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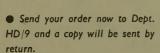
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BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

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

DECEMBER, 1943.



I.—SUB-ATOMICS.

Continuum in the 1849 A. region in the afterglow spectrum of mercury. A. Wattenberg and H. W. Webb (*Physical Rev.*, 1943, [ii], 64, 39—40).—A continuum reported by Garth (cf. A., 1941, I, 437) is confirmed, and a microphotometer record, with and without O₄ absorption bands, is given.

N. M. B.

Determination of absolute intensities of spectral lines. G. S. Kvater (J. Physics, U.S.S.R., 1942, 6, 210—217).—The discrepancy between the author's results (J. Exp. Theor. Phys., 1941, 11, 402) for abs. intensity of Tl lines at 3776 and 5350 a. by the anomalous dispersion method and those of Kuhn and Müller by absorption and magnetic rotation methods is discussed. Recalculation of Müller's results shows that the discrepancy resides in v.p. vals. for Tl. The absorption method affords an accurate measure of v.p.

New crystals to be used in chemical X-ray spectrography. G. Aminoff (Arkiv Kemi, Min., Geol., 1943, 16, B. No. 10, 5 pp.).— Intensity and dispersion of the Ka_1 radiation of Ag, Mo, Cu, Fe, Cr, and Sc, reflected from the scalenohedron 2131 of calcite and the 110 face of baryta (Dana's notation), have been determined, and the vals. compared with those of other crystals used in X-ray spectrography. W. R. A.

Origin of the $M\zeta_1$ and $M\zeta_2$ X-ray satellite groups. F. R. Hirsh, jun. (Physical Rev., 1943, [ii], 64, 39; cf. Munier, A., 1940, I, 424).— The satellites are ascribed to initial MN ionisation involving the radiationless transition $M_{\rm III} \rightarrow M_{\rm V}$. N. M. B.

Thermo-electromotive force. K. F. Herzfeld (*Physical Rev.*, 1943, [ii], 64, 37—38).—Mathematical. A simple kinetic interpretation, applicable in quantum and classical theory, is given. The usual expression can be transformed to agree with this result.

Spatial asymmetry of Cerenkov radiation as a function of electron energy. H. O. Wyckoff and J. E. Henderson (Physical Rev., 1943, [ii], 64, 1—6).—A study, as a function of bombarding particle energy, of the Cerenkov radiation emitted when high-speed electrons traverse transparent media shows that the direction of emission of the radiation for mica over the range 240—815 kv. is given by the Frank-Tamm relation (cf. A., 1937, I, 220) $\cos \theta = 1/\beta n$, where θ is the angle of progression of the radiation with the electron beam and n is the refractive index of the mica target. In this range β [= (velocity of electrons in medium)/c] changes markedly, providing a significant test of the relation as a function of bombarding particle energy. N. M. B.

Positive column of a helium discharge. N. A. Karelina (J. Physics, U.S.S.R., 1942, 6, 218—223).—The dependence of potential gradient, electron temp. (T_e), and electron concn. on the radius and gas pressure (p) of the positive column in a He discharge has been investigated for $p=10^{-2}$ —1 mm. and discharge current 300 ma. in a tube 32 mm. in diameter. The results agree with calculations for low-pressure plasma by Klarfeld's method (ibid., 1941, 5, 155). At p=0.007 mm. the val. of T_e is 188,000° k.

L. J. J.

Chemical elements and natural atomic types according to the position of isotope and nuclear research (addendum to report on work from the end of 1939 to the end of 1940). O. Hahn (Ber., 1941, 74, [A], 24, 27; cf. A., 1940, I, 185).—Few changes are noted since the previous report. From the relative abundance of Mo isotopes the at. wt. is given as 95.92 ± 0.01 (formerly 95.90). The deviation from the val. (95.95) in the International at. wt. table is therefore < before.

Electron mass in relation to energy of formation of the atoms: calculation of isotopic and atomic weights. H. D. K. Drew (Chem. and Ind., 1943, 390—393).—It is suggested that there is a numerical connexion between the mass of the electron, m, and that of the proton, M_P , and the neutron, M_N , and the mass of 16 O. The isotopic wt. $I_W = AM_N - k$, where $A = \max$ no. It is found that aA + b = k (a = const., and b = a drifting const. common to two or more atoms in some of its vals. but in other cases applying to one atom only). a = 18m, so that if every term is expressed in electron masses, 18A + b = k. Hence, when free particles coalesce to form atoms, a sum of energy = 18Am is withdrawn. It is divided into two

parts, k disappearing in so far as it is not represented as mass in the atom, and b appearing as mass. b is always negative. k/Z (Z = the no. of protons or planetary electrons in the atom) is integral and is the mass-contraction distribution index, Y, for a given atom. The integral relationship of Z and Y enables both k and b to be calc. if I_W is known with sufficient accuracy, since k = ZY and b = ZY - 18A. When Y can be calc. from experimentally determined I_W , the true val. of I_W can be obtained from $I_W = AM_N - ZY$. Hence the at. wt. can be calc. if the Y nos. of all the isotopes are known. The vals. thus obtained agree well with experimental vals. The electron mass is thus an integral measure of the energy changes occurring in the formation of the atom. k/A is a convenient alternative to Aston's packing fraction, since it does not vary in sign, and compares the contraction of the atoms as a whole, and not with respect to $I^{16}O$. The interpretation of k and k is discussed. Both the nucleus and the planetary system of an element can be regarded as formed by the fusion of two lighter atoms, or of two atoms of a single lighter element.

A. J. M.

Nuclear chemistry. R. Fleischmann (Z. Elektrochem., 1941, 47, 8—16).—A review in which the types of nuclear reaction, and the particles which can bring them about, are discussed. Artificial radioactivity and nuclear isomerism are also dealt with. Laws governing nuclear reactions, and the applications of nuclear chemistry, are outlined.

A. J. M.

Electrons in equilibrium with the penetrating component of cosmic rays in lead at 10,000 feet and at sea level. W. E. Hazen (Physical Rev., 1943, [ii], 64, 7—10).—Measurements with Wilson cloud chambers containing Pb plates show that the no. of electrons (N) in equilibrium is $7\cdot4\pm0\cdot2\%$ at 10,000 ft. and $6\cdot8\pm0\cdot6\%$ at sea level. Comparison with calc. vals. of N shows that if the loss of lowenergy electrons as a result of scattering in the Pb is taken into account, the calc. vals. are only slightly > the experimental vals. If the calc. vals. are assumed correct, the measurements provide additional evidence that protons constitute only a small fraction of the cosmic-ray particles in the lower atm.

N. M. B.

Space distribution of particles in "Auger showers." D.V. Skobeltzin (Compt. rend. Acad. Sci. U.R.S.S., 1942, 37, 14—19).—Auger's coincidence data (A., 1939, I, 400) are shown to be in agreement with calculations based on Euler's space distribution equation, $p^{r} = \rho_{0}e^{-r/R}$, relating the no. of particles (ρ) passing through unit cross-section with the distance (r) from centre of shower and the "half-radius" (R) of the shower.

L. J. J.

Excited states of elementary particles. V. L. Ginzburg (Compt. rend. Acad. Sci. U.R.S.S., 1942, 37, 9—13).—Two types of difficulty in relativistic quantum particle theory are discussed: (a) difficulties arising from the infinite proper energy of elementary particles; (b) difficulties arising from not taking into account the effect of the proper field of the particle on its scattering properties. If the proper field of the magnetic moment is taken into account, excited spin states of the particle must be postulated, and the wave equation must contain an empirical const.

L. J. J.

Electron configuration as the basis of the periodic table. W. F. Luder (J. Chem. Educ., 1943, 20, 21—26).—Charts based on electron configuration of the elements are reproduced and discussed. The at. structure chart recommended should replace arrangements of the elements based on Mendeléeff's classification.

L. S. T.

Approximate equations of transfer of radiation in a scattering and absorbing medium. E. S. Kuznetzov (Compt. rend. Acad. Sci. U.R.S.S., 1942, 37, 209—214).—Mathematical. W. R. A.

II.—MOLECULAR STRUCTURE.

Intensity theories in band spectra. I. Hutchisson's theory. II Langstroth's theory. N. R. Tawde and V. S. Patankar (Proc. Physical Soc., 1943, 55, 396—403, 403—409).—I. Integrated intensity vals. (I) for all measurable bands of the second positive system of Nexcited by an induction coil (without spark-gap or condenser), were determined by photographic photometry. Transition probabilities for bands in emission are calc. from known mol. consts with the help of Hutchisson's formula. Observed I/ν^4 vals. for

bands of different v''-progressions do not agree satisfactorily with calc. emission probabilities, but agreement is improved by interchanging the vibrational quantum numbers. Explanations are discussed.

II. Vals. of I were determined, as above, for 24 bands, compared with only 3 estimated by Langstroth. From calc. $P^2v'v''$ vals. and excitation probabilities P^2v^0v' the "complete intensities" $P^2vv' \times P^2v'v'$ are calc., as suggested by Langstroth. Observed I/v^4 vals. for different bands of the system do not show satisfactory agreement with calc. "complete intensities," but agreement is improved if, in the calculation of the complete intensity for the (x, y) band, the emission probability $P^2v'v''$ calc. for the (x, y) band is used. Reasons for discrepancies are given and discussed.

Intensity anomalies and perturbations in the CN bands. A. T. Wager (Physical Rev., 1943, [ii], 64, 18—31).—The rotational structures of the (0, 0) violet and (9, 4) red CN bands, developed by CHCl₃ in active N, were measured on plates in the first and second orders of a 30-ft. grating. Data for rotational consts., Λ -doubling, spin doubling, perturbations, and shifts are given. The vals. of the perturbation matrix elements are obtained for the various levels. Anomalies of R branch lines in the (0, 0) band are noted. The mechanism of enhancements of the main and extra lines of this band is discussed. Collisions involving interstate transfer (${}^2\Pi \rightarrow a^2\Sigma$) occur, or are enhanced, at each perturbed level; rapid redistribution of mols. among rotational levels by collisions must also occur. Where spin doublets are resolvable in the violet band, rotational redistribution occurs without change of spin direction.

Continuous emission bands in the spectrum of carbon tetrachloride. R. K. Asundi, N. L. Singh, and J. P. Mishra (Current Sci., 1943, 12, 204—205).—Bands in the range 4620—2450 A., except those at 4620 and 3340 A., are identical*with those obtained in a discharge through Cl₂, and are probably due to Cl₂ or Cl₂*. The strong 4620 A. band is attributed to a transition in the CCl₄ mol. from the ground level of CCl to the repulsive curve of CCl₂, and the weak band at 3340 A. to the transition from the same initial level to the repulsive curve of CCl₃, in complete analogy to the continuous spectra in SnCl₄.

N. M. B.

N. M. B.

Configuration of Δαγ-butadiene. R. S. Rasmussen, D. D. Tunnicliff, and R. R. Brattain (J. Chem. Physics, 1943, 11, 432—433).—Ultraviolet absorption by (CH₂:CH)₂ vapour at 2200—2400 A. increases markedly with temp. in the range 10—40°, probably owing to rapidly-changing cis-trans equilibrium. Of 10 infra-red bands at 520—1500 cm.⁻¹ measured, 6 frequencies coincide with Bradacs and Kahovec's Raman frequencies (A., 1943, I, 31) measured at low temp., indicating predominance of the cis-form at low temp. Hence the cis- is the form of lower energy.

L. J. J.

Ultra-violet absorption spectrum of formic acid. B. Sugarman (Proc. Physical Soc., 1943, 55, 429—430).—Data are reported for bands photographed in the range 2260—2600 A., and an expression for $1/\lambda$ is found. N. M. B.

Absorption spectra of substituted nitrosobenzenes. Resonance effect of substituents. Y. Tsuzuki, T. Uemura, and N. Hirasawa (Ber., 1941, 74, [B], 616—621; cf. A., 1942, I, 39).—Absorption measurements are recorded for o-, m-, and p-C_eH₄Me·NO and for p-C_bH₄X·NO (X = Cl, Br, I). In every case the absorption max of PhNO is displaced towards greater $\lambda\lambda$, the effect being in the order p > o > m-Me, I > Br > Cl. Considered in conjunction with published data the results indicate that parallelism exists between the op-directing activity of substituents and their effect on light absorption. F. L. U.

Mesomeric anions containing nitro-groups. G. Kortüm (Ber., 1941, **74**, [B], 409—416).—The displacement in the absorption max. towards the red of o-, m-, and p-NO $_2$ -C $_6$ H $_4$ -O $^-$ (in H $_2$ O or dioxan) indicates that each ion exists in a limiting quinonoid form (which is not dependent on hydration). For s-C $_6$ H $_3$ (NO $_2$) $_3$ (I), the "quinonoid" anion is undoubtedly hydrated. Thus (I) and NH $_3$ in dioxan show no colour change until H $_2$ O is added. H. B.

Absorption of light by organic molecules and ions according to quantum mechanics. T. Forster (Z. Elektrochem., 1941, 47, 52—54).—The application of quantum mechanics to light absorption by org. mols. is considered, with special reference to the polyenes and $(\mathrm{CPh_3})^+$, and its mono-, di-, and tri-substitution derivatives. A theoretical substitution rule is deduced stating that the absorption range of an unsubstituted ion breaks into two regions, one of shorter and the other of longer λ , when the first auxochromic group is substituted. When the second auxochromic group is substituted both regions are shifted to longer $\lambda\lambda$, and when the third is substituted, the two regions merge into one of intermediate λ . This is verified by experiment.

Ultra-violet absorption of some resins of the formaldehyde-phenol type. E. Mayer-Pitsch and H. Troger (Z. Elektrochem., 1941, 47, 60—65).—The dialcohol, 4-cyclohexyl-2: 6-di(hydroxymethyl)-phenol (I), loses $\rm H_2O$ on heating, ${}^{\circ}\rm CH_2{}^{\circ}\rm O{}^{\circ}\rm CH_2{}^{\circ}$ bridges linking the

mols. Further heating may result in loss of $\mathrm{CH_2O}$, and formation of a ${}^{\circ}\mathrm{CH_2O}{}^{\circ}$ bridge to the 1-position. (I) may also give 2:6-diformyl-4-cyclohexylphenol (II). The formation of these compounds was followed by determination of ultra-violet absorption spectra. When the resin from (I) was strongly heated, (II) was found in the sublimate. When the resin itself was dissolved in cyclohexane, ultra-violet absorption indicated the presence of (II). A. J. M.

Physico-chemical properties of chromophoric groups. Complete analysis of absorption spectra. III. E. Hertel (Z. Elektrochem., 1941, 47, 28—34).—The question whether chromophoric properties are associated with single atoms of a group, or with the whole group, is discussed. In some cases the effect of a group cannot be analysed to that of the component atoms. The connexion between the position of the long- λ absorption range and the polarity of the chromophoric group is considered. No simple relationship connects polarity and absorption. In the case of cinnamylidene derivatives, the absorption is largely independent of substituents, although these alter considerably the distribution of charges within the mol., but this is not always the case. The transition of an atom into the ionic state alters the properties of chromophoric groups only in degree (i.e., it causes displacement or intensification). Phenolic O, N in NHPh₂ derivatives, and C in CHPh₃ derivatives are not chromophoric.

A. J. M.

Assignment of absorption bands in conjugated systems of chromophores. G. Kortüm (Z. Elektrochem., 1941, 47, 55—59).—Two classes of absorption bands may be distinguished, those due to individual double bonds ("localised"), which are comparatively weak, and the more intense, fundamental bands, due to conjugation of localised double bonds, which cannot be ascribed to any particular double bond. Although conjugation may exist, the absorption due to individual chromophores may often still be recognised. This is due to the fact that certain electromeric limiting structures participate largely or exclusively in the stationary states of the mol. Localised bands disappear when such participation does not occur. The systematic change in the absorption of the anion of nitronic acids by the introduction of various groups is explained on this view.

A. J. M.

Conjugation of chromophores and constitution of organic compounds. M. Pestemer (Z. Elektrochem., 1941, 47, 20—28).—The possibility of using ultra-violet absorption spectra to determine the constitution of org. mols. is discussed. Groups of conjugated chromophores can readily be recognised in a mol. when limited by CH₂ groups. The position of chromophores with respect to each other, and of substituents, gives rise to characteristic differences in the ultra-violet absorption spectrum. Examples drawn from cistrans isomerism, tautomerism, chain-conjugation of chromophores, the nature of condensed rings in hydrogenated and dehydrogenated isocyclic hydrocarbons, and the detection of definite NH₂-acids in proteins are given.

A. J. M.

Effect of acidifying substituents on chromophoric systems. B. Eistert (Z. Elektrochem., 1941, 47, 35—40).—The effect of groups such as NO₂, SO₂R, COR, and CN, when substituted in CH₄ and more complex compounds, on chromophoric groups is reviewed, the acidic properties of the resultant mol. and the possibility of mesomerism being particularly considered. There is no simple relationship between the position of the absorption bands of the anion and the acid-producing effect of the substituent. The SO₂R group affects absorption by its inductive effect, whilst the other groups exert also a secondary electromeric effect on the stability and structure of the anion. Thus, CHPh(C₆H₄·NO₂·p)₂ (I) (colourless gives intensely violet-coloured salts with NaOH, but colourless CHPh(C₆H₄·SO₂Me-p)₂ remains colourless in NaOH. In the latter, the inductive effect of the SO₂Me on the methane-C is small, as such effects are short-ranged. Mesomerism is thus very small, whereas in (I) mesomerism can occur, and (I) is coloured. The introduction of acidifying groups into cation-halochromic systems is also considered. Here the effect is essentially inductive, and COR and SO₂R produce similar effects.

A. J. M.

Acidity constants, resonance energies, and light absorption of simple dyes. G. Schwarzenbach (Z. Elektrochem., 1941, 47, 40—52).—It is possible to study the colour changes of substances with pH from -10 to +17 by using solvents other than $\rm H_2O$. In passing through this range of pH, there is usually a periodic change of colour. In the case of dyes with two auxochromic groups, a bathochromic change of colour always follows a hypsochromic one, and vice versa. The larger is the no. of auxochromic groups, the more complicated is the periodicity. A new theory of colour in org. compounds covers these and other properties of dyes. The position of the long- λ absorption band is decided by the symmetry of the coloured particle, which affects the resonance energies of the various limiting structures. It is also affected by the length of the resonance chain between the auxochromic groups, and by sp. effects due to the constitution and nature of these groups. The resonance energies of the majority of coloured particles can be estimated from acidity consts.

Light absorption and energy propagation by loose complexes in organic dyes. G. Scheibe (Z. Elektrochem., 1941, 47, 73—80).— Previous work on ψ -isocyanine diethochloride (I) in aq. solution is reviewed (cf. A., 1937, I, 165, 494; 1938, I, 117, 434; 1939, I, 452). As concn. is increased, a new absorption band appears at a definite concn. It is very narrow, and of longer λ than the bands normally given by (I), and is accompanied by resonance fluorescence. When diluted or warmed the solution loses this absorption. Similar phenomena are shown by mixtures of these dyes with others. The new narrow band appearing in this case is not characteristic of either component but is intermediate in λ , and must indicate the formation of a new absorption complex. Several series of compounds related to (I) have been prepared, and their absorptions determined. Replacement of Me by Et on the N of simple ψ -isocyanines produces very little shift of the principal absorption band, but with the 3-Me derivative of (I), replacement of NMe by NEt in the substituted quinoline ring causes considerable displacement towards the red. A similar replacement in the unsubstituted quinoline ring, however, has very little effect. This is due to steric hindrance. These and effects of a similar kind observed with related dyes are considered in connexion with the polarisation of light reflected from and absorbed by the mols.

Polarisation of adsorbed substances. IV. Colour change and catalytic effect as a consequence of polarisation due to absorption of surface-active substances. E. Weitz [with F. Schmidt and J. Singer] (Z. Elektrochem., 1941, 47, 65—73).—Largely a summary, with experimental data, of work previously described (cf. A., 1940, I, 109, 158, 319), showing that polarisation of a colourless mol. at the surface of a solid adsorbent may cause it to become coloured. When the adsorbate is eluted, the colour disappears. Certain coloured compounds, which are feebly ionised, become colourless when adsorbed. Many examples are given.

A. J. M.

Fluorescence and phosphorescence of crystal phosphors. A. Schleede (Angew. Chem., 1940, 53, 378—383).—A review dealing with the structure of crystal phosphors and the mechanism of phosphorescence, with special reference to ZnS phosphors.

Chemical and physical properties of luminescent materials. J. W. Strange (*Proc. Physical Soc.*, 1943, **55**, 364—371).—A lecture survey of development, application, and theory. N. M. B.

