

# BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

**MAY, 1944**



## A I—GENERAL, PHYSICAL, AND INORGANIC CHEMISTRY

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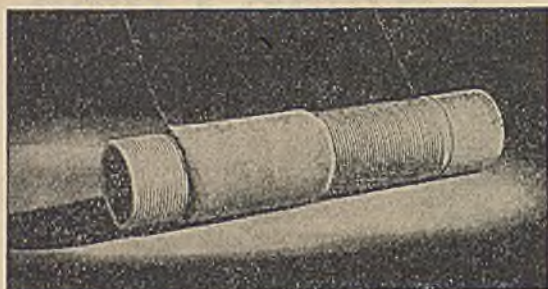
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MAY, 1944.

## I.—SUB-ATOMICS.

**Polarisation of lines in the night-sky luminescence spectrum.** V. L. Ginzburg (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 38, 237—240).—A discussion of the degree of polarisation in the lines  $\lambda$  5577 and 6300 Å. of O and the D lines of Na, assuming that the luminescence is due to fluorescence and multiple scattering of the sun's rays. The possibility of polarisation in the aurora spectrum is also discussed.

H. J. W.

**Spectrum of doubly ionised cadmium.** K. C. Mazumder (*Indian J. Physics*, 1943, 17, 229—238).—The spark spectrum of Cd has been investigated from 2200 to 370 Å. and the lines corresponding with different stages of ionisation have been sorted out. 134 new lines of Cd III have been classified, identifying 29 new terms with  $4d^6s$ ,  $4d^5d$  configurations, and 7 undesignated terms. Term vals. have been calc. The deepest term,  $4d^{10}1S_0$ , is 308,463 cm.<sup>-1</sup> and the ionisation potential  $\sim 33$  v.

W. R. A.

**Observation of very small Stark effects.** L. Jenckel and H. Kopfermann (*Z. Physik*, 1941, 117, 145—155).—A beam of atoms is illuminated at right angles from a source emitting the resonance frequency for which the inverse Stark effect is to be examined, and an electric field of  $>300,000$  v. per cm. is applied at right angles to the light and atom beams. The absorption in the "continuum" provided by the emitted line is observed by means of a Fabry-Perot étalon. The Ca  $^1S_0-^1P_1$  ( $\lambda$  4227 Å.) line first shows measurable red displacement at  $\sim 200$  kv. per cm. Higher potential gradients are required than those predicted by theory, e.g., 300 kv. per cm. produces  $\Delta\nu = 1.8 \times 10^{-2}$  cm.<sup>-1</sup>

L. J. J.

**Probable X-ray mass absorption coefficients for wave-lengths shorter than the K critical absorption wavelength.** J. A. Victoreen (*J. Appl. Physics*, 1943, 14, 95—102).—Graphic analysis of all available experimental data leads to an expression for absorption coeffs.  $\mu/\rho = a\lambda^3Z^2(2Z/A) - \beta\lambda^4Z^6(2Z/A) + \sigma_e N_0(Z/A)$ , valid for all elements, where  $a = aZ^2 + bZ - c$  and  $\beta = dZ^2 - eZ + f$ . Different vals. of  $a$ ,  $b$ ,  $c$ ,  $d$ ,  $e$ , and  $f$  are required for each side of the crit. absorption  $\lambda\lambda$  and for either side of  $Z = 5$ , and are given for the short- $\lambda$  side of the K crit. absorption  $\lambda\lambda$ . Vals. of  $aZ^2(2Z/A)$  and  $\beta Z^6(2Z/A)$ , calc. for all elements, are tabulated. Calc. mass absorption coeffs. agree well with published data as shown by comparative tabulations for a representative range of elements and  $\lambda\lambda$ .

N. M. B.

**L Spectra and characteristic levels of thallium.** (Mlle.) Y. Cauchois (*Compt. rend.*, 1942, 215, 413).—Vals. of  $\lambda$  and  $\nu/R$  are reported for transitions, in emission and absorption, from the  $L_I$ ,  $L_{II}$ , and  $L_{III}$  levels.  $\nu/R$  vals. for levels from K to  $O_V$  (except  $N_{VI}$ ,  $VII$  and  $O_I$ ) are derived.

A. J. E. W.

**L Spectra and characteristic levels of gold.** (Mlle.) Y. Cauchois (*Compt. rend.*, 1942, 215, 465—466).—Corresponding data are reported for Au (cf. preceding abstract).

A. J. E. W.

**"Avalanche products," discharge depressions, and falling characteristics.** W. Rogowski (*Z. Physik*, 1941, 117, 265—284).—The effect of irradiation on electrical discharge characteristics in  $H_2$ ,  $N_2$ , air, A, Ne, Kr, and Xe is discussed.

L. J. J.

**Thermionic emission from an oxide-coated cathode.** H. Y. Fan (*J. Appl. Physics*, 1943, 14, 552—560).—Electrons emitted from an indirectly heated BaO-coated cathode have a Maxwellian distribution corresponding with the temp. of the cathode in the range 582—951° K. With accelerating voltages up to 2500 v. per cm., the current increases much more rapidly than is predicted by Schottky's theory. Both the work function and factor  $A$  vary with the physical state of the cathode. No decay of emission with time is found.

L. J. J.

**Secondary electron emission from metals in the low primary energy region.** (Miss) I. Gimpel and (Sir) O. Richardson (*Proc. Roy. Soc.*, 1943, A, 182, 17—47).—A new method and apparatus for measuring secondary electron emission from non-gaseous material are described. One of the essential features of the experimental arrangement is the control of the primary beam of electrons by an electrostatic lens system. The method is applied to pure, gas-free Cu, using primary electrons with energies as low as 0.35 v. It is concluded that for low-energy electrons the secondary electrons are just re-

flected electrons and that the coeff. of reflexion is independent of the energy. No manipulation of the electrode potentials can reduce the mean energy of electrons from a thermionic source at temp.  $T$  below  $2kT$ .

G. D. P.

**Electron affinity of oxygen.** D. T. Vier and J. E. Mayer (*J. Chem. Physics*, 1944, 12, 28—34).—Measurements of the ratio of negative ions to electrons leaving a hot filament surface exposed to  $O_2$  at 0.1—2  $\mu$ . and 2030—2230° K. give  $70.8 \pm 2.0$  kg.-cal. per g.-mol. for the reaction  $e^- + O_{gas} \rightarrow O_{gas}^-$  at 0° K.

L. J. J.

**Condensation nuclei made visible by the electron microscope.** F. Linke (*Naturwiss.*, 1943, 31, 230—231).—A magnification of 30,000, obtained with the electron microscope, makes visible the nuclei (radius 25—100 m $\mu$ .) responsible for condensation of  $H_2O$  vapour. Photographs are given, and the structure of the nuclei is discussed.

A. J. M.

**Control of rare-gas-filled low-pressure arcs by means of a grid in the discharge plasma.** E. Leimberger (*Z. Physik*, 1941, 117, 621—641).—The anode current can be controlled by means of a positive space charge layer produced by a grid. At relatively high pressures control is limited by constriction of the arc. The dependence of the control effect on a no. of variables has been studied.

L. J. J.

**Electric spark discharge in different gases.** T. E. Allibone and J. M. Meek (*J. Sci. Instr.*, 1944, 21, 21—27).—A survey, with illustrative data and curves, of breakdown of the nearly uniform and the diverging field for const. and low-frequency alternating voltage and for impulse voltage.

N. M. B.

**Mechanism of electrical removal of gas at pressures below  $10^{-4}$  torr.** H. Schwarz (*Z. Physik*, 1941, 117, 23—40).—Sudden changes in electron current between 0.1 and 30 ma., observed in high-vac. hot-cathode tubes with annular anodes, at 4000 v. anode potential, are caused by reversal of the charge on the glass wall. The charge is independent of pressure between  $2 \times 10^{-7}$  and  $2 \times 10^{-3}$  torr., and is determined by the secondary electron emission yield ( $\delta$ ) of the wall. The charge on the wall is positive for  $\delta > 1$  and negative for  $\delta < 1$ . The electrical conditions can be reproduced by the introduction of a metal wall, the potential of which can be varied. The change in the anode current from a higher to a lower val. is accompanied by a sudden fall in pressure from  $10^{-4}$  to  $10^{-6}$  torr., caused by capture of positive ions by the wall. When a wide-meshed wire network is used, absorption of gas is found only in the range +30 to +140 v.

L. J. J.

**At. wt. of samarium.** O. Hönigschmid and F. Hirschbold-Wittner (*Z. physikal. Chem.*, 1941, A, 189, 38—43).—Pure  $Sm_2O_3$  was prepared, and converted into  $SmCl_3$  by pptg. as oxalate, igniting, and dissolving in HCl. The pure  $SmCl_3$  was titrated against Ag by the nephelometric method, and compared with Ag by weighing the pptd.  $AgCl$ . The average val. of the at. wt. was 150.38.

A. J. M.

**Scattering of rapid neutrons at protons and deuterons.** M. Ageno, E. Amaldi, D. Bocciarelli, and G. C. Trabacchi (*Naturwiss.*, 1943, 31, 231—232).—With an arrangement of three proportional counters in coincidence the total cross-sections of neutrons of 4.1, 12.5, and 13.5 Me.v. are measured with respect to C, H, and D. The results agree with Bethe's theory.

A. J. M.

**$\beta$ - and  $\gamma$ -Rays from artificially radioactive  $^{74}As$ .** K. Philipp and F. Rehbein (*Naturwiss.*, 1943, 31, 235—236).—The  $\beta$ -spectrum of  $^{74}As$  has been investigated with a magnetic  $\beta$  spectrograph. There are 3 components with limiting energies  $1.1 \pm 0.1$ ,  $2.7 \pm 0.2$ , and  $3.15 \pm 0.05$  Me.v. Weak electron lines were also found in the region of 0.3—0.7 Me.v. The energies of  $\gamma$ -radiations obtained from these data agree with experimental results.

A. J. M.

**Continuous  $\beta$ -ray spectrum emitted by radiovanadium,  $^{55}V$ .** (Mlle.) T. Yuasa (*Compt. rend.*, 1942, 215, 414—415).—The  $\beta$ -ray spectrum of radio-V prepared by neutron bombardment of  $V_2O_5$  in a cyclotron has been examined by the Wilson cloud-chamber method. The spectrum is simple; with a source containing 24 mg. of  $V_2O_5$  per sq. cm. the upper energy limit is  $2.65 \pm 0.05$  Me.v.; the most probable and mean energies, respectively, are  $0.90 \pm 0.05$  and 1.1 Me.v.  $\gamma$ -Radiation of mean energy  $1.57 \pm 0.10$  Me.v. and a small no. of positrons of energy 0.15—0.97 Me.v. are observed.

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The  $\beta$ - and  $\gamma$ -radiations are ascribed to the reactions  ${}^{52}_{22}\text{V} \rightarrow {}^{52}_{22}\text{Cr}^* \rightarrow {}^{52}_{22}\text{Cr}$ .  
A. J. E. W.

**Active strontium and yttrium isotopes obtained in uranium fission.** O. Hahn and F. Strassmann (*Naturwiss.*, 1943, 31, 249—250).—Preliminary. Two new isotopes, Sr with half-life  $\sim 2$  min., and its daughter element Y of half-life 20 min., have been detected in the product from active U. The half-life of the Y isotope from 7-min. Sr is  $11.5 \pm 0.5$  hr. instead of the earlier val. 9 hr. The half-life of the Sr isotope, found by Götte (*ibid.*, 1941, 29, 496), is 10 hr. instead of the earlier val. 8.5 hr.  
J. F. H.

**Theory of mesons.** K. Nikolski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 38, 173—175).—Mathematical.  
N. M. B.

**Production of cosmic-ray mesons.** L. Jánossy (*Physical Rev.*, 1943, [ii], 64, 345—349).—The cross-sections given (cf. Hamilton, *et al.*, A., 1944, I, 2) for the production of mesons in collisions between heavy particles are so large that a heavy particle crossing an atom nucleus must be expected to collide several times inside the same nucleus. This accounts for cloud-chamber observations showing the production of several mesons in one point. Anticoincidence experiments can be interpreted by the theory (*ibid.*), when the occurrence of multiple collisions is assumed.  
N. M. B.

**Mesotron temperature coefficient.** F. A. Benedetto (*Physical Rev.*, 1943, [ii], 64, 317—318; cf. A., 1942, I, 37).—Causes of the discrepancy between observations by counter train and by ionisation chamber are discussed.  
N. M. B.

**Applications of the  $\lambda$ -limiting process to the theory of the meson field.** W. Pauli (*Physical Rev.*, 1943, [ii], 64, 332—344).—Mathematical. The Wentzel-Dirac  $\lambda$ -limiting process for the interaction of an electron with an electromagnetic field is applied to the interaction of a heavy particle (nucleon) with the meson field.  
N. M. B.

**Stellar model built in complete accordance with Bethe's formula of energy-generation.** N. R. Sen and U. R. Burman (*Physical Rev.*, 1943, [ii], 64, 317).—Bethe's scheme for stars produced by the "C cycle" requires a temp. of  $\sim 20 \times 10^6$  degrees. A preliminary investigation to find what types of core with that central temp.,  $\text{H}_2$  content 35%, He content 0, and average mol. wt. 1, conform to Bethe's formula is reported. Distinguishing a convective and an energy core, for central density  $\rho < 31$  g. per sq. cm. there is no convective core, for  $\rho$  31—51 g. per sq. cm. there is a convective core, and for  $\rho \geq 51$  g. per sq. cm. the model is entirely convective. Other characteristics are evaluated and discussed.  
N. M. B.

## II.—MOLECULAR STRUCTURE.

**Molecules in stellar atmospheres.** P. P. Dobronravín (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 91—94).—The temp. of stars and the conditions of some mol. at their surfaces are deduced from the mol. bands in stellar spectra.  
J. J. B.

**Resonance emission of cadmium hydride bands in cadmium-photo-sensitised reactions of hydrocarbons.** E. W. R. Steacie and D. J. LeRoy (*J. Chem. Physics*, 1944, 12, 34—36).—The resonance excitation of CdH bands in mixtures of  $\text{C}_2\text{H}_4$  or  $\text{C}_2\text{H}_2$  with Cd vapour illuminated with  $\lambda$  3261 and 2288 Å. has been examined. With  $\lambda$  2288 Å. no resonance emission was found. With  $\lambda$  3261 Å., no resonance excitation was found with  $\text{C}_2\text{H}_4$ , but CdH bands were emitted with  $\text{C}_2\text{H}_2$ . Thus the primary process in Cd-sensitised reactions of paraffins is  $\text{Cd}(^5P_1) + \text{RH} \rightarrow \text{CdH} + \text{R}$ .  
L. J. J.

**Band spectrum of  $\text{N}_2$ ; weak systems in the visible region.** A. G. Gaydon (*Proc. Physical Soc.*, 1944, 56, 85—95).—Data are reported for the Goldstein-Kaplan bands at  $\lambda$  4165, 4432, and 4728, which appear readily in the spectrum produced by mild excitation with a silent, ozoniser-type discharge, and with a Tesla coil. Measurements support Kaplan's vibrational analysis, but other bands in the ultra-violet probably belong to a different system. The rotational structure and probable type of electronic transition are discussed. A weak new system observed in the green has, provisionally,  $\omega_1' = 896$ ,  $\omega_1'' = 740$   $\text{cm}^{-1}$ . The electronic levels of  $\text{N}_2$ , effect of excitation conditions on the band systems, and the bearing of results on the determination of dissociation energy are discussed.  
N. M. B.

