  $H_2$ . Under controlled conditions, the C and F lines of  $H_2$  and the D line of Na are emitted simultaneously. The tube operates efficiently as a source of Na line over a wide pressure range, and has a long life. L. S. T.

Electronic relays. S. Redfern (*Ind. Eng. Chem. [Anal.]*, 1942, 14, 64—65).—The circuit described for use with a.c. has a diode beam-power amplifier tube with a separate, independent, rectified grid-bias voltage. L. S. T.

Drift of selenium barrier-layer photo-cell. K. A. Houstoun (*Phil. Mag.*, 1941, [vii], 31, 498—506).—The current given by an illuminated Se barrier-layer photo-cell decreases with time, and the cell slowly regains its original sensitivity in darkness. The fatigue effect is more pronounced in green than in red light. Exposure to light of one colour reduces the sensitivity of the cell to light of other colours, e.g., when the cell is exhausted for red it is also exhausted for green, irrespective of the colour of the light which produced the exhaustion. L. J. J.

Formula of the selenium barrier-layer photo-cell. R. A. Houstoun (*Phil. Mag.*, 1942, [vii], 33, 226—237).—The cell is connected to a micro-ammeter and resistance of combined resistance  $R$  and exposed to  $L$  ft.-candles illumination. The recorded current  $I$  is then a function of  $L$  and  $R$  and an investigation of the form of this function is reported. Data were obtained for the variation of  $I$  with  $L$  and  $R$  with 5 cells of different origin. Results confirm a formula deduced from consideration of the action of the cell,  $1/I = (k/EL) + R(1 + k/rL)/E$ , where  $r$  is the internal resistance, and  $E$  the e.m.f. of the cell. The addition of an empirical term  $ae^{-R/b}$  to the right-hand side of the equation is necessary to represent deviation from the straight line. The formula is justified theoretically. N. M. B.

Induction accelerator generating 20 Me.v. D. W. Kerst (*Physical Rev.*, 1942, [ii], 62, 93—94).—The design follows that of a 2.3-Me.v. accelerator (cf. A., 1941, I, 358), but by means of a pulse of flux generated by auxiliary coils the electrons are caused to spiral outwards to impinge on the W injector structure serving as a target for the production of X-rays and for the scattering of primary electrons. N. M. B.

184-in. cyclotron at Berkeley, California. M. L. Oliphant (*Nature*, 1941, 148, 717).—A brief description, with a photograph, of the apparatus designed to give 100-Me.v. deuterons. L. S. T.

Discharge mechanism of fast Geiger-Müller counters from the dead-time experiment. H. G. Stever (*Physical Rev.*, 1942, [ii], 61, 38—52).—A simple oscilloscopic method is given for measuring the dead-time (an insensitive time of  $\sim 10^{-4}$  sec. between registration of a count and recovery sufficient to register another count). A theory of this dead-time, in good accord with experiment, involves the formation of a positive ion space-charge sheath about the wire of the counter, this sheath expanding to the cylinder. The dead-time experiment shows the internal action of the counter, and also that the discharge spreads throughout the length of the counter but can be stopped by a small glass bead on the wire. N. M. B.

Discharge characteristics of self-quenching counters. W. E. Ramsey and E. L. Hudspeth (*Physical Rev.*, 1942, [ii], 62, 95—96; cf. A., 1941, I, 439).—Montgomery's counter discharge mechanism for a non-self-quenching gas mixture (cf. A., 1940, I, 306) satis-



factorily explains the dependence of pulse size on counter wire capacity and counter length for the case also of self-quenching gases. Data and curves for the dependence are given and the essential difference between the two types of counter is illustrated and discussed. N. M. B.

**Directional properties of self-quenching counters.** W. E. Ramsey (*Physical Rev.*, 1942, [ii], 62, 96—97).—Stever's method of producing directional properties by means of glass beads on the counter wire is discussed (cf. A., 1941, I, 349). In a self-quenching mixture the entire ionisation process is confined to the vicinity of the wire and spreads along it from a starting point initiated by the ionising ray. Hence the discharge may be confined to any desired section of the counter by any procedure which interferes with this step-by-step process of propagation. The procedure of reducing the electric field at points where it is desired to interrupt the discharge, using a segmented counter (cf. A., 1940, I, 424), is described and discussed. Particles may thus be counted and their ionising capacity simultaneously measured within the same counter. N. M. B.

**Counter as a measuring instrument.** W. Kolhörster and E. Weber (*Physikal. Z.*, 1941, 42, 13—19).—Types of counter and auxiliary apparatus (amplifiers, boosters, counting devices, and coincidence mixing circuits) suitable for reliable continuous recording of cosmic rays are reviewed and discussed. A. J. E. W.