Light emission of solid insulators. F. Möglich (Angew. Chem., 1940, 53, 405—409).—A theoretical explanation, based on the quantum theory, of the emission of light from hot insulating material, e.g., quartz or thoria, is offered.

A. R. P.

Infra-red and Raman spectra of polyatomic molecules. XVIII. Trideuteronitromethane. XX. cycloButane. T. P. Wilson (J. Chem. Physics, 1943, 11, 361—368, 369—378).—XVIII. The infra-red (3—25 μ .) and Raman spectra of CD₃·NO₂ have been investigated; combined with the data of Wells and Wilson (A., 1941, I, 241) on MeNO₂, they lead to the assignment of all the fundamental $\nu\nu$, except the C–N bond torsion. A potential function has been derived by a normal co-ordinate treatment.

XX. Raman and infra-red $(2-25\,\mu)$ spectra of cyclobutane have been determined, and a tentative assignment of fundamental $\nu\nu$ has been made. Δ^a -Butene has been recognised as a product of liquid-phase photolysis of cyclopentanone. W. R. A.

Detection of carbonyl groups in aldols by means of Raman spectra.
—See A., 1943, II, 319.

Structure of the Rayleigh line and the viscosity of liquids. E. Gross and A. Siromiatnikov (Compt. rend. Acad. Sci. U.R.S.S., 1941, 31, 219—221).—Measurements of the spectra of scattering of pcresol (I) and of PhOH at room temp. and at 140° for (I) and 74° for PhOH confirm the view, derived from theoretical considerations, that in viscous liquids the intensity of the depolarised undisplaced component of the Rayleigh line is connected with the depolarised background observed near the components of the triplet. On heating (I) or PhOH η decreases markedly; the undisplaced line decreases in intensity, and a strong depolarised continuous background appears in its neighbourhood.

L. S. T.

Photo-conductivity of lead chromate. J. E. Goldman and A. W. Lawson (Physical Rev., 1943, [ii], 64, 11—18).—The conductivity referred to unit intensity of the incident radiation is a max. in the blue, corresponding with a val. of 5×10^{-3} amp. per w. at saturation. There are subsidiary max. in the red and near ultra-violet. Results conflict with those of previous investigations. Data on the spectral scattering of PbCrO₄ are presented. The dependence of photo-conductivity on time, electric field, and previous history of the specimen is illustrated. On the basis of unit quantum efficiency, the mean displacement distance of photo-electrons in PbCrO₄ is 3×10^{-3} cm. Various explanations of the observed behaviour are discussed.

Electrical properties of polyvinyl acetate. T. W. Dakin (Trans. Electrochem. Soc., 1943, 83, Preprint 27, 309—317).— ϵ and loss factors were determined for five samples of polyvinyl acetate of

different mol. wt. and at different frequencies. In general, the loss factor–frequency curves were displaced uniformly to higher frequencies with decreasing mol. wt., apart from one exception. The material probably has at least three regions of ϵ dispersion in the frequency spectrum: the largest occurs at low frequencies and will occur in the audio-frequency range when the polymer starts to soften; the second is at room temp. at a few megacycles frequency; and the third, which has not been detected, is anticipated at an extremely high frequency at 25° . The observations are discussed in relation to mol. structure and thermodynamic considerations.

Effect of pressure on the dielectric constants of liquids. B. B. Owen and S. R. Brinkley, jun. (Physical Rev., 1943, [ii], 64, 32—36).—An empirical equation containing two parameters A and B expresses the isothermal variation of ϵ of liquids with pressure. Comparisons with experimental data are tabulated for 21 liquids. The equation is analogous to the Tait equation for the variation of liquid d with pressure; B is common to both and can be obtained from ϵ or d. Elimination of B between the two equations gives a linear relationship between the reciprocals of ϵ and d, and this relationship can be derived from Tammann's hypothesis and electrostatic theory.

Theory of insulators. P. Boning (Kolloid-Z., 1940, 92, 136—141).—A theory of insulators, based on the assumption that all insulators are solid dispersions, is proposed. In liquid dispersions, the particles are charged, and are surrounded with ions of opposite charge. If H₂O is removed from such a disperse system, the colloidal particles retain their charges, and the ions remain in the pores of the material as adsorbed ions. Over these is a layer of less firmly held ions, with an equal and opposite charge. The fact that such a system of charges exists, e.g., in clay particles, is shown by electroendosmosis. All substances which can be used as diaphragms in electro-endosmosis are colloidal, and usually contain, in addition to the adsorbed ions and the ions of opposite charge, a certain no. of ordinary dissociated ions. If such a substance is subjected to an electric field, a current flows through the pores and channels, being carried by the dissociated ions. When the field strength reaches a certain min. val. the upper ions move; the adsorbed ions are thus freed and, at a certain field strength, begin to move. This theory accounts for the potential distribution and space charge in dielectrics, clapacity changes, and dielectric loss, better than the absorption or dipole theories.

Dielectric behaviour of nitrogenous heterocyclic compounds in aqueous solution. W. Hückel and W. Jahnentz (Ber., 1941, 74, [B], 652—656).—Dielectric consts. (ϵ) of aq. solutions of glyoxaline (II), 4-methylglyoxaline (II), pyridazone (III), pyrazole, and 1:2:4-triazole have been measured, also their dipole moments (μ) in C_6H_6 and/or dioxan solution. The dielectric increment ($d\epsilon$: $d\epsilon$) is zero for (I) and negative for all the other substances examined. Considerations advanced by Devoto (A., 1932, 794) are applied to the calculation of μ , and the calc. vals. agree with those observed only for the compounds (I), (II), and (III), which are believed on independent evidence to form zwitterions; the failure of these substances to increase the ϵ of H_2O is attributed to the proximity of their ionising groups. Data are recorded for the mol. refraction and μ of (III).

Magneto-optical rotation of hydrogen peroxide. P. A. Giguère and H. Feeny (Canad. J. Res., 1943, 21, A, 69—73).—The Verdet consts. for H_2O_2 at 10° , obtained by extrapolation of data for the magnetic rotatory power of aq. solutions of H_2O_2 , are 0-01148, 0-01190, 0-01352, and 0-02265 min. per gauss-cm. at $\lambda\lambda$ 5893, 5780, 5461, and 4359 A., respectively.

Kerr electro-optical effect in solutions of p-azoxyanisole. N. Tolstoi and V. Tzvetkov (Compt. rend. Acad. Sci. U.R.S.S., 1941, 31, 230—232).—Average vals. of the Kerr consts. are $(0.83\pm0.05)\times10^{-32}$ for p-azoxyanisole (I) in C_6H_6 , and $(0.31\pm0.11)\times10^{-32}$ in CCl₄. The corresponding angles (calc.) between the dipole and the axis of the mol. are 47° and 55°, showing that (I) contains p-OMe· C_6H_4 ·NO:N· C_6H_4 ·OMe-p. L. S. T.

Internal rotation in gaseous molecules. I. A. Maccoll ($J.\ Proc.\ Austral.\ Chem.\ Inst.,\ 1943,\ 10,\ 91-99).$ —Free rotation about the C-C linking in mols. of the C_2H_6 type is discussed, reference being made to appropriate potential functions. Dipole moment and electron diffraction measurements on $(CH_2Cl)_2$ support the view that rotation about the C-C linking is restricted, being of a vibrational type at lower temp. and becoming free only at high temp.

Internal rotation in gaseous molecules. II. A. Maccoll (J. Proc. Austral. Chem. Inst., 1943, 10, 161—168; cf. preceding abstract).—Comparison of observed and calc. thermodynamic quantities and of Raman and infra-red spectra indicates restricted rotation around the C-C single linking. Theoretical attempts to account for the restricting potentials are examined, and the isolation of rotational isomerides is discussed.

N. M. B.

Chemical linking. H. G. Grimm (Angew. Chem., 1940, 53, 288—292).—A review of the nature of the four types of chemical linking, and of methods of detecting them. The connexion between the type of linking and the structure of the atoms concerned is discussed. There is a periodicity in regard to the nature of the linking corresponding to position in the periodic table.

Structure of boron hydrides. II. M. E. Diatkina and J. K. Sirkin (J. Phys. Chem. Russ., 1943, 17, 20—23).—It is suggested that in B_2H_6 two BH_2 groups are in one plane and the remaining two H are on a perpendicular axis. The electron diffraction results (cf. Russer, A. 1927, L. 207) against this between the contractions and the contraction of the (cf. Bauer, A., 1937, I, 397) agree with this structure.

Statistical length of paraffin molecules. L. R. G. Treloar (Proc. Physical Soc., 1943, 55, 345—361).—Methods are outlined for representing the distribution of lengths of a thermally fluctuating paraffin mol. over the whole range of any chain length. Results for paraffin chains of 3, 4, 5, 10, 20, 40, and 80 links are given. For the higher members of the series results diverge rapidly from the Kuhn formula as the length approaches that of the extended chain; this is important in the development of the kinetic theory of elasticity

Measurement of the temperature coefficient of the surface tension of mercury. A. M. Didenko and N. L. Pokrovski (Compt. rend. Acad. Sci. U.R.S.S., 1941, 31, 233—236).—Apparatus for measuring γ of Hg by Kantor's method is described. Measurements of γ at 0—300° are recorded graphically. $\gamma = 459\cdot10 - 0\cdot20\theta$ dynes per

Parachors of thymol, menthol, and p-toluidine in different solutions. S. S. Deshapande, S. N. Kaweeshwa, and W. V. Bhagwat (J. Indian Chem. Soc., 1942, 19, 149—152).—The parachors of thymol in PhNO₂ and in AcOH, of menthol in PhNO₂ and in CCl₄, and of ptoluidine in PhNO₂ have been determined at different concns. and temp. Vals. calc. from Hammick and Andrew's equation deviate from the theoretical at low concns., but are not appreciably affected by temp. (whether > or < the m.p.) or by the nature of the solvent.

Parachor of some organic compounds and their chemical constitution. S.S. Deshapande, S. N. Kaweeshwar, and W. V. Bhagwat (J. Indian Chem. Soc., 1942, 19, 153—158).—Parachor determinations in EtOAc and PhNO₂ show that pyrone and diethylpyrone have the simple ring structure (II), but favour structure (II)

for dimethylpyrone and (III) for diacetylacetone. Dehydracetic acid has the simple ring structure. Diacetylacetone probably has the bridged ring structure. The method of calculation for the bridged ring system is confirmed by determinations on oximinocamphor.

III.—CRYSTAL STRUCTURE.

New aspects of X-ray analysis. I. Index of X-ray diffraction ata. II. Non-Laue diffuse reflexions in X-ray diffraction patterns. data. II. Non-Laue diffuse reflexions in X-ray diffraction patterns. III. Examination of fine structural characteristics by X-ray powder methods. IV. Absolute accuracy of X-ray wave-lengths. H. P. Rooksby (Elect. Times, 1943, 104, 212—214, 242—244, 270—274, C. P. P. 300-302).

Graphical evaluation of Debye-Scherrer photographs. F. Feher (Z. Elektrochem., 1941, 47, 369-374).—A graphical method which permits the rapid determination of the lattice consts. from the observed positions of interference rings on Debye-Scherrer records. together with a knowledge of the mol. wt. and d of the material investigated, is described and illustrated.

MX₂ layer lattices with close-packed X atoms. G. Hagg (Arkiv Kemi, Min., Geol., 1943, 16, B, No. 3, 6 pp.).—Notations by which layer lattices of different types may be represented are described. Possible types of ordered and random layer lattices for compounds Possible types of ordered and random layer lattice factors govern-of the MX₂ type are discussed, with reference to lattice factors govern-disorder transformation.

A. J. E. W.

Crystal structures of cadmium bromide and cadmium iodide. G. Hägg, R. Kiessling, and E. Lindén (Arkiv Kemi, Min., Geol., 1943, 16, B. No. 4, 9 pp.).—CdBr₂ cryst. from a melt, or obtained by dehydration of CdBr₃,4H₂O at 200°, has the Cl9 structure. Dehydration at room temp., grinding of the Cl9 structure, or crystallisation from EtOH, MeOH, or COMe₂ leads to a random layer lattice. Transformation of this lattice into the Cl9 structure occurs only at temp. $(e.g., 300^\circ)$ at which recrystallisation occurs. CdI₂ cryst. from a melt or slowly from H₂O has a C27 structure. Crystallisation from liquid SO₂, condensation from the vapour, or grinding produces

a random layer lattice. MeOH solutions deposit a random layer lattice tending towards the C6 structure; specimens from H_2O (cryst. rapidly), EtOH, or COMe₂ are similar, but often contain some of the C27 form. The form deposited depends on the rate of crystallisation (k), the random layer lattice and the C6 and C27 structures, respectively, being obtained as k decreases; the three forms have identical sp. vol. Transformation of the random lattice into the other structures occurs only at $>300^\circ$, at which temp. recrystallisation is also observed.

A. J. E. W. A. J. E. W. recrystallisation is also observed.

X-Ray studies on the system cadmium bromide—cadmium iodide. G. Hagg and E. Einden (Arkiv~Kemi,~Min.,~Geol.,~1943,~16,~B,~No. 5,~10~pp.).—The CdBr $_2$ phase (C19 structure) can dissolve 43 mol.-% CdI $_2$, and the CdI $_2$ phase (C27) 44 mol.-% CdBr $_2$; CdBrI occurs as an intermediate phase. All cryst. phases give a random layer structure when ground. CdBrI forms a layer lattice in which the halogen atoms are close-packed, 12 layers being arranged in the order ABCBCABABCAC (cchh); Cd atoms are inserted between every second halogen layer. CdBrI has a rhombohedral translation group, with a unit cell (2 mols.) having r 13·46 A., a 17° 56′; Laue symmetry, D_{3d} —3m; space-group C_{3v}^{5} —R3m (Br and I in separate layers) or D_{3d}^{5} —R3m (Br and I distributed at random). At. parameters for both possible space-groups are given. A. J. E. W.

Structure of liquid carbon tetrachloride. E. E. Bray and N. S. Gingrich (J. Chem. Physics, 1943, 11, 351-354).—Radial electron density distribution curves have been calc. from the X-ray diffraction patterns of liquid CCl_4 at 25° and -20° . Discrete peaks correspond with interat. distances of 1.7 and 2.9 A. at -20° , and 1.74 and 2.92 A. at 25° . Non-discrete peaks (3.6, 4.1, 6.4 A. at -20° ; 4.0, 6.3 A. at 25°) due to atoms in different mols. have been obtained.

Morphology of finest sublimed lead oxide [minium]. I. R. Meldau and M. Teichmüller (Z. Elektrochem., 1941, 47, 95—97).—Pb₃O₄, prepared by vaporising Pb in an electric arc in the presence of definite quantities of O₂, was rapidly cooled, and the sublimate examined by the electron microscope. The particles are mostly rounded, but some appear with an octagonal outline, which represents a prism with terminal pyramids. X-Ray analysis showed definite interference rings. It is concluded that the crystals belong to the tetragonal system.

X-Ray study of chrysotile asbestos.—See A., 1943, I, 268.

X-Ray diffraction investigation of sodium stearate from room temperature to the m.p. A. de Bretteville, jun., and J. W. McBain (J. Chem. Physics, 1943, 11, 426—429).—Diffraction of Cu K_a radiation by the γ -form of Na stearate at seven temp. (25—301°) shows const. long spacing (44·3—44·7 a.) up to 132°, the subwaxy-waxy transition point, followed by a decrease with increasing temp. to 31·9 a. at 301°. The two most intense short spacings increase in learnth from 4.68 and 4.05 at 4.25° when the way the subsequence in the state of the subsequence in the subsequence of the subsequence in the subsequence of the su length from 4.68 and 4.05 A. at 25° up to the waxy cryst.-superwaxy transition point at 167°, and then coalesce to a single spacing up to the liquid cryst.-liquid m.p. at 288°. A monoclinic space-lattice, with hexagonal close packing of the chains above 167°, is

Fine structure of the cellulose fibre. K. H. Meyer and A. J. A. van der Wyk (Z. Elektrochem., 1941, 47, 353—360).—A review of experimental investigations indicates that the principal valency chains in dry cellulose fibre lie closely packed and parallel to the axis of the fibre, the planes of the glucose rings being oriented in a definite manner with respect to the cell wall. The presence of cavities interrupting the packing accounts for the fibrillar structure.

Structure of molecular compounds. II. H. M. Powell and G. Huse (J.C.S., 1943, 435—437; cf. A., 1943, I, 177).—M.p. and intensities of reflexion of X-rays, including diffuse spectra, of crystals of the mol. compounds of C₆Me₆ with picryl halides have been determined, and year to choose that the them. been determined, and used to show that the crystals consist of weakly-bound alternate layers of the two components. The weakly-bound alternate layers of the choosing existence of ions in crystals of mol. compounds is unlikely.

W. R. A.

IV.—PHYSICAL PROPERTIES OF SUBSTANCES.

Physical data of p-alkyltoluenes. A. W. Schmidt and V. Schoeller (Ber., 1941, 74, [B], 258—264).—p-C₆H₄Me·C_nH_{2n+1}, where $n=1-8, 10, 12, \text{ and } 14, \text{ were prepared by reducing } (N₂H₄ + NaOEt) the ketones obtained from PhMe and the appropriate acyl chlorides in the Friedel-Crafts reaction. Mol. wt., b.p., m.p., <math>d_4^{20}$, and n_D^{20} data produced and network given.

Dimensions of physical magnitudes. III. Electric and magnetic magnitudes. H. Dingle (Phil. Mag., 1943, [vii], 34, 588—599).—An extension and amplification of previous work (ibid., 1942, 33, 321). The definition of the magnitude of an electrical or magnetic quantity (e.g., e.m.f.) consists of a statement of a process of measurement involving ultimately only mechanical quantities. The quantity thus defined is therefore expressible dimensionally in terms

of [M], [L], and [T]; the dimensional equation is regarded as an indication not of the physical nature of the quantity, but of the defining process adopted. Experimental relations between the various quantities necessitate the introduction of two "dimensional consts.," which replace, but are not identical with, μ and κ of the usual scheme. H. I. W.

Electrical conduction of textiles.—See A., 1943, I, 258.

Variation of superconductivity of tin under non-uniform tension. B. G. Lazarev and A. A. Galkin (Compt. rend. Acad. Sci. U.R.S.S., 1942, 37, 91—92).—Sn wires (diameter $\sim\!0.06$ mm.) cooled under tension (in liquid He?) show increases in crit. superconductivity temp. from 3.715° to $\sim\!9^{\circ}$, in $H_c^{2\circ}$ from $\sim\!2.10$ to $\sim\!2.5\times10^4$ gauss, in dHc/dT from $\sim\!130$ to $\sim\!2000$, and in $R_{4\cdot2^{\circ}}/R_{290^{\circ}}$ from 1.5×10^{-3} to $\sim\!0.3$, and a decrease in $I_c^{2\circ}$ from $\sim\!3$ to 0.067. It is concluded that local strains as large as 10^5 kg. per sq. cm. exist, and that irregular deformation of the crystal lattice has occurred. M. H. M. A.

Magnetic susceptibilities of metals dissolved in liquid ammonia. S. Freed and N. Sugarman (J. Chem. Physics, 1943, 11, 354—360).— Magnetic susceptibilities of liquid NH $_3$ solutions of K, Cs, Ba, and Ca have been measured at 200° and 240° κ ., by a low-temp. modification of the Gouy method. The magnetic behaviour resembles that of a free-electron gas, overlaid by effects characteristic of the solution. A structure is proposed for the solutions, with reference to the electrons which conduct electricity. W. R. A.

Scientific significance of ferromagnetism. F. Bitter (J. Washington Acad. Sci., 1943, 33, 235—238).—A lecture. L. S. T.

Magnetic and other properties of crystalline horse-liver catalase and derivatives.—See A., 1943, III, 841.

Supersonic measurements in carbon dioxide and water vapour at 98°. W. H. Pielemeier and W. H. Byers (J. Acoust. Soc. Amer., 1943, 15, 17—21).—Previously reported results (cf. A., 1940, I, 104) suggest that there are two overlapping absorption regions for supersonic waves in $\mathrm{CO_2}$ — $\mathrm{H_2O}$ vapour mixtures at 28°. The present measurements of absorption in $\mathrm{CO_2}$ — $\mathrm{H_2O}$ and sound velocity in dry $\mathrm{CO_2}$, all at 98°, were made in the expectation, which was not fulfilled, that the resolution of the absorption max. would be improved. The results lead to a satisfactory calc. val. for the sp. heat of $\mathrm{CO_2}$. H. J. W.