**Band spectrum of NO:  $\gamma$  and  $\epsilon$  systems.** A. G. Gaydon (*Proc. Physical Soc.*, 1944, 56, 95—103).—Data are reported for the  $\gamma$ ,  $\delta$ , and  $\epsilon$  bands of NO excited by transformer discharge and silent ozoniser-type discharge. Measurements and intensity distribution show that, contrary to the findings of Herzberg (cf. A., 1940, I, 191), the  $\gamma$  and  $\epsilon$  systems arise from separate upper electronic states. There is no evidence of predissociation in the  $\gamma$  and  $\epsilon$  systems. It is difficult to reconcile observations with a heat of dissociation as low as 5.29 e.v.  
N. M. B.

**Spectroscopic study of the diffuse discharge in nitrogen at atmospheric pressure.** J. Janin (*Compt. rend.*, 1942, 215, 505—506).—The ultra-violet spectrum includes bands of the second positive system of  $\text{N}_2$ , a few of the negative bands of  $\text{N}_2^+$ , and the Vegard-

Kaplan ( $A \rightarrow X$ ) bands of  $\text{N}_2$ . The forbidden  $^4S \rightarrow ^3P$  line of N also appears at  $3466.5 \pm 0.1$  Å., its intensity variation being parallel to that of the  $A \rightarrow X$  bands.  $\lambda$  of eight of the band-heads of the  $A \rightarrow X$  system are recorded, and a  $\nu$  formula is proposed; all the bands have P and R branches. Details of fine structure are given for the (1, 8) and (1, 9) bands (2997, 3198 Å.).  
A. J. E. W.

**Green phosphorescence of active nitrogen.** (Mme.) R. Herman (*Compt. rend.*, 1942, 215, 506—508).—The phosphorescence is produced by a high-voltage discharge in purified  $\text{N}_2$  at 10—20 mm. pressure. The spectrum contains high vibrational lines of the first positive system of  $\text{N}_2$  at high intensity; in addition to the levels  $\nu' = 13$ —20 of the sequence  $\nu' - \nu'' = 5$ , the sequence  $\nu' - \nu'' = 6$  ( $\nu' = 17$ —24) is observed. Although first positive  $\text{N}_2$  and first negative  $\text{N}_2^+$  bands occur simultaneously in the spectrum, a comparison of intensities shows little similarity to auroral spectra.  
A. J. E. W.

**New ultra-violet band-system of antimony monoxide (SbO).** A. K. Sengupta (*Indian J. Physics*, 1943, 17, 216—222).—A new ultra-violet band system, probably a  $^3\Sigma \rightarrow ^3\Pi$  transition, has been photographed in the region 2910—2450 Å. in the emission spectrum of SbO. The bands are double-headed and degraded towards the violet. The vibrational structure analysis shows that the lower state of the new system is identical with that of other SbO systems already known.  
W. R. A.

**Ultra-violet spectra and electron configuration of HgF and related halide molecules.** H. G. Howell (*Proc. Roy. Soc.*, 1943, A, 182, 95—112).—The high-frequency ultra-violet emission spectrum of HgF was photographed and analysed into two systems, each due to a  $^3\Pi \rightarrow ^3\Sigma$  transition between Hg atom-like levels. Predicted analogies with the Zn and Cd halides are verified. The electron configuration of the states involved is discussed and an energy-level diagram is given.  
G. D. P.

**Assay of potassium *p*-phenolsulphonate, its pH range, and its ultra-violet absorption spectrum.** E. E. Sager, M. R. Schooley, and S. F. Acree (*J. Res. Nat. Bur. Stand.*, 1943, 31, 197—204; cf. also C., 1944, Part 2).—The purification of *p*-OH·C<sub>6</sub>H<sub>4</sub>·SO<sub>3</sub>K (I) and its determination through the quantity of Br used in its dibromination are described. The absorption spectrum of (I) has been determined over the  $\lambda$  range 2100—3100 Å. The main absorption band has a peak at 2300 Å. but this is sharply defined only in dil. solutions. The absorption spectrum is changed considerably on the addition of NaOH, owing to the production of the bivalent ion.  
J. W. S.

**Ultra-violet absorption spectra and resonance in benzene derivatives: sulphanilamide, metanilamide, *p*-aminobenzoic acid, benzenesulphonamide, benzoic acid, and aniline.** W. D. Kumler and L. A. Strait (*J. Amer. Chem. Soc.*, 1943, 65, 2349—2354).—Ultra-violet absorption spectra of sulphanilamide (I), metanilamide (II), *p*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H (III), PhSO<sub>2</sub>·NH<sub>2</sub> (IV), BzOH (V), and NH<sub>2</sub>·Ph (VI) have been determined in acidic, basic, H<sub>2</sub>O, and aq. NaCl solutions. The spectra are correlated with the known resonance forms. Spectra of (I) and (II) in acid are similar to that of (IV) in H<sub>2</sub>O. The spectrum of an unsubstituted or alkyl-substituted aromatic NH<sub>2</sub>-compound reverts, in a solution sufficiently acid to cause conversion into the salt, to that of the compound in which NH<sub>2</sub> is replaced by H or an alkyl group. (I) and (III) have higher extinction coeffs. in basic solution than in H<sub>2</sub>O or aq. NaCl, indicating a greater contribution by the main resonance form to the ion than to the undissociated mol. The reverse is true for (IV) and (V). Solvent effects in the spectra of compounds of the type of *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub> (VII) are due to solvation differences and not to differences in dielectric const. Differences in the spectra of (VII) in C<sub>6</sub>H<sub>6</sub>, dioxan, and H<sub>2</sub>O are attributed to differences in H-bonding. The similarity of the spectra of (VI) and (II) is attributed to the incompatibility of NH<sub>2</sub> and SO<sub>2</sub>·NH<sub>2</sub> resonance in (II), that due to NH<sub>2</sub> effectively concealing the resonance of SO<sub>2</sub>·NH<sub>2</sub>.  
W. R. A.

**Ultra-violet absorption spectra of ethanol lignins.**—See A., 1944, II, 115.

**$\gamma$  Bands in absorption spectra.** G. N. Lewis and J. Bigeleisen (*J. Amer. Chem. Soc.*, 1943, 65, 2102—2106).—When one of the equiv. groups of crystal-violet is replaced by a different group, the single absorption band becomes resolved into  $\alpha$  and  $\gamma$  bands. The larger is the difference in auxochromic nature of the new and old groups, the wider is the separation of the  $\alpha$  and  $\gamma$  bands. The second band in malachite-green is proved to be a  $\gamma$  band by production of oriented mol. in a rigid solvent and by polarised fluorescence. It is shown that the electronic oscillations of two excited states are perpendicular to each other. The negative fluorescent polarisations in fluorescein and rhodamine-B accord with Lewis and Calvin's theory. A new method of measuring small degrees of polarisation is described. (See also C., 1944, Part 2.)  
W. R. A.

**Second order  $\alpha$ -bands in absorption spectra.** G. N. Lewis and J. Bigeleisen (*J. Amer. Chem. Soc.*, 1943, 65, 2107—2110).—Additional second-order  $\alpha$  bands in the absorption spectra of cyanines and other dyes are reported and discussed.  
W. R. A.



**Ultra-violet absorption spectra of alicyclic di- and tri-ketones.**—See A., 1944, II, 138.

**Absorption spectra and structure of pyrethrins I and II.** A. E. Gillam and T. F. West (*J.C.S.*, 1944, 49—51; cf. A., 1942, I, 31).—The presence in pyrethrolone enol semicarbazone (I) of conjugated, and not cumulated, ethylenic linkings in the side-chain is proved by absorption max. at 2260—2270 and 3085—3090 Å. in EtOH. (I) has m.p. 255—256°, but  $\epsilon$  varies for different samples (12,000—17,600 and 16,500—20,300 for the two bands, respectively). For the enol itself (II) (modified prep.) the two bands overlap, giving a max. at 2440 Å. ( $\epsilon$  12,600). Pyrethrolone (III) has a max. at 2260 Å. ( $\epsilon$  ~29,000). (II), (III), and the Me ether of (III) are either unchanged or converted into high-boiling compounds by  $\text{Al}(\text{OPr}^i)_3$ - $\text{Pr}^i\text{OH}$ . R. S. C.

**Volatile vegetable matter. XXVIII. Ultra-violet absorption and Raman spectra of ionones and related substances.** Y. R. Naves and P. Bachmann (*Helv. Chim. Acta*, 1944, 27, 97—104).—For a solution of the ionones (I) in hexane there is a series of fine bands in the ultra-violet which are connected with the states of vibration of the normal mol. In  $\alpha$ -ionone and methyl- $\alpha$ -ionone the R absorption bands are continuous with the K bands. The frequencies characteristic of different double-bond effects and the displacements which cause coupling can be determined by comparison of the Raman spectra of (I) with those of the dihydroionols. Secondary effects in the spectra are mostly explicable by conjugation. J. O'M. B.

**Fluorescence and absorption spectra of naphthalene and its derivatives at low temperatures.** A. F. Prichotko and K. G. Schabaldas (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 120—125).—The absorption and fluorescence spectra of  $\text{C}_{10}\text{H}_8$  and the fluorescence spectra of 2- $\text{C}_{10}\text{H}_7\text{Me}$ , 2:6- $\text{C}_{10}\text{H}_6\text{Me}_2$ ,  $\alpha$ - and  $\beta$ - $\text{C}_{10}\text{H}_7\text{OH}$ ,  $\alpha$ - and  $\beta$ - $\text{C}_{10}\text{H}_7\text{NH}_2$ , and dinaphthyl are determined at 20.4° K. Several new electron transitions are reported. J. J. B.

**Fluorescence of anthracene in the presence of naphthalene.** S. C. Ganguly (*Proc. Indian Assoc. Cult. Sci.*, 1943, 26, 7).—Fluorescence of naphthalene (I) has been studied in solid solution with anthracene (II) and chrysene, also in EtOH and in an EtOH solution of (II). In solid solution the excited fluorescence bands of (I) are shifted slightly, depending on the solvent. Comparison of the fluorescence of mixed EtOH solutions of (I) and (II) with solutions containing only (I) or (II) shows that the fluorescence of one component is not affected by the presence of the other. Absorption spectra of the solutions confirm this result. W. R. A.

**Raman spectra of solutions of silver perchlorate in toluene and in water.** M. J. Murray and F. F. Cleveland (*J. Amer. Chem. Soc.*, 1943, 65, 2110—2112).—A band at 167  $\text{cm}^{-1}$  in the Raman spectrum of a conc. solution of  $\text{AgClO}_4$  in PhMe, which has no counterpart in aq.  $\text{AgClO}_4$ , but appears in aq.  $\text{Hg}(\text{ClO}_4)_2$ , is thought to arise from a covalent linking of the metal and  $\text{ClO}_4$ . W. R. A.

**Raman effect. CXXVIII. Oxalic acid.** L. Kahovec, K. W. F. Kohlrusch, and J. Wagner. **CXXIX. Nitrogen compounds. XIX. Amides of dicarboxylic acids and related compounds.** L. Kahovec and J. Wagner. **CXXX. Nitrogen compounds. XX. Tetranitromethane.** K. W. F. Kohlrusch and H. Wittek (*Z. physikal. Chem.*, 1941, B, 49, 145—155, 156—162, 163—169).—CXXVIII. The Raman spectra of anhyd. cryst.  $\alpha$ - and  $\beta$ - $\text{H}_2\text{C}_2\text{O}_4$  are obtained. They differ markedly between themselves and also differ from that of  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ .  $\beta$ - $\text{H}_2\text{C}_2\text{O}_4$  gives four lines at 2600—3100 Å., and the  $\alpha$ -form two at 3100 and 3260 Å., ascribed to O—H—O bridges. No satisfactory explanation of the observed vibrational spectra can be obtained by discussion of the results of X-ray, Raman, and infra-red spectra.

CXXIX. The Raman spectra of cryst.  $(\text{CO}\cdot\text{NH}_2)_2$  (I),  $\text{CH}_2(\text{CO}\cdot\text{NH}_2)_2$ ,  $(\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2)_2$ ,  $\text{NH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$  (II),  $\text{NH}_2\cdot\text{CO}\cdot\text{CO}_2\text{Me}$ ,  $\text{NH}_2\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ ,  $(\text{CH}_2\cdot\text{CO})_2\text{O}$ ,  $(\text{CH}_2\cdot\text{CO})_2\text{NH}$ , allantoin, and  $(\text{CO}\cdot\text{NH})_2\text{CO}$  are obtained. The  $\delta(\text{NH}_2)$  and  $\nu(\text{NH}_2)$  frequencies and the similarity of the spectra of (I) and (II) to those of  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{N}_2\text{O}_4$  are briefly discussed.

CXXX. The Raman spectra of  $\text{C}(\text{NO}_2)_4$  as solid, liquid, and dissolved in  $\text{CCl}_4$  are obtained. The results confirm those of Médard (A., 1935, 564). The results of polarisation measurements are best explained by a structure with symmetry  $S_{4w}$ . J. F. H.

**Rectifying property of carborundum.** J. T. Kendall (*Proc. Physical Soc.*, 1944, 56, 123—129).—A technique is described for obtaining non-rectifying C-carborundum contacts. Current-voltage curves for single rectifying contacts show that (I) green, and (II) blue or black carborundum are essentially different types of semi-conductor; in (I) rectification takes place so that easy electron flow is from semi-conductor to metal, and in (II) rectification is in the opposite direction. Experiments show that all rectification takes place at the contact surface and that vol. rectification (if any) is a second-order effect. N. M. B.

**Dielectric constant of ionised air in a discharge tube in the range of wave-lengths 80—1500 cm.** N. Alam and S. R. Khastgir (*Indian J. Physics*, 1943, 17, 204—215).—The effective dielectric const.,  $\epsilon$ , of the ionised air in a discharge tube has been determined, using

the Lecher-wire method, for  $\lambda$  80—1500 cm. Three distinct min. were observed at 175, 310, and 370 cm., corresponding with weak oscillations, of  $\lambda$  169, 310, and 362 cm., produced within the tube under the conditions of measurement. W. R. A.

**Hydrogen cyanide. XIII. Dielectric constant of anhydrous hydrogen cyanide.** G. E. Coates and J. E. Coates (*J.C.S.*, 1944, 77—81).—The dielectric const. ( $\epsilon$ ) of anhyd. HCN can be represented by  $\log \epsilon = 2.199 - 0.0079\theta + 5 \times 10^{-5}\theta^2$  for  $\theta$  -13.3° (f.p.) to 18°, and by  $\log \epsilon = 2.1869 - 0.00633\theta$  for  $\theta$  18—25.7° (b.p.). The high vals. of  $\epsilon$  and temp. coeff. are interpreted in terms of linear polymerisation and the existence of mol. units with large dipole moments. C. R. H.

**Scattering of light by small drops of water.** R. Ruedy (*Canad. J. Res.*, 1943, 21, A, 99—100).—When small drops increase in size to  $2r = 0.25\lambda$ , they scatter light according to Rayleigh's law, but for  $2r = 0.25-0.5\lambda$  the intensity of light scattered towards the source decreases almost to zero, the change being most marked for  $2r = 0.25-0.375\lambda$ . The sharp increase,  $\propto r^3$ , of scattered light with increase in size continues in the main direction of radiation by the particle. As scattering deviates from Rayleigh's law, colours other than blue appear strongly; the dispersion of the colours increases with increasing particle size until mainly red light remains. N. M. B.