**Helium-filled Geiger-Müller counters.** P. L. Kapur, H. R. Sarna, and Charanjit (*Current Sci.*, 1941, 10, 521—522).—The characteristics of counters filled with mixtures of He with the vapours of various alcohols at different partial pressures have been investigated. Curves for no. of counts against the potential of the wire of the counter are given for He mixed with MeOH, EtOH, Pr<sup>n</sup>OH, and Et<sub>2</sub>O. There is at first a rapid rise, followed by a plateau, and then a further rise. The plateau is longest for He-MeOH, where it extends over 400 v. He-EtOH is also good, but the threshold potential is higher. The threshold potential increases with increasing concn. of org. vapour. This may be due to the fact that the greater amounts of org. vapour decrease the effective mean free path for ions by increasing their size considerably, by condensation or formation of clusters. This makes it necessary to use larger fields to produce ionisation by collision, and thus to start a discharge. The threshold potentials are lower for counters filled with He-MeOH than for those with A-MeOH. A. J. M.

**Simpler weighing.** G. W. Harris (*J. Chem. Educ.*, 1941, 18, 81—82).—The single deflexion method is recommended. L. S. T.

**Recording automatic balance.** P. Ewald (*Ind. Eng. Chem. [Anal.]*, 1942, 14, 66—67).—The instrument described is suitable for investigations of rock phosphate sedimentation, dehydration, hygroscopicity, rapid corrosion, and changes in  $\rho$ . L. S. T.

**Tapless micro-burette with a stock bottle and its application to old and new analytical methods.** I. Lüttger and E. Schröer (*Z. physikal. Chem.*, 1941, B, 49, 257—270).—The apparatus is described, and its use in the usual volumetric processes is outlined. The % errors in these processes are evaluated. The micro-burette gives results equal in accuracy to those obtained by macro-methods. A. J. M.

**Automatic quadruple pipetting machine for rapid and accurate delivery of measured small amounts of fluid.** R. J. Lebowich, H. D. Gursky, C. F. Ackerbauer, and F. A. Opps (*J. Lab. clin. Med.*, 1941, 27, 244—247). C. J. C. B.

**Attachment for pipettes for precise transfer of dangerous fluids.** W. R. Thompson (*Ind. Eng. Chem. [Anal.]*, 1942, 14, 73).—The apparatus described and illustrated has been used for dangerous reagents, and for precise work with bacterial and virus suspensions. L. S. T.

**Du Pont type semi-micro-nitrometer.** P. J. Elving and W. R. McElroy (*Ind. Eng. Chem. [Anal.]*, 1942, 14, 84—88).—Construction and operation of two types of nitrometer, one hand- and the other motor-shaken, are described. Various inorg. and org. nitrates, including those of cellulose, have been analysed by means of this apparatus, which can be applied with economy of time and Hg to other determinations for which the Lunge nitrometer is used. Precision and accuracy are slightly < those obtainable on the macro-scale. L. S. T.

**Simple gas-testing appliance.**—See B., 1942, I, 179.

**Instrumental methods of chemical analysis.** R. H. Müller (*Ind. Eng. Chem. [Anal.]*, 1941, 13, 667—754; cf. A., 1941, I, 59).—An illustrated review of instrumental methods relating to  $\rho$ , gas analysis, spectroscopic analysis, colorimetry, fluorescence, refractometric methods of analysis, polarimetry, potentiometric and conductometric analyses, the polarograph, electrographic methods of analysis,  $\epsilon$ , radiometric and mass spectrographic methods. L. S. T.

**Apparatus for photo-electric titrations.** H. N. Alyea (*J. Chem. Educ.*, 1941, 18, 57). L. S. T.

**Nomenclature of optical processes in colorimetric analyses.** R. Havemann (*Z. physikal. Chem.*, 1941, A, 188, 182—190).—A dis-

cussion on the correct use of the terms "absolute colorimetry" and "spectrophotometry." F. J. G.

**Dithizone method for determination of lead: mechanical shaker for separatory funnels.** L. R. Crisp and S. H. Webster (*J. Lab. clin. Med.*, 1941, 27, 269—270). C. J. C. B.

**Inexpensive specific gravity apparatus.** H. L. Motley (*J. Lab. clin. Med.*, 1941, 26, 1959—1961). C. J. C. B.

**Tube for centrifuging 16 specimens in a 4-place centrifuge.** E. E. Holmes (*J. Lab. clin. Med.*, 1941, 27, 252—253).—7 10-mm. centrifuge tubes are packed into each 50-c.c. brass cup supplied with the centrifuge. C. J. C. B.