Supersonic measurements in carbon dioxide at 0° to 100° . W. H. Pielemeier (J. Acoust. Soc. Amer., 1943, 15, 22—26).—Experimental data due to a no. of observers are discussed. Most probable velocity-temp. curves for dry CO_2 are plotted for long and short $\lambda\lambda$. The effect of adding H_2O vapour is examined. Evidence for the existence of two relaxation times (cf. preceding abstract) is reviewed.

Specific heats of carbon tetrafluoride from supersonic measurements. W. H. Byers (J. Chem. Physics, 1943, 11, 348—350).—Velocity and absorption of supersonic waves of 290.7 and 615.6 kilocycles in CF_4 have been measured at 0.3—3 atm. The sp. heat for equilibrium conditions (13.5 \pm 0.5 g.-cal. per g.-mol. at const. vol.), the sp. heat due to intramol. vibrations (7.5 \pm 0.7 g.-cal. per g.-mol.), and the mean life of a quantum of vibrational energy [(7.6 \pm 0.5) \times 10-7 sec.] have been calc. from the dispersion and absorption curves. W. R. A.

Vapour pressure of the sulphides of antimony, lead, cadmium, and zinc. B. K. Veselovski (J. Appl. Chem. Russ., 1942, 15, 422—436).— Knudsen's effusion method was used and checked on KCl between 886° and 971° k. Log p (in mm. Hg) of stable $\mathrm{Sb}_2\mathrm{S}_3$ at $665-809^\circ$ k. is $12\cdot546-11200/T$, of CdS at $828-1030^\circ$ k., $9\cdot823-11256/T$, and of ZnS (sphalerite) at $1038-1496^\circ$ k., $9\cdot495-14200/T$. Log p of PbS is $3\cdot242$ at 879° and $1\cdot586$ at 1069° k. The error is $\pm5\%$ except for ZnS, for which it is larger because of oxidation. Thermodynamic functions of the sulphides are calc.; it is necessary to assume that $\mathrm{Sb}_4\mathrm{S}_6$ is the correct formula of Sb sulphide. Freshly sublimed $\mathrm{Sb}_4\mathrm{S}_6$ has a higher v.p. than recryst. $\mathrm{Sb}_4\mathrm{S}_6$. J. J. B.

Thermal conductivity of non-metallic single crystals. W. J. Knapp J. Amer. Ceram. Soc., 1943, 26, 48—55).—Measurements of the thermal conductivity (C) of single crystals (1 cm.³) of quartz, corundum, sapphire, beryl, tourmaline, synthetic LiF, topaz, zircon, and periclase and samples of electrocast mullite and a Na₂O-CaO glass, Pyrex, and pure fused SiO_2 were made at 100— 500° . The C of crystals along the various crystallographic axes differed markedly, but the difference decreased at higher temp. Single crystals give a min. C with rising temp., which agrees with Compton's theory. C of glasses increases approx. linearly with temp. J. A. S.

Viscosity at the b.p.: the rheochor. J. N. Friend and W. D. Hargreaves (Phil. Mag., 1943, [vii], 34, 643—650),—The rheochor is defined as $R=(\eta^{1/8}\times \text{mol. wt.})/d$, η and d being measured at the b.p. For monomerics R is α mol. crit. vol. It is, with some reservations (notably for H), const. for a given atom or group, and is additive. Vals. of R are given for 12 simple org. liquids, for which η and d vals. are determined. H. J. W.

Structural mechanics of viscous-elastic systems. IV. Piezometry of viscosity. H. Umstätter (Kolloid-Z., 1940, 92, 169—179).—

An equation is deduced connecting η with pressure, and is tested with data obtained by Bridgman, with satisfactory agreement. For every liquid there is a characteristic internal pressure which decides the frictional strength of the liquid and is a definite multiple of the surface tension. This leads to the deduction of an equation of state for the liquid. The mol. wt. of a liquid can be calc. from the η -temp. and the η -pressure curves. A. J. M.

Viscosity of natural gases.—See B., 1943, I, 439.

Influence of ionic radius and cation valency on fluidity of silicate melts.—See B., 1943, I, 448.

Viscosimetric investigation of higher fatty acids and triglycerides. G. B. Ravitsch (Acta Physicochim. U.R.S.S., 1942, 17, 55—72).— η for the C_{18} -fatty acids (linolenic, linoleic, oleic, and stearic) is linear with I val. (I); an equation giving η as f(I,I) is obtained. $\eta = Ae^{B|R^T}$ holds for the above and for palmitic acid, triolein, tristearin, tripalmitin, and hydrogenated sunflower oil. The liquid structure of these compounds is discussed in relation to H bonding and mol. aggregation. The temp.-dependence of η for hydrogenated sunflower, mustard, cottonseed, linseed, dolphin, and seal oils is investigated. Hydrogenated cottonseed oil shows a decrease in η to a limit with increase in rate of flow. After irradiation with ultra-short waves η for castor oil increases, and shows a variation with time of flow and an increased temp.-dependence. J. H. Ba.

Self-diffusion of copper. C. L. Raynor, L. Thomassen, and L. J. Rouse (Trans. Amer. Soc. Met., 1942, 30, 313—325).—Radioactive Cu, prepared by bombardment with deuterons in a cyclotron, was dissolved, introduced into a cyanide plating bath, and deposited (mixed with ordinary Cu) to a thickness of 0·0015—0·003 in. on the surface of a Cu block. Intensity measurements were made of the β -rays emerging from the plated surface before and after heating for various periods at 650°, 750°, and 850°; coeffs. of self-diffusion of Cu at these temp. are calc. to be 3·20 \times 10⁻¹², 2·49 \times 10⁻¹¹, and 2·62 \times 10⁻¹⁰ cm.² per sec., respectively.

V.—SOLUTIONS, DISPERSIONS, AND MIXTURES.

Refractive indices of hydrogen peroxide and its aqueous solutions. P. A. Giguère (Canad. J. Res., 1943, 21, B, 156—162).—Vals. of n_0 , n_0 , n_1 , and n_0 at 16°, 20°, 24°, and 28° are tabulated and vals. of other physical consts. have been calc. from the data. C. R. H.

Supersaturation limits of solutions. I. R. Gopal (J. Indian Chem. Soc., 1943, 20, 183—188).—When saturated solutions of certain inorg. Na and K salts are cooled under controlled conditions the difference between the temp. of saturation (T_i) and the temp. of spontaneous crystallisation (T_i) is approx. const. for a given solute. For monobasic salts of Na and K the mol. heat of dissolution $\propto 1/(T_i-T)$. The val. of T_i-T for solutions of T_i and T_i and succinic acid increases as the solutes are successively redissolved and recryst. Certain salts show no spontaneous crystallisation. C. R. H.

Colloid osmotic pressure of mixtures of protein and thymus-nucleate.—See A., 1943, III, 914.

Diffusion [of ions] in glass.—See B., 1943, I, 448.

Magnetic evidence regarding the valency of colourant ions in glass. II. N. A. Yajnik, Ram Chand, and D. C. Jain (J. Indian Chem. Soc., 1943, 20, 169—170; cf. Bhatnagar et al., A., 1941, I, 8).— Magnetic susceptibility (χ) measurements and chemical analysis have been used to determine the valency of colourant Fe ions in reduced and oxidised glasses prepared from borax and NaNH₄HPO₄. Calculations of χ from analysis data and the Stoner-Van Vleck formula give good agreement with the experimental val. throughout. Agreement is best when the orbital moment l is regarded as quenched. Measurements of χ for Fe'' ions in oxidised borax glass furnish the vals. $\theta = 2\cdot 3$, $\mu_{\beta} = 5\cdot 74$. The latter is in fair agreement with the theoretical val. of $5\cdot 9$ (l quenched).

Effect of gelatin on the solubility of thallous salts at 40°. W. G. Eversole and F. S. Thomas (f. Physical Chem., 1943, 47, 421—424).—Data for the solubility (s) of TlCl, Tl_2SO_4 , and TlCNS at 40° in solutions of gelatin show that s increases with gelatin content (g) and that the increase in s for a given pH and g is greatest for TlCNS and least for Tl_2SO_4 . The electrical condition of the gelatin seems to be of secondary importance in determining s. C. R. H.

Distribution in systems with anomalous mixed crystals. I. Systems of the type $\mathrm{NH_4Cl}$ -FeCl₃ and $\mathrm{NH_4Cl}$ -MnCl₂-H₂O. II. Systems of the type inorganic salt-organic dye. III. Equilibrium between anomalous mixed crystals and solution. E. M. Joffe and B. A. Nikitin (Acta Physicochim. U.R.S.S., 1942, 17, 93—105, 106—115, 116—124).—I. The distribution coeff. D of FeCl₃ between saturated solution and solid $\mathrm{NH_4Cl}$ (found by crystallising $\mathrm{NH_4Cl}$ in the presence of FeCl₃) is const. up to concns. of FeCl₃ 0.055M., but below this D decreases, indicating a lower limit for mixed crystal formation. MnCl₂ is similar, with D > for FeCl₃ and const. up to

4 × 10-6 m. in MnCl₂. Experiments with radioactive Mn at lower concns. indicate a decrease in D. The results show a microdisperse

structure for these systems.

II. The distribution coeff. D of crystal-ponceau (I) between the saturated solution and solid, on crystallising K_2SO_4 , is const. for the same initial concn. of (I) (amount of K_2SO_4 pptd. being varied), but decreases with this initial concn. Methylene-blue (II) is similar with $Ba(NO_3)_2$ solutions (D vals. < those of Chlopin and Tolstaja, A., 1941, I, 462) but here the dye is adsorbed on the crystals. Both are collected microdiners of themselves. are colloidal microdisperse systems.

III. The equilibrium for the distribution between saturated soluand (II)—Ba(NO₃)₂ (A), and Ra(NO₃)₂—Ba(NO₃)₂ is approached slowly when the distributed component is stirred with the other component suspended in its saturated solution. (I) and Ra(NO₃)₂ distribute at equal rates in system (A), indicating that recrystallisation of Ba(NO₃)₂ is the governing factor and that anomalous mixed crystals can be in true equilibrium with the solution. (II) decreases the can be in true equilibrium with the solution. (II) decreases the rate of distribution of Ra(NO₃)₂ in system (A) by adsorption on the

Kinetics of sorption by grains. J. Zabeshinski (J. Phys. Chem. Russ., 1943, 17, 32—44).—A cylinder, or a layer of cylinders, of activated anthracite C is kept in streaming air containing EtOH, and the rate da/dt of wt. increase is determined; then pure air is and the rate a/at or wt. Increase is determined; then pure air is passed through, and the rate $-da_1/dt$ of desorption is measured. It is found that $da/dt = \beta(c_0 - c)$ and $-da_1/dt = \beta c_1$, c_0 being [EtOH] in air, c and c_1 the [EtOH] which would have been in equilibrium with the adsorbed amount a and a_1 , respectively. If the relation between a and c (i.e., the adsorption isotherm) is known, the sorption and desorption rates can be calc. The agreement with experiment is satisfactory, and the const. θ is identical for sorption and desorption. factory, and the const. β is identical for sorption and desorption. is also independent of [EtOH] between 3 and 9 mg. per l. $\beta \propto v^{0.4} d^{-2}$, vbeing the velocity of air (between 75 and 1300 c.c. per sq. cm. per min.) and d the diameter of the cylinder (0.14—0.2 cm.). Vals. of β for birch charcoal and for fruit-stone charcoal differ from that for anthracite C by only 30—40%. These results agree with the theory that β depends mainly on the external diffusion. Sorption isotherms are determined also for H_2O , MeOH, $Pr^{\beta}OH$, and $Pr^{\alpha}OH$. H₂O is the only substance the desorption of which is more rapid than the sorption.

(i) Absolute method for determination of the area of a fine crystalline powder. (ii) New adsorption isotherm valid over a very wide range of pressure. (iii) Adsorption method for the determination of the area of a solid without the assumption of a molecular area, and the area or a solid without the assumption of a molecular area, and the area occupied by nitrogen molecules on the surfaces of solids. W. D. Harkins and G. Jura (J. Chem. Physics, 1943, 11, 430, 430—431, 431—432).—(i) The powder particles are coated with a layer, several mols. thick, of a liquid having zero angle of contact with the solid, by condensation of saturated vapour on the outgassed powder. The wetted powder is immersed in the liquid and the surface coarse change massured calorimetrically. The surface surface energy change measured calorimetrically. The surface energy of the adsorbed liquid film is assumed equal to that of the

(ii) The adsorption isotherm $\log p/p_0 = B - A/v^2$ gives much better agreement than that (I) of Brunauer, Emmett, and Teller (A., 1938, I, 190) with experimental data for the vol. (v) of N_2 adsorbed on TiO₂ (anatase) powder up to ~600 mm. pressure (p). At higher A both isotherms give too high vals.

At higher p, both isotherms give too high vals.

(iii) Areas of surface calc. from the above equation agree with those calc. from (I) within $\pm 9\%$ for 56 non-porous and 4 porous solids. For 60 solids, vals. calc. for the area occupied by an adsorbed N_2 mol. lie between $13\cdot6-16\cdot9$ sq. A., with most frequent vals. $14\cdot0-14\cdot1$, $15\cdot2-15\cdot3$, and $16\cdot2-16\cdot3$. L. J. J.

Disperse structure of solid crystalline systems, and its thermodynamic basis. III. D. Balarev (Kolloid-Z., 1940, 92, 179—182).— CaF_2 , $CaCO_3$, and $BaCO_3$ were heated to various temp. and the adsorption of dyes (Congo-red, tropæolin OOO, and hæmatoxylin) on the powders was studied. The results indicate that the processes are reversible, in agreement with former work (cf. A., 1942, I, 391)

Definition of surface tension. G. Antonoff (J. Physical Chem. 1943, 47, 463-464).—Surface tension and interfacial tension should not be defined as force per unit length at right angles to the surface or as force per unit area tangential to the surface as is often done, but as force per unit length tangential to the surface or, alternatively,

Contact angles. E. J. Irons (Phil. Mag., 1943, [vii], 34, 614—624).—By a combination of the methods of Ferguson and Dowson and of Jäger for the measurement of surface tension it is possible to evaluate the (receding) contact angle θ of a liquid in a capillary tube. Results for H_2O , C_8H_6 , CCl_4 , $COMe_2$, NH_2Ph , and pinene in contact with Al, Fe, Ni, Cu, Ag, and Pt, and for these liquids and AcOH, cyclohexanone, Et₂O, and liquid paraffin in contact with glass, show that in every case $\cos \theta = 1$ to a few parts in $\frac{1}{1000}$ Relation between surface tension and vapour pressure of liquids and liquid mixtures. R. C. Tripathi (J. Indian Chem. Soc., 1943, 20, 197—199).—An equation on the type $\log p = A + B/(C - \gamma)$ satisfactorily represents the variation of v.p. (p) with surface tension (y). Vals. for the consts. A, B, and C are recorded for 18 inorg. and 34 org. liquids. The equation is applicable to liquid mixtures and vals. of A, B, and C for $\text{Et}_2\text{O-C}_6\text{H}_6$, $\text{CCl}_4\text{-C}_6\text{H}_6$, and $\text{AcOH-C}_6\text{H}_6$ mixtures have been calc. mixtures have been calc.

Surface activity of some sodium sulphonate solutions, and chemical constitution of the hydrocarbon radical. N. Turkiewicz (Kolloid-Z., 1940, 92, 208—217).—Naphthenesulphonates with a primarily bound sulphone group, unlike the alkanesulphonates of corresponding mol. wt., are readily sol., crystallise well, and show a distinct capillary activity. Sulphonates with a cyclopentane ring substituted with short aliphatic side-chains are particularly active. Derivatives of cyclopentane are more active than those of cyclohexane. Sulphonates with a cyclopentane ring have min. in the surface tensions of their aq. solutions. These min. are displaced towards smaller concns, with increasing mol. wt. Naphthenesulphonates prepared from naphthenic acids by replacement of CO₂H by CH₂·SO₃Na are considerably more active than the usual technical surface-active substances.

Condensation in the form of clouds and dew. J. W. Archbold (Phil. Mag., 1943, [vii], 34, 632—642).—Statistical mechanics are used for the determination of the size distribution of drops in clouds subject to gravity. In the absence of electrical charges the drops tend to be large, with a min. size agreeing with Kelvin's result for the stability of single drops. When there are charges, a cloud of small drops may also occur. The distribution law for dewdrops is of a similar type to that for drops in a cloud. H. J. W.

Dragging of a liquid by a moving plate. L. Landau and B. Levitsch (Acta Physicochim. U.R.S.S., 1942, 17, 42—54).—Expressions derived for the thickness (h) of the liquid layer carried along by a plate moving through the liquid take the forms: (1) $h = A(v\eta)^{2/5}/\gamma^{1/6}v(\rho g)^{1/2}$ for small vals. of v, the velocity of the plate, (2) $h = \sim Av\eta/\rho g$ for large vals. of v, and (3) $h = (v\eta/\rho g)^{1/2}f(v\eta/\gamma)$ for intermediate vals., the last function, and the numerical const. A, having to be determined by experiment having to be determined by experiment. η , γ , and ρ are the viscosity, surface tension, and density of the liquid. J. H. BA.

Film formation by pure liquids. C. W. Foulk and J. E. Barkley (Ind. Eng. Chem., 1943, 35, 1013—1016).—The ease of film formation with H₂O, Et₂O, COMe₂, and MeOH decreased to zero as the liquids were purified and, in the case of the org. liquids, traces of H₂O were removed. NH₂Ph did not form films even before purification, and repeated purification of n-C₇H₁₆ did not reduce film formation to

Determination of mol. wt. of organic substances by dialysis. H. Spandau and W. Gross (Ber., 1941, 74, [B], 362—373).—Membranes of "Cellophane 300" and of "Cuprophane 15," recommended by Brintzinger (A., 1931, 416) for determining mol. wts. by dialysis, are unsuitable since the val. of $\lambda \sqrt{M}$ (λ = dialysis coeff., M = mol. wt.), which should be const., decreases with increasing M. Satisfactory results are obtained with "Cella-filters 100 sec.," in which the average pore radius is 25 times that of the other membranes. Experiments with 8 org. non-electrolytes with M ranging from 46 to 584 indicate that "Cella-filters" give M with an accuracy of $\pm 3\%$, whilst the results with Cellophane and Cuprophane membranes are completely misleading. Measurements of the mol. wt. of digitalin and digitonin in aq. solution give vals. twice as great as these proposed in the literature. as those recorded in the literature.

Permeability of porous solids to gases and liquids.—See B., 1943,

Permeability through sugar-beet membranes.—See A., 1943, III, 838.

Electroviscous effect. B. N. Finkelstein and M. P. Tschursin (Acta Physicochim. U.R.S.S., 1942, 17, 1—13).—A formula is derived for the viscosity of colloidal solutions, taking into account the diffuse ionic atm., its deformation with flow, and the reverse action of the cataphoretic potential.

J. H. BA.

Streaming double refraction and double diffraction of herapathite suspensions. H. H. Pfeiffer (Kolloid-Z., 1940, 92, 182—188).—Flow experiments with herapathite suspensions, carried out with a Diesselhorst and Freundlich flow-chamber, indicate that double refraction increases with increasing flow-gradient, up to a saturation limit. This shows the suspension to have a high η . Streaming double refraction increases with concn. and depends on the previous history, age, coloration, and mechanical treatment of the suspension. During flow, the disc-shaped particles orient themselves parallel to the broad side of the chamber. This is also indicated by investigation of double diffraction. The degree of polarisation depends on the degree of aggregation of the particles, and on their symmetry, n, and absorption coeff., and on those of the medium. It also depends on the concn. and degree of hydration of the suspension, and on the λ of the transmitted light. A. J. M.

Dielectric measurements on pigment-linseed oil suspensions. Determination and computation of the dielectric constant of mixed systems. F. Wachholz and A. Franceson (Kolloid-Z., 1940, 92, 75—93, 234).—The "Dielkometer" high-frequency resonance capacitymeter is described. Measurements of ϵ are carried out on the pigment suspended in a liquid of lower ϵ and repeated with one of higher ϵ . Typical vals. are given for a no. of common pigments. The most suitable frequency is 2×10^6 cycles per sec. A specially designed cell is described. Linseed oil-pigment systems show deviations from a linear ϵ -composition relation which can be calc. in an analogous manner to the conductivity of disperse systems. Geometrical models are given which provide a basis for the calculations described. The course of the ϵ -conc. curve is strongly dependent on the shape of the particles, but not on their size. Unsymmetrical particles give an orientational effect in flowing systems.

Relations between electrical conductivity and degree of dispersion of lyophilic colloids. I. General. E. Angelescu. II. Conductivity of sodium and potassium palmitate and stearate solutions in presence of o-cresol. E. Angelescu and A. Woinarosky (Kolloid-Z., 1940, 92, 94—98, 99—105).—I. Factors affecting electrical conductivity (κ) in colloidal electrolyte solutions, e.g., soap solutions, are reviewed. Soap solutions with addition of varying proportions of cresols provide suitable systems for the study of the effect of

ionic dispersity and solvation on k.