**Rotation dispersion of some  $\alpha$ -hydroxy-acids. Configuration of  $\alpha$ -hydroxy-acids.** P. Szarvas (*Z. physikal. Chem.*, 1941, A, 188, 235—245).—The rotatory dispersions of (+)-lactic (I), (-)- $\alpha$ -hydroxybutyric (II), (-)-malic, and (+)-tartaric acids in the visible and near ultra-violet regions have been determined. The results indicate that (II) has the *l*-configuration similar to (I). The contrary observation of Levene and Haller (A., 1927, 1053) is attributable to the presence of  $\text{BaCl}_2$ . J. W. S.

**Possibility of determining experimentally the coefficient of damping of elastic waves of the Debye spectrum from observations on the fine structure of lines of Rayleigh scattering.** V. V. Vladimirovski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 38, 201—202).—Determination of coeff. of damping may be possible from investigation of the fine structure in a non-uniformly heated body. F. R. G.

**Interferometric studies of light scattering in binary liquid mixtures. I.** K. S. Bai (*Proc. Indian Acad. Sci.*, 1943, 18, A, 210—217).—The light scattered by  $\text{H}_2\text{O}$  and a series of org. liquids when illuminated with the  $\lambda$  4810 Å. line of Zn is found to have Brillouin components. These are present also in the scattered light from ordinary mixtures, e.g.,  $\text{EtOH-H}_2\text{O}$  and  $\text{C}_6\text{H}_6-n\text{-C}_6\text{H}_{14}$ , but are absent in that from the crit.-composition mixtures of  $\text{MeOH}$  and  $n\text{-C}_6\text{H}_{14}$  and of  $\text{Pr}^i\text{CO}_2\text{H}$  (I) and  $\text{H}_2\text{O}$  at the crit. solution temp. (~20°), and at temp. up to 40° for  $\text{MeOH}-n\text{-C}_6\text{H}_{14}$ . For (I)- $\text{H}_2\text{O}$  the components appear weakly at 90°. It is concluded that the mixtures remain as emulsoids over a range of temp. above 20°, the mol. aggregates being of a size comparable with  $\lambda$ . H. J. W.

**Diffuse reflexion of light by a foggy medium.** V. A. Ambarzumian (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 38, 229—232).—The scattering power of a medium of infinite thickness with a plane boundary is unaltered by the addition of a further thin layer. Hence an integral equation, the solution of which determines the scattered intensity in any direction outside the boundary, is deduced. The method is also applicable to a finite slab. Solutions of the equations are not given. H. J. W.

**Distribution of light intensity within a scattering medium.** R. R. Newton (*J. Appl. Physics*, 1943, 14, 481—486).—An integral-differential equation is derived for intensity as a function of position and direction. L. J. J.

**Doppler effect in a refractive medium.** I. M. Frank (*J. Physics U.S.S.R.*, 1943, 7, 49—67).—Theoretical. A. J. M.

**Valency states of sulphur.** E. N. Gurjanova (*J. Phys. Chem. Russ.*, 1943, 17, 65—74).—The energies of various possible structures of  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{SOCl}_2$ , and  $\text{SO}_2\text{Cl}_2$  are calc. The most probable structures are  $\text{O}:\overset{\cdot}{\text{S}}:\overset{\cdot}{\text{O}} \rightleftharpoons \overset{\cdot}{\text{S}}:\text{O}:$ ,  $\text{Cl}:\overset{\cdot}{\text{S}}:\overset{\cdot}{\text{O}} \rightleftharpoons \text{Cl}:\overset{\cdot}{\text{S}}:\overset{\cdot}{\text{O}}:$ ,  $\text{O}:\overset{\cdot}{\text{S}}:\overset{\cdot}{\text{O}}:$ , and  $\text{Cl}_2\overset{\cdot}{\text{S}}:\overset{\cdot}{\text{O}}:$ . Other chemical evidence confirms the presence of a trivalent S' ion in "quadrivalent," and of a quadrivalent S'' ion in "sexavalent" S. J. J. B.

**Co-ordination and valency.** A. A. Blanchard (*J. Chem. Educ.*, 1943, 20, 454—460). L. S. T.

**Stereochemistry of co-ordination number eight. Isomerides for the trigonal prism with symmetry  $C_{2v}$ .** L. E. Marchi (*J. Amer. Chem. Soc.*, 1943, 65, 2257—2258).—The trigonal prism with two extra bonds along the normals to two of the rectangular faces and with symmetry  $C_{2v}$  is discussed in respect of compounds showing co-ordination no. 8, and the isomerides for mono- and bi-dentate groups are listed. The nos. of isomerides for class 4AA of the trigonal prism and the dodecahedron are identical. Conclusions regarding the structure of the  $[\text{U}(\text{C}_2\text{O}_4)_4]^{4-}$  ion (cf. A., 1943, I, 194) must be altered to include the prism. W. R. A.

**Electrical energy of two cylindrical charged particles.** G. P. Dube (*Indian J. Physics*, 1943, 17, 189—192).—Using the approx. Debye-



Hückel theory the electrical energy of two cylindrical particles has been worked out. The energy is min. for a certain val. of interparticle distance and this may be important in explaining thixotropic properties. W. R. A.

**Statistical mechanics of liquids, and the gas of hard elastic spheres.** O. K. Rice (*J. Chem. Physics*, 1944, 12, 1—18).—General principles are formulated for a model of the liquid state. A gas of hard elastic spheres has a "communal entropy"  $3R$  per mol., fully excited in each direction of space, arising from sharing of the available space by all the atoms. The geometry, equation of state, and partition function for an assemblage of hard elastic spheres are considered, and a partition function for a monat. liquid is derived, consisting of terms representing vibrational motion in terms of the Debye characteristic temp. of the solid, and a translational term. Each term contributes to the communal entropy. L. J. J.

**Surface tensions and parachors of methyl- and ethyl-amines.** E. Swift, jun. and C. R. Calkins (*J. Amer. Chem. Soc.*, 1943, 65, 2415—2417).—Vals. of  $\gamma$ , accurate to 0.5%, are given for mono-, di-, and tri-methyl- and -ethyl-amines at 15°, 25°, and 35°. Parachors show no structural abnormalities in the liquid state. W. R. A.

### III.—CRYSTAL STRUCTURE.

**Chemistry of oriented growth of crystals of organic compounds.** II. Significance of the hydrogen bond for production of oriented growth of organic compounds. J. Willems (*Naturwiss.*, 1943, 31, 232—233).—A no. of cases of oriented growth of crystals seem to depend on the existence of a H bond between the O of the substance and that of the material on which the crystal is grown. Thus, 1 : 2 : 4- $C_6H_5(OH)_2$ ,  $p$ - $C_6H_4(N-OH)_2$ , and 2 : 5- $C_6H_3Cl_2 \cdot C(OH)_2 \cdot N-OH$  on the (100) face of calcite and related carbonates,  $\alpha$ -quinol, and  $p$ - $NH_2 \cdot C_6H_4 \cdot CO_2H$  on the (010) face of gypsum, and  $(CH_3 \cdot CO_2H)_2$  on talc, show the effect.  $C_6Cl_5 \cdot OH$  (I) grows from  $C_6H_6$  solution in needle-shaped crystals on the (100) face of CsCl, NaCl, KCl, KBr, RbBr, and  $NH_4Cl$ , oriented either parallel to the edges or along the diagonals of the face.  $C_6Br_5 \cdot OH$  grows similarly on NaCl and KCl. A linking of the two lattices by a H bond between the O of the phenol and the Cl of the halide is to be expected; it can only be weak.  $C_6Cl_4$  does not orient itself in the same way on NaCl although formally similar to (I); this indicates that the H atom is responsible for the orientation. Orientation of the (I) lattice has also been obtained on carbonates of the calcite series,  $NaNO_3$ ,  $KClO_3$ , gypsum, anhydrite,  $Sb_2S_3$ , various micas (e.g., muscovite and phlogopite), chlorites (e.g., pennine), sulphanilamide, sulphanilic acid, and sucrose. A. J. M.

**X-Ray patterns of hydrated calcium silicates.** H. F. McMurdie and E. P. Flint (*J. Res. Nat. Bur. Stand.*, 1943, 31, 225—228; cf. A., 1939, I, 154).—X-Ray diffraction data for powder samples of seven natural and eight synthetic hydrated Ca silicates are recorded. J. W. S.

**Crystal structure of boron carbide.** H. K. Clark and J. L. Hoard (*J. Amer. Chem. Soc.*, 1943, 65, 2115—2119).—X-Ray investigation of B carbide confirms the data of Shdanov and Sevastianov (A., 1943, I, 82) and yields for the rhombohedral lattice const.  $a$  5.19 Å.,  $\alpha$  66° 18', space-group  $D_{3h}^6$ — $R\bar{3}m$ , 3  $B_4C$  mols. per unit cell. Corresponding hexagonal lattice const. are  $a$  5.60,  $c$  12.12 Å., 9 mols. per unit cell. Structural units are a linear chain of 3 C with 12 B arranged at the vertices of a nearly regular icosahedron and distributed formally in an approx. NaCl structure. Each B has 6-fold co-ordination and is approx. at the centre of a pentagonal pyramid. Each B is bonded to 5 others in the same icosahedral group and also to either a C in  $2c$  (B in  $6h_1$ ) or a B in  $6h_2$  in an adjacent icosahedron (B in  $6h_2$ ). There is, therefore, a continuous three-dimensional network of B throughout the crystal, which accounts for the great hardness and electrical conductivity of  $B_4C$ . The apparent existence of room in the structure for more atoms explains why commercial  $B_4C$ , having a B/C ratio  $>4$ , is a solid solution. W. R. A.

**X-Ray pattern of boron carbide.** N. G. Sevastianov (*Zavod. Lab.*, 1939, 8, 1317—1318).—In the system B—C only one carbide,  $B_4C$ , is formed. The spacing 3.39 Å. is due to contamination by graphite. J. J. B.

**Crystal chemical studies of the alums.** V. Gallium alums. H. P. Klug and G. L. Kieffer (*J. Amer. Chem. Soc.*, 1943, 65, 2071—2072).—Lattice const. and vals. of  $\rho$  from X-ray data have been determined at 25° for  $M(Ga)(SO_4)_2 \cdot 12H_2O$  ( $M^I = NH_4, K, Rb, Cs, Tl$ ). The Cs and Tl alums have the  $\beta$  structure; the others have the  $\alpha$  structure. W. R. A.

**Crystal structure of LaAl<sub>3</sub>.** G. E. R. Schulze (*Z. Krist.*, 1942, 104, 257—260).—LaAl<sub>3</sub> is a typical cubic Laves phase having the  $MgCu_3$  (C 15) structure;  $a$  8.115 Å.;  $\rho$  4.76. Intensities in the powder X-ray diagram are tabulated. A. J. E. W.

**Co-ordination of starch in the starch-iodine complex.** IV. X-Ray diffraction of butanol-precipitated amylose. R. E. Rundle and F. C. Edwards (*J. Amer. Chem. Soc.*, 1943, 65, 2200—2203).—Diffraction

patterns from wet and dried BuOH-pptd. amylose confirm the helical starch chain with a helix diameter of  $\sim 13.7$  Å., a length per turn of  $\sim 8$  Å., and 6 glucose residues per turn. The helices approximate to a close-packed arrangement in both wet and dried pptts., with alternate helices directed in opposite directions and the probable space-group  $D_{12}^2$ — $P2_12_12_1$ . Spatial relations between the starch-I complex (I) and dried BuOH ppt. confirm that the I in (I) occupies the interior of the helix. It is suggested that BuOH in the BuOH-pptd. amylose also occupies the interior of the helix. The cell previously reported for (I) (A., 1944, I, 5) must be a pseudo-cell with only pseudo-hexagonal symmetry. W. R. A.

**X-Ray fibre pattern from amylose with a glycerol plasticiser.** R. E. Rundle and L. W. Daasch (*J. Amer. Chem. Soc.*, 1943, 65, 2261—2262).—The fibre spacing in an amylose with a glycerol plasticiser is 7.5 Å., compared with 10.6 Å. for "B" starch. This indicates a flexibility of the starch chain not found in the cellulose chain. The ascertained spacing suggests that the chains are extended linearly, but they must be folded to account for the spacing. W. R. A.

**Molecular structure of fibres made from native egg-albumin.** K. J. Palmer and J. A. Galvin (*J. Amer. Chem. Soc.*, 1943, 65, 2187—2190).—Fibres were made from native egg-albumin by complex formation with detergent and drawing under steam. They are composed of parallel bundles of polypeptide chains, having a  $\beta$ -keratin structure, running parallel to the fibre axis. The tensile strength depends on the degree of mol. orientation and can be as high as 38,000 lb. per sq. in. W. R. A.

**Electron beam interferences from molten alloys.** R. Glocker and H. Richter (*Naturwiss.*, 1943, 31, 236).—Liquid binary alloys give two types of electron interference pattern: (a) superposition of the interference systems of the two components (immiscibility in the liquid state), and (b) occurrence of a new interference pattern (due to miscibility). In the case of Sn—Bi the curve of electron density for the strongest innermost interferences against at. concn. of Bi is linear. Vegard's additive rule for mixed-crystal formation in the solid state can therefore also be applied to the liquid state. The equilibrium diagram for this system in the solid state does not show continuous mixed-crystal formation, such as is indicated for the liquid state by the density-concn. curve. A. J. M.

**Variations with temperature of optical properties of conine hydrochloride crystals.** J. Jaffray (*Compt. rend.*, 1942, 215, 489—491; cf. A., 1942, I, 231).—Data are recorded for the temp. variation (0—50°) of the  $\lambda$  at which the crystals become uniaxial, and for the  $\lambda$  and temp. variations of the birefringence of plates cut parallel to  $g^1$ , and of the external angle between the optic axes. A. J. E. W.

**Retrograde transformation.** III. A. Smits (*Z. physikal. Chem.*, 1941, B, 49, 126—130).—In the retrograde transformation tetragonal-cubic observed with  $ND_4Br$ , increase of pressure decreases the temp. range of existence of the tetragonal modification. The possible forms of the pseudobinary ( $T, \pi$ ) diagram and the corresponding unary ( $p, T$ ) diagram are discussed theoretically. Two cases are outlined, in which the region of coexistence of the two phases is either open or closed by a crit. max. (Cf. A., 1942, I, 139.) J. F. H.

**Thermal analysis in the heated microscope.** III. Polymorphic and isomorphous phenomena with *s*-trinitrobenzene, picric acid, and 2 : 4 : 6-trinitrotoluene. A. Kófer (*Z. physikal. Chem.*, 1941, A, 188, 201—228).—Besides the stable form (m.p. 123.5°), *s*- $C_6H_3(NO_2)_3$  (I) exists in unstable enantiomorphic modifications of m.p. 106° and 110°, with transition point 85°. Picric acid (II) occurs in stable (m.p. 122°) and unstable (m.p. 75°) forms isomorphous with the forms of (I) of m.p. 110° and 123.5°, respectively. 1 : 2 : 4 : 6- $C_6H_2Me(NO_2)_3$  (III) occurs in one form only. (I) shows complete miscibility with (II), but in the systems of (III) with (I) or (II) there are several crystallographically distinct mixed crystal series. J. W. S.

### IV.—PHYSICAL PROPERTIES OF SUBSTANCES.

**Magnetic studies on permanganates.** A. Mookherjee (*Proc. Indian Assoc. Cult. Sci.*, 1943, 26, 8—9).—Consideration of the effect of the electric field surrounding the  $MnO_4^-$  ion in  $KMnO_4$  and  $Ba(MnO_4)_2$  shows that the paramagnetism of these compounds arises from the high-frequency portion of the orbital moment. Comparison with  $K_3Fe(CN)_6$  and the small anisotropy (0.07) support this view. W. R. A.