**Immersion still-head for low-pressure distillation of organic mixtures.** A. J. Bailey (*Ind. Eng. Chem. [Anal.]*, 1942, 14, 71).—The still-head described has been used successfully with mixtures characterised by high b.p., viscous or tarry consistency, and a marked tendency to bump, froth, or spatter. Still-heads of this type fill the gap between vac. and mol. distillation. L. S. T.

**Improved distilling column head.** A. Turk and A. Matuszak (*Ind. Eng. Chem. [Anal.]*, 1942, 14, 72).—The column head described for total reflux-variable take-off distillation has been used on ~30 columns of various types with compounds boiling from 36° to 168°. L. S. T.

**Laboratory flowmeter with interchangeable precision-bore capillaries.** F. C. Croxton (*Ind. Eng. Chem. [Anal.]*, 1942, 14, 69—70).—Details of construction and performance are given. L. S. T.

**Applications of determinants.** A. Alison (*Ind. Chem.*, 1941, 17, 156—161).—The application of determinants to elimination, solution of equations, and nomography is illustrated. L. J. J.

## XII.—LECTURE EXPERIMENTS AND HISTORICAL.

**Lecture experiments in general chemistry. VI. Liquefaction and fractionation of air. VII. Liquefaction and fractionation of natural gas.** S. Morris and A. J. W. Headlee (*J. Chem. Educ.*, 1941, 18, 79—80). L. S. T.

**John Mayow, 1641—79.** D. McKie (*Nature*, 1941, 148, 728).—Evidence that Mayow was born in Cornwall in December, 1641, is presented. L. S. T.

**John Mercer.** H. Rheinboldt (*J. Chem. Educ.*, 1941, 18, 80). L. S. T.

**V. V. Markovnikov.** H. M. Leicester (*J. Chem. Educ.*, 1941, 18, 53—57). L. S. T.

## XIII.—GEOCHEMISTRY.

**Spectroscopic studies of base exchange materials.**—See A., 1942, I, 124.

**Experimental flow of rocks under conditions favouring recrystallisation.** D. Griggs (*Bull. Geol. Soc. Amer.*, 1940, 51, 1001—1022; cf. A., 1939, I, 110).—Pressure alone changes the behaviour of rocks and simulates some types of natural deformation, but it is inadequate to explain all natural flow because of the large increase in rock strength involved, its inability to produce plastic behaviour in quartz (I), and the development of too intense mechanical twinning in calcite aggregates. Preliminary experiments at high pressure indicate that temp. alone produces unimportant effects on the deformation of rocks. Creep tests show that the flow of Solenhofen limestone loaded to 1400 kg. per sq. cm. is so slow that deformation would be negligible in >10<sup>6</sup> years. When conditions are such that dissolution and recrystallisation may occur, the observed characteristics of rock flow are quite different. At high temp. and in presence of solutions, (I) appears to show recrystallisation flow; the flow of marble is also altered. Creep tests on Ohio alabaster, which shows little deformation when dry, indicate relatively rapid flow in presence of solutions. The rate of flow increases exponentially with stress. The important rôle that dissolution and recrystallisation may play in rock deformation is emphasised. L. S. T.

**Cosmical abundance of the elements.**—See A., 1942, I, 125.

**Sedimentary basins of Ontario. Possible sources of oil and gas.** A. E. Wilson, J. S. Stewart, and J. F. Caley (*Trans. Roy. Soc. Canada*, 1941, [iii], 35, IV, 167—185).—Information concerning the numerous attempts to find oil and gas is summarised, and related to the Palaeozoic basins, as basins. The Delaware-Onondaga strata of the Ontario peninsula provide the greatest oil-producing formation in Ontario. Devonian rocks in the Hudson Bay area have yielded no oil. Oil occurs in small quantities in the Guelph dolomite and in the Whirlpool sandstone at the base of the Silurian; otherwise, it does not occur in the Silurian of Ontario. Gas is produced in large quantities from the Silurian rocks in the Niagara peninsula region. Commercial amounts of oil are found in rocks of Trenton age only in Dover West in the Ontario peninsula. Gas occurs at two levels in the Ordovician, in rocks of Gloucester and Trenton ages. Gas is reported from wells in the black shales of Central and Eastern Ontario. No oil or gas has been reported from the Ordovician strata in the Hudson Bay area. L. S. T.



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