II. The conclusions of the foregoing paper are tested by measurements of κ in Na and K stearate and palmitate solutions at concns. 0·1 and 0·2n, and temp. 20—60°, with and without addition of o-cresol. All four soaps show a max. val. of κ with increasing cresol concn.; the max. is the more pronounced the greater is the colloidal character of the soap, and its form is independent of concn. and temp. The effect of 'CH₂· chain length is > any effect of differing ionic mobility or dissociation const. The effect of change of cation is marked with stearates but inappreciable with palmitates. The effect of dilution is inappreciable except with Na stearate, for which Λ increases with dilution.

Effect of hydrogen-ion concentration on the time of setting of thorium phosphate gel-forming mixtures. (Miss) A. Nathan (f. Indian Chem. Soc., 1943, 20, 159—165).—The method of Hurd and Letteron (A., 1932, 464) has been employed to determine the time of setting, t, of Th phosphate gel-forming mixtures, prepared from $\text{Th}(\text{NO}_3)_4$ and varying quantities of H_3PO_4 and HCl, at 35° and pH vals. <1.7. Above this val. pptn. without gel-formation occurs. In all cases, for const. amounts of H_3PO_4 , the effect on t of decreasing the pH was to cause first an increase, then a decrease to a min., and finally a continuous increase. The pH at the min. was observed to decrease as the proportion of H_3PO_4 decreased. The concns. of the two acids at the min. exhibited a linear relationship. The pH-log t relationships were not linear as they are with silicic acid (cf. Hurd et al., A., 1934, 730). Increasing the pH with NaOH increased t until pptn. occurred. The presence of increasing amounts of EtOH, while not affecting the pH, increased t to a max. followed by a decrease. In no case was the pH observed to have changed after gelation.

L. H. L.

Time of setting and changes in hydrogen-ion concentration during the setting of gels formed by the interaction of oppositely charged sols. II. Interaction of nickel hydroxide and manganese dioxide sols with aluminium hydroxide sol. M. Prasad and S. D. Mehta (J. Indian Chem. Soc., 1943, 20, 166—168; cf. A., 1943, 1, 180).—The method of Hurd and Letteron (A., 1932, 464) has been employed to determine the time of setting, t, of the gels obtained by mixing positively charged $Al(OH)_3$ sol with negatively charged sols of $Ni(OH)_2$ and MnO_2 at 35° . The gels formed were transparent and thixotropic. For a const. vol. of $Ni(OH)_2$ or MnO_2 sol, $t = Rv^{-m}$, where v is the vol. of $Al(OH)_3$ sol and R and m are const. (cf. Prasad and Hattiangadi, A., 1929, 1235). Electrometric measurement showed that no appreciable change of pH occurred during gelation. L. H. L.

Ageing of alumina and silica gels and the precipitates obtained from mutual coagulation of alumina and silicic acid sols. S. P. Raychaudhuri and A. H. Miah (J. Indian Chem. Soc., 1943, 20, 195—196).—Freshly prepared gels of SiO₂, Al₂O₃, and alumino-silicates have a smaller buffer capacity than gels which have been aged for 1 year. The buffer capacity of aged gels increases as $\mathrm{SiO}_2/\mathrm{Al}_2\mathrm{O}_3$ increases, whereas the buffer capacity of fresh gels rises to a max. as $\mathrm{SiO}_2/\mathrm{Al}_2\mathrm{O}_3$ increases, max. capacity occurring when $\mathrm{SiO}_2/\mathrm{Al}_2\mathrm{O}_3=3$. C. R. H.

Reactions of solids. CXXII. Processes occurring in a kaolin on gradual heating in presence of air and other gases. G. F. Hüttig and E. Herrmann (Kolloid-Z., 1940, 92, 9—35).—Measurements of solubility in HCl and H₂SO₄, and of sorption of MeOH, HCl, SO₂, and dyes, are recorded for preps. of kaolin after treatment with air, H₂O vapour, O₂, N₂, NO₂, HCl, and SO₂ at varying pressures and temp. up to 700°. The order of decreasing catalytic activity for

dehydration of kaolin in the presence of gases is (NO₂, HCl), $4NO_2+O_2$, O₂, N₂ (inactive), H₂O (inhibitory). H₂O acts by displacing the equilibrium. L. J. J.

Constitution of dilute soap solutions. III. Theory of hydrolysis. P. Ekwall (Kolloid-Z., 1940, 92, 141—157; cf. A., 1937, I, 78; 1938, I, 618).—The activity of OH' of soap solutions is nearly const. at high concis,, and the degree of hydrolysis in a range almost coincident with that between the limiting and crit. concis. increases instead of decreasing. The products of hydrolysis are: below the limiting concn., the fatty acid; between the limiting and crit. concns., a cryst. acid soap with 1 mol. of soap to 1 mol. of fatty acid, and cryst. liquid acid soap with 2 mols. of soap, 1 mol. of fatty acid, and x mols. of H_2O ; and above the crit. concn., colloidal acid soaps. Above a concn. of $O\cdot In$, both the hydrolysis products and the soap are associated. The theory that the ions of the fatty acid associate in a step-wise manner, and are then hydrolysed, the hydrolysis occurring the more readily the higher is the degree of association, is examined in detail. Different hydrolysis products are formed at different stages of the association of the anions. The hydrolysis curve breaks up into several sections, each with its own equilibrium. Within each section, the course of the curve depends on the initial association, the hydrolysis const. and the depends on the initial association, the lightlysis collist and the solubility of the products. Narrow transition ranges separate the main sections. An attempt is made to obtain equations for the OH' activity and degree of hydrolysis in the different sections. Below the limiting concn. where the soap acts as a normal electromagnetic production of balanchesis degrees with increasing concn. lyte, the degree of hydrolysis decreases with increasing concn. in the usual way, until the solution is saturated with fatty acid, when it becomes const. At the limiting concn. double ions begin to form. After a narrow transition range, in which the fatty acid disappears, the second main section begins, in which the acid soap, NaL, HL (L = fatty acid radical), and its ions predominate. below the crit. concn. the association reaches a new stage, but the nature of the anions in this region is not definitely known. At higher temp. triple ions exist, whilst at lower temp. triple or quadruple ions are formed. Beyond the crit. concn. the degree of association increases rapidly. The course of the hydrolysis in this region is considered in detail.

Solid soap phases. R. H. Ferguson, F. B. Rosevear, and R. C. Stillman (Ind. Eng. Chem., 1943, 35, 1005—1012).—The application of X-ray diffraction methods to the identification and determination of the proportions of α , β , δ , and ω solid soap phases in Na soaps is described. The δ and ω phases have not hitherto been recognised, although the ω phase is possibly the same as the y structure of Na stearate mentioned by McBain and de Bretteville (cf. A., 1943, I, 147). Much of the evidence for the ω phase has been mistakenly attributed to β , but examination of the phase has established ω as a separate structure. Formation of the ω phase is favoured by high temp., low H_2O content, and low mol. wts., whereas the formation of δ phase is favoured by low temp., low soap content, and high mol. wts. The influence of the four phases on the properties of soaps is discussed.

Structure of rubber. R. Houwink (J. Physical Chem., 1943, 47, 436—442).—Modern ideas on the structure of raw and vulcanised rubber are discussed. The exponent n in Kuhn's equation ($\eta_{ap} = KcM^n$, where c = concn., $\eta_{ap} = \text{sp.}$ viscosity, M = real mol. wt. determined osmotically, K = const.) is a measure of the degree of compactness of the ''knäuels.'' The calc. val. of n for raw rubber is 1·6, indicating a very loose "knäuel." Diagrams illustrating the structure of raw and vulcanised rubber are presented. C. R. H.

Colloid-chemical and physical properties of starch solutions as guides to the study of its organic structure. M. Samec (Kolloid-Z., 1940, 92, 1—8).—The effect of P content on the viscosity of potato starch solutions is examined. Electrodialysis separates such solutions into sol and gel phases, the P content being conc. in the latter, which contains invariably $\sim 0.17\%$ P_2O_6 . The electrometric titration curve of the gel closely resembles that of H_3PO_4 . Natural phosphatases do not produce a similar separation. Acid and diastatic hydrolysis of the gel give fragments which on further electrodialytic separation give a higher P content in the gel phase. Phosphorylation of the P-free sol phase with POCl₃ gives a gel. Gels obtained from different forms of starch by electrodialysis differ widely in physical properties, but in a series of starches of different origin the P content, electrical conductivity, and [H⁺] show a parallel variation. P-rich starches (e.g., potato) show characteristic differences in X-ray spectrum from low-P starches (e.g., wheat).

Detection of acid groups in native cellulose by salt formation with crystal-violet base. M. Rebek (Kolloid-Z., 1940, 92, 217—221).— To detect CO_2H groups in native cellulose, the latter is allowed to react with a colourless pseudo-base, which will combine with acid groups to form a dye. Cotton-wool was treated with the colourless base of crystal-violet in Et_2O , H_2O , C_8H_6 , and light petroleum, and after removal of excess of dye from the thread, the N content of the fibre was determined. The amount of dye taken up in C_6H_6 , H_2O , and light petroleum was practically the same (indicating 0.04%

 ${\rm CO_2H}$), but a lower val. was obtained in ${\rm Et_2O}$, which is considered to be due to the inhibiting effect of ${\rm Et_2O}$ on the ionisation of the dyebase. The ${\rm CO_2H}$ vals. obtained are < those obtained by Schmidt by conductometric titration (0·282%) (A., 1935, 201), and this may be due to the fact that only strong ${\rm CO_2H}$ groups will react with crystal-violet base. A. J. M.

Degradation of cellulose fibres.—See B., 1943, II, 345.

Swelling of cellulose hydrates in the presence of protein substances. E. Elöd and G. Schmitt (Kolloid-Z., 1940, 92, 105—112).—The effect of addition of varying proportions of gelatin (I), casein (II), and hæmalbumin (III) to cellulose xanthate solutions on the swelling of viscose films made from them, in air at const. R.H., has been examined. With (I), swelling has a sharp min. val. at 10% (I), and rises with increasing concn. of (I) to a val. > that for cellulose. With (II), swelling is a min. with 50% (II). The effect of (III) is similar to that of (I) and (II). In all cases, films treated with CH₂O show decreasing swelling with increasing protein content. The tanning effect of CH₂O, Cr^{III}, Ce^{III}, and Zr^{IV} is a max. at pH 5, and gives greatly increased stability to H₂O at 100°. L. J. J.

Electrodialysis—electrophoresis apparatus for preparative colloid-chemical purposes. O. Dahl (Kolloid-Z., 1940, 92, 70—75).—A three-chamber apparatus consisting of anode- and cathode-cells and electrodialysis—electrophoresis vessel is described. It permits simultaneous electrodialytic purification and electrophoretic fractionation of colloidal systems. Fractionation results for separation of amylose and amylopectin from starch are given. L. J. J.

Coagulation of colloids by electrolytes. XV. Electrochemical and chemical investigations on monodisperse gold sols. V. N. Volkov and A. J. Rabinovitsch. XVI. Electrophoresis cell and measurements on monodisperse gold sols. A. J. Rabinovitsch and V. N. Volkov (Acta Physicochim. U.R.S.S., 1942, 17, 14—24, 25—41).—XV. Zsigmondy Au sols show a decrease in κ and an increase in pH on dialysis. Displacement of H' by added salts reaches a limiting val. (Al > Ba > K) and the amounts displaced are equiv. to the amounts of adsorbed cations. Titration of an undialysed sol with AgNO₃ and VOSO₄ indicates the presence of unreduced Au compounds (H₂AuCl₃O) adsorbed on the particles (not removed by ultrafiltration).

XVI. Improvements on the electrophoresis cell of Smith and Lisse (A., 1936, 697) are described and the theory is confirmed. Dialysed Au sols show a decrease in mobility and ζ on addition of KCl, Bacl2, and AlCl2, to a limit corresponding to max. H' displacement. The effect of HCl on ζ is > of KCl, while NaOH gives a ζ -concn. curve with a flat max. In general the decrease in ζ for non-dialysed sols is less but KCl, HCl, and NaOH all give ζ -concn. curves with small max. Changes in ζ are accounted for by variations in the electrolytic dissociation. The theory of Müller (cf. A., 1928, 1322) is applicable only when the H' displacement (KCl and dil. BaCl2 but not AlCl2) (cf. A., 1939, I, 610) is very small. Calculations of radii of particles on this theory agree with the counting method, but the calc. charge differs widely from the titration val. J. H. Ba.

Mechanism of the mutual coagulation process. III. H. B. Weiser and W. O. Milligan (J. Physical Chem., 1943, 47, 424—436).—On mixing two hydrophobic sols of opposite sign of charge, mutual adsorption of the oppositely charged particles takes place with lowering of the ζ -potential (or mobility) of the mixed particles, accompanied in most cases by displacement of the counter ions of the double layer surrounding the particles of the respective sols. Fe₂O₃ was used as positive sol, the stabilising ions being H' and Fe'' and the counter ion Cl', and Cu₂Fe(CN) ₈. SnO₂, As₂S₃, and Congored acid were used as negative sols. The behaviour of each sol pair is described.

Electrophoretic study of action of alkylbenzenesulphonate detergents on ovalbumin.—See A., 1943, III, 838.

VI.—KINETIC THEORY. THERMODYNAMICS.

Equilibrium in hydrogen-water systems containing tritium. J. F. Black and H. S. Taylor (J. Chem. Physics, 1943, 11, 395—402).— Equilibrium measurements over a Pt-charcoal catalyst at 289—576° K. give for the reaction HT + H₂O = H₂ + HTO: log $K=0.292\log T+336.5/T-1.055$, $\Delta F^{\circ}=4.83T-1.34T\log T-1540$, $\Delta H^{\circ}=0.58T-1540$, $\Delta S^{\circ}=1.34\log T-4.25$, $\Delta C_{p}^{\circ}=0.58\pm0.05$ g.-cal. per degree per mol., $\Delta H_{p}^{\circ}=-1540\pm160$ g.-cal., per mol., I=-1.055, in agreement with Libby's calculations (A., 1943, I, 175) and the assumption that force fields are unaffected by nuclear mass changes. L. J. J.

Magnetic study of colour changes in copper chloride. N. A. Yajnik, R. Chand, and D. C. Jain (J. Indian Chem. Soc., 1943, 20, 203—206).—The change of magnetic susceptibility with temp. and with changes in [Cl'] has been investigated for 5% solutions of CuCl₂, [Cl'] being varied by addition of HCl. At 35° the colour of the solution changes from blue to green as [HCl] is raised beyond 4N.

At higher temp, this colour change occurs at lower [HCl], thus showing that rise in temp, brings about the same change as increase in [Cl']. The data support the view that the colour change is due to complex ion formation.

Absorption spectrum of reversible polymers of quinoline dyes. H. Ecker (Kolloid-Z., 1940, 92, 35—70).—An apparatus for the measurement of absorption spectra of dye solutions in the range 4600—6800 A. with an accuracy within 2—3% is described. The spectral data recorded for aq. solutions of dyes consisting of two variously substituted mols. of quinoline or indole linked through one or more CH show a variation with temperature and concn., attributable to reversible polymerisation by a co-ordination mechanism. Polymerisation leads by way of double mols. to highly polymerised, fluorescent, thixotropic, viscous and elastic products, while a sharp narrow absorption band appears. H₂O and D₂O solutions show these effects, but not H₂S, NH₃, HCN, or EtOH as solvents. The heat of polymerisation is ~7 kg.-cal. per single mol. Strong mol. resonance effects are shown by the absorption band referred to.

Thermal analysis of binary systems. H. Rheinboldt (Ber., 1941, 74, [B], 756—758).—A claim for priority over Kofler and Wannenmacher (ibid., 1940, 73, 1388).

F. L. U.

System silver nitrate-water. A. N. Campbell and M. L. Boyd (Canad. J. Res., 1943, 21, B, 163—169).—The temp.-concn. diagram for the system from 0 to 100% of AgNO₃ and from -7° to 195°, which has been determined with a degree of accuracy > hitherto employed, confirms the eutectic at -7.57° and 46.9% of AgNO₃ and the break in the curve at $\sim 159^{\circ}$ corresponding with the rhombic \rightleftharpoons rhombohedral transformation of AgNO₃. C. R. H.

System n-hexane—methylcyclopentane—aniline. B. de B. Darwent and C. A. Winkler (J. Physical Chem., 1943, 47, 442—454).—The system has been investigated at 25.0°, $34\cdot5°$, and $45\cdot0°$, and the data are recorded in tabular and diagrammatic form. The methods which yielded straight consolute lines for the system $n\cdot C_7H_{16}$ -methylcyclohexane—NH $_2$ Ph have been applied to the present system with satisfactory results for mixtures which contain large amounts of $n\cdot C_6H_{14}$ and are far removed from the plait point. The val. of $\beta = y_nx_p/y_px_n$ (y_n and x_n are mol. fractions of naphthene in solvent and in $n\cdot C_6H_{14}$ respectively and y_p and x_p are the mol. fractions of $n\cdot C_6H_{14}$ in solvent and in $n\cdot C_6H_{14}$ layer respectively) is reasonably const., not only for tie lines at each temp. but also over the temp. range investigated. C. R. H.

Behaviour of hydroxyapatite in solutions. R. Klement and R. Weber (Ber., 1941, 74, [B], 374-386).— $3Ca_3(PO_4)_2$, $Ca(OH)_2$ (I) does not dissolve congruently in H_2O . At 25° the amounts of Ca and PO_4 in solution increase with the proportion of solid phase present, and the ratio $Ca:PO_4$ varies from 1:1 to $1:1\cdot26$. For a given solid: liquid ratio the total quantity dissolved decreases slightly with rise of temp., with a min. at 40° , at which temp. the ratio $Ca:PO_4$ is a min. $(1:1\cdot46)$. The solubility of (I) in aq. NH_2 -acids is > in H_2O , and is much greater in 1% aq. gelatin. When (I) is shaken with Tyrode's (Ringer) solution the amounts of Ca and PO_4 in solution decrease, the decrease being smaller in presence of 1% gelatin. Solutions of org. acids have a strong solvent action on (I), lactic acid being the most effective of those studied. Electrical conductivities and diffusion coeffs. are recorded for some of the solutions.

Thermochemical study of processes taking place during heating of kaolin. B. S. Schvetzov and C. O. Gevorkian (J. Appl. Chem. Russ., 1942, 15, 302—318).—Certain exothermic effects suggested by the heating curve of kaolin are, on the basis of a study of the X-ray spectra of the products, and of their heat of dissolution in HF, interpreted as being due to formation of metakaolin at <900°, to its decomp., with crystallisation of γ -Al₂O₃, at 900—1050°, and to formation of mullite at 1200—1300°. R. T.

Heat of formation of iron disulphide. S. V. Lipin, V. S. Uskov, and V. R. Klokman (J. Appl. Chem. Russ., 1942, 15, 411—421).—Pyrite and marcasite, both containing >1% of SiO_2 and other admixtures, gave in a calorimetric bomb the heats of combustion to $\mathrm{Fe}_3\mathrm{O}_4$ and SO_2 of 188.4 and 194.0 kg.-cal. per g.-mol., respectively. The error, mainly due to the chemical inhomogeneity of the material, was ± 1.5 kg.-cal. The difference between the heats of formation of pyrite and marcasite is, therefore, real.

Thermodynamics of humic acid reactions. The systems humic acid-calcium acetate-water, and methoxyhumic acid-calcium acetate-water. W. Fuchs (Fuel, 1943, 22, 112—116).—The equilibrium conditions of the above systems have been investigated. On the assumption of a homogeneous system the mass action law was applied and the thermodynamic equilibrium const., heat of reaction, and changes of free energy were computed. On the assumption of a heterogeneous system, the distribution law was applied, and distribution coeffs. and the thermal effects of phase distribution were computed. The results obtained by these two different methods of approach checked reasonably well.

H. C. M.

VII.—ELECTROCHEMISTRY.

Conductivity of adsorptive charcoal. G. M. Schwab and B. Karkalos (Z. Elektrochem., 1941, 47, 345—353).—The electrical conductivity of commercial forms of active charcoal is increased considerably during the adsorption of vapours, particularly Br. At const. C vol. the effect is independent of the rate of passage of Br vapour or its concn., and with rise of temp. decreases in proportion to the amount of Br adsorbed. With const. external pressure on the C the effect is independent of temp. and increases with increasing pressure. The changes observed are $> \alpha$ the vol. changes of the C particles, and are explained by assuming that on adsorption of Br the vol. of the C increases reversibly, whilst its modulus of elasticity decreases reversibly. J. W. S.