**Magnetic properties of iron included in active charcoals.** C. Courty (*Compt. rend.*, 1942, 215, 461—463; cf. A., 1938, I, 321).—Data are recorded for  $\chi$  (−0.187 to +5.087) and the  $Fe_2O_3$  content (0.0021—0.0152%) of four activated and one unactivated coconut shell charcoals. The contained  $Fe_2O_3$  has an effective  $\chi$  val. of  $\sim 15,000 \times 10^{-6}$  (pure  $Fe_2O_3$ , +68,000  $\times 10^{-6}$ ). A. J. E. W.

**Magnetic susceptibility of iron tetracarbonyl.** H. G. Cutforth and P. W. Selwood (*J. Amer. Chem. Soc.*, 1943, 65, 2414—2415).—



The magnetic susceptibility,  $\chi$ , of  $\text{Fe}_3(\text{CO})_{12}$  (I), at room temp., when corr. for ferromagnetic impurity, is  $-0.07 \times 10^{-6}$ . On keeping in the dark (I) undergoes a slow change, and  $\chi$  increases.

W. R. A.

**Complex ions. VI. Magnetic moments of ferric complex ions.** B. Werbel, V. H. Dibeler, and W. C. Vosburgh (*J. Amer. Chem. Soc.*, 1943, **65**, 2329—2334).—The magnetic moment,  $\mu$ , of  $\text{Fe}^{III}$  has been determined in aq.  $\text{Fe}(\text{ClO}_4)_3$  containing various complex-forming anions. When  $[\text{HClO}_4]$  is  $>0.1\text{M}$ ,  $\mu = 5.93 \pm 0.01$ , which agrees well with the theoretical spin moment,  $\mu = 5.92$ . Low vals. of  $\mu$ , observed when  $[\text{HClO}_4]$  is  $<0.1\text{M}$ , are attributed to the presence of  $[\text{FeOH}]^{2+}$ .  $\mu$  remains unchanged when  $\text{C}_2\text{O}_4^{2-}$ , 8-hydroxyquinoline-5-sulphonate,  $\text{Cl}^-$ ,  $\text{CNS}^-$ , and dichloroacetate complexes are formed.  $\mu$  has lower vals. in  $\text{OAc}^-$ , chloroacetate,  $\text{HPO}_4^{2-}$ ,  $\text{P}_2\text{O}_7^{4-}$ , lactate, tartrate, citrate, and aminoacetate complexes. Variation of  $\mu$  in the latter group with concn. of excess anion and pH indicates the existence of  $>1$  complex.

W. R. A.

**Magnetic susceptibility of cobaltous complexes and their constitution.** P. Ray and S. P. Ghosh (*J. Indian Chem. Soc.*, 1943, **20**, 323—328).—The magnetic moments of the central Co atoms in diaquo- $\text{Co}^{II}$ -ethylenediaminebisacetylacetonate,  $\text{Co}^{II}$ -ethylenediguanidium sulphate, diguanidinium sulphate and hydroxide show that these complexes are of the penetration type. The average moment is 2.66 Bohr magnetons, which is slightly  $<$  that calc. on the supposition that the orbital moments are not quenched but are free to orient independently. The discrepancy suggests that the quenching is incomplete.

C. R. H.

**Magnetic measurements on catalytically active substances.**—See A., 1944, I, 109.

**Effect of torsional vibrations on the Barkhausen effect.** K. M. Koch (*Naturwiss.*, 1943, **31**, 233—234).—If a stretched Fe wire, magnetised longitudinally, is twisted, the longitudinal component of the magnetisation decreases. This can be demonstrated by surrounding the wire with a coil, amplifying the induced current, and passing it into a loud-speaker. A note of the frequency of the torsional vibration is heard. If the magnetisation is changed during the vibration, the frequency of the note is doubled while the magnetisation is changing, but reverts to the original when it becomes const. If the wire is not vibrating and the magnetisation is altered, the normal Barkhausen noise is heard. If the wire is now slowly set into torsional vibration, the Barkhausen effect gives place to a note of double the vibrational frequency. The effect is well shown by means of an oscillograph.

A. J. M.

**Specific heats at low temperatures of hydrates of magnesium chloride.** K. K. Kelley and G. E. Moore (*J. Amer. Chem. Soc.*, 1943, **65**, 2340—2342).—Sp. heat measurements on the mono-, di-, tetra-, and hexa-hydrates of  $\text{MgCl}_2$  at 52—298° K. are recorded. An anomaly is found for the hexahydrate with a peak at 136.7° K. Calc. entropies at 298.16° K. are  $32.8 \pm 0.5$ ,  $43.0 \pm 0.5$ ,  $63.1 \pm 0.7$ , and  $87.5 \pm 1.0$  g.-cal. per degree per g.-mol. Free energies of formation of the hydrates from the elements and from anhyd.  $\text{MgCl}_2$  and liquid  $\text{H}_2\text{O}$  are listed.

W. R. A.

**Specific gravity of butadiene.** M. R. Dean and T. W. Legatski (*Ind. Eng. Chem. [Anal.]*, 1944, **16**, 7—8).—The  $d$  of 99.6 mol.-%  $(\text{CH}_2=\text{CH})_2$  over the range 0—140° F. is recorded; the val. of  $d$  (60°/60° F.) is  $0.6274 \pm 0.00015$ .

J. D. R.

**Viscosity and structure of pure hydrocarbons.** H. A. Kierstead and J. Turkevich (*J. Chem. Physics*, 1944, **12**, 24—27).—The fluidity of hydrocarbons can be satisfactorily represented by the expression  $Ae^{-E/kT}$ . Vals. of the consts.  $A$  and  $E$  are given for  $n$ -paraffins ( $\text{C}_5$ — $\text{C}_{12}$ ,  $\text{C}_{14}$ ,  $\text{C}_{16}$ ,  $\text{C}_{18}$ , and  $\text{C}_{22}$ ) and 17 aromatic and branched-chain hydrocarbons. The effect of structure on the vals. of these consts. is discussed.

L. J. J.

**Equation of diffusion in a turbulent medium.** W. G. L. Sutton (*Proc. Roy. Soc.*, 1943, **A**, 182, 48—75).—A mathematical investigation of the two-dimensional form of the equation of diffusion is presented. The results are applied to the theory of evaporation into a turbulent medium.

G. D. P.

**Evaporation from a plane, free-liquid surface into a turbulent air stream.** F. Pasquill (*Proc. Roy. Soc.*, 1943, **A**, 182, 75—95).—Experimental investigation of the rate of evaporation from a plain liquid surface into a tangential air stream demonstrates the importance of the type of boundary layer flow. In the case of turbulence the results are in agreement with a theory due to Sutton (cf. B., 1935, 1), a generalisation of which is developed. Applied to the analogous process of the turbulent diffusion of heat in the boundary layer, substantial verification of the theory is obtained.

G. D. P.

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

**Growth of crystals from solution.** E. Hofer (*Z. physikal. Chem.*, 1941, **A**, 188, 265—271).—Theoretical. Assuming that the effectiveness of foreign nuclei in causing crystallisation depends on the collecting action of the surface of the heterogeneous particles, the

crystal size should be  $\propto$  the square of the concn., in agreement with the author's experimental results (A., 1939, I, 252). A crystal of great solubility will take up more from the mother solution than one of small solubility. The assumption on which these deductions are made, that the concn. gradient in the neighbourhood of the crystal is uniform, is strictly valid only in the special case of the salt in solvents of nearly the same physical properties. The results and deductions support the concept that it is the excess % surface concn. which is effective in causing crystallisation.

J. O'M.-B.

**Diffusion thermo-effect.** L. Waldmann (*Naturwiss.*, 1943, **31**, 204).—Mathematical. An exact solution of the equation governing the effect is possible for a cylindrical diffusion vessel. The results are quoted.

A. J. M.

**Temperature coefficient of diffusion constant of copper in aqueous solutions of sulphuric acid containing copper sulphate.** W. A. Patterson and J. T. Burt-Gerrans (*Canad. J. Res.*, 1944, **B**, 22, 5—15).—On the basis of Rosebrugh and Miller's theory of changes of concn. at the electrode (A., 1911, ii, 181), diffusion coeffs. are calc. from the time,  $t$ , required for the concn. potential to reach a max., using an oscillograph for time measurements. Use of a new point on the oscillograph potential curve for determining  $t$  brings the results into line with those obtained by a different method. Diffusion coeffs. increase linearly with temp. from 10° to 25°, the change being related to the change in  $\eta$  in accordance with the Stokes-Einstein equation.

R. H. F.

**Variation in equilibrium pressure of compounds during fusion in the case of miscibility in the solid state.** M. Dodé (*Compt. rend.*, 1942, **215**, 436—437; cf. A., 1943, I, 62).—The case is considered in which a solid dissociates into a gas (pressure  $p$ ) and a second solid, the two solid phases forming an ideal series of mixed crystals. An expression (involving the gradient of the liquidus) giving  $d(\log p)/dT$  is derived for the univariant system formed during melting, and possible types of  $p$ - $T$  relation are considered.

A. J. E. W.

**Energy coefficients of crystalline lattices (VEC) and the structure of binary metallic alloys.** O. E. Zvjagintzev (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **38**, 28—32).—A theoretical treatment of the nature of binary metallic alloys.

L. S. T.

**Volume changes in alloys in the heterogeneous solid-liquid range.** II. F. Sauerwald (*Metallwirts.*, 1941, **20**, 1211—1213).—Temp.-vol. curves covering the solidification ranges of saturated solutions in the Al-Cu, Al-Zn, Al-Si, Al-Mg, and Mg-Zn systems have been plotted from published data. The results are discussed in relation to conditions when equilibrium is not attained.

C. E. H.

**Continuous transition between the daltonide and the berthollide phases in the system iron-nickel-antimony.** N. V. Ageev and E. S. Makarov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **38**, 20—21).—Results obtained in an experimental investigation of the transition between the berthollide phase of the system Fe-Sb and the daltonide phase of the system Ni-Sb, both with Ni arsenide structure, are presented in the form of a Stokes diagram.

L. S. T.

**[Solubility of lithium carbonate.]** I. T. Poljanitschka (*Zavod. Lab.*, 1939, **8**, 1052—1054).—1 l. of saturated aq. solution contains at 0° 0.417 and at 100° 0.197 g.-equiv. Vals. are given for the solubility of  $\text{Li}_2\text{CO}_3$  in salt solutions and 40% EtOH. (See also C., 1944, Part 2.)

J. J. B.

**Solubility of carbon as graphite in gamma iron.** R. W. Gurry (*Amer. Inst. Min. Met. Eng.*, 1942, *Tech. Publ.* 1440, 7 pp.; *Metals Tech.*, **9**, No. 3).—The solubility of graphite in austenite was determined by carburising pure Fe in an atm. of  $\text{H}_2$  and PhMe, and determining the C content of the quenched steel at equilibrium. Microscopical examination showed the steel to be free from graphite. The solubility at 957° was 1.39%, and at 1110° was 1.89%. By extrapolation, the max. solubility, at 1135°, is 1.98%.

R. KE.

**Determination of ionic adsorption in the Helmholtz-Gouy (electrical) layers by the combination of electrokinetic and interfacial tension measurements.** W. Dickinson (*Trans. Faraday Soc.*, 1944, **40**, 48—59).—Data recorded in a previous paper (cf. A., 1940, I, 366) on the effect of KCl, KI, and KCNS on the electrophoretic mobilities of emulsions of cetyl acetate (I) and on the interfacial tension between (I) and the aq. solutions are used to calculate the ionic composition of both the rigid and the mobile parts of the Stern double layer.  $\text{I}^-$  and  $\text{CNS}^-$  are strongly positively adsorbed throughout the range of concn. examined (0.01—0.2N.).  $\text{Cl}^-$  shows slight positive adsorption below 0.05N. and slight negative adsorption at higher concns.  $\text{K}^+$  from KI and KCl is negatively adsorbed, and the surface excess of  $\text{K}^+$  from KCNS is  $\sim 0$ , over the whole concn. range.

F. L. U.

**Density of dilute solutions of strong electrolytes.** F. Sauter (*Z. physikal. Chem.*, 1941, **A**, 188, 220—234).—A general relationship between the  $d$  and osmotic pressure of a solution is derived and is applied to dil. solutions of strong electrolytes. This leads to a correction of the formula of Redlich and Rosenfeld (A., 1931, 906).

J. W. S.



**New group of colloidal electrolytes.** N. R. Dhar and S. Ghosh (*J. Indian Chem. Soc.*, 1943, 2, 282—288).—Observations on  $\Lambda$  and on pptn. by electrolytes in absence of alkali or in presence of traces of alkali indicate that sols of  $\text{HSbO}_3$ ,  $\text{HVO}_3$ ,  $\text{H}_2\text{MoO}_4$ , and  $\text{H}_2\text{WO}_4$  are typical colloidal electrolytes. F. J. G.

**Sedimentation volumes and rigidity in suspensions of sodium soaps in mineral oils.** W. Gally and I. E. Puddington (*Canad. J. Res.*, 1944, B, 22, 16—20).—The sedimentation vol. of Na soaps increases with temp. and with decreasing viscosity index of the oil. Large sedimentation vol. is due to attraction between particles resulting in a scaffolding structure. Flow measurements on such suspensions show the existence of a yield point, indicating rigidity of the suspension. R. H. F.

**Stress-strain data for vulcanised rubber under various types of deformation.** L. R. G. Treloar (*Trans. Faraday Soc.*, 1944, 40, 59—70; cf. A., 1944, I, 15).—Data are recorded for two types of vulcanised rubber under (a) two-dimensional extension, (b) simple elongation, (c) pure shear, and (d) combined elongation and shear. Comparison with the theoretical relations based on the mol. network model shows good agreement for (a), less good for (b) and (c). The effect of (d) is accounted for satisfactorily. The theory provides a satisfactory explanation of rubber-like elasticity, and a useful basis for the description of the mechanical properties of rubber under large deformations of any type. F. L. U.

**Anomalous viscosity and flow-birefringence of protein solutions.** I. General behaviour of proteins subjected to shear. A. S. C. Lawrence, J. Needham, and S. C. Shen. II. Dilute solutions of proteins from embryonic and other tissues. A. S. C. Lawrence, M. Miall, J. Needham, and S. C. Shen (*J. Gen. Physiol.*, 1944, 27, 201—232, 233—271).—I. Viscometric methods of investigating the shape of protein particles are discussed. The application of a new viscosimeter (cf. C., 1944, Part 2) to the measurement of relative and anomalous  $\eta$  and of flow-birefringence of dil. protein solutions is described. The general behaviour of protein solutions subjected to shear is summarised.

II. Examination of a no. of proteins suggests that they can be conveniently classified into four groups. Group A consists of proteins which show flow anomaly both in bulk and in the surface film with flow-birefringence, and which are fibrillar in bulk and in film, e.g., tobacco mosaic virus, myosin. Groups  $B_1$  and  $B_2$  consist of proteins which show flow anomaly in film but not in bulk and no flow-birefringence in the bulk phase. In bulk the particles are spherical but are fibrillar in film.  $B_1$  proteins show flow anomaly immediately after formation, e.g., mammalian serum-egglobulin and -pseudoglobulin, avian ovoglobulin, amphibian embryo-egglobulin  $b$ , and, possibly, plasmosins.  $B_2$  proteins show flow anomaly only after an interval, e.g., cryst. avian ovalbumin, amphibian embryo-pseudoglobulin. Group C consists of proteins which show flow anomaly neither in bulk nor in film, e.g., cryst. insulin and methæmoglobin, amphibian embryo-egglobulin  $c$ , amphibian egg-jelly-mucoprotein, human umbilical cord-mucoprotein. The theoretical significance of fibrillar proteins is discussed in relation to experimental morphology and cytology. A bibliography of 262 references is appended. C. R. H.

**Yeast-ribonucleic acid.** VII, VIII.—See A., 1944, II, 112.

## VI.—KINETIC THEORY. THERMODYNAMICS.

**Equilibrium composition of gaseous mixtures under high pressure.** A. I. Brodski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, 36, 237—238).—Theoretical. The activity coeffs. of the components of a compressed gaseous mixture are given by  $\log f_1 = 9/128 \pi_1/\theta_1 \cdot (1 - 6/\theta_1^2)$ , where  $\pi_1$  and  $\theta_1$  are reduced pressures and temp. F. J. G.

**Second dissociation constant of phenol-*p*-sulphonic acid and the pH values of phenolsulphonate-chloride buffers from 0° to 60°.** R. G. Bates, G. L. Siegel, and S. F. Acree (*J. Res. Nat. Bur. Stand.*, 1943, 31, 205—223).—From e.m.f. measurements on cells containing  $\text{H}_2$  and Ag-AgCl electrodes in the presence of various concns. of  $p\text{-OH-C}_6\text{H}_4\text{SO}_3\text{H}$  (I), NaOH, and NaCl the thermodynamic dissociation const. of the OH-group of (I) has been measured at 0—60° as  $\text{p}K_2 = 1961.2/T - 1.1436 + 0.012139T$ . Formulae relating  $\Delta G^\circ$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta C_p$  with  $T$  for this dissociation are deduced. At 25° these quantities have the vals. 12,351 and 4036 g.-cal., and -27.9 and -33 g.-cal. per degree per g.-mol., respectively. The pH vals. of solutions containing various ratios of uni- to bi-valent ion ( $\frac{3}{2}$ -1) at various temp. are recorded. These are suitable buffer solutions for the pH range 8.6—9.0. J. W. S.

**Potentiometric determination of solubility product.** R. Näsänen (*Z. physikal. Chem.*, 1941, A, 188, 272—283).—The theory of pptn. titrations is examined and an equation for the difference between the end-point and the inflexion on the titration curve is deduced. This is experimentally determined by reference to the alkalimetric determination of Mg and depends only on the val. of  $m$  and  $n$  in the pptd.  $\text{A}_m\text{B}_n$ . The solubility product can be determined from the min. of the buffer capacity curve. The concn. solubility product

of  $\text{Mg}(\text{OH})_2$  is determined at the min. p.d. for different KCl concns. For the thermodynamic solubility product the val. of  $3.07 \times 10^{-11}$  is obtained so that this electrolyte obeys the Debye-Hückel theory. The results here reported are > those in the literature, but the latter are not const., owing perhaps to the carbonate content of the solutions and to the solubility of the glass vessel. The latter does not affect the present method owing to the short duration of the experiments. J. O'M.-B.

**Solidification point curves of binary [fatty] acid mixtures. III. Tetracosanoic to triacontanoic acids.** H. A. Schuette, R. M. Christenson and H. A. Vogel (*Oil and Soap*, 1943, 20, 263—265; cf. B., 1940, 222; A., 1941, I, 35).—The solidification point (s.p.) diagrams (and tabulated experimental figures) for binary mixtures of synthetic tetracosanoic (s.p. 83-82°, 83-45°), hexacosanoic (s.p. 87-38°, 87-06°), octacosanoic (s.p. 90-48°), and triacontanoic acids (s.p. 93-10°) are presented. Starting with erucic acid, which was reduced and converted into Et behenate, each homologue was successively synthesised by reducing the ester to the corresponding alcohol, converting this into the iodide, and interaction with malonic ester; the prep. of triacontanoic acid from Et octacosanoate is described in detail. Attempts to separate the fatty acids of Chinese insect wax into binary mixtures by fractional distillation of the Et esters with a Widmer column were unsuccessful. E. L.

**Salting-out effect.** T. J. Morrison (*Trans. Faraday Soc.*, 1944, 40, 43—48).—The salting-out of  $\text{PhOH}$ ,  $\text{CH}_3\text{PhCO}_2\text{H}$ , and  $\text{BzOH}$  in aq. solution by some uni-univalent electrolytes has been investigated over a range of temp. and for various concns. (c) of electrolyte. The results are tabulated. Factors that determine the temp. variation of solubility are predominant in determining the variation in salting-out effect. If  $c$  is in mols. per 1000 g. of  $\text{H}_2\text{O}$ , the data are better expressed by  $\log s_0/s = k_1 c^\beta$  than by  $\log s_0/s = kc$ ,  $s_0$  and  $s$  being the solubilities in  $\text{H}_2\text{O}$  and salt solution respectively. Both  $k_1$  and  $\beta$  vary with temp. F. L. U.

**Effect of the physical state of the solid reactants on the equilibrium  $\text{Fe}/\text{Fe}_3\text{O}_4$  with  $\text{H}_2\text{O}/\text{H}_2$ .** R. Fricke, K. Walter, and W. Lohrer (*Z. Elektrochem.*, 1941, 47, 811).—Use of a better val. for the heat of formation of  $\text{Fe}_3\text{O}_4$  at room temp. does not influence the conclusions made in a previous paper (A., 1944, I, 37). J. F. H.

**Structure and composition of the double carbides of the system W-Co-C determined from the relative intensity of Debye lines.** E. N. Kisliakova (*J. Phys. Chem. Russ.*, 1943, 17, 108—114).—The system W-Co-C shows two distinct phases, with compositions near  $\text{W}_2\text{Co}_3\text{C}$  (spacing 11.19 Å.) and  $\text{W}_3\text{Co}_5\text{C}$  (spacing 10.89 Å.), the unit cell of which contains 96 metal atoms. J. J. B.

**Spectroscopic determination of the heat of association of methyl alcohol in  $\text{CCl}_4$ .** R. Mecke and H. Nüchel (*Naturwiss.*, 1943, 31, 248).—Spectroscopic measurements confirm that for normal alcohols in  $\text{CCl}_4$  no double mols. are formed ( $k_{12} \sim 0$ ). The mean association const.  $\bar{k}_n = (k_{1n})^{1/(n-1)}$  ( $n > 2$ ) can be taken as independent of  $n$ . Vals. for the heat of association per g.-mol. of  $\text{MeOH}$  in  $\text{CCl}_4$  are 4.59 kg.-cal. (10—20°), 4.72 kg.-cal. (20—30°), and 4.82 kg.-cal. (30—40°). J. F. H.

## VII.—ELECTROCHEMISTRY.

**Conductivity of strong electrolytes.** J. Lange (*Z. physikal. Chem.*, 1941, A, 188, 284—315).—The re-evaluated conductivity results for 560 electrolytes are tabulated and shown to conform to a simple relation the coeffs. of which can be calc. from the Debye-Hückel-Onsager theory. The poorest agreement is obtained for non-aq. media and for electrolytes of high valency; the inherent difficulty for the former is the almost unavoidable presence of a trace of  $\text{H}_2\text{O}$ . A new method is given for obtaining the limiting equiv. conductivity from an assumption of the validity of the interionic attraction theory at low concns. Vals. of  $\lambda_\eta$  are tabulated; they show Walden's rule to be obeyed only very roughly except for large ions. The results are sufficient to prove that the conductivity of strong electrolytes is a function only of the electrostatic forces. J. O'M.-B.

**Irreversible electrode potentials of metals.** G. B. Clark and G. V. Akimov (*Trans. 2nd Russ. Conf. Corrosion Metals*, 1943, 2, 33—51).—The electrode potential  $V$  of Si and 21 metals is determined in 3% NaCl, 0.1N-HCl, 0.1N- $\text{HNO}_3$ , and 0.1N-NaOH 1 and 5 min. after immersion in the stationary electrolyte, when the solution is stirred, and when the electrode is being abraded with a  $\text{CSi}$  disc. The effect of time and of stirring on  $V$  is small, usually 20—70 mv. The effect of abrasion is very large for the elements of the sub-groups  $a$  of the periodic system (Be, Mg, Al, Si, Nb, Cr, Mo, and Mn), and  $V$  becomes more negative (less noble) by 300—1000 mv.; this is due to destruction of the protective film and increase of the anodic area of the local elements. The  $V$  of the transition group (Fe, Co, Ni) is lowered by abrasion by 200—500 mv., and the  $V$  of the sub-groups  $b$  (Cu, Ag, Au, Zn, Cd, Hg, Tl, Sn, Pb, Sb, and Bi) is lowered by <200 mv. or not at all. The effect of abrasion is small when the cathodic and the anodic areas of an undisturbed electrode have similar magnitudes. J. J. B.



**Piezoechemical studies. XXXII. Piezodynamical examination of the Gladstone-Tribe mechanism of the lead accumulator.** E. Cohen and G. W. R. Overdijkink (*Z. physikal. Chem.*, 1941, 188, 316—330).—The pressure coeff. of the e.m.f. of an accumulator is more accurately measurable than the temp. coeff. and is used to determine the chemical reaction taking place in the accumulator. The val. obtained agrees closely with that derived from the vol. contraction which takes place on working, assuming the equation of the theory, which is hence considered verified. J. O'M.-B.

**Anodic passivation of lead in sulphuric acid.** B. N. Kabanov (*Trans. 2nd Russ. Conf. Corrosion Metals*, 1943, 2, 67—85).—The anodic overvoltage  $\eta$  on Pb in  $H_2SO_4$  slightly increases with c.d. and with concn. of  $H_2SO_4$  (2—13N.) and is lowered by a temp. increase (—35° to 45°). PhOH raises and gelatin lowers it. At c.d. of  $10^{-6}$  to  $10^{-8}$  amp. per sq. cm.  $\eta = \text{const.} + 0.18 \log \text{c.d.}$ , and the  $\eta$  is due to a supersaturation of  $PbSO_4$  caused by the slowness of its crystallisation. At c.d.  $> 0.03$  amp. per sq. cm.  $\eta$  increases linearly with c.d. and is due to a retardation of the ionisation of Pb. Müller's theory of the passivity of Pb is not correct as the ohmic resistance of the electrolyte layer at the electrode is  $\sim 0.01$  of that postulated by Müller. The extent of covering of Pb by  $PbSO_4$  is determined by measuring the capacity of the electrode in the course of its passivation. The charge  $Q$  required to raise the potential of Pb by 0.1—0.2 v. is the larger the more dil. is  $H_2SO_4$  and the higher is the temp., and  $Q \propto (\text{c.d.})^{-0.1}$  to  $(\text{c.d.})^{-0.4}$ . If c.d. varies during the polarisation,  $Q$  depends only on the average c.d. EtOH reduces  $Q$ , gelatin and methylene-blue raise it. These results are accounted for by the proportionality between  $Q$  and the thickness of the passivating  $PbSO_4$  layer; this thickness increases with the solubility and the rate of diffusion, and when the rate of crystallisation is lowered. Equations for the rate of growth of the passivating layer are derived. J. J. B.

**Theory of passivity phenomena. XXXIII. Connexion between anodic behaviour of iron and corrosion accompanying potential oscillations in chromic acid-sulphuric acid solutions.** W. J. Müller and E. Löw (*Z. physikal. Chem.*, 1941, A, 189, 70—87).—Fluctuations of potential occurring when Fe is immersed in  $H_2CrO_4$ - $H_2SO_4$  mixtures can be explained by supposing that passivity is due to a surface film. The connexion between passivity and anodic oxidation indicates that potential fluctuations can occur only when the surface is covered with a film of oxide. In anodic oxidation, passivity depends on c.d. When high c.d. is used the pores in the surface are covered with a film of oxide. The time elapsing before the sudden decrease in current occurs is the smaller the larger is the initial c.d. This passivation time also depends on the diffusion of  $H_2CrO_4$  into the neighbourhood of the electrode. The passivation time is short with high  $[H_2CrO_4]$ , with unprotected electrodes, and particularly if the electrodes are immersed after the circuit has been closed, even if the c.d. is low. The potential fluctuation is due to the fact that after the decrease of the current, the surface film is dissolved by the  $H_2SO_4$ . The fluctuations vary with  $[H_2CrO_4]$  and in presence of  $N-H_2SO_4$  occur with concns. of  $H_2CrO_4$  between 2 and 7%. The fraction of free surface of Fe when potential oscillations occur is  $\sim 0.001$ ; this increases with increase of passivation time. A. J. M.

**Passivity of platinum.** B. V. Erschler (*Trans. 2nd Russ. Conf. Corrosion Metals*, 1943, 2, 52—66).—Earlier results (cf. A., 1941, I, 470) are reviewed. J. J. B.

**Mechanism of the depolarisation of local cathodes in corrosion involving oxygen depolarisation.** N. D. Tomashev (*Trans. 2nd Russ. Conf. Corrosion Metals*, 1943, 2, 11—32).—The current strength between a Zn plate and a smaller Cu plate in 0.5N-NaCl, measured at various areas  $f$  of the Cu plate, is  $I = k(2.25\sqrt{f} + f/\delta)$ ,  $k$  being a const. which can be calc. from the diffusion coeff. of  $O_2$ , and  $\delta$  the thickness of the diffusion layer. Experiments give  $\delta \sim 1$  mm. Only at  $f > 6$  sq. cm. is  $I \propto f$ . If a Cu plate and a Zn ring surrounding it in the horizontal plane are covered with a layer,  $d$  cm. thick, of 3% NaCl,  $I$  has a sharp max. at  $d = 0.05$  mm.; at lower  $d$  vals.  $I$  is smaller because of the increased ohmic resistance, and at higher  $d$  because of the longer diffusion path for  $O_2$ ; at  $d > 1$  mm.  $I$  is independent of  $d$ .  $I$  is raised by agitating the air above the NaCl solution. The term  $2.25\sqrt{f}$  is due to the c.d. being larger near the edge of the cathode. Measurements of  $I$  between a Zn plate and a set of concentric Cu rings show that the c.d. 0—0.5 mm. from the edge is 4.5 times that in the centre of the cathode. If, at a const.  $f$ , the cathode consists of several spots instead of one plate,  $I$  in 3% NaCl is increased since the cross-section of the diffusion path for  $O_2$  is raised, but the difference is negligible in  $N-HCl$ , in which  $H_2$  is evolved. If the layer of 3% NaCl covering the cathode is  $< 1$  mm. thick, the difference between a single and a composite cathode is reduced. If  $d$  is larger, an increase of the  $f$  of the composite cathode (or of the amount of cathodic inclusions in a corroding metal) does not cause a marked increase of  $I$ , the cross-section of the diffusion path being nearly equal to the total area of the corroding metal independently of the area of the cathodic inclusions. J. J. B.

**Capacity of the double electric layer on Wood's metal.** S. Karpatshev, N. Ladigin, and V. Zikov (*J. Phys. Chem. Russ.*, 1943, 17, 75—78).—The capacity was measured directly with a.c. at 50 cycles per sec. At the e.m.f. of  $Hg|HgCl, N-KCl|Wood's\ metal = 1$  v. the capacity in  $N-KCl$  had a min.; it was  $\sim 15 \mu F$ . per sq. cm. at 75° (liquid cathode) and  $\sim 20 \mu F$ . per sq. cm. at 65° (solid cathode). It rose to  $\sim 100 \mu F$ . per sq. cm. when the e.m.f. was  $\sim 0.85$  v.