Contact potential difference between mercury and thallium amalgam. S. Karpatschev and A. Stromberg (J. Phys. Chem. Russ., 1943, 17, 1—3).—The characteristics of two two-electrode thermionic valves are compared, the anode of one being a thin stream of Hg, and of the other a similar stream of 12% Tl amalgam. The voltage difference between the characteristics is 0·35—0·42 v. This agrees with the difference between the potentials of the electrocapillary max. of Hg and of Tl amalgam (cf. A., 1941, I, 81).

J. J. B.

Passivity of platinum. B. V. Erschler (Compt. rend. Acad. Sci. U.R.S.S., 1942, 37, 226—229).—The velocity of dissolution of a Pt electrode in HCl depends on the potential of the electrode and [Cl'].

F. R. G.

Electrochemical mechanism of passivation of platinum. B. V. Erschler (Compt. rend. Acad. Sci. U.R.S.S., 1942, 37, 230—232).—Retardation of dissolution of Pt by O is attributed to a weakening of the field of the double layer owing to displacement of Cl by O. F. R. G.

E.m.f. measurements in liquid sulphur dioxide. K. Cruse (Z. Elektrochem., 1941, 47, 411—413; cf. A., 1943, I, 229).—Reasons for preferring Brönsted's definition of acids and bases to that of Wickert (A., 1937, I, 306; 1943, I, 258) are detailed. J. W. S.

Relation between the height of the polarographic wave of a cation and the concentration of the background. T. A. Kriukova (Zavod. Lab., 1940, 9, 699—702).—The height of the polarographic wave of, say, 0.0005m-Pb" in KCl solution depends on [KCl]. This is due to movements of solution near Hg drops as the rate v of the movement depends on the nature and concn. of the "background electrolyte." If this concn. is >1N., v is independent of the salts present in small concns. The current increase Δi due to v is $\propto vC$, C being the concn. of, say, Pb". If v for a given background electrolyte is known for all polarising voltages, C can be calc. by measuring the height of the Pb wave without and in presence of gelatin which reduces v to zero. The calculation gives correct results for Pb, Cd, Mn, Co, Fe, Cr, and Th in saturated KCl.

Hydrogen overpotential in alkaline electrolytes under reduced pressure. G. Schmid and E. K. Stoll (Z. Elektrochem., 1941, 47, 360—368).—The H-overpotential (η) at Cu, Ni, Pb, Ag, Fe, Zn, and Sn cathodes in 0·1n-NaOH has been measured at c.d. 10^{-2} — 10^{-4} amp. per sq. cm. and at H₂ pressure (p) 15—760 mm. For all metals η increases with decreasing p, the vals. for Cu, Ni, Pb, and Ag following the relation $\eta = \eta_0 - k \log p$. With the other metals no simple relationship has been derived. The cathode potential relative to a non-pressure-dependent auxiliary electrode is for Cu, Ni, Pb, and Ag independent of p and the variation of q is therefore due only or principally to the variation of the equilibrium potential of the auxiliary H₂ electrode. It is suggested that, since the electrode reaction is under these conditions almost unidirectional, it is to be expected that the kinetics of the reaction will be independent of the conen. of the products, i.e., the cathode potential is independent of p whereas the potential of the reference electrode varies with p in the usual way.

J. W. S.

Polarographic study of cis-trans isomerism of azo-compounds.—See A., 1943, II, 361.

VIII.—REACTIONS.

Temperature, pressure, and specific volume changes of a gas under dissociation and re-association conditions. W. J. Walker (Phil. Mag., 1943, [vii], 34, 486—488).—Mathematical. The temp. and pressure of explosion of a mixture of fuel and air have been computed, taking dissociation into account. The method applies to the re-association correction required for temp., pressure, and sp. vol. changes during the subsequent expansion. W. R. A.

Kinetics of the thermal decomposition of n-propyl and isopropyl formates. R. B. Anderson and H. H. Rowley (J. Physical Chem., 1943, 47, 454—463).—The initial reaction in the thermal decomposition of HCO_2Pr^a and $\text{HCO}_2\text{Pr}^\beta$ over the range 300—400° is decomposited to C_3H_6 and HCO_2H . HCO_2H then decomposes according to HCO_2H \rightarrow CO_2 + H_2 , HCO_2H \rightarrow CO_2 + H_2 , HCO_2H \rightarrow CO_2 + CO_2 +

formation can be represented by $k=2.94\times 10^9\times {\rm e}^{-39,660/R^T}$ for HCO₂Pr^a and $k=2.47\times 10^{12}\times {\rm e}^{-44,230/R^T}$ for HCO₂Pr^β. C. R. H.

Kinetics of the rearrangement of cis-trans-isomerides in the gaseous state under the influence of foreign gases. II. Dichloroethylene. B. Tamamushi, H. Akiyama, and K. Ishii (Z: Elektrochem., 1941, 47, 340—345; cf. A., 1939, I, 151).—The conversion of cis- into trans-(CH₂Cl)₂ in the gaseous state has been followed at 200° by measurements of dielectric const. At const. partial pressure of (CH₂Cl)₂ the addition of foreign gas increases the unimol. velocity coeff., the effects of O₂ and NO being particularly marked and attributed to sp. catalytic action, whilst the effects of C₂H₈, CO₂, and N₂ are relatively small. In the absence of foreign gas the unimol velocity coeff. k is dependent on the (CH₂Cl)₂ pressure at pressures <80 mm., but is independent of this at higher pressure. The position of equilibrium (~60% cis at 200°) is not appreciably affected by the addition of O₂, suggesting that its action is one of homogeneous catalysis. Comparative measurements of the rates of reaction at 200°, 225°, and 250° indicate that the heat of activation of the reaction is ~16,000 g.-cal. per g.-mol.

J. W. S.

Reaction between chlorohydrins and ammonia or amines.—See ${\rm A}$, 1943, II, 354.

Rates of dissociation of penta-arylethanes.—See A., 1943, II, 360.

Solid-phase inversions of calcium orthosilicate, constituent of dolomite-silica brick. S. Zerfoss and H. M. Davis $(J.\ Amer.\ Ceram.\ Soc.,\ 1943,\ 26,\ 302-307)$.—The solid solution of P_2O_5 in $2CaO_5iO_2$ (I) was studied by thermal and optical methods and the $a\to\beta$ inversion point was found to be lowered by P_2O_5 . The inhibition of the $\beta\to\gamma$ inversion of (I) by 1% of P_2O_5 , B_2O_3 , Cr_2O_3 , As_2O_3 , or V_2O_5 may be due to: (1) purely physical separation and restraint of the crystals by sufficient compatible cryst, or vitreous phase [this method is probably effective only in the case of bodies low in (I)1, or (2) the crystal-chemical effect of a solid solution of certain acid oxides in the β form, their insolubility in the γ -form lattice, and their sluggish pptn. from the β form. This type of inhibition involves the preservation of part of the Ca atoms in a low co-ordination (i.e., 4 instead of 8 O neighbours).

Kinetics of reduction of Cu" to Cu' by carbon monoxide in ammonia solution. E. I. Dontzova (J. Appl. Chem. Russ., 1942, 15, 447—452).—A solution of CuCl₂ in 5·85n-NH₃ was kept under CO, and the e.m.f. between a Pt electrode immersed in the solution and a Hg/Hg₂Cl₂ electrode measured every 20—120 min. The [Cu"] calc. from this e.m.f. increases at first very slowly, then at almost const. rate up to >95% of reduction. The first period is, e.g., 8 hr. at 24°, 5 hr. at 30°, 3 hr. at 41°, and 2 hr. at 49°, and the reduction is nearly complete within 24, 14, 9, and 8 hr., respectively. The autocatalytic progress of the reaction is attributed to formation of the CuCO' ion which is the real reducing agent.

J. J. B.

Olation of some chromium salts. A. Lottermoser, R. Schmied, and P. C. Chü (Kolloid-Z., 1940, 92, 129—136).—Solutions of $\mathrm{CrCl_3}$ to which had been added $\frac{1}{3}$ equiv. of NaOH were titrated conductometrically and potentiometrically with HCl back to the hexa-aquosalt. The conductivity of the final solution was the same as that of a solution of $[\mathrm{Cr}(\mathrm{OH_2})_6]\mathrm{Cl_3}$ to which an equiv. quantity of NaCl had been added. It follows that the monohydroxo-salt gives the hexa-aquo-salt with acids without any side-reaction. pH determinations lead to the same result. The velocity of olation is small at 0°; at 50° a const. rate of olation is reached after 168 hr. Investigations with Cr chloride, nitrate, and perchlorate in aq. solution show that the anion is without effect on the velocity of olation. Olated solutions were titrated at 0° with equiv. amounts of HCl. Conductivity and pH determinations show that the acid is not used up.

Influence of oxygen and sulphur atoms on the velocity of hydrolysis of the carbon-halogen bond. H. Böhme (Ber., 1941, 74, [B], 248—256).—Halogen atoms in compounds containing halogen and O or S linked to the same C atom are very reactive. Such substances often have pronounced physiological action, e.g., COCl₂, CSCl₂, (CH₂Cl)₂O, CiCO₂Et. Characteristic of all these substances is their hydrolysis by H₂O with formation of HHal. Qual. statements in literature appeared to indicate that O compounds were more stable than S compounds. The course of hydrolysis is studied for a no. of cases using 0·1M-dioxan solutions with varying amounts of H₂O and titrating the halogen acid with N(CH₂Ph)₃, using NMe₂·C₆H₄·N.NPh as indicator, a technique which is not interfered with by unchanged material. It is found that O compounds are much more easily hydrolysed than S compounds; e.g., half-time vals. are: 9 min. for CH₂Cl·OEt and 10 days for CH₂Cl·SEt; 5 hr. for (CH₂Cl)₂O and 19 days for (CH₂Cl)₂S with 200-fold excess of H₂O at 25°. COCl₂ is hydrolysed much more rapidly than CSCl₂. The reactions are first-order reactions but in the case of α-halogenated ether and thioether an induction period is observed and the accumulation of a definite amount of HHal is necessary before a normal first-order reaction rate is observed. Electronic mechanisms are discussed.

J. WA.

Zone behaviour of enzymes.—See A., 1943, III, 842.

Ether-like compounds. XXIV. Synthesis and reaction velocities of higher ether-acids.—See A., 1943, II, 351.

Physico-chemical investigations of solutions in liquefied gases. XXIX. Catalytic activity of nitro-indicators in liquid ammonia. Salt effect in the ammonolysis of pilocarpine. E. A. Izrailevitsch and A. I. Schattenschtein (*J. Phys. Chem. Russ.*, 1943, 17, 24—31).— The rate of ammonolysis of santonin in liquid NH₃ at 20—25° is almost unaffected by NEt₄Cl, o-NO₂·C₆H₄·NEt₂, p-NO₂·C₆H₄·NHMeAc, o-NO₂·C₆H₄·NHMe, m-NO₂·C₆H₄·NH₂, or 2:4:1-(NO₂)₂C₆H₃·NEt₂, and raised in the order o-NO₂·C₆H₄·NH₂ (I) < o-NO₂·C₆H₄·NHAc < 2:4:1-(NO₂)₂C₆H₃·NH₂ < phenolphthalein < CH₂Ac₂ < m-NO₂·C₆H₄·OH, 2:4:6:1-(NO₂)₃C₆H₂·NH₂ < p-NO₂·C₆H₄·OH (II); N-(I) raises the rate 4 times, and N-(II) 700 times. The catalytic activity increases with the acid strength of the catalyst. The rate of ammonolysis of pilocarpine in liquid NH₃ + Physico-chemical investigations of solutions in liquefied gases. catalyst. The rate of ammonolysis of pilocarpine in liquid $\mathrm{NH_3} + 0.09\mathrm{n-NH_4NO_3}$ at 20° is raised by $\mathrm{NaNO_3}$ (1.3 times) $< \mathrm{LiNO_3} < \mathrm{Ba(NO_3)_2} < \mathrm{Sr(NO_3)_2} < \mathrm{Ca(NO_3)_2}$ (13.5 times for a N. solution). The salt effect of cations is the stronger the more ''acid '' is the cation.

Preferential paths in contact catalysis. A. A. Balandin (Acta Physicochim. U.R.S.S., 1942, 17, 73—81).—Calculations of the probabilities of reactions on Ni catalysts based on the multiplet theory (cf. A., 1929, 519; 1941, I, 341) are revised, using new bond strength data. The results (in general unchanged by the new data) agree with experiment. Several new reactions are considered on this J. H. BA.

Contact decomposition of hydrocarbons. Conversion of n-butane under the action of carbon dioxide over nickel-alumina catalysts. A. A. Balandin, M. N. Maruschkin, and M. M. Afanasiev (Acta Physicochim. U.R.S.S., 1942, 17, 82—92).—With rise in temp. (θ) from 400° to 600°, [CO] and [H₂] of the product from C₄H₁₀ and CO₂ over a Ni-Al₂O₃ catalyst increase, and the vol. increases tenfold. The hydrocarbon content is all CH₄ at 600° (amount decreasing with θ). For low initial CO₂ content CH₄ is > original C.H₄. with θ). For low initial CO₂ content, CH₄ is > original C₄H₁₀, indicating decomp. of C₄H₁₀, and decrease in the C and H content of products indicates decomp. to C. C₂H₆ is found in some experiments but is not due to pyrolysis since no olefines are produced. The results are explained on the multiplet theory (cf. preceding abstract). With the catalyst the C_4H_{10} first suffers rupture of a primary C-H linking followed by that of C-C to give H, CH₂, and Pr. Pr and H recombine to give C_3H_8 , and CH_2 with CO_2 gives CO and H_2 . The shortened chain repeats the process (calculation shows it to be more favourable). Alternatively CH_2 gives C and H_2 or is hydrogenated to CH_4 . CO_2 and PrCHO under similar conditions give olefines (amount increases with A) or well as pressed as (amount increases with θ) as well as paraffins, but θ must be higher than with C_4H_{10} . This indicates that PrCHO is not an intermediate in the C_4H_{10} -CO₂ reaction.

J. H. BA.

Relationship between particle size and efficiency of palladium-polyvinyl alcohol (Pd-PVA) catalysts. L. D. Rampino, K. E. Kavanagh, and F. F. Nord (Proc. Nat. Acad. Sci., 1943, 29, 246—256).—Pd-PVA was prepared by reducing PdCl₂ in PVA solution by H₂ or by allowing the slow reduction by PVA itself to proceed to completion. pletion. No appreciable difference of function was observed in the two preps. Electron micrographs showed no significant difference in particle size, the Pd being present mainly as hexagonal crystals. Partial separation of the particles by centrifuging revealed, in the comparison of rates of catalytic hydrogenation of PhNO₂, that the activity was mainly associated with the particles of smaller size. Statistical evaluation of the particle size from electron micrographs indicated the existence of a rough quant, relationship between the catalytic activity and surface area. An additional quality factor is to be attributed to the superiority of the synthetic polymer-supported catalyst over the gum arabic-supported type. L. H. L.

Catalytic hydrogenation of carbon monoxide: methane synthesis from water-gas.—See B., 1943, I, 437.

Nikel-chromic oxide catalysts for hydrogenation of peanut oil.— See B., 1943, II, 351.

Anodic polishing of lead.—See B., 1943, I, 457.

Photochemical decomposition of platinum complexes. I. Photochemical decomposition of the platinum complexes with oxalic acid and malonic acid. T. Banerjee, H. Chakravorty, and S. Sarker (J. Indian Chem. Soc., 1943, 20, 207—212).—The photochemical decomp. of the complexes formed between H₂PtCl₆ and K₂C₂O₄ or CH₂(CO₂K)₂ follows a unimol. course in blue light but in ultra-violet light the unimal value of the complexes. CH₂(CO₂K)₂ follows a unimol. course in one light out in utra-violetlight the unimol. velocity coeffs. decrease with time. The val. of the ratio $[CH_2(CO_2K)_2]/[H_2PtCl_6]$ (= R) affects the quantum yield (γ) in the second reaction. When R is ~3 γ is ~1, but as R increases γ suddenly increases so that when R = 6 $\gamma = 4$ and an induction period appears. It is assumed that when R is >3 some other complex is involved. Possible morphoxima are discussed. is involved. Possible mechanisms are discussed.

Mercury-photosensitised decomposition of *n*-butane. A. W. Hay and C. A. Winkler (Canad. J. Res., 1943, 21, B, 149—155).—The Hg-photosensitised decomp. of $n\text{-}\mathrm{C_4H_{10}}$ at 100°, 175°, and 250° leads to the formation of H_2 , octanes, and dodecanes. Discussion of the

decomp. mechanism leads to the view that liberated H atoms react with unchanged C_4H_{10} to give Bu^α and H_2 by rupture of a C-H linking, and that Bu^α radicals then unite to form higher paraffins.

IX.—PREPARATION OF INORGANIC SUBSTANCES.

Complex compounds of diguanide with bivalent metals. V. Copper and nickel m-phenylenebisdiguanidine and their salts.—See A., 1943, II, 361.

Air-free carbon dioxide from the Kipp apparatus for the Dumas nitrogen determination. R. Kraus (Z. anal. Chem., 1943, 125, 405—406; cf. A., 1943, İ, 321).—Merck's Na K carbonate cast into rods gives with 20% H₂SO₄ pure air-free CO₂, containing no trace of H₂S, without any pre-treatment being necessary. L. S. T.

Concentration of hafnium. Preparation of hafnium-free zirconia. E. M. Larsen, W. C. Fernelius, and L. L. Quill (Ind. Eng. Chem. [Anal.], 1943, 15, 512—515).—Zr and Hf can be satisfactorily extracted from cyrtolite by heating 1 part of the 200-mesh ore with extracted from cyrtofite by fleating 1 part of the 200-mesh ore with 2 parts of conc. H₂SO₄ at a max, temp. of 210—220°, and pouring the cooled digest into 5 parts of H₂O. Acid solutions of dil. ZrO-HfO sulphate sprayed into 10% H₂SO₄ at 70—75° simultaneously with dil. H₃PO₄ yield a dense, compact ppt. that is easily filtered. Treatment of a cold slurry of the phosphates with ice-cold NaOH-Na₂O₃ solution, followed by digestion at 70° yields an acid-sol hydrate. Conditions for the fractional separation of 7r and Hf by direct and Conditions for the fractional separation of Zr and Hf by direct pptn. of the phosphates in dil. solution have been investigated. mother-liquor from a partial pptn. of the total oxides as phosphate, when purified by oxychloride recrystallisation, gave Hf-free ZrO₁. The Hf-free oxide prepared by ignition of the hydrated oxide at 900° has ρ 5.64. Details of procedure, including a method of analysis by ρ determinations of the ignited Zr-Hf oxides, are given.

Silicates. XI. Further experiments with pyrophyllite and comparison of its reactions with those of tale. E. Thilo and U. Schwarz (Ber., 1941, 74, [B], 196—204; cf. A., 1937, I, 206, 256).—The thermal decomp. of anhyd. pyrophyllite (I), Al₂[Si₄O₁₀]O, which is first detectable at 1150° in the absence of impurities, occurs at 900° in mixtures of (I) with MgO, this being also the decomp. temp. of tale, the Mg analogue of (I). The primary products are Mg spinel and free SiO₂ or Mg₂SiO₄ with some MgSiO₃, according to the amount of MgO used. Some decomp. of (I) into mullite and SiO₂ also occurs at 1060° (instead of at 1150° in the absence of MgO). CuO reacts with (I) similarly to MgO, transformation into CuAl₂O₄ CuO reacts with (I) similarly to MgO, transformation into CuAl₂O₄ and SiO₂ being almost complete in 6 hr. at 950°. In presence of MgO or CuO the SiO₂ appears as cristobalite at a temp. much lower than that (1200°) needed when (I) is heated alone. Whereas MgCl₂ reacts with (I) to form a compound analogous to cordierite, CoCl₂ reacts at 800° to give CoAl₂O₄, SiO₂, and HCl. In the course of this reaction a bright lavender-blue compound is formed, the nature of which is discussed. A review of the evidence available indicates that the thermal decomp. of (I), like that of tale, consists primarily in the disruption of the tetrahedral, Si-O-Si layers into simple

Phosphates. II. Neutral and basic phosphates of alkaline-earth metals. W. Rathje. III. Hydroxyfluorapatite. F. Giesecke and W. Rathje. IV. Neutral and basic phosphates of heavy metals. V. Low crystallisation velocity of tertiary phosphates. W. Rathje (Ber., 1941, 74, [B], 342—349, 349—356, 357—362, 546—552).—II. Phosphates of Mg, Ca, Sr, and Ba are prepared by the method of "acidimetric pptn.," which consists in the slow addition of aq. KH₂PO₄ (or Na₂HPO₄) to a dil. solution of the nitrate or chloride of the metal, a neutral reaction being maintained by the simultaneous addition of aq. NaOH of known concn. From the simultaneous addition of aq. NaOH of known concn. From the amount of NaOH used during the pptn. the composition of the ppt. can be calc. To ensure equilibrium and preclude the copptn. of diphosphates the liquid is kept boiling, the solutions are dil., and the precipitant is added slowly. The phosphates stable under these conditions are $Mg_3(PO_4)_2$, $3Ca(PO_4)_2$, $Ca(OH)_2$ (Γ), $Ba_3(PO_4)_2$, and $Ca(OH)_3$ ($Ca(OH)_3$).

conditions are Mg₃(PO₄)₂, 3Ca(PO₄)₂,Ca(OH)₂ (1), Ba₃(PO₄)₂, and 3Sr₃(PO₄)₂,Sr(OH)₂.