J. J. B.  
**Formation and growth of electrodeposited crystals.** K. M. Gorbunova (*Trans. 2nd Russ. Conf. Corrosion Metals*, 1943, 2, 142—152).—Theories of crystal growth, based on consideration of elementary processes, often fail to agree with the observed rate of growth, since the latter is determined by the conditions of diffusion. Zn was electrodeposited from 4.7N- $ZnSO_4$  on to various faces of a single Zn crystal. At a const. overvoltage the c.d. on the basis (0001)  $<$  prism (1010)  $<$  prism (1120); these c.d. are  $\propto$  the rate of growth of the crystal face. J. J. B.

## VIII.—REACTIONS.

**Primary reactions induced by nuclear processes.** H. Suess (*Z. Elektrochem.*, 1941, 47, 765).—A brief summary. J. F. H.

**Kinetics and reaction mechanisms.** K. H. Geib (*Z. Elektrochem.*, 1941, 47, 761—765).—An attempt is made to limit the uncertainty of determining reaction mechanisms by recourse to theoretical considerations. The mechanism of several reactions is discussed on the basis of mol. structure and the principle of least motion, formulated by Rice and Teller (A., 1938, II, 425). J. F. H.

**Chemical kinetics and the second law.** E. Baur (*Z. Elektrochem.*, 1941, 47, 747—749).—A brief discussion of partial equilibrium and anti-catalysis. J. F. H.

**Calculations of velocity coefficients from experimental data.** J. A. Christiansen (*Z. physikal. Chem.*, 1941, A, 189, 126—134).—The weighting of different results in a series of determinations in kinetic experiments is discussed. The assumption is made that the wts. should be so chosen that the sum of the squares of the deviations,  $\Sigma(D_{\text{min.}}^2)$ , should be equal to the sum of the squares of the errors in reading,  $\Sigma(\delta x)^2$ . The mean val. of  $k$  is readily calc. from the individual vals. from the relationship  $\bar{k} \Sigma G = \Sigma Gk$ , where  $G$  is the function governing the order of reaction. Tables for  $G$  are given for the case of first- and second-order reactions.

A. J. M.  
**Thermal decomposition of higher hydrocarbons.** W. Jost and L. von Muffing (*Z. Elektrochem.*, 1941, 47, 766—773).—The homogeneous thermal decomp. of  $n-C_6H_{14}$ ,  $n-C_7H_{16}$ ,  $n-C_8H_{18}$ ,  $\beta$ -dimethylhexane,  $\beta\beta$ -trimethylpentane, cyclohexane, PhMe, PhEt, PhPr $^\alpha$ , and PhPr $^\beta$  was studied by pressure measurements and analysis. No definite conclusions could be reached as to the reaction mechanisms. In the  $n$ -paraffins, addition of  $\cdot CH_2\cdot$  approx. doubles the rate of decomp. Increased chain branching leads to greater quantities of  $H_2$  and  $C_1$ ,  $C_2$  and higher fractions, but less  $C_3$  fraction. Addition of  $HgMe_2$  accelerates the rate of pressure increase owing to the extra Me radicals produced. One Me radical decomposes 1.5—2 mols. of paraffin. Increase of side-chain in the  $C_6H_6$  derivatives by  $\cdot CH_2\cdot$  approx. doubles the rate of decomp. J. F. H.

**Homogeneous thermal decomposition of cyclohexane and methylcyclohexane.** G. R. Schultze and (Frl.) G. Wassermann (*Z. Elektrochem.*, 1941, 47, 774—778).—Preliminary. The thermal decomp. of cyclohexane (I) and methylcyclohexane (II) was investigated at temp. up to 550° and at initial pressures of 100—400 mm. The primary reaction is of the first order; for (I),  $\log k = -64.100/2.3RT + 13.8$ ; for (II),  $\log k = -57.900/2.3RT + 12.65$ . Both decmps. are preceded by an induction period, which is more marked with (I); no further evidence of a chain reaction was found. Approx.  $-\Delta G$  vals. for some of the possible reactions were calc. J. F. H.

**Kinetics of ring polymerisation. XII. Explosive polymerisation reactions.** G. V. Schulz and F. Blaschke (*Z. Elektrochem.*, 1941, 47, 749—761).—Polymerisation of  $CH_2=CMe\cdot CO_2Me$  in presence of  $O_2$  or peroxides occurs with a steady increase in reaction velocity, until, after induction periods ( $\tau$ ) of varying length, the unused monomer reacts violently with an increase in temp. (up to 90°).  $\tau$  may last several hr., and is the smaller the higher is the temp. Measurements of composition, degree of polymerisation, viscosity, and temp. during the reaction show that the explosiveness of the reaction is caused by chain-branching. J. F. H.

**Kinetics of formaldehyde-phenol condensation.** H. von Euler and S. von Kispéczy (*Z. physikal. Chem.*, 1941, A, 189, 109—121).—The reaction of xylenol with  $CH_2O$  in acid and in alkaline solution has been investigated. The  $[CH_2O]$  in the supernatant liquid was determined from time to time by pptn. as the trinitrophenylhydrazone, treating the ppt. with NaOH in EtOH, and determining the coloured compound formed by means of a photometer. The reaction is approx. bimol. For the condensation of *o*-4-xylene (I)



with  $\text{CH}_2\text{O}$ ,  $k$  is  $\sim 124$ , and for the *o*-3-compound it is 110 in either acid or alkaline solution.  $k$  for PhOH in place of xylenol is  $\sim 75\%$  greater. In the acid condensation of (I) with  $\text{CH}_2\text{O}$ , xylenol alcohol is formed. The bromination of various xylenol derivatives was investigated in order to determine the no. of reactive positions on the xylenol nucleus. This is  $>$  the no. of free *o*- and *p*-positions. Hence the side-chain must also be brominated. A. J. M.

**Consecutive competitive reactions.** R. M. Fuoss (*J. Amer. Chem. Soc.*, 1943, 65, 2406—2408).—Mathematical. The amounts of the five substances present in the reaction system  $\text{AX}_4 \rightarrow \text{RAX}_3 \rightarrow \text{R}_2\text{AX}_2 \rightarrow \text{R}_3\text{AX} \rightarrow \text{R}_4\text{A}$ , the reagent in each reaction being RY, have been calc. as functions of the total added RY, and reaction probability ratios. W. R. A.

**Chain transfer in the polymerisation of styrene. Reaction of solvents with free radicals.** F. R. Mayo (*J. Amer. Chem. Soc.*, 1943, 65, 2324—2329).—Assuming that certain solvents reduce the mol. wt. of polymerising styrene by transferring H or Cl atoms to the growing polymer radicals, a "transfer const." may be defined, which is characteristic of the solvent. Transfer consts. of cyclohexane,  $\text{C}_6\text{H}_6$ , PhMe, PhEt, and a  $\text{C}_6\text{H}_4\text{Et}_2$  have been calc. and quantitatively support the theoretical development. The coexistence of transfer between polymer radicals and both polymer and monomer mols. is suggested. W. R. A.

**Formation of chlorate in hypochlorite solutions.** H. Ramstetter and G. Hantke (*Z. physikal. Chem.*, 1941, A, 189, 122—125).—In alkaline solution the decomp. of  $\text{NaOCl}$  at  $45^\circ$  is bimol. In acid solution, the uni- and bi-mol. coeffs. show a decided trend. The formation of  $\text{NaClO}_3$  proceeds to completion in slightly alkaline solution but the rate is slow. A. J. M.

**Polarographic determination of the velocity coefficients for the oxidation of haem and other ferro-complexes by hydrogen peroxide.** R. Brdička and K. Wiesner (*Naturwiss.*, 1943, 31, 247).—Preliminary. A new explanation of the displacement of the polarographic reduction potential of  $\text{H}_2\text{O}_2$  by Fe-porphyrin complexes (cf. A., 1937, III, 163) is given. The mechanism involves a cyclic alteration of the valency of Fe; haemin (I) is electrolytically reduced to haem (II), which is then chemically oxidised by  $\text{H}_2\text{O}_2$  to (I). The process continues until the concn. ratio of (I) and (II) is that required by their redox potential equation. The rate-determining step of the oxidation is  $\text{Fe}^{2+} + \text{H}_2\text{O}_2 = \text{Fe}^{3+} + \text{OH}^- + \text{OH}$ . An equation is deduced which enables  $\mu^k$  to be determined,  $\mu$  being the thickness of the phase boundary layer and  $k$  the velocity coeff.  $k$  for  $\alpha$ -chlorohaemin determined in this way is  $2 \times 10^7 \text{ sec}^{-1} \text{ g.-mol./l.}$  J. F. H.

**Oxidation of oxalic acid solutions by elementary oxygen in the presence of manganese.** (Fr.) K. von Bazcko and E. Schreier (*Z. Elektrochem.*, 1941, 47, 801—805).—The oxidation of  $\text{H}_2\text{C}_2\text{O}_4$  by gaseous  $\text{O}_2$  in aq.  $\text{H}_2\text{SO}_4$  in the presence of  $\text{MnSO}_4$  was studied at various concns. of reactants and at temp.  $100$ — $118^\circ$ . Typical chain phenomena are observed. A mechanism is proposed in which the  $\text{Mn}^{2+}$  ions first disproportionate to  $\text{Mn}^{3+}$  and  $\text{Mn}^+$ . The subsequent reactions are: (a)  $\text{Mn}^{3+} + \text{HC}_2\text{O}_4 \rightarrow \text{Mn}^{2+} + \text{CO}_2\text{H} + \text{CO}_2$  (start of chain), (b)  $\text{CO}_2\text{H} + \text{O}_2 \rightarrow \text{CO}_2 + \text{HO}_2$ ,  $\text{HO}_2 + \text{HC}_2\text{O}_4 \rightarrow \text{CO}_2 + \text{CO}_2\text{H} + \text{HO}_2'$  and  $\text{HO}_2' + \text{H}^+ \rightarrow \text{H}_2\text{O}_2$  (chains), and (c)  $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$  (breaking of chain). J. F. H.

**Proof of accuracy of hydrodynamic-thermodynamic theory of detonation for solid and liquid explosives.** A. Schmidt (*Z. physikal. Chem.*, 1941, A, 189, 88—94).—For solid and liquid explosives the hydrodynamic-thermodynamic theory for the calculation of detonation velocity is difficult to apply owing to the fact that the equation of state of the gases formed is unknown. Using Aberl's modification of van der Waals' equation,  $p/d = vRT/(v - nb)$  ( $p$  = pressure,  $v = 1/d$ ,  $n$  = no. of g.-mols. of gas per kg. of explosive,  $b$  = co-val. of mols.) the following equation was deduced for the propagation velocity  $D$  of the wave:  $D = \{v/(v - n_2b)\} \mu \sqrt{(8 \cdot 32 \gamma n_2 T_2)}$  ( $\mu = d$  in wave/d of explosive;  $\gamma = c_p/c_v$ ). The effect of  $d$  on detonation velocity was confirmed experimentally. Compressed nitrocellulose has a higher detonation velocity when it contains 20% of  $\text{H}_2\text{O}$ . The explosion temp. is lowered, but the increase in vol. of gas  $>$  compensates for this. The detonating power of an explosive can be determined by finding the distance away from another explosive at which it will cause detonation. The detonating power of an explosive decreases with increasing  $d$ . This is explained by supposing that the explosion of the first substance produces a compression shock on the surface of the second, and this must be maintained if detonation is to occur. If the  $d$  of the second explosive is too high no detonation occurs as the shock is not maintained. A. J. M.

**Reaction of 2- $\alpha$ -chloroalkylbenzimidazoles with potassium iodide.**—See A., 1944, II, 83, 84.

**Philosophy in catalysis, catalysis in philosophy.** A. Mittasch (*Z. physikal. Chem.*, 1941, A, 189, 44—62). A. J. M.

**Possibility of auto-vibrations in a homogeneous chemical system involving a quadratic auto-catalysis.** D. A. Frank-Kamenetzki and I. E. Salnikov (*J. Phys. Chem. Russ.*, 1943, 17, 79—86).—Some

conditions under which periodic catalytic reactions can occur are discussed. J. J. B.

**Acceleration by iron of reduction by hydrogen peroxide.** K. Yamafuji, K. So, and H. Takaishi (*Biochem. Z.*, 1941, 308, 29—36).— $\text{H}_2\text{O}_2$  is decomposed with production of reducing activity [shown by Thunberg's methylene-blue (I) method] by aq. suspensions and, to a greater extent, solutions (in 0.1N-NaOH) of haematin. The decomp. of  $\text{H}_2\text{O}_2$  is also effected by  $\text{OH}^-$ , but with haematin the amount of  $\text{H}_2\text{O}_2$  decomposed is much less, and the rate of decolorisation of (I) is greater, than that due to alkali. Absence of air has no effect on the reduction of (I) or decomp. of  $\text{H}_2\text{O}_2$ . The reducing activity is also produced by inorg. Fe,  $\text{Fe}^{2+}$  being more active than  $\text{Fe}^{3+}$  and  $\text{FeSO}_4$  than  $\text{FeCl}_2$ .  $\text{Cu}^{2+}$ , which is very active in decomp.  $\text{H}_2\text{O}_2$ , does not produce reducing activity. Zn haematoporphyrin is inactive. The mechanism of the reducing activity is discussed. F. O. H.

**Reaction of sulphur dioxide with olefines. Ceiling-temperature phenomena.** R. D. Snow and F. E. Frey (*J. Amer. Chem. Soc.*, 1943, 65, 2417—2418).—Simple olefine hydrocarbons and  $\text{SO}_2$  undergo a catalysed reaction in a homogeneous liquid phase to form polysulphones of high mol. wt. but on raising the temp. the reaction is arrested at a characteristic temp. called the "ceiling temp." The characteristic temp. is unaffected by proportions of reactants and by the nature of the catalyst. It is considered that the olefine acts as inhibitor to the reaction and that the ceiling temp. is lowest for olefines most susceptible to acid-catalysed polymerisation. W. R. A.

**Activation of aluminium chloride by the catalytic action of chlorides of elements of the fourth group of the periodic classification.** E. Ott (*Angew. Chem.*, 1941, 54, 142—144).—A review of published data. The catalytic activity of  $\text{AlCl}_3$  for Friedel-Crafts and Gattermann-Koch syntheses, and for reaction of  $\text{CCl}_4$  with aliphatic and aromatic hydrocarbons to give polymerisable olefines, can be increased by addition of chlorides of any elements of the 4th periodic group. L. J. J.

**Catalytic isomerisation of paraffin hydrocarbons. I. Butanes.** P. A. Leighton and J. D. Heldman (*J. Amer. Chem. Soc.*, 1943, 65, 2276—2280).—The homogeneous liquid-phase isomerisation of  $n\text{-C}_4\text{H}_{10}$ , catalysed by  $\text{AlBr}_3\text{-HBr}$  mixtures, has been studied. Anhyd.  $\text{AlBr}_3$  has no catalytic action, but traces of moisture induce catalysis;  $\text{HALBr}_4$  is regarded as the true catalyst.  $\Delta E$  of activation of isomerisation of  $n\text{-C}_4\text{H}_{10}$  is 9.2 kg.-cal. per mol. The calc. temp.-independent rate factor of  $10^{6.4}$  is  $\ll$  that predicted from collision rate considerations. W. R. A.

**Kinetics of enzyme-substrate compound of peroxidase.**—See A., 1944, III, 284.

**Peroxy-compounds of quinquevalent vanadium and their action as active intermediates in the catalytic decomposition of hydrogen peroxide.** K. F. Jahr (*Z. Elektrochem.*, 1941, 47, 810).— $\text{V}^{\text{V}}$  reacts with  $\text{H}_2\text{O}_2$  to give two peroxy-compounds, which in solution enter into the equilibrium:  $[\text{V}(\text{O}_2) \cdot \text{aq.}]^{+++} + \text{H}_2\text{O}_2 + 2\text{H}_2\text{O} \rightleftharpoons [\text{VO}_2(\text{O}_2)_2 \cdot \text{aq.}]^{+} + 6\text{H}^+$ . In solutions not strongly acid the anion of the diperoxyvanadic acid (I) is formed. Hydrated  $\text{V}_2\text{O}_5$  dissolves in aq.  $\text{H}_2\text{O}_2$  to give (I). This decomposes with evolution of  $\text{O}_2$ , forming orthovanadic acid, which in presence of  $\text{H}^+$  ions finally gives pentavanadic acid. Octavanadic acid is formed as an unstable intermediate, which is very active as a catalyst for the decomp. of  $\text{H}_2\text{O}_2$ . J. F. H.

**Catalytic investigation on alloys. X. Catalytic activity of alloys of copper with nickel, palladium, and platinum.** G. Rienacker (*Z. Elektrochem.*, 1941, 47, 805—809).—The catalytic action of alloys of Cu with Ni, Pd, and Pt on the dehydration of  $\text{HCO}_2\text{H}$  and the hydrogenation of  $\text{C}_2\text{H}_4$  was studied. Each system forms a continuous series of solid solutions with face-centred cubic lattices. In each case Cu is the least active element. The catalytic properties are not additive. Use of kieselgur as support increases the activity of the pure components, but not for mixed catalysts. Catalysts with ordered lattices are more effective than disordered types. J. F. H.

**Kinetics of the catalytic oxidation of acetylene on active manganese dioxide.** V. Roiter and M. Rusov (*J. Phys. Chem. Russ.*, 1943, 17, 87—96).—30—100 l. of air containing 0.04—0.57% of  $\text{C}_2\text{H}_2$  were passed per 1 hr. through 1 g. of commercial active  $\text{MnO}_2$ . The rate  $v$  of oxidation was determined from the temp. of the air before and after passing the catalyst; this method was more exact than chemical analysis, provided that the temp. of the catalyst was kept const. by adjusting the temp. of the oncoming air. At  $142^\circ v \propto [\text{C}_2\text{H}_2]$ , at  $190^\circ v \propto [\text{C}_2\text{H}_2]^{0.75}$ , and at  $220^\circ v \propto [\text{C}_2\text{H}_2]^{0.5}$ ; at lower temp. it is determined by the rate of reaction, and at higher temp. by the rate of diffusion. At  $142^\circ v$  is nearly independent of the speed of air flow and of the grain size of  $\text{MnO}_2$ , but at  $220$ — $250^\circ$  it increases with this speed and the degree of dispersity (1—5 mm.) of  $\text{MnO}_2$ . The apparent heat of activation at  $<170^\circ$  is 14—23 kg.-cal. per g.-mol. J. J. B.

**Kinetics of the hydrogenation of acetylene on palladium.** E. Cremer, C. A. Knorr, and H. Plieninger (*Z. Elektrochem.*, 1941, 47,



737—747).—The reaction of  $C_2H_2-H_2$  mixtures on Pd as catalyst at room temp. was investigated by measuring (1) the pressure change in the gas vessel, (2) the electrical resistance of the Pd to determine the amount of  $H_2$  in the Pd, and (3) the  $C_2H_2$  concn. by analysis of a sample of gas. The main reaction is  $C_2H_2 + H_2 = C_2H_4$ . The reaction is autocatalytic, the velocity increasing almost up to complete conversion, due to the decreasing inhibition by the  $C_2H_2$ . The pressure change follows the equation  $-dp/dt = k \cdot p_{H_2} / (1 + b'p_A)$ , where  $p_{H_2}$  and  $p_A$  are the pressures of  $H_2$  and  $C_2H_2$  respectively,  $b'$  is the adsorption coeff. of  $C_2H_2$ , and  $k$  is the velocity coeff. J. F. H.

**Palladium-synthetic high polymer catalysts.** K. E. Kavanagh and F. F. Nord (*J. Amer. Chem. Soc.*, 1943, **65**, 2121—2125).—Polyvinyl acetate (I) in EtOH and  $COMe_2$  is an effective colloidal support for Pd hydrogenation catalysts but the particle size of a polymer can be so large that catalytic activity diminishes. Further, acetals of (I) (a long-chain polyhydroxy linear polymer) in AcOH or dioxan can be used for Pd catalysts. Stability and efficiency of the polymer catalysts are enhanced by the presence of small amounts of  $H_2O$ . In the presence of thiophen gum arabic-Pd catalysts are inferior to (I)-Pd. W. R. A.

**Magnetic measurements on catalytically active substances.** H. Morris and P. W. Selwood (*J. Amer. Chem. Soc.*, 1943, **65**, 2245—2252).—Magnetic susceptibilities at different field strengths and temp. have been measured for catalysts for the hydrogenation of  $C_6H_6$  by Ni-activated Cu, Ni on Mg, and Ni-activated Mo oxide. Ni-activated Cu consists of a continuous series of solid solutions containing 66—92.5% Ni. Thermal deactivation of such catalysts is accompanied by a lowering of the Curie point and indicates diffusion of Cu into the Ni-rich alloys. Thermal deactivation of Ni on MgO is accompanied by a decrease in magnetisation but the Curie point remains unchanged. Poisoning by  $H_2S$ , CO, Hg, and Pb affects only a small fraction of the Ni atoms presumably on the surface of active microcrystals. Ni-activated Mo oxide contains no metallic Ni. W. R. A.

**Catalytic agents for synthesis of carbon disulphide.**—See B., 1944, II, 61.

**Theory of passivity phenomena.** XXXIII.—See A., 1944, I, 105.

**Electrolytic reduction of amides.**—See B., 1944, II, 61.

**Photochemical oxidation-reduction of carbon monoxide and water to carbon dioxide and hydrogen.** W. Seitz (*Biochem. Z.*, 1941, **308**, 103—108; cf. A., 1938, I, 315).—When CO in  $H_2O$  is strongly illuminated (temp.  $>30^\circ$ ) the reaction  $CO + H_2O = CO_2 + H_2$  occurs. Similar reactions occur with CO in EtOH, MeOH, or  $COMe_2$ . The  $CO_2$  produced is determined by fixing with alkali and titrating. The  $H_2$  produced decolorises H acceptors, e.g., methylene-blue;  $CO_2$ ,  $N_2$ , and, in absence of CO,  $H_2$  do not cause decolorisation. In neutral solution, illumination and presence of basic or buffered acid H acceptor are necessary for the reaction but in slightly alkaline solution illumination or presence of H acceptor suffices. In strongly alkaline solution, CO is oxidised to  $CO_3$  in the dark in absence of H acceptor. If photosensitiser (e.g., adrenaline) is present, illumination by diffuse daylight is adequate. The reaction proceeds almost as rapidly at  $5^\circ$  as at  $30^\circ$ . It is not affected by  $CH_3O$ ,  $HCO_2H$ ,  $Fe^{II}$ ,  $Fe^{III}$ ,  $Cu^I$ , or  $Cu^{II}$ . The results must be borne in mind when the effect of CO on the respiration of cells is studied. W. McC.

**Effect of temperature on the photographic process.** II. J. Eggert and F. G. Kleinschrod (*Z. physikal. Chem.*, 1941, A, **189**, 1—9).—The blackening produced on photographic plates by X-rays at temp. between  $14^\circ$  and  $-173^\circ$  has been investigated. There is a general decrease in sensitivity as temp. is decreased. The behaviour of some reversal effects (Villard effect, and solarisation) at temp. between  $20^\circ$  and  $-160^\circ$  was examined. The Villard effect, which is marked at higher temp., gradually disappears as temp. is reduced. A. J. M.

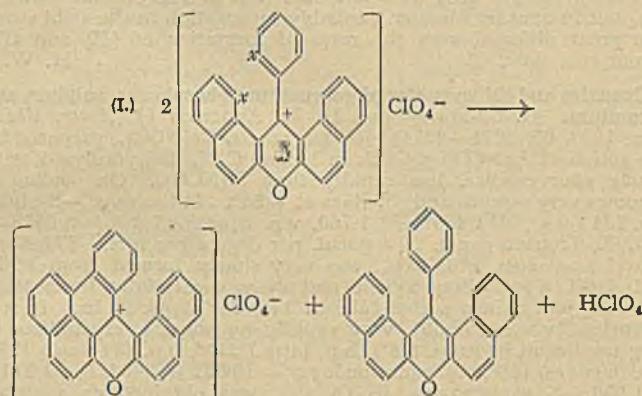
**Photochemical nitration of benzene and nitrobenzene with nitrogen oxides.** I. O. Gorislavetz (*J. Phys. Chem. Russ.*, 1943, **17**, 102—107).—Nitration of  $C_6H_6$  vapour by  $NO_2$  at  $20-60^\circ$  is only slightly accelerated by illumination; visible light raises mainly the yield of  $PhNO_2$ , and ultra-violet light that of  $C_6H_4(NO_2)_2$  etc.  $PhNO_2$  vapour yields with  $NO_2$  in light a mixture of  $C_6H_4(NO_2)_2$  and  $C_6H_3(NO_2)_3$ . J. J. B.

**Photo-oxidation in rigid media.** G. N. Lewis and J. Bigeleisen (*J. Amer. Chem. Soc.*, 1943, **65**, 2424—2426).—The rôle of electron-ejection in photochemical processes is discussed by reference to the odd-electron ions and radicals produced on illuminating org. substances, e.g., diarylamines, derivatives of  $Ph_2$  and of  $C_6H_5$ , in rigid media. W. R. A.

**Photochemical reactions of leuco-dyes in rigid solvents. Quantum efficiency of photo-oxidation.** G. N. Lewis and J. Bigeleisen (*J. Amer. Chem. Soc.*, 1943, **65**, 2419—2423).—Absorption spectra of oxazine (I), thiazine (II), leuco-methylene-blue (III), leucothionine (IV), and Michler's hydride (V) in an EtOH-iso- $C_6H_{12}$ -Et<sub>2</sub>O mixture G (A., 1)

at liquid air temp. have been determined. (I) and (II) give, on illumination, two semiquinone forms, one by ejection of an electron and the other by loss of  $H^+$  from the first on keeping. (III), (IV), and leuco-Capri-blue give, on illumination, five different substances, two of which are semiquinones, one is the completely oxidised dye ion, and the others are derived from the dimeric form of the leuco-base. Leuco-crystal-violet, leuco-malachite-green, and (V) behave similarly. Quantum yield of Wurster's-blue ions in the photo-oxidation of leuco-Wurster's-blue is 0.10 at the commencement of illumination. With (III), the quantum yield increases with concn. of leuco-base and decreases with increasing illumination; in conc. solutions the initial yield is 0.04. This behaviour demonstrates the existence of a dimeric leuco-base responsible for most of the oxidation products. W. R. A.

**Mechanism of a photo-disproportionation reaction.** E. Hertel and G. Sock (*Z. physikal. Chem.*, 1941, A, **189**, 95—108; cf. A., 1936, 1120).—The photochemical disproportionation of 13-phenyl-dibenzoxanthemium perchlorate according to the scheme:



has been investigated. The reaction is truly photochemical with a quantum yield of 0.03—0.05. This is independent of intensity and frequency of the incident light, and of the concns. of starting materials and products, and of the presence of foreign substances ( $N_2$ ,  $H_2$ ,  $O_2$ , *p*-benzoquinone). The extent of reaction is  $\propto$  quantity of light absorbed. Temp. coeff. is 1.1 for  $10^\circ$ . Since the quantum yield is independent of intensity only 1 mol. requires to be activated for reaction to occur. The reaction is intramol., consisting of a dehydrogenation leading to ring-closure at the positions marked  $x$  in (I), or to an initial step in this ring-closure. A. J. M.

## IX.—PREPARATION OF INORGANIC SUBSTANCES.

**Theory of isotope separation by exchange reactions.** L. Waldmann (*Naturwiss.*, 1943, **31**, 205—206).—Mathematical. The application of the law of mass action to Urey's method of separating isotopes (A., 1939, I, 211) is considered in two limiting cases: (1) when the gas mols. dissolve unchanged in the liquid, (2) when there is extensive ionisation in the liquid. The general rule is obtained that in the equilibrium, gas  $\rightarrow$  dissolved mols. and ions, the heavier isotope is always enriched in the liquid if the ions have more internal degrees of freedom than the gas mols. Where there are fewer degrees of freedom of the ion, separation of the heavier isotope may occur in either phase. A. J. M.

**Action of charcoal on potassium nitrate.** II. T. M. Oza and M. Shah (*J. Indian Chem. Soc.*, 1943, **20**, 261—270; cf. A., 1943, I, 133).—A detailed study of the reactions between  $KNO_3$ ,  $KNO_2$ , and C under different conditions, shows that the first reaction is  $4KNO_3 + 3C = 4KNO_2 + 2CO_2$ , and this may be followed by  $4KNO_2 + 3C = 2K_2CO_3 + CO_2 + 2N_2$ , proceeding smoothly to completion, or may become explosive when the reaction is  $KNO_3 + KNO_2 + 2C = K_2CO_3 + CO_2 + N_2$ . F. J. G.

**More care with mercury.**—See A., 1944, III, 362.

**Chemical investigations of silicates.** X. Topaz,  $Al_2SiO_4(F,OH)_2$ , and its synthesis; new aluminium oxide containing fluorine. R. Schober and E. Thilo (*Ber.*, 1940, **73**, [B], 1219—1240).—Comparison of the analytically determined F content of 3 topazes with the gitter vals. obtained by exposure of powders shows that there is no simple relationship between these magnitudes. Thermal hydrolysis of  $AlF_3$  leads, according to the temp., to an *Al oxyfluoride* (I) of the approx. composition  $Al_2O_3F$  or to  $\alpha-Al_2O_3$  (II). Up to  $600^\circ$  only (I) is produced, between  $600^\circ$  and  $800^\circ$  a mixture of (I) and (II) and  $>800^\circ$  only (II). (I) has its proper lattice. The intensities of the lines in the Debye diagrams differ according as (II) has been prepared up to  $550^\circ$  or at  $>600^\circ$ . Very sharply defined limits of temp. are observed for the reaction,  $2AlF_3 + 2SiO_2 = topaz$  (III) +  $SiF_4$ . (III) is produced between  $750^\circ$  and  $950^\circ$ . Above and below these temp. there is



much loss of  $\text{SiF}_4$  and a product (IV) results with a lattice closely resembling that of mullite. (IV) contains 5–6% F. The mechanism of formation of (III) through the gas phase of  $\text{SiF}_4$  is shown by use of an excess of  $\text{AlF}_3$  or  $\text{SiO}_2$  to be:  $4\text{AlF}_3 + 6\text{H}_2\text{O} = 2\text{Al}_2\text{O}_3 + 12\text{HF}$ ;  $12\text{HF} + 3\text{SiO}_2 = 3\text{SiF}_4 + 6\text{H}_2\text{O}$ ;  $2\text{Al}_2\text{O}_3 + \text{SiF}_4 + \text{SiO}_2 = 2\text{Al}_2\text{SiO}_4\text{F}_2$ , or, summarising,  $4\text{AlF}_3 + 4\text{SiO}_2 = 2\text{Al}_2\text{SiO}_4\text{F}_2 + 2\text{SiF}_4$ . The sharp limits of temp. are ascribed to the need by  $\text{SiF}_4$  of a definite energy of activation. The same limits of temp. are imposed for the production of (III) from  $\text{SiF}_4$  and  $\text{Al}_2\text{O}_3$ , or from a mixture of  $2\text{Al}_2\text{O}_3 + 1\text{SiO}_2$ . Under defined conditions it is possible to prepare topazes with enlarged lattice, the phenomenon appearing parallel with the inclusion of  $\text{Al}_2\text{O}_3$ , which must be in a particularly active form. Lattice enlargement follows when (III) is formed in presence of an excess of  $\text{AlF}_3$ , which yields this active  $\text{Al}_2\text{O}_3$  by hydrolysis or reaction with  $\text{SiO}_2$  or when  $\gamma\text{-Al}_2\text{O}_3$  is treated with  $\text{SiF}_4$  at  $700-800^\circ$ ; at this temp. (III) is not obtainable from  $\alpha\text{-Al}_2\text{O}_3$ . A substance resembling (IV) is not obtained by the reaction of  $\text{SiF}_4$  with  $\text{Al}_2\text{O}_3 + \text{SiO}_2$  at temp. not exceeding  $1050^\circ$ . Formation of (IV) from  $\text{AlF}_3 + \text{SiO}_2$  does not, like that of (III), occur through  $\text{SiF}_4$  but in another manner, probably by reaction in the solid state. The great differences in the rates of formation of (II) and (IV) favour this view. H. W.