III. Attempts to prepare fluorapatite by acidimetric pptn. of Ca(NO₃)₂ by KH₂PO₄ in presence of NaF resulted in the formation of mixtures of 3Ca₃(PO₄)₂,CaF₂ with (I). Treatment of (I) with conc. aq. NaF leads to decomp. with formation of CaF₂, but with dil. NaF the liquid becomes alkaline owing to partial exchange between OH and F. No evidence could be obtained for the formation of corresponding compounds having Cl₂, Br₂, I₂, SO₄ or CO₃ in place of F.

ation of corresponding compounds having C_2 , D_2 , D_3 , D_4 , or CO_3 in place of F_2 .

IV. Heavy metal phosphates formed by acidimetric pptn. under neutral conditions have the following compositions: $M_3(PO_4)_2$, $M_3($

phosphates are produced. This behaviour is attributed to the low velocity of crystallisation of the tertiary salts, and is discussed in relation to the softening of hot H₂O, "phosphating" of metals, hardening of Zn phosphate cement, manufacture of superphosphate, and the action of fertilisers.

F. L. U.

Hydrides of nickel. R. B. N. Sahai and R. C. Ray (J. Indian Chem. Soc., 1943, 20, 213—217).—An apparatus for preparing large quantities of Ni hydrides from MgPhBr, NiCl₂, and H₂ is described. The decomp. pressure curve of the hydrides from 30° to 150° consists of two straight lines intersecting at 56°. Below and above 56° NiH₂ and NiH are formed respectively. No other hydride appears to exist within this temp. range. The transition from NiH₂ to NiH is irreversible. The calc. heats of formation, extrapolated to 18° in each case, are NiH₂ 35,200, NiH 17,100 g.-cal. C. R. H.

X.—ANALYSIS.

Colorimetric test of pH in alkaline solution by means of permanent colour standard solutions, with special reference to electroplating solutions.—See B., 1943, I, 456.

Salts of tervalent thallium as indicators in alkalimetry and acidimetry. V. K. Zolotuchin (Zavod. Lab., 1940, 9, 133—134).—TI" gives in alkaline solutions a yellow sol of Tl(OH)₃. The colour change is so abrupt that it can be used in titration, especially in presence of oxidising substances which destroy org. indicators. The solution must contain much Cl', so that NaCl is added to H₂SO₄ or HNO₃ before titration. Examples are given for solutions containing Cl₂, Br, and NO₂.

J. J. B.

Determination of water. E. Eckert and P. Wulff (Angew. Chem., 1940, 53, 403—405).—Modern methods of determining $\rm H_2O$ in org. substances, salts, minerals, etc. are briefly described.

Determination of hygroscopic moisture in crystalline hydrates. A. T. Sveschnikov and N. V. Koleva ($Zavod.\ Lab.$, 1940, 9, 357).—When hydrates, e.g., BaCl₂,2H₂O, CuSO₄.5H₂O, or KAl(SO₄)₂,12H₂O, are mixed with CaC₂, the hygroscopic H₂O reacts first and can be calc. from the vol. of C₂H₂ evolved during the first 15 sec.

Rapid determination of water in by-product sulphur.—See B.,

Determination of small concentrations of electrolytes by a galvanic method. B. A. Raschkovan (Zavod. Lab., 1940, 9, 728—731).— The solution is placed between a Hg cathode and an anode of amalgamated Cu, and the current in the external circuit measured. The method is applied to the determination of HCl and of o-C₆H₄(CO)₂O in air. J. B.

Dynamic determination of free halogens. M. M. Raines, A. I. Krupkin, and P. V. Rodzevitsch (Zavod. Lab., 1940, 9, 135—138).—Gas containing Cl_2 or Br (or both) is passed through a 0·15% solution of KI and the colour obtained measured with a photo-cell. If the [Cl₂] or [Br] is <0·1 mg. per l. of air, starch is added to KI. o-Tolidine can be used instead of KI for Cl_2 or Br alone but not for their mixtures.

Determination of halogens. M. B. Schtschigol (Zavod. Lab., 1940, 9, 310—313).—The solution containing Cl', Br', and I' is divided into three parts. In (a) all three halogens are exactly pptd. using Q mols. of AgNO₃. In (b) I is determined by adding HMnO₄ and starch and titrating with AgNO₃. (c) is mixed with aq. NH₃ (final [NH₃] = 0.5s..) and with Q mols. of AgNO₃; AgI and AgBr are pptd., but Ag(NH₃)₂Cl remains in solution and is determined in the filtrate.

J. J. B.

Colorimetric determination of chlorine residuals [in water] up to 10 p.p.m. with o-tolidine.—See B., 1943, III, 283.

Volumetric determination of iodide ion in mercury compounds. V. D. Ponomarev (Zavod. Lab., 1940, 9, 299—300).—HgI₂ or K₂HgI₄ is shaken with Zn amalgam and 2n-H₂SO₄, and I' is determined in the resulting solution as usual.

J. J. B.

Volumetric determination of iodides [in presence of chloride and bromide.] P. Kainrath (Z. anal. Chem., 1942, 125, 1—5).—The iodide solution, or the Ag halide ppt., is treated with glacial AcOH + 20% NaOAc, and the I'oxidised to IO₃' by aq. Br, excess of which is removed by means of 80% HCO₂H (not PhOH). 5% KI and dil. H₂SO₄ are added, and the liberated I is titrated by 0·1N·Na₂S₂O₃. The I' content of a photographic film can be similarly determined after removal of AgI from the film by means of 5% Na₂S₂O₃.

L. S. T.

Colorimetric micro-method for [determination of] dissolved oxygen [in water].—See B., 1943, III, 259.

Electrochemical determination of dissolved oxygen in water.—See B., 1943, I, 426.

Determination by Winkler's method of free oxygen in water containing unsaturated compounds.—See B., 1943, III, 284.

Oxalate method of determining sulphate ion.—See B., 1943, III, 259.

Reaction of selenic acid with silver ion and the consequent separation of selenic from sulphuric acid. R. Ripan (Z. anal. Chem., 1942, 125, 38—40).—4—5 drops of $0\cdot 1\text{M-AgNO}_3$ are added to the neutral solution of a selenate or to $H_2 \text{SeO}_4$ neutralised to pH 6·7 by NaHCO_3. Pptn. of Ag_SeO_4 can be ensured by adding 2n-NaOAc and COMe_2. The limit of identification is 10^{-7} g. For the quant. pptn. and separation of SeO_4" from SO_4", the solution should be neutral and should contain 2n-NaOAc and 20% of COMe_2, and should be $\Rightarrow 0\cdot05\text{M}$. with respect to SeO_4". The Ag_SeO_4 is pptd. by $0\cdot1\text{M-AgNO}_3$ and washed with 20% COMe_2. L. S. T.

Determination of selenium in sulphur.—See B., 1943, I, 446.

Detection of nitrates in presence of interfering anions. B. I. Soibelman and F. Bresler (Zavod. Lab., 1940, 9, 359—360).— NO_3' is detected with NHPh₂. To remove the interfering anions the solution is twice evaporated to dryness with 10% aq. NH₃ saturated with SO₂ (thus destroying NO_2' , MnO_4' , ClO_3' , OCl', CrO_4'' , etc.) and the residue pptd. with cryst. Ag_2SO_4 (eliminating halogens etc.).

Aminosulphonic acid in the determination of nitrites. W. M. Cumming and W. A. Alexander (Analyst, 1943, 68, 273—274).— NO_2 ' is determined by addition of excess of $NH_2 \cdot SO_3H$ and back-titration with standard $NaNO_2$, using $\alpha \cdot C_{10}H_1 \cdot NH_2 + p \cdot NH_2 \cdot C_0H_4 \cdot SO_2 \cdot NH_2$ in AcOH as external indicator. NaOAc is added as a buffer in titrating strongly acid solutions.

M. H. M. A.

Determination of nitric oxide in manufactured gases.—See B.,
1943, I, 436.

Separation of phosphoric acid as bismuth phosphate in quantitative analysis. I. A. Keschan (Kešans) (Z. anal. Chem., 1942, 125, 6—22).—The pptn. of PO₄ "by BiONO₃ in dil. HNO₃, and separation from Li', Na', K', Ca", Sr", and Ba", have been investigated. Data on the solubility of BiPO₄ in 0·25—2N-HNO₃ are recorded and discussed; the solubility in 0·5N-HNO₃ is 24·0 mg. per l. Solubility increases in presence of Cl', Br', I', and SO₄". Pptn. can be made quant. (2 mg. PO₄" per l.) by using excess of precipitant (0·5 g. of BiONO₃ in 0·5N-HNO₃). C₂O₄", S", S₂O₃", CNS', IO₃', and AsO₄" interfere and must be present only in small amounts. Supersaturation of EiPO₄ is marked, but can be overcome by digestion for 6—8 hr. on the water-bath or, preferably, by shaking for 1—2 hr. Small amounts of H₃PO₄ (<0·2 g. per l.) are not pptd., and addition of known amounts of H₃PO₄ or of freshly-pptd. BiPO₄ is then necessary. Cations the hydroxides of which are strong bases are generally co-pptd. in small quantities with the BiPO₄. Cl' does not interfere, but SO₄" increases co-pptn. of the alkalis. The order of co-pptn. is K > Na > Li, and Ca > Sr > Ba. Conditions of pptn. under which contamination of the BiPO₄ is negligible are recorded. Excess of Bi in the filtrate from the phosphate pptn. is removed by means of H₂S at room temp., and cations remaining in the filtrate are determined by the usual methods.

Determination of phosphorus in chalk in the form of a complex of phosphoric acid, molybdenum, and 8-hydroxyquinoline.—See B., 1943, I, 444.

Determination of phosphate in plant ash.—See B., 1943, III, 262, 263.

Photometric determination of phosphoric acid in fertilisers.—See B., 1943, III, 263.

Chemical determination of minute amounts of boron in plants.—See B., 1943, III, 263.

Colorimetric determination of boron in steel, using the quinalizarin reaction.—See B., 1943, I, 456.

Detection of silicic acid and hydrofluoric acid by the tetrafluoride and oily drop tests. R. Albrecht and H. Bast [in part with M. Büttner] (Z. anal. Chem., 1943, 125, 321—335).—Success in getting the SiF₄, liberated by heating with H_2SO_4 , to give a white stain on wet, black filter-paper depends on the ratio of $SiO_2: CaF_2$. Limiting mol. ratios for pptd. SiO_2 are $\sim 1:10$, for sea-sand $\sim 1:2$, for $Na_2SiF_6 \sim 1:6$, for $BaSiF_6 1:<0.17$. By using a drop of H_2O on a rubber rod, transferring to a cellulose acetate slide, adding HCl and $BaCl_2$, and examining microscopically for $BaSiF_6$ crystals, the limiting ratios can be raised, e.g., to 1:66 for pptd. SiO_2 containing 11% of H_2O . For sand and anhyd. pptd. SiO_2 , the only limiting factor for excess of SiO_2 is the min. actual wt. of CaF_2 required ($\sim 0:2$ mg.), but for hydrous SiO_2 there is a limiting ratio ($\sim 25:1$). Quartz, however fine, fails to give a positive test. $Na_2B_4O_7$, if > 0:2 molar with reference to the CaF_2 , inhibits the reaction. The characteristic oily drops formed when fluorides are heated with H_2SO_4 in glass are inhibited by a $CaF_2: Na_2B_4O_7$ ratio of 1:2, but the Zr-alizarin lake test is not affected by ratios of even 1:25.

S. A. M.

Determination of silicon in steel with a photocolorimeter.—See B., 1943, I, 456.

Gravimetric determination of potassium, rubidium, and cæsium. O. G. Scheintzis ($Zavod.\ Lab.,\ 1940,\ 9,\ 162-163$).—0·2—0·005 g. of K, Rb, or Cs is pptd. by 3% Mg salt of dipicrylamine, the ppt. is washed with H_2O -free Et₂O at 10°, dried at 80—90°, and weighed.

Sedimentary determination of potassium and its use in soil investigations.—See B., 1943, III, 230.

Determination of sodium in presence of molybdenum. C. H. Hale (Ind. Eng. Chem. [Anal.], 1943, 15, 516—517).—Mo interferes by forming a ppt., presumably of UO2MOO4, with the Zn UO2 acetate reagent. The interference is overcome by adding citric or tartaric acid to form the sol. complex with MoO4". Details of procedure and test data are given.

Rapid determination of sodium chloride in presence of protein.—See B., 1943, III, 250.

Sensitivity of chemical reactions. VI. Reactions giving rise to supersaturated solutions. Z. Karaoglanov (Z. anal. Chem., 1943, 125, 336—349; cf. A., 1943, I, 163).—The sensitivity of the reaction Ca" + SO₄" is raised by increasing the reaction time or the concnof reagent, or (for shorter reaction times) by seeding with CaSO₄,2H₂O or BaSO₄, or scratching with a glass rod, or by starting the reaction by warming for 5 min.; it is markedly lowered by the presence of HCl. CaSO₄ forms supersaturated solutions, which, however, are much less stable than those of Mg₂C₂O₄. In the separation of Ba from Ca by the SO₄" method, pptn. is carried out slowly, at room temp., and in presence of HCl. The reaction Sr" + CrO₄" is much less affected by the above factors, except that there is a marked decrease in sensitivity in presence of AcOH. SrCrO₄ forms only unstable supersaturated solutions. Ba" + CrO₄" is a highly sensitive reaction, not greatly affected by factors other than the concn. of reagent and the presence of AcOH; BaCrO₄ does not form supersaturated solutions. To separate Ba from Sr by the CrO₄" method, pptn. is carried out with a slight excess of pptg. agent at room temp. in presence of dil. AcOH, the ppt. being filtered off at once. The reaction Hg" + CNS' is much more sensitive when the reagents are in equiv. proportions than under the usual conditions, owing to the solubility of Hg(CNS)₂ in either Hg(NO₂)₂ or NH₄CNS; seeding, scratching, and longer reaction times increase the sensitivity.

Determination of active calcium oxide in quicklime.—See B., 1943, I, 444.

Rapid analysis of technical magnesium chloride.—See $\rm B.,\ 1943,\ I,\ 444.$

Determination of traces of zinc with Pulfrich's photometer. L. Kulberg and F. Jurovskaja (Zavod. Lab., 1940, 9, 295—296).—A solution containing 10^{-5} — 10^{-6} g. of Zn, and similar amounts of Fe, Al, Mn, Cu, Ca, and Mg, is mixed with 0.5 ml. of 10% KI and completely evaporated. The solid is dissolved in 2 ml. of H_2O ; Cu remains in the residue. To the liquid NH₄ citrate and HCO₂H are added, and ZnS is pptd. with H₂S. ZnS is transformed into Zn salt of 8-hydroxyquinoline, which is decomposed with HCl, and 8-hydroxyquinoline is coupled with diazotised sulphanilic acid. The NH₄ salt of the dye obtained has an absorption max. near 470 m μ . Its amount is determined with a photocolorimeter, using a green filter.

Determination of small amounts of cadmium in air.—See B., 1943, III, 257.

Separation of lead from copper, cadmium, and iron, as lead chromate. I. Sarudi (v. Stetina) (Z. anal. Chem., 1943, 125, 370—372).—1% K₂CrO₄ is added dropwise to a boiling solution of the nitrates or acetates (not chlorides) in very dil. HNO₃, to which NaOAc and AcOH have been added, and the pptd. PbCrO₄ washed with 1% AcOH, EtOH and Et₂O, and dried at 100°. The Cu is determined electrolytically after reduction of excess of CrO₄" with CH₃O, or is pptd. as CuS and Cu₂S by Na₂S₂O₃ and ignited to CuO. The Cd is pptd. as CdS and determined as such or as CdNH₄PO₄, H₂O or Cd₂P₂O₇. The method is quicker and simpler than the SO₄" method, and satisfactory results are obtained. S. A. M_{*}

Determination of lead in air by means of dithizone.—See B., 1943, III, 257.

Volumetric determination of lead.—See B., 1943, III, 277.

Work involved in and efficiency of colorimetric methods. A. Schleicher (Z. anal. Chem., 1943, 125, 385—405).—The energy requirements and the rate of performance of colorimetric methods are discussed in relation to the determination of Cu' colorimetrically by the following methods, for which data obtained with the Lange photo-electric colorimeter are recorded: NH₃, sulphide, benzidine, ferrocyanide, dithizone, salicylic acid, iodide, and diethyldithiocarbamate methods.

L. S. T.

Detection of copper ion. N. A. Tananaev and V. N. Podtschainova (Zavod. Lab., 1940, 9, 168—169).—0.5 mg. of Cu in 1 l. is detected by introduction of CdS into the solution; if [Cu] is not too low, the CdS becomes dark, otherwise it is dissolved in dil. HCl and CuS observed in the residue. If the solution contains Bi, Ag, or Hg in addition to Cu, the ppt. of the sulphides is dissolved in aqua regia and the solution treated with conc. NH₃; 10 mg. of Cu per I, give a blue colour.

Application of compensation in polarographic determination of copper in zinc sulphide.—See B., 1943, I, 444.

Volumetric thiocyanate process for determining mercury. Z. Karaoglanov (Z. anal. Chem., 1943, 125, 406—416).—Data showing the effect of varying conditions on the titration of Hg" by CNS' are recorded and discussed. The method is trustworthy when the titration is made at room temp. in presence of sufficient HNO₃ and indicator solution. Fe(NO₃)₃ or Fe alum can be used as indicator, the Hg salt can be either nitrate or sulphate, and Hg" can be titrated by CNS', or CNS' by Hg". Deviations occur when titration is effected in hot solution, or when [HNO₃] is too low, or the solution is too dil. with respect to Hg". In presence of PO₄"', extra indicator and HNO₃ are needed. Cl' and Br' must be absent. Hg dissolved in HNO₃, with subsequent removal of oxides of N, is the best substance for standardisation of the NH₄CNS. AgNO₃ can be used as reference substance, but the titration by CNS' must then be carried to the second, permanent red coloration.

L. S. T.

X-Ray analysis of the rare elements of the cerium group. I. B. Borovski, M. A. Blochin, and L. A. Grschibovskaja (Zayod. Lab., 1940, 9, 740—741).—When the relation between the amount of an element and the intensity of its X-ray lines is found by experiment, unknown concus. of this element can be found from X-ray spectra. The method is applied to minerals containing Ce, La, Nd, Pr, and Sm; the error usually is <7%.

J. J. B.

Direct volumetric and gravimetric determinations of cerium and thorium by the iodate method. J. A. Tschernichov and T. A. Uspenskaja (Zavod. Lab., 1940. 9, 276—283).—The ppt. obtained from Ce(NO₃)₄ and a large excess of 10% KIO₃ + 2·5% HNO₃, after being washed with 95% EtOH and Et₂O, is 2Ce(IO₃)₄, KIO₃,8H₂O (I). It can be weighed directly or titrated with KI; one Ce liberates 28 equivs. of I. An analogous ppt. from Th(NO₃)₄ is 4Th(IO₃)₄, KIO₃, 18H₂O (II). It liberates 25·5 equivs. of I per one Th. If the solution contains both Th and Ce, Ce^{***} is reduced to Ce^{***} by H₂O₂, (II) is pptd., and Ce^{***} in the filtrate is treated with KBrO₃, when (I) is formed. J. J. B.

Determination of traces of aluminium with aluminon. L. M. Kulberg and E. I. Rovinskaja (Zavod. Lab., 1940, 9, 145—148).— 10^{-6} — 10^{-5} g. of Al can be determined in presence of <4 mg. of Ca, <0.5 mg. of Mg, <2 × 10^{-5} g. of Cu, Mn, and Zn, and <3 mg. of PO₄", if the solution contains also 0.5—2 mg. of Fe". Al + Fe are pptd. with 8-hydroxyquinoline in dil. AcOH at 50°, and the ppt. is transformed into chlorides and extracted with 50% KCNS and Et₂O. The residue is transformed into Al aurintricarboxylate and the colour intensity measured with a photo-cell using a green filter since the absorption max. of the salt is at 530 m μ . J. J. B.

Determination of aluminium oxide in aluminium.—See B., 1943, I. 458.

Improved manganese separation for the phosphate method and for general use. G. J. Austin (Analyst, 1943, 68, 274—275).—The solution left after removal of Ni, Co, and Zn with (NH₄)₂S, containing Mn, Ca, and Mg, is buffered to pH 4·4 —4·8 with AcOH-NH₄OAc and Mn is pptd. as MnO₃ by adding a slight excess of NaIO₄ and a little HCO₂H to inhibit further oxidation. The ppt. is freed from traces of Ca and Mg with hot 0·1n-HNO₃. Excess of P₂O₅ causes the MnO₂ to be slightly sol. in hot 0·1n-HNO₃ and the original solution must be diluted to >0·1% P₂O₅ before oxidation.

M. H. M. A.

Separation of the metals of the third group from calcium, magnesium, and alkalis by means of hydrogen sulphide in presence of hexamethylenetetramine. E. A. Ostroumov and R. I. Bomschtein (Zavod. Lab., 1940, 9, 139–142).—If Mn", Fe"', Al'", Cr''', and Zn' are pptd. by H_2S in presence of $(CH_2)_6N_4$ at 60—99°, the pH of the solution increases gradually and every sulphide is pptd. more or less separately, forming crystals which do not adsorb Ca, Mg, or alkali metals. To a solution containing 0·3 g. of the metals 20—25 g. of N_4 Cl are added; after heating to 60° 7 g. of $(CH_2)_6N_4$ are added and H_2S is passed through at a slowly rising temp. for ~1'hr. If N_1 '' or Co'' is also present, a little C_5H_5N , HCl is added before the $(CH_2)_6N_4$.

Application of the photocolorimeter in volumetric analysis. J. J. Lurie and E. M. Tal (Zavod. Lab., 1940, 9, 702—714).—In the simplest cases the light absorption of the solution is measured at three additions of standard solution, one being before and two after the end-point has been reached; the end-point is the crossing of the straight lines drawn through the zero point and the first measured

point, and through the two other measured points. This method is used for permanganatometry (determination of Fe in presence of coloured cations, e.g., Ni and Co) and alkalimetry in presence of phenolphthalein. A suitable light filter facilitates the titration. In more complicated cases, when the solution is coloured throughout (titration with Me-orange, Me-red, etc.), the light absorption must be measured for many additions, and the end-point found graphically. The method is indicated for coloured solutions, e.g., for determining the acidity of technical Ni and Co sulphates and of Ni and Co electroplating baths.

J. J. B.

Determination of small amounts of tervalent chromium in chromic acid. V. E. Kuteinikov (Zavod. Lab., 1940, 9, 305—306).—Cr'' is separated from a large excess of CrO_4 " or Cr_2O_7 " by pptg. with Na_2HPO_4 in an acid solution; Cr phosphate is oxidised with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ to CrO_4 ", which is titrated. J. J. B.

Determination of chromium in steel, alloys, and chromite.—See B., 1943, I, 456.

Determination of molybdenum by internal electrolysis. J. A. Tschernichov and E. V. Schtutzer (Zavod. Lab., 1940, 9, 723—728).— Mo is electrodeposited from a solution containing AcOH 0·3, NH₄OAc 0·17, and NH₄Cl 1%, at 70—75°, as a compound Mo₂NO₄,5H₂O. It can be weighed as such. If Fe''' is present, it is reduced to Fe'' by NH₂OH, and Mo is deposited as before. Large amounts of salts like NaCl, Na₂SO₄, etc. increase the wt. of the electrodeposit. If VO₃' is present, it must first be removed by NH₃. The method is used for the analysis of wulfenite. J. J. B.

Use of pyridine in determination of uranium and its separation from the alkaline-earth metals. L. E. Kaufman (Zavod. Lab., 1940, 9, 228—229).—U is pptd. by C_5H_5N only if the [(NH₄)₂CO₃] is low. If the solution contains U, Fe, and alkaline earths, U and Fe are pptd. by C_5H_5N , U is extracted from the ppt. by conc. (NH₄)₂CO₃, and Fe determined in the residue. Th is pptd. by C_5H_5N like U, but the pptn. of Ce is slow.

Effect of germanium on iodometric determination of tin. I. P. Alimarin and B. N. Ivanov-Emin (Zavod. Lab., 1940, 9, 356).—Ge does not interfere with the titration of Sn. so long as its concn. is <0.1%.

J. J. B.

Gravimetric determination of tin in steel (other than chrome steel).—See B., 1943, I, 456.

p-Hydroxyphenylarsonic acid as selective precipitant for titanium in the analysis of titanium ores.—See B., 1943, I, 457.

Rapid determination of zirconium. T. A. Uspenskaja, E. I. Guldina, and M. S. Zverkova (Zavod. Lab., 1940, 9, 142—145).—A solution of 0·2 g. of Zr in 5% HCl is mixed with 1·5 ml. of 0·03% alizarin (I) and with enough 0·1n-NaF to produce a yellowish-pink colour. To another solution containing the same amounts of HCl, (I), and NaF a titrated solution of ZrOCl₂ is added to give the same colour. Fe" and SO₄", but not Fe", interfere.

J. J. B.

Spectrochemical analysis of solutions and minerals. VIII. Direct determination of germanium in coal ash.—See B., 1943, I, 436.

Polarographic studies. III. Determination of vanadium. J. E. Page and F. A. Robinson (Analyst, 1943, 68, 269—271).—Org. V compounds are heated with conc. $H_2\mathrm{SO}_4 + \mathrm{HNO}_3$ or fused with $\mathrm{Na}_2\mathrm{CO}_3 + \mathrm{KNO}_3$ to form $\mathrm{VO}_4^{\prime\prime\prime}$, which is determined polarographically in presence of conc. aq. NH₃. i_4 \propto [V] in the range 5 \times 10^{-3} –5 \times 10^{-4} M. Vals. obtained agree to ± 4 % with vals. obtained volumetrically. M. H. M. A.

Simplified cell unit for internal electrolysis. [Determination of bismuth in lead.]—See B., 1943, I, 457.

Spectral analysis of small amounts of iridium and rhodium in platinum preparations. A. V. Babaeva, V. I. Belova, and S. A. Borovik (Compt. rend. Acad. Sci. U.R.S.S., 1942, 37, 101—103).—
Ir and Rh are determined in Pt compounds by their spark spectra, ~3 mg. of material being fixed in a hollow in the lower C electrode with collodion. The method is sensitive to 0.001% with an accuracy of ±4.5%.

M. H. M. A.

XI.—APPARATUS ETC.

Vacuum furnace. W. Ehrenberg and F. Ansbacher (J. Sci. Instr., 1943, 20, 164—165).—The apparatus eliminates the disadvantages of external heating by the use of an internal heater of Ni (Ta or Mo) strips wound on ceramic rods and surrounded by a Cu reflecting screen. Performance data are given.

N. M. B.

Electric furnace for intensive heating of crucibles. K. A. Karajanopulo (Zavod. Lab., 1940, 9, 366).—The heating elements are CSi rods. The furnace can be used up to 1520°. J. J. B.

Thermostat keeping an exactly controlled temperature. K. P. Florenski (Zavod. Lab., 1940, 9, 189—191).—A Hg thermometer immersed in the thermostat is placed between a source of light and a

photo-cell so that the top of the Hg column casts a shadow on the cell when the temp. is too high; when the photocurrent ceases, the heating is switched off. When the stirring is intensive enough, the temp. can be kept for several hr. within 0.001°.

J. J. B.

Water thermoregulator. W. E. Boyd (Ind. Eng. Chem. [Anal.], 1943, 15, 523).—The portable apparatus described maintains a variation of $\pm 0.5^{\circ}$. L. S. T.

Compensated hot-wire air thermometer. M. A. El-Sherbini and Y. L. Yousef (*Proc. Physical Soc.*, 1943, **55**, 427—428).—A simple instrument for measuring currents at frequencies up to radio-frequency is constructed from a thermally screened Roberts-type micromanometer, with a hot wire in each limb. Paraffin oil manometric liquid encloses a bubble in the capillary. Performance, sensitivity, and calibration are outlined.

N. M. B.

Temperature determination with a photocell. A A. Novikov (Zavod. Lab., 1940, 9, 750—754).—The ratio of the red to the blue radiation of a heated body is determined using a red and a blue filter and Sb-Cs photocells. The temp. is calc. from this ratio for 15 incandescence lamps.

J. J. B.

Practical colour measurement. S. Rösch (Z. Elektrochem., 1941, 47, 18—19).—The introduction of suitable colour standards and new and improved instruments for the determination of colour have made it possible to some extent to interpret data obtained in colour measurements on one system with respect to those obtained on another.

A. J. M.

Visual photometry in the region of low brightnesses. A. Gerschun (Compt. rend. Acad. Sci. U.R.S.S., 1942, 37, 125—126).—Accuracy of photometric measurements is greatest when the light from the field of comparison has a definite spectral composition, the measured brightness is not weakened, the angle subtended by the field of vision is ~>6°, and the exit pupil of the apparatus is > that of the pupil of the eye by ~7 mm.

L. S. T.

Photo-electric photometer. P. W. Cunliffe (J. Text. Inst., 1943, 34, 755—60).—The photometer described is constructed from a vac. emission photo-cell and the valve potentiometer part of a glass-electrode pH-meter. Its use is exemplified by absorption of dyes from their solutions, chemical analysis by colorimetric methods, and spectrophotometry.

F. O. H.

Surface replicas containing dye for use in the light microscope. V. J. Schaefer (Met. Progr., 1943, 44, 72—74).—A solution of dye in resin is placed over the micrographic specimen, and when dry the replica is removed and examined under the microscope. Variations in colour density on the photomicrograph are directly related to variations in depth on the original surface of the specimen.

Manipulation of the microscope. Observations on technique. I—III. F. D. Armitage (Ind. Chem., 1943, 19, 447—454, 495—500, 549—554).—The general use of the microscope, the measurement of area, the interpretation of images and possible sources of error, and the choice of a technical microscope are described and illustrated.

Recording microphotometer for the examination of X-ray diffraction films. H. R. Ronnebeck $(J.\ Sci.\ Instr.,\ 1943,\ 20,\ 154—161)$.—The mechanical features (lathe bed, roller gears, half-speed drive, etc.) are described. The recording system is a photocell-photometer unit with an amplifier and Einthoven string galvanometer. The performance is discussed and a full bibliography given. N. M. B.

Determination of the integral energies of X-ray lines in structure analysis. III. Rapid method of integral photometry of diffraction spots. V. P. Kotov and A. C. Breger (J. Phys. Chem. Russ., 1943, 17, 51—56).—A wide photometer slit is used allowing the photometry of a whole spot at once. The val. obtained is corr. using an empirical relation between the total absorption on the one hand and the ratio (area of spot): (area of slit) and the average blackness of the spot on the other.

J. J. B.

X-Ray methods of determining size and shape of submicroscopic crystals. G. S. Shdanov (Zavod. Lab., 1940, 9, 732—740).—A review.

Apparatus for making X-ray powder photographs at controlled, elevated temperatures. M. J. Buerger, N. W. Buerger, and F. G. Chesley (Amer. Min., 1943, 28, 285—302).—Complete details (A., 1943, I, 210) are given. L. S. T.

Million-volt portable radiographic X-ray unit. E. E. Charlton and W. F. Westendorp (*Proc. Amer. Soc. Test. Mat.*, 1942, 42, 1088—1098). R. B. C.

Exposure meter for X-ray radiography. H. Friedman and A. L. Christenson (Proc. Amer. Soc. Test. Mat., 1942, 42, 1145—1153).

Universal source of excitation of spectra. N. S. Sventitzki (Compt. rend. Acad. Sci. U.R.S.S., 1942, 37, 205—208).—An a.c. arc, which can produce both arc and spark spectra by variation of the capacity and inductance of a steadying superimposed high-frequency discharge, is described.

W. R. A.

Method of feeding in spectrochemical analysis. S. I. Safonov (Zavod. Lab., 1940, 9, 187—188).—Spectra are produced in a vertical C arc. The powder to be analysed is fed into the flame through a channel along the axis of the upper electrode; it is gradually shaken into this channel by the hammer of an electric bell. If the powder sinters within the electrode, sparks must be used instead of arc.

Spectrophotometric method for the analysis of multi-component mixtures and its infra-red application. R. R. Brattain, R. S. Rasmussen, and A. M. Cravath $(f.\ Appl.\ Physics,\ 1943,\ 14,\ 418-428)$.— The method is based on the assumption that the optical density of a mixture is an additive property, although the transmissions of the separate components may not follow Beer's law. The application of the method to infra-red absorption of vapour samples is described in detail, and the results of tests using a 6-component C_4 hydrocarbon mixture are given. The method is particularly suited to the rapid routine analysis of large nos. of liquid or vapour samples containing the same components. It is the only practical method of analysis of mixtures such as the isomerides of $\Delta \beta$ -butene. L. S. T.

Apparatus for studying transformations in alloys by means of electric resistance. M. E. Blanter (Zavod, Lab., 1940, 9, 332—335).— An apparatus which continuously records the temp. of the specimen, the potential drop in it, and the current strength is described. The temp. of transformations can be measured within $\pm 2\%$.

Silver chloride electrode. O. Redlich and L. F. Maranville (J. Chem. Educ., 1943, 20, 10).—Advantages of the AgCl electrode (prep. described) over the calomel electrode are emphasised.

Vacuum-tube voltmeter for measuring high negative potentials. M. Kupferberg (Rev. Sci. Instr., 1943, 14, 254).—A circuit capable of measuring negative voltages from 0 to 5000 v. with a max. error of 2% is presented. The meter has a zero adjustment and two voltage ranges, 0—3000 v. and 0—5000 v. J. L. E.

Theoretical problems in the practical polarographic work. T. A. Kriukova (Zavod. Lab., 1940, 9, 691—698).—Some difficulties of polarography are reviewed, including the polarographic max., its dependence on the movement near the cathode and on the concn. of the supporting electrolyte, the extinguishing of the max. and the secondary effects of the extinguishing substances, the influence of the concn. of the supporting electrolyte on the position and shape of polarographic waves, polarographic waves of ions reducible in steps, and also substitution of solid cathodes for Hg drops.

Apparatus for micro-determination of magnetic susceptibility. H. Theorell (Arkiv Kemi, Min., Geol., 1943, 16, A, No. 1, 8 pp.).—
A micro-modification of the Gouy method is described. A thin tube divided centrally into two sections, one of which contains the solution under test, is suspended horizontally in a magnetic field by two long fibres. The horizontal displacement on application of the field is observed with a microscope, oscillations being damped by a rod attached to the tube and dipping into glycerol. The second section of the tube may be filled with aq. NaCl or FeCl₃ to correct any displacement due to the tube itself.

A. J. E. W.

Cooling hydrogen discharge tubes. Chao-wang Hsueh (Rev. Sci. Instr., 1943, 14, 250—253).—A method for cooling H_2 discharge tubes to 56° κ . by means of rapidly evaporating liquid air under reduced pressure is described. The temp. is measured with a Cu–constantan thermocouple.

Electron reflecting microscope; a new ultra-microscope. H. Mahl and A. Pendzich (Z. tech. Physik, 1943, 24, 38—42).—Details are given of an electron microscope having an electron mirror as projective. By reversal of the electron beam a "stage-microscope" which is very compact can be obtained.

Technique of neutron probes. W. Bothe (Z. Physik, 1943, 120, 437—449).—Errors involved in measurements of neutron density by probes are analysed and conditions for accurate measurement of neutron streams are discussed.

L. J. J.

Apparatus used in radium radiography. L. W. Ball and D. R. Draper (*Proc. Amer. Soc. Test. Mat.*, 1942, 42, 1134—1143).—
R. B. C.

Weighing method of sedimentometric analysis. S. J. Starodubtzev (Zavod. Lab., 1940, 9, 758—760).—A simplified Oden balance allows measurement of time of sedimentation of every 0·1 mg. (or of every 5 mg.) of suspension.

J. J. B.

Apparatus for semi-micro-evaporations. S. Gaddis (*J. Chem. Educ.*, 1943, 20, 28).—Kurtz' method (A., 1942, I, 281) is modified. L. S. T.

Testing of measuring flasks. L. A. Mindalev (Zavod. Lab., 1940, 9, 365).—A known amount of solid is dissolved in the contents of the flask, and its amount in 50 ml. or 100 ml. taken from the flask is determined.

J. J. B.

Analytical washing bottle. V. A. Alexandrov (Zavod. Lab., 1940, 9, 245).—A Bunsen valve is attached to the injector tube for use with unpleasant liquids.

J. J. B.

Apparatus for filtering in a stream of inert gas. N. I. Stognii (Zavod Lab., 1940, 9, 236—237).—An apparatus is described made up of a separating funnel, two filtering funnels, and an aspirator.

Convenient arrangement for rapid dialysis. W. H. Seegers (J. Lab. clin. Med., 1943, 28, 897—898).

Dispenser for corrosive liquids. S. Zuffanti (*J. Chem. Educ.*, 1943, 20, 28).—An arrangement for aspirating definite vols. of liquid, particularly Br, into a graduated cylinder is described. L. S. T.

Laboratory stirrer. V. M. Muchatschev (Zavod. Lab., 1940, 9, 244—245).—The reaction vessel is rotated along a conical surface.

J. J. B.

Mol. wts. of high polymers. M. L. Huggins (Ind. Eng. Chem., 1943, 35, 980—986).—Methods for determining the above are subjected to crit. mathematical consideration. The osmotic or cryoscopic data yield ordinary "no.-average" mol. wts., whereas η data, if properly interpreted, yield " η average" results in which the heavier mols. are relatively more important. For characterisation of a polymer it is desirable to know the dependence of the osmotic pressure and η on concn. and that of the intrinsic η on mol. wt., whereby, from a single measurement of η and of osmotic pressure, it is possible to calculate the two distinct mol. wt. vals. D. F. T.

Purification of substances by partial fusion and warm absorption. J. Lindner (Ber., 1941, 74, [B], 231—237).—Mixtures of substances are warmed to suitable temp. < that of complete fusion and the liquid portion is absorbed by porous material, such as porous plate or filter-paper. Limitations of the method are recognised and an illustrative example is the mixture of Ph2 and NHPh2, which gives a simple m.p. diagram with a eutectic point at 29.5°. The method is applicable to small amounts.

Determination of densities of reactive gases. H. von Wartenberg (Z. Elektrochem., 1941, 47, 92—94).—A column of the reactive gas is balanced in a xylene (I) manometer against a column of air. A buffer space containing air prevents the reactive gas from coming in contact with the (I). The pressure difference is read by means of a microscope, and gives d to 1%. The construction and calibration of the apparatus are described.

A. J. M.

McLeod gauge of great accuracy and sensitivity. G. Haase (Z. tech. Physik, 1943, 24, 27—34).—Inaccuracies, present in the usual instruments with very narrow capillaries, caused by irregular motion of the Hg, are eliminated by weak etching of the capillary with aq. or gaseous HF, without impairing the visibility of twalls. Contact of the Hg with air or O_2 must be avoided. Before each determination, all parts of the gauge, except the Hg reservoir, are heated to the softening point of the glass. By these means the McLeod gauge can be used down to pressures of $\sim 4 \times 10^{-7}$ mm. Hg.

Method for determining the coefficients of friction μ_0 and μ . B. Piesker (Z. tech. Physik, 1943, 24, 34—38).—The apparatus used consists of the usual inclined plane with the addition of an electromagnetic system above the sliding body. The inclined plane is set an angle a ($<\rho$) and the field strength increased until sliding occurs. The process is then repeated with an additional wt. on the pan. The measurements made permit the calculation of μ_0 . The determination of μ is carried out similarly from the increase of kinetic energy in the magnetic field ($a > \rho$). By the use of a.c., an imitation of actual machine conditions can be obtained.

J. F. H.

Berthelot method of measuring tension in liquids. R. S. Vincent and G. H. Simmonds (*Proc. Physical Soc.*, 1943, 55, 376—382; cf. A., 1943, I, 72).—A modified method in which the pressure at the moment of sealing is known gives vals. >25 atm. compared with ~150 atm., which are considered likely to be falsely high, by the normal method. The order of magnitude agrees with the vals. obtained by the viscosity tonometer method. N. M. B.