**Cyanates and thiocyanates of germanium, phosphorus, sulphur, and chromium.** G. S. Forbes and H. H. Anderson (*J. Amer. Chem. Soc.*, 1943, **65**, 2271–2274).—*Ge isocyanate*,  $\text{Ge}(\text{NCO})_4$ , prepared by the action of  $\text{AgNCO}$  on  $\text{GeCl}_4$  in boiling  $\text{C}_6\text{H}_6$ , is hydrolysed, with strong effervescence, less rapidly than  $\text{Si}(\text{NCO})_4$ . On cooling it becomes very viscous and solidifies at  $-65^\circ$ . It has m.p.  $-8 \pm 0.5^\circ$ , b.p.  $204 \pm 0.4^\circ$ ,  $n_D^{20} 1.4858$ ,  $\rho^{25} 1.760$ , v.p. equation  $\log p = 8.6578 - 2757/T$ , Trouton const.  $26.4$  g.-cal. per degree per mol. *Thiophosphoryl isocyanate*,  $\text{PS}(\text{NCO})_3$ , was very slowly formed from  $\text{PSCl}_3$  and  $\text{AgNCO}$  in boiling xylene and more successfully by heating  $\text{P}(\text{NCO})_3$  and S in a sealed tube at  $140^\circ$  for about 12 hr. It is a colourless, viscous liquid, very rapidly hydrolysed, crystallises in long needles at  $0^\circ$  (m.p.  $8.8^\circ$ ), b.p. (atm.)  $215^\circ$ , b.p. (30 mm.)  $135^\circ$ , b.p. (60 mm.)  $150^\circ$ , v.p. equation  $\log p = 10.032 - 3492/T$ ,  $n_D 1.5116$ ,  $\rho 1.538$ . *S monocyanate*,  $[\text{S}_2(\text{OCN})_2]_n$ , was obtained as a stable yellow solid by heating  $\text{AgNCO}$  and  $\text{S}_2\text{Cl}_2$  in  $\text{C}_6\text{H}_6$ ; the  $\text{C}_6\text{H}_6$  solutions deposited also a brownish-yellow solid, unstable in air, and presumably *thionyl cyanate*,  $[\text{SO}(\text{OCN})_2]_n$ . *S monothiocyanate* was obtained as  $\text{S}_2(\text{SCN})_2$  in solution but polymerised to an insol. red solid when  $\text{S}_2\text{Cl}_2$  and  $\text{AgSCN}$  were boiled in  $\text{C}_6\text{H}_6$ . Its chemical and physical properties are almost identical with those of thionyl thiocyanate  $[\text{SO}(\text{SCN})_2]_n$  and sulphuryl thiocyanate  $[\text{SO}_2(\text{SCN})_2]_n$ . *Chromyl isocyanate*,  $\text{CrO}_2(\text{NCO})_2$ , formed when  $\text{AgNCO}$  and  $\text{CrO}_2\text{Cl}_2$  are refluxed in  $\text{CCl}_4$  is stable in solution only. On evaporation under reduced pressure a brown solid is obtained which explodes when dry. *Chromyl isothiocyanate*,  $\text{CrO}_2(\text{NCS})_2$ , may exist for a short time as a dark purple substance in  $\text{CCl}_4$  at room temp. but decomposes explosively at higher temp. The following have been prepared (details not given): *Silicic acid* (b.p.  $\sim 129^\circ$ ) and *POCl<sub>2</sub>SCN* (b.p.  $\sim 173^\circ$ ). W. R. A.

**Preparation of pure heavy oxygen isotope  $^{18}\text{O}_2$ , and nitrogen  $^{14}\text{N}^{15}\text{N}$ .** K. Clausius, G. Dickel, and E. Becker (*Naturwiss.*, 1943, **31**, 210).—A separation tube consisting of six units with a total length of 82 m. was used. With the wire at  $700^\circ$ , the equilibrium  $2^{16}\text{O}^{18}\text{O} \rightleftharpoons ^{16}\text{O}_2 + ^{18}\text{O}_2$  was set up, and  $^{18}\text{O}_2$  separated at the heavy end, together with a little  $^{17}\text{O}^{18}\text{O}$ . This was further separated in another apparatus.  $^{18}\text{O}_2$  has mol. wt. 35.99.  $\text{N}_2$  containing 4% of  $^{14}\text{N}^{15}\text{N}$ , obtained from  $\text{NH}_4\text{Cl}$  containing an enrichment of  $^{15}\text{N}$ , was separated. In the case of  $\text{N}_2$ , the equilibrium  $2^{14}\text{N}^{15}\text{N} \rightleftharpoons ^{14}\text{N}_2 + ^{15}\text{N}_2$  is not set up at the Pt wire. The mol. wt. of  $^{14}\text{N}^{15}\text{N}$  separated was 29.015, the small difference between this and the theoretical val. (29.004) being ascribed to the presence of a small amount of  $^{15}\text{N}_2$ . The use of a suitable catalyst in the tube brings about the above equilibrium, and enables pure  $^{15}\text{N}_2$  to be separated. A. J. M.

**Application of the isotopic method to the investigation of the mechanism of chemical reactions. III. Mechanism of reaction of acid anhydrides with alcohols. IV. Reaction of xanthation, reaction of cellulose mercerisation, and structure of alkali-cellulose.**—See A., 1944, II, 119, 122.

**Recovery of elementary sulphur from gases containing hydrogen sulphide.** J. K. Chowdhury and R. M. Datta (*J. Indian Chem. Soc.*, 1943, **20**, 253–260).—Incorporation of  $\text{Al}_2\text{O}_3$  or to a smaller extent of  $\text{MnO}_2$  increases the efficiency of  $\text{Fe}_2\text{O}_3$  as an absorbent for the recovery of S from gaseous mixtures containing  $\text{H}_2\text{S}$ . F. J. G.

**Problems of systematic affinity theory.** W. Biltz (*Z. physikal. Chem.*, 1941, **A**, 189, 10–37).—The affinity of S and P for metals is examined. There is a periodicity in the no. of sulphides and phosphides which a metal can form with position in the periodic table. Max. occur with the elements of group I which is due to the existence of stable poly-compounds, in which the valency of the metal is increased. Max. in groups IV and VIII are due to the

formation of sub-compounds. The stability of polysulphides increases on the left-hand side of the periodic system with increasing at. no. The stability of the sulphides agrees in general with the rule that of homologous elements of the principal groups and transition series the compounds of the lighter are less stable than those of the heavier elements. The types of linkage and lattice structure present in sulphides and phosphides are discussed, and the energy content of these compounds is considered. A. J. M.

**Synthesis of ethylene complexes of platinum with four different substituent groups in the inner sphere.** A. Gelman (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **38**, 310–313).—The geometrical isomerides  $\text{C}_2\text{H}_4 \left\langle \begin{array}{l} \text{Cl} \\ \text{NH}_3 \end{array} \right\rangle \text{Pt} \left\langle \begin{array}{l} \text{Cl} \\ \text{Br} \end{array} \right\rangle$  (I) and  $\text{C}_2\text{H}_4 \left\langle \begin{array}{l} \text{Br} \\ \text{Cl} \end{array} \right\rangle \text{Pt} \left\langle \begin{array}{l} \text{Br} \\ \text{NH}_3 \end{array} \right\rangle$  (II) have the following properties: (I), greenish-yellow prismatic crystals,  $n_D > 1.783$ ,  $n_p 1.758$ , insol. in cold HCl, decomposed by cold  $\text{AgNO}_3$ ; (II), yellow crystals,  $n_D 1.783$ ,  $n_p 1.708$ , sol. in cold HCl giving  $\text{NH}_4[\text{Pt}(\text{C}_2\text{H}_4)\text{BrCl}_2]$ , giving a very feeble opalescence with cold  $\text{AgNO}_3$ . Attempts to obtain the anion  $[\text{Pt}(\text{C}_2\text{H}_4)\text{ClBr}]^-$  led to displacement of  $\text{C}_2\text{H}_4$  from the complex. L. J. J.

## XI.—GEOCHEMISTRY.

**Apparatus and methods for measuring the conductivity of natural waters in marine and semi-marine conditions.** P. Ulylyott and O. Ilgaz (*Rev. Fac. Sci. Istanbul*, 1943, **7**, 190–227).—Conductivity data and composition of Black Sea and Mediterranean waters are recorded. (See also C., 1944, Part 2.) A. A. E.

**Sediments of four woodland lakes, Villas Co., Wisconsin.** I. W. H. Twenhofel, V. E. McKelvey, S. A. Carter, and H. Nelson (*Amer. J. Sci.*, 1944, **242**, 19–44).—The sediments are described, and mechanical and chemical analyses given. L. S. T.

**Age of the Universe and of three Spanish minerals.** J. de D. L. Luna (*Inst. Geol. Min. España*, 1943, **11**, 149–213).—A survey of methods for determining geological time. The age of the following minerals was studied by radioactive methods: pitchblende, from a middle carboniferous layer, (411), betafite from Cordoba (0.8), and torbernite from the granites of Colmenarejo (Madrid) ( $424 \times 10^6$  years). F. R. G.

**Chromium minerals of Beni-Buscera (Gomara [Spanish Morocco]).** A. de Gálvez-Cañero and J. de Lizaur y Roldán (*Inst. Geol. Min. España*, 1943, **11**, 109–124).—Irregular deposits of chromite occur in association with serpentine, magnesia, and amorphous silicates. Cr does not occur in Spain. F. R. G.

**Tantalites or niobates?** A. de Larragán (*Inst. Geol. Min. España*, 1943, **11**, 225–232).—Columbite (I) containing some Ta occurs in Galicia (Spain). Good quality (I) has a market val. similar to that of tantalite. F. R. G.

**Structural type of perovskite.**—See A., 1944, I, 79.

**Spectrum analysis data on gypsum from Permian deposits of Tართა.** L. M. Miropolski and S. A. Borovik (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **38**, 33–36).—Of the 55 elements sought spectrographically in 17 samples of gypsum only 15, viz., Li, Be, B, Mg, Al, Si, Ca, Ti, Mn, Fe, Cu, Sr, Y, Zr, and Bi, were found. There are no marked differences in composition of samples taken from different stratigraphical horizons. Secondary gypsum has a simpler composition than primary. Fe, Ti, and Cu appear to be responsible for colour. Mg, Si, Ca, Ti, Fe, and Sr are always present; Li, Be, Y, Zr, and Bi occur sporadically, and only as traces. L. S. T.

**A monchikite from Takob (Tadjik Soviet Socialist Republic).** S. D. Tschetverikov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **38**, 37–41).—An unusual occurrence of a dyke of black lamprophyric rock (monchikite) in a biotite granite is described. A chemical analysis [I. Tuchin] is recorded. L. S. T.

**Effect of salt admixtures on the dissociation of dolomite.** L. G. Berg (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **38**, 24–27).—The effect of mixing NaCl with dolomite (I) on the time-temp. curves of (I) is illustrated graphically and is discussed. L. S. T.

**Oxidation by potassium hydrogen sulphate as a distinguishing feature between amphiboles and pyroxenes.** M. R. A. Iyer (*Current Sci.*, 1943, **12**, 271–272).—Data which show that in amphiboles the proportion of  $\text{FeO}$  oxidised to  $\text{Fe}_2\text{O}_3$  by fusion with  $\text{KHSO}_4$  is  $>$  in pyroxenes of similar composition are tabulated. The extent to which oxidation takes place depends in some measure on the composition of the substance, e.g., a high % of  $\text{MgO}$  reduces the degree of oxidation. L. S. T.

**Kaolin seams.** J. R. O. de Villacián (*Inst. Geol. Min. España*, 1943, **11**, 3–31).—Kaolin is considered to be formed from felspar by  $\text{H}_2\text{O}$  at temp.  $< 400^\circ$ . More prolonged action or higher temp. produce cryst. kaolin. The formation of sericite from plagioclase occurs similarly with  $\text{H}_2\text{O}$  containing K. F. R. G.



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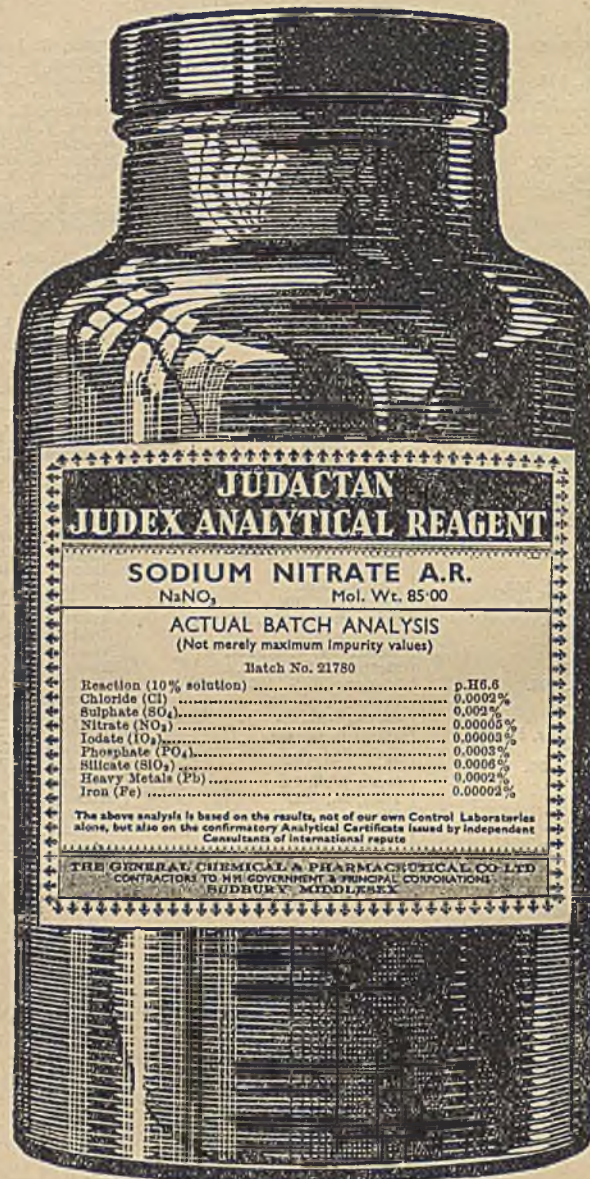




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