Cellulose acetate capillaries for Debye-Scherrer photographs. R. Fricke, O. Lohrmann, and W. Schröder (Z. Elektrochem., 1941, 47, 374—379).—A method of forming cellulose acetate capillaries of definite dimensions by moulding on Cu wires, and the accurate determination of their diameters, are described. The capillaries are suitable for the study of powders by the Debye-Scherrer method, since the "amorphous ring" due to the cellulose acetate is smaller than that due to glass.

J. W. S.

Use of Wood's metal in vacuum systems. A. L. Hughes and C. S. Pao (Rev. Sci. Instr., 1943, 14, 254—255).—The use of Wood's metal as a substitute for the usual greases in the lubrication of standard taper joints and in a device for the replacement of stopcocks is described.

Equivalent penetrometers in radiographic testing. R. J. Schier and G. E. Doan (Proc. Amer. Soc. Test. Mat., 1942, 42, 1166—1168).

Laboratory penetrometer. N. D. Talanov (Zavod. Lab., 1940, 9, 794—795).—A penetrometer made from a hand balance is described. It is used for testing C electodes.

J. J. B.

Improved Kipp apparatus. G. N. Evetzki and I. L. Degtiarev (Zavod. Lab., 1940, 9, 364—365).—The vol. of gas produced is measured in a burette attached to the Kipp apparatus. J. J. B.

Air-free carbon dioxide from a Kipp apparatus for the Dumas nitrogen determination. H. Brintzinger ($Z.\ anal.\ Chem.,\ 1942,\ 125,\ 5-6$).—Before the marble is placed in the Kipp apparatus, air trapped in the capillary spaces of the marble lumps is removed by covering the lumps with H_2O or aq. CaCl₂ in a well-closed flask which is attached to a H_2O -pump for several hr. L. S. T.

Gas-absorption apparatus. L. Bolstad and R. E. Dunbar (Ind. Eng. Chem. [Anal.], 1943, 15, 498).—The apparatus described fits into a filter-flask and ensures prolonged and intimate contact of gas and liquid. It has been used successfully in the prep. of org. acetates.

L. S. T.

Determination of volumes by the use of carbon dioxide. W. W. Barkas and J. M. Paton (J. Sci. Instr., 1943, 20, 163—164).—A method is given, with illustrative data, for calibrating an unknown irregular vol. by filling with CO_2 to a known pressure and determining the wt. of the CO_2 after absorption in soda—asbestos.

Simple volumometer. L. A. Gontscharski (Zavod. Lab., 1940, 9, 795—796).—A vessel is rigidly connected to a glass capillary in which a short column of parafin oil can move. When the vessel is tilted so that the capillary points downwards, the oil descends until the pressure in the vessel reaches a definite min. val. When the vol. of air in the vessel is reduced by placing a solid in it, the oil descends less; this permits the vol. of the solid to be calc. J. J. B.

Dilatometers for thermal analysis of metals.—See B., 1943, I, 458.

Absolute method for determining the area of a fine crystalline powder. Adsorption method for determining the area of a solid without the assumption of a mol. area.—See A., 1943, I, 303.

Method of sealing fused silica tubes. W. McCavock (*J. Chem. Educ.*, 1943, 20, 20).—Technique for joining or welding sand surface fused SiO₂ tubing ⇒3 in. in diameter is described and illustrated.

Recent developments in hygrometry. J. H. Awbery (J. Sci. Instr., 1943, 20, 153—154).—A brief summary of improved technique and refinements with the gravimetric, dew-point, and wet-and-dry-bulb methods, and hair, Cellophane, glycerol, and electrical resistance hygrometers.

N. M. B.

Condensers with intensive cooling. K. A. Bogdanov (Zavod. Lab., 1940, 9, 237).—A distillation column like that of Lebel and Henninger is surrounded by a H₂O-jacket. J. B.

XII.—LECTURE EXPERIMENTS AND HISTORICAL.

Photochemical reaction of hydrogen and chlorine. Lecture demonstration. C. M. Furgason and J. W. Moore (J. Chem. Educ., 1943, 20, 41—42).

L. S. T.

Lecture demonstration of mixture versus compound. A. Scattergood (J. Chem. Educ., 1943, 20, 40).—The formation of SbI_2 by heating Sb with I dissolved in an org. solvent such as C_2Cl_4 or CCl_4 is utilised. L. S. T.

Nicholas Leblanc, 1742—1806. R. E. Oesper (J. Chem. Educ., 1943, 20, 11—20). L. S. T.

Chemistry of the solid state. R. Schenck (Z. Elektrochem., 1941, 47, 1—8).—An historical review, dealing chiefly with the work of the author.

A. J. M.

XIII.—GEOCHEMISTRY.

Hydrochemical facies of the fluvial waters and their zoning. G. A. Maximovitsch (Compt. rend. Acad. Sci. U.R.S.S., 1942, 37, 185—190).—Hydrochemical facies, i.e., the portions of a river bed characterised by the predominance in its ${\rm H_2O}$ of a dissolved substance or group of substances, are tabulated from data showing the mineralisation of numerous rivers of the world.

Origin and geochemistry of connate waters in West Virginia. E. T. Heck, C. E. Hare, and H. A. Hoskins (Bull. Geol. Soc. Amer., 1940, 51, 1995).—Plotting % of Na against total solids shows that there has been a relative loss of Na in brines that contain > 140,000 p.p.m. of total solids. This loss is probably caused by fractional pptn. of halite. The chemical composition of the Carboniferous sea was probably similar to that of present-day sea-H₂O. L. S. T.

Ground water and hydrothermal deposits. C. H. Behre, jun., and R. M. Garrels ($Econ.\ Geol.$, 1943, 38, 65—69).—Evidence for the hypothesis that deposits are localised to near-surface positions by reaction between mineralising rising solutions and cool, neutralising ground H_2O is advanced. L. S. T.

Time relations in ocean sediments. C. S. Piggot and W. D. Urry (Bull. Geol. Soc. Amer., 1942, 53, 1187-1210).—Time-intervals in

ocean-bottom cores, and the rate of deposition of ocean sediments are discussed.

L. S. T.

Source of beach and river sands on gulf coast of Texas. F. M. Bullard (Bull. Geol. Soc. Amer., 1942, 53, 1021—1043).—Heavy mineral analyses are recorded and discussed. The origin of the sands is also discussed.

L. S. T.

Black beach sands of Guatemala, Central America. M. F. Boos (Bull. Geol. Soc. Amer., 1940, 51, 1921).—66% of the sand is magnetite (I), the amount of which decreases markedly close to mouths of streams. Chemical analysis shows traces of W and Ti and 20—30% of SiO₂. Rare yellow topaz, quartz, sphene, and andesite occur with (I).

L. S. T.

Boron distribution in recent organogenic deposits. L. A. Guliaeva (Compt. rend. Acad. Sci. U.R.S.S., 1942, 37, 28—31).—Highly org. fresh $\rm H_2O$ deposits (sapropels) do not show appreciable B enrichment in comparison with average B content of soils and earth crust; similar deposits from saline waters, containing fatty algae (balkhasite), are relatively rich in B.

Organic content of cores from Gulf of Mexico off Mississippi delta. H. J. Bissell (Bull. Geol. Soc. Amer., 1940, 51, 1920).—>200 samples from 24 cores have been analysed. Excluding a few thin beds of coarse silt and sand, the samples show a min. of 2% of org. matter, with many beds containing >4%. The darker-coloured near-shore samples have only a slightly higher org. content than the light-coloured deep-H₂O sediments. Deep-H₂O cores show a slight decrease in org. content with depth; all cores show a decrease in N with depth, the C:N ratio increasing towards the bottom of the core. L. S. T.

Structural history of iron meteorites. J. O. Lord (Bull. Geol. Soc. Amer., 1940, 51, 2040). L. S. T.

Meteorites and an earth-model. R. A. Daly (Bull. Geol. Soc. Amer., 1943, 54, 401—455).—The hypothesis that the earth represents meteoritic material is discussed. The principal characteristics, e.g., chemical and mineralogical composition, of meteoritic stones and irons are summarised, and reasons for supposing them to be fragments of a disrupted parental planet given.

L. S. T.

Cooling of the earth. L. B. Slichter (Bull. Geol. Soc. Amer., 1941, 52, 561—600).—Data and hypotheses relevant to the cooling problem of the earth are reviewed, and the theory of the cooling of a solid radioactive earth is developed by a method which identifies the problem with an equiv. one in the cooling of a non-radioactive earth. It is probable that the mantle solidified from the bottom upwards, beginning at the boundary of the core. Little correlation exists between radioactivity at depth and observed surface heat flux. It is unknown whether the earth is heating or cooling at depth. There is no need for a marked rate of decrease of radioactive substance with depth. The view that the indicated amounts of radioactivity in the earth are unnecessarily large and ≫ the amounts to be expected from observed surface heat flows is fallacious.

Some petrological concepts and the interior of the earth. A. F. Buddington (Amer. Min., 1943, 28, 119—140).—An address.

Radioactivity of rocks. R. D. Evans and C. Goodman (Bull. Geol. Soc. Amer., 1941, 52, 459—490).—Several hundred radioactivity measurements are tabulated and, with results of other investigators, are used to obtain the following average vals. for rocks of various types: acidic igneous rocks (43), $1.37\pm0.17\times10^{-12}$, intermediate igneous rocks (7), $0.51\pm0.05\times10^{-12}$, basic igneous rocks (54), $0.38\pm0.03\times10^{-12}$, sedimentary rocks (28), $0.57\pm0.08\times10^{-12}$, g. Ra per g. of rock; acidic igneous rocks (26), $3.0\pm0.3\times10^{-6}$ g. U per g., $13\pm2.0\times10^{-6}$ g. Th per g. (Th/U ratio 5.0); intermediate igneous rocks (6), $1.4\pm0.2\times10^{-6}$ g. U per g., $4.4\pm1.2\times10^{-6}$ g. Th per g. (Th/U 2.6); basic igneous rocks (34), $0.96\pm0.11\times10^{-6}$ g. U per g., $3.9\pm0.6\times10^{-6}$ g. Th per g. (Th/U 4.0). The vals. show a more marked decrease of radioactivity with increasing basicity, and are \ll those generally accepted; the Th: U ratios are also greater, and are in better agreement with those expected from geochemical considerations. Inaccuracies in earlier investigations are discussed. Estimates, based on the above vals., of the rate of production of heat by radioactive decay show that Holmes' estimates may have to be substantially decreased.

Porosity of geospheres. G. A. Maximovitsch (Compt. rend. Acad. Sci. U.R.S.S., 1942, 37, 215—216).—Porosity data have been collated, and average, min., and max. porosities calc. for the various geospheres. W. R. A.

Large magnesia-rich triphylite crystals in pegmatite. C. A. Chapman (Amer. Min., 1943, 28, 90—98).—Crystals of triphylite occur in a quartz-albite pegmatite at Newport, New Hampshire. The chemical analysis recorded shows a high FeO: MnO and 7.38% MgO. This abnormally high MgO content may account for the relatively low vals. of n and p. Curves showing the variation in composition and optical properties of the lithiophyllite-triphylite series are discussed.

L. S. T.

Age of pegmatite veins of the Ilmen Reserve in the Urals. E. K. Gerling and M. E. Vladimirova (Compt. rend. Acad. Sci. U.R.S.S., 1942, 37, 179—184).—The age of the granite intrusions and their pegmatites has been obtained from samarskite (I) and eschinite (II) by the He method. (I) from the Blumovskaya mine has He 3·41 mg. per g., U 0·1038 g. per g., and Th 0·0503 g. per g. The corresponding figures for (II) are 0·591, —, 0·0901. The ages are 248 × 10° and 218 × 10° years, respectively. Curves showing the He evolved by heating (I) at different temp. are reproduced. (II) retains He when heated, only 20% of its total amount being liberated by heating to 1200°.

Stability and formation of minerals of abyssal geospheres in the stratisphere. V. P. Baturin (Compt. rend. Acad. Sci. U.R. S.S., 1942, 37, 32—34).—Evidence is reviewed to show that only those abyssal minerals which are most resistant to weathering (e.g., quartz, rutile, zircon, tourmaline, and felspars) are capable of synthesis in sedimentary formations.

L. J. J.

Pyroxenes of basaltic magma. F. Walker (Amer. J. Sci., 1943, 241, 517—520).—The nomenclature of common clinopyroxenes, the relationship between pigeonite and augite (I), the order of crystallisation of pyroxenes, and the exsolution of (I) from orthopyroxene are discussed (cf. A., 1942, I, 251).

L. S. T.

Phosphorite deposits on the sea floor off Southern California. R. S. Dietz, K. O. Emery, and F. P. Shepard (Bull. Geol. Soc. Amer., 1942, 53, 815—847).—Nodular phosphorite in abundance has been dredged from the sea-floor off Southern California. The nodules are composed of irregular layers of collophane usually enclosing phosphatic oölites, glauconite, and formaniniferal tests. Chemical analyses (recorded) show a high F content, and X-ray data reveal a typical apatite structure. Origin, probably direct pptn. from ocean H₂O, is discussed.

Geology of phosphate deposits in the United States. G. R. Mansfield (Bull. Geol. Soc. Amer., 1940, 51, 2040—2041). L. S. T.

Presence of cobalt in iron ore from Divrik, Turkey. M. Gysin (Arch. Sci. phys. nat., 1942, [v], 24, Suppl., 142—147).—The Fe ore contains small amounts of Co, localised in the Fe pyrite, and traces of Ni. The ore also contains an unidentified yellowish-grey mineral containing Fe and S, but no Co, Ni, or Cu, and probably no As or Sb.

L. S. T.

Magnetite-hæmatite relations in the banded iron formation of W. Australia. K. R. Miles (Proc. Austral. Inst. Min. Met., 1941, No. 124, 193—201).—Evidence that the existing primary Fe oxide of the banded Fe formations of the Older Pre-Cambrian series is magnetite (I) is presented. The Fe was deposited originally probably as the hydroxide or carbonate which, under moderate temp, and pressure, was converted into (I). The later alteration of (I) to hæmatite is widespread, but is confined commonly to the zone of oxidation in W. Australia, where it has been a supergene process.

Relation between ferro-nickel and nickel ores of the Urals. B. P. Krotov. (Compt. rend. Acad. Sci. U.R.S.S., 1942, 37, 141—143). L. S. T.

New silicate structures. N. V. Below (Compt. rend. Acad. Sci. U.R.S.S., 1942, 37, 139—140).—Structures of dioptase, ramsayite, and "Egyptian blue," CaCu(Si₄O₁₀), are discussed. L. S. T.

Uraninite in Minas [Geraes]. W. Florencio and C. de Castro (Anais Acad. Brasil. Cienc., 1943, 15, 19—29).—Uraninite from Engenho Central contains 240·10 mg. of Ra per metric ton and 77·91% U. F. R. G.

Origin of sulphides in the nickel deposits of Mount Prospect, Connecticut. E. N. Cameron (Bull. Geol. Soc. Amer., 1943, 54, 651—686; cf. A., 1943, I, 211).—The Ni deposits occur within masses of olivine norite, quartz norite, and hypersthene pyroxenite intruded in the order given; they are regarded as high-temp. hydrothermal.

Gold-nickel mineralisation at Alistos, Sinaloa, Mexico. P. Krieger and A. F. Hagner (Amer. Min., 1943, 28, 257—271).—An occurrence of Au-Ni ore from Alistos, Mexico, is described. It consists of (i) Au-niccolite, containing minor amounts of gersdorffite (I) and maucherite, and (ii) Au-millerite with associated (I), pentlandite, and violarite. The mineral assemblage, particularly the association of native Au with niccolite and primary millerite, is unusual. The ore minerals may have originated from a peridotite stock by hydrothermal alteration; end-stage solutions from the peridotite magma removed Ni and probably Au from the peridotite and deposited them in latite as veins of Ni arsenides and sulphides, and native Au.

L. S. T.

Abrigo [Arizona] limestone. J. H. Wiese (Bull. Geol. Soc. Amer., 1940, 51, 1964).—The limestone was deposited in the neritic zone of a warm sea, the calcite being derived mainly from calcareous

shell fragments and, in part, by pptn. Most of the formation consists of thin alternating layers of limestone and shale. Differential dissolution under pressure explains many of the irregularities in thickness of the alternating layers. Dolomitisation is widespread.

Crystallisation of salt as a factor in rock weathering. E. Blackwelder (Bull. Geol. Soc. Amer., 1940, 51, 1956).—Crystallisation of salt disrupts rocks along joints, cleavage, and other lines of weakness.

Origin of caliche. W. A. Price (Bull. Geol. Soc. Amer., 1940, 51, 1939).—Caliche is the end-product in well-drained, well-developed soils of the process of "soil-lime" accumulation. Concn. occurs well above H₂O table in lower soil zones and in weathered or porous parent materials through normal soil processes of dry climates where rates of weathering, soil development, and soil erosion are balanced.

L. S. T.

Industrial limestones in Virginia. A. Bevan (Bull. Geol. Soc. Amer., 1940, 51, 2039).

L. S. T.

Geology of the Cœur d'Alene mining district, Idaho. K. Whiting (Bull. Geol. Soc. Amer., 1940, 51, 2036—2037). L. S. T.

Geology of the Shasta copper belt. G. F. Seager (Bull. Geol. Soc. Amer., 1940, 51, 2031—2032). L. S. T.

Solution effects on limestone as a function of slope. J. F. Smith, jun., and C. C. Albritton, jun. (Bull. Geol. Soc. Amer., 1941, 52, 61—78).—Corrosive effects in the Sierra Bianca area are primarily a function of the degree of slope on which the meteoric H₂O falls.

L. S. T.

Late Tertiary geology southeast of Mono Lake, California. C. M. Gilbert (Bull. Geol. Soc. Amer., 1941, 52, 781—815).—Chemical analyses [E. S. Shepherd] are recorded. L. S. T.

Geology of the Stony Mountain stock, San Juan Mountains, Colorado. M. Dings (Bull. Geol. Soc. Amer., 1941, 52, 695—720).—Chemical analyses of the Governor diorite and of a gabbro are recorded.

L. S. T.

Chemical and physical properties of the clay minerals nontronite, attapulgite, and saponite. O. G. Caldwell and C. E. Marshall (Univ. Missouri Agric. Exp. Stat., Oct., 1942, Bull. 354, 51 pp.).—Nontronite (I) (Carolina), attapulgite (II) (Georgia), and saponite (III) (California) were examined for dispersion and mechanical analysis (down to 50 m\(mu) and chemical composition. Electrodialysis caused slight decomp. of (I) and (III), whereas (III) decomposed completely, with Si and Mg moving to the cathode. The base exchange of the various fractions of the clays (using NH4 at pH 7 and Ca" at pH 5, 7, and 9) varied little with the particle size or treatment. (I), (II), and (III) gave 65, 21, and 80 m.-equiv. per 100 g. of calcined clay, respectively. Titration curves are given. (I) has the beidellite, (II) the amphibole, and (III) the montmorillonite type of structure. The dehydration behaviour of the various fractions was studied. Flakes or films gave much higher H₄O contents than did ground clays, probably due to H₂O trapped in the structure. Bradley's structure for (II) is modified slightly by providing for 10 (OH) per cell instead of 4 H₂O and 2 (OH). Determinations of d of the fractions were made in HgCl₂ solutions. The effects of drying and heat-treatment up to 870° on the n of the various clay fractions were determined. On heating to 110°, n of (I) and (III) increased and rehydration restored the original val., but n of (II) decreased and was not restored by rehydration. The Wisner theory of the birefringence of regular aggregates is discussed in connexion with superimposed lattice and film structures, the latter type being well illustrated by (II), which has a non-expanding lattice structure. It is likely that clay minerals could be identified and estimated in mixtures by means of n determined under three or four different conditions. Grinding a clay film, by destroying the film structure, decreases the H₂O content, but very fine grinding causes it to increase again. More study is needed before i

Decomposition of kaolin by diatoms. A. P. Vinogradov and E. A. Boitschenko (Compt. rend. Acad. Sci. U.R.S.S., 1942, 37, 135—138).—Bacteria-free diatoms (Nitzschia palea and Navicula minuscula) decompose nacrite (I) liberating Al_2O_3 , nH_2O , probably by the action of their pectinous slime. Azotobacter chroococcum without diatoms does not decompose (I).

Eccene anauxite clays and sands in the coast range of California. V. T. Allen (Bull. Geol. Soc. Amer., 1941, 52, 271—293).—Mineral and chemical analyses are recorded.

L. S. T.

Clays and soils in relation to geologic processes. C. S. Ross (J. Washington Acad. Sci., 1943, 33, 225—235).—A review, illustrated by sp. studies, of certain geological problems on which clay and soil materials have a bearing.

L. S. T.

Organic matter of ball clays.—See B., 1943, III, 229.